

Highlights of Analytical Sciences in Switzerland

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Improving the Sensitivity of pH Glass Electrodes Towards Ultrasensitive Environmental Monitoring

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pH measurements are routinely performed with the well-known glass electrode, which is regarded as the gold standard. Its output is accepted as the practical pH value, traceable across laboratories, when combined with a reference electrode containing 3M KCl in contact with the sample through a liquid junction. Unfortunately, the potentiometric readings suffer from limited measurement reproducibility, making it difficult to use in applications that require very high precision. One example is anthropogenic oceanic acidification owing to increasing atmospheric carbon dioxide levels. The resulting pH change is estimated to -1.7 mpH per year and may have important adverse consequences if not properly monitored.



Fig. 1. Submersible probe platform developed by our group at the University of Geneva. Photo Credit: Eric Bakker.

Our group previously reported an increased sensitivity and reproducibility using constant potential coulometric readout with polymeric membrane-based pH electrodes.^[1] In this protocol, the cell potential is kept constant and a capacitor (C in Fig. 2) is placed in series of the pH electrode. The sample pH is then compared to that of a reference solution. Because the cell potential is fixed, any potential change at the pH electrode induces an opposite potential change over the capacitor and consequently a transient current is observed. The latter is integrated to obtain the charge, which is used as the analytical signal. Unfortunately, however, as the current needs to flow through the pH electrode, it was impossible to use glass electrodes owing to their high impedance of tens of M Ω .

This problem has now been overcome.^[2] We recently reported on a novel electronic circuit that uses a high-impedance input volt-

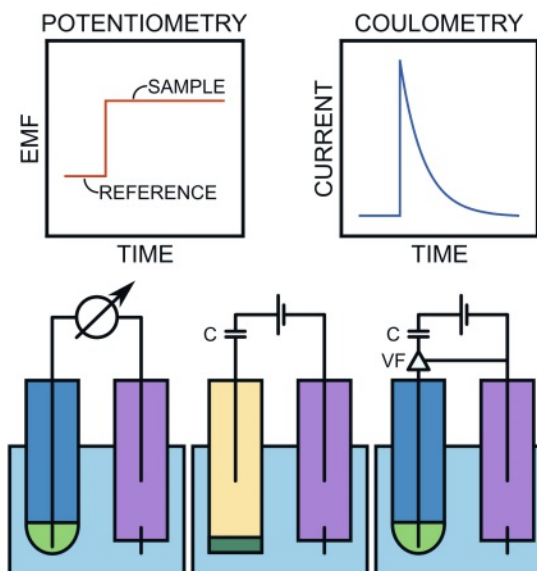


Fig. 2. Increasing the sensitivity of pH glass electrodes by constant potential coulometry. Left: Traditional potentiometric setup. The potential between the two electrodes is recorded over time, making very small potential steps difficult to distinguish from background drift. Center: Original experimental setup for coulometric readout with membrane-based pH electrodes. The cell potential is held constant, forcing a capacitive element to charge. This allows one to record current spikes that are easier to identify than potential changes, resulting in increased sensitivity. Unfortunately, a transient current must pass through the measurement cell. Right: Novel arrangement using a voltage follower, achieving constant potential coulometry without passing any current through the cell. Highly resistive membranes such as the pH glass electrode can now be used in this mode for the first time.

age follower (VF in Fig. 2) that separates the capacitive current entirely from the electrochemical cell. Thus, even glass electrodes can now be used in this configuration for enhanced sensitivity. The work resulted in an attractive measurement reproducibility of just 64 μ pH for steps of 10 mpH units. pH determination was also achieved over the entire pH range, which was not previously possible. We now aim to implement this principle in a submersible probe to achieve *in situ* ultrasensitive pH sensing in natural waters. This increased precision may also be correlated with *in situ* trace metal detection developed in our group and could provide new insights on metal speciation. **This novel experimental setup is appropriate for high precision pH sensing with a glass electrode, but may be applied to any other ion-selective electrode for enhanced sensitivity.**

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[1] P. Kraikaew, S. Jeanneret, Y. Soda, T. Cherubini, E. Bakker, *ACS Sens.* **2020**, 5, 650, <https://doi.org/10.1021/acssensors.0c00031>.

[2] R. Nussbaum, S. Jeanneret, E. Bakker, *Anal. Chem.* **2024**, 96, 6436, <https://doi.org/10.1021/acs.analchem.4c00592>.

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