Aquatrode Plus – water analysis at the highest level

Metrohm
Ion analysis

The Aquatrode Plus guarantees the highest precision in pH measurement and pH titration

The Aquatrode Plus is a new combined pH glass electrode that has been specially designed for pH measurements and pH titrations (e.g. the determination of the carbonate alkalinity) in ion-deficient, poorly conducting samples such as natural surface waters or deionized water. It is highly suitable for a wide range of applications covering not only drinking water analysis but also field measurements, research and training at universities as well as online pH measurements.

Tricky pH measurements

Measuring the pH value in low-conductivity media is far more complicated than a simple routine measurement in a highly conducting, buffered solution. In order to obtain correct results and to prevent interferences, certain aspects have to be taken into consideration.

Carbon dioxide

In the case of samples with low buffer capacity even atmospheric CO_2 will cause considerable pH shifts. Pure water containing no carbon dioxide has a pH value of 7.0. When allowed to stand in air it will eventually reach a pH value of about 5.7 due to absorption of CO_2. For this reason samples with low conductivity and low buffer capacity ought to be measured under a protective gas such as nitrogen or argon.

Electrical resistance of the measuring system

pH measurements in ion-deficient solutions are additionally complicated by the extremely high electrical resistance of these media. In general, the overall resistance of the measuring system should be kept as low as possible to avoid long response times and drifting pH values. The new type of membrane glass developed for the Aquatrode Plus is characterized by its comparatively low resistance and guarantees very short response times. The special construction of the glass membrane as a thin-walled bulb serves to further reduce its electrical resistance.

Diaphragm

According to DIN 19264 [1] the electrical resistance of the reference electrode should not exceed 5 kΩ. The overall resistance of the reference system is made up of several individual resistances, one of the most important being that of the diaphragm. As the conductivity of the solution decreases, the diaphragm resistance increases. Also of great importance is the so-called «propagation resistance», which is dependent on the geometry of the respective diaphragm [2]. By using a fixed ground-joint diaphragm the propagation resistance can be kept low even in poorly conducting media. In a solution of 10 µS/cm, e.g., a ceramic pin diaphragm (diameter 1 mm) exhibits a propagation resistance of 31.7 kΩ, whereas the resistance of a separable ground-joint diaphragm (length 60 mm) is only 4.9 kΩ. Our novel Aquatrode Plus has a specially designed fixed ground-joint diaphragm that exhibits an extremely low resistance and thus allows rapid and accurate pH measurements in low-conductivity samples.

Reference electrolyte

The double-junction construction of the Aquatrode Plus with a maintenance-free inner reference system (gel) allows the outer reference electrolyte to be exchanged and thus be adapted to the particular measuring conditions. The electrolyte outflow through the diaphragm is in the range 5…20 µL/h and remains constant with time. Compared to a ceramic pin diaphragm (electrolyte outflow 3…25 µL/h, decreasing greatly with blockages) and a separable ground-joint diaphragm (higher outflow rate between 20 and 100 µL/h), the fixed ground-joint diaphragm thus guarantees accurate and reproducible pH measurements while at the same time minimizing sample contamination by the electrolyte.

Innovative shielding

The inner chamber of the Aquatrode Plus is electrically shielded with a special metal coating. pH measurements in high-resistance samples benefit as this shielding prevents interferences by static electricity, which would otherwise lead to very noisy signals and drifting pH values.

Excellent precision in titration

The determination of the carbonate alkalinity by SET titration to pH = 5.4 according to EN ISO 9963-2 (C24) [3] is a really hard test for pH glass electrodes. On the one hand a SET titration requires a rapid response of the glass membrane, on the other hand the measured pH values should be falsified as little as possible by the stirring of the solution. With extremely weakly buffered solutions, sample carryover can result in very long response times as the system reaches equilibrium only very slowly. The specially designed fixed ground-joint diaphragm of the Aquatrode Plus virtually eliminates cross-contamination and undesirable memory effects. Compared to other diaphragm types, the annular fixed ground-joint diaphragm is also characterized by a considerably smaller streaming potential (see Fig. 1).

The precision of a SET titration is determined by the pH values measured in the stirred solution at the start and end of the titration. The Aquatrode Plus shows hardly any dependence of the measured pH value or the determined endpoint volume on the stirring speed (see Figs. 2 and 3), whereas the endpoints obtained with a pH glass electrode with ceramic diaphragm differ more and more from the theoretical value with increasing stirring speed (Fig. 3).

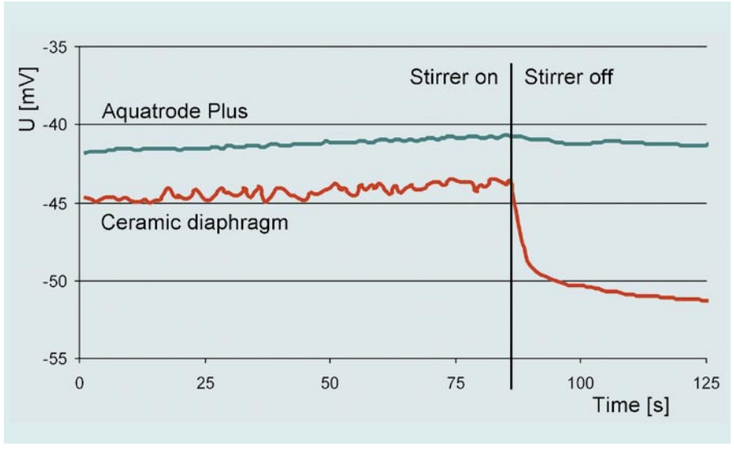

Fig. 1: Simultaneous potential measurement with the Aquatrode Plus and a pH electrode with ceramic diaphragm in a c($NaHCO_3$) = 0.15 mmol/L solution. Apart from the considerably less noisy measuring signal, the Aquatrode Plus shows only a minimal dependence of the measured potential value on the stirring speed.

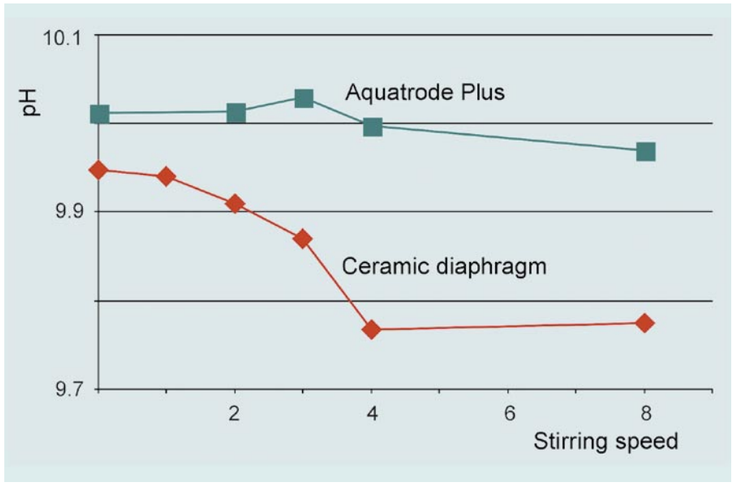

Fig. 2: Measured pH values of a c(Na_2CO_3) = 0.14 mmol/L solution at different stirring speeds. Even under vigorous stirring the Aquatrode Plus differs only by approx. 0.05 pH units (corresponding to approx. 3 mV) from the value measured in the unstirred solution. The pH electrode with ceramic diaphragm shows a deviation of about 0.2 pH units.

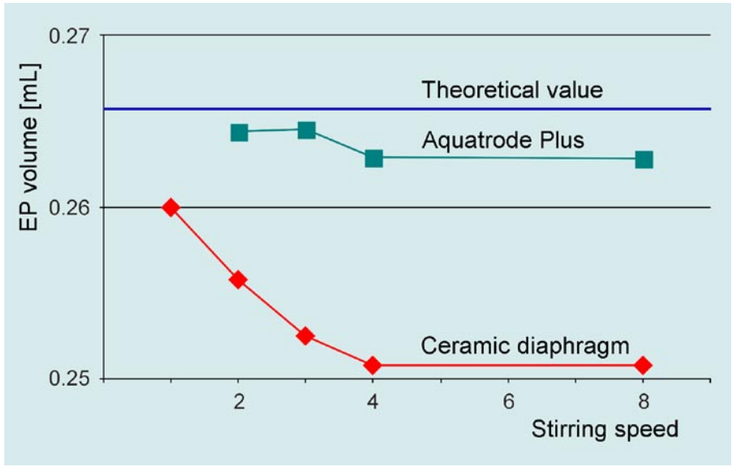

Fig. 3: Endpoint volumes obtained by SET titration at different stirring speeds [in each case the c(Na_2CO_3) = 0.14 mmol/L sample solution is titrated with c(H_2SO_4) = 0.035 mol/L to pH = 5.4]. The endpoints determined with the Aquatrode Plus are virtually independent of the stirring speed and are very close to the theoretical value of 0.2657 mL. At higher stirring speeds the endpoints obtained with the pH electrode with ceramic diaphragm differ from the theoretical value by about 5%.

Storage of the Aquatrode Plus

On contact with aqueous media, glass forms a thin hydrated layer, which is essential for the use of glass as pH membrane material. The structure of the Aquatrode Plus's membrane glass has been optimized so that, as far as possible, only protons can penetrate the membrane. However, as a result of the slow but continuous hydration process, other ions will eventually penetrate the glass as well. Particularly storage in solutions containing plenty of sodium or potassium ions will lead to an increased response time of the glass membrane as the protons must first replace the «foreign ions» from the hydrated layer. In order to ensure a rapid response of the Aquatrode Plus over a long period of time, Metrohm recommends to use the 6.2323.000 storage solution. If c(KCl) = 3 mol/L is additionally used as the reference electrolyte then the optimized composition of the storage solution guarantees that the pH glass electrode is always ready for immediate use. Conditioning prior to the measurement is not necessary, no matter how long the electrode has been stored.

pH measurements according to ISO 10523

The international standard ISO 10523 dealing with the determination of the pH value of water [4] requires grounding of any low-conductivity sample by an external metal electrode in order to eliminate electrostatic effects. The Metrohm 780 pH Meter and 781 pH/Ion Meter are equipped with separate grounded inputs where a Pt electrode or another metal electrode can be connected.

Literature

[1] DIN 19264
pH-Messung – Messfertige Bezugselektroden
Beuth Verlag GmbH, Berlin, 1985

[2] Helmuth Galster
pH-Messung – Grundlagen, Methoden, Anwendungen, Geräte
Wiley-VCH Verlag GmbH, Weinheim, 1990
ISBN 3-527-27836-2

[3] EN ISO 9963-2 (C24)
Water quality – Determination of alkalinity – Part 2: Determination of carbonate alkalinity
International Organization for Standardization, Geneva

[4] ISO 10523
Water quality – Determination of pH
International Organization for Standardization, Geneva

Technical specifications

Shaft length	178 mm
Shaft diameter	12 mm
Shaft material	Glass
Minimum immersion depth	20 mm
Glass membrane	Bulb
Membrane resistance	80...200 MΩ
Electrode zero point	0 ± 15 mV (pH = 7)
Electrode slope	>0.97
Diaphragm	Fixed ground-joint diaphragm
Reference electrolyte	KCl gel with a(KCl) = 3 mol/L
Electrolyte outflow	5...20 µL/h
pH range	0...13
Temperature range	0...60 °C

Ordering information

6.0253.100	Aquatrode Plus, combined LL pH glass electrode with fixed ground-joint diaphragm and Metrohm plug-in head G
6.0257.000	Aquatrode Plus, combined LL pH glass electrode with integrated Pt 1000 temperature sensor, fixed ground-joint diaphragm and fixed cable [length 2 m, Metrohm plug F + 2 x plug B (4 mm)]
6.2308.020	Electrolyte solution c(KCl) = 3 mol/L, 250 mL
6.2323.000	Storage solution for combined pH glass electrodes, 250 mL
6.2307.100	Buffer solution pH = 4.00, 500 mL
6.2307.110	Buffer solution pH = 7.00, 500 mL
6.2307.120	Buffer solution pH = 9.00, 500 mL
6.2104.020	Electrode cable 1 m for Metrohm plug-in head G, with Metrohm instrument plug F
6.2104.050	Electrode cable 1 m for Metrohm plug-in head G, with instrument plug E (DIN 19262)
6.2104.090	Electrode cable 1 m for Metrohm plug-in head G, with BNC instrument plug
6.2104.130	Electrode cable 1 m for Metrohm plug-in head G, with Radiometer instrument plug

Longer electrode cables (2 m or 3 m) on request.

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