1 PRINCIPLE OF METHOD

pH is a measure of acidity and is defined by equation (1)

\[
pH = -\log a_{H^+}
\]  

(1)

where \(a_{H^+}\) = activity of \(H^+\) ion

Combination glass electrode: The glass membrane is in equilibrium with \(H^+\)

\[
\text{Si-O-Na} + H^+ - \text{Si-O-H} + Na^+
\]  

(2)

On each surface and \(Na^+\) ions transport charge across the membrane so that one side still senses the other side. The response to changes in pH is nearly Nerstian and can be described by equation (3).

\[
E = E^0 + 0.059\log([H^+] + K[Na^+])
\]  

(3)

Where:

- \(E\) = observed potential
- \(E^0\) = potential dependent on the electrode system used
- \(K\) = selectivity coefficient for \(H^+\) over \(Na^+\)

1.2 SCOPE

Working Range: pH = 2-12

1.3 SAMPLE STORAGE & PRESERVATION

Analyze within 24 hours of collection (preferably as soon as possible after sampling).
1.4 INTERFERENCES

- The glass electrode is relatively free from interferences from colour, turbidity, colloidal matter, oxidants, reductants or high salinity except for a sodium error at pH > 10 (in this case use special electrodes).
- pH measurement is affected by temperature, mechanical effects that are issued by changes in the properties of the electrodes and chemical effects caused by equilibrium changes.
- Always report temperature with pH measurements.

1.5 EQUIPMENT

WTW pH 320, 330 or 340 meter and Sentix 41 probe with range 0-14 pH scale and temperature sensor.

1.6 REAGENTS

- Pre-prepared certified standard solutions of Technical Buffers 7.00 and 4.01
- 3 molar solution of Potassium Chloride, KCl

1.7 INSTRUMENT CALIBRATION (WTW 320, 330 and 340)

i. Remove the rubber protective seal covering the electrode.
ii. Bring the buffers to 20-25°C (room temperature).
iii. Switch on meter. Ensure [T] is present at bottom RHS of screen to indicate temperature sensor is connected.
iv. Press [Cal] button until CTI appears on screen ([AutoCal] [TEC] at bottom of screen).
v. Rinse electrode in distilled water and gently pat dry.
vi. Immerse electrode in pH 7.00 and allow to stabilise.
vii. Press [Run/Enter]. AR will flash on screen and the mV reading for pH 7.00 appears and should be within 0 ± 30 mV. Record value.
viii. CT2 will then appear.
ix. Rinse electrode in distilled water and gently pat dry.
x. Immerse in pH 4.01 buffer and allow to stabilise.
xi. Press [Run/Enter]. AR will flash on screen and the mV reading for pH 4.01 appears and should be within 170 ± 30 mV. Record value.
-xii. Meter will then give slope value (S), which must be within range of minus 57-60mV. Record slope value.
xiii. Press [pH/mV] button to convert to pH units. Record value for pH 4.01 buffer.
xiv. Rinse electrode in distilled water and gently pat dry.
xv. Immerse in pH 7.00 buffer, allow to stabilise and record pH reading for same.

1.8 INSTRUMENT CALIBRATION (WTW 340i)

Calibration for WTW 340i is the same as that outlined in section 1.7. with the following amendments:

- (vii) is amended in that the mV reading for pH 7.00 does not appear and therefore is not recorded. pH 7.00 remains on the screen until CT2 appears.
- (xi) is amended in that the mV reading for pH 4.01 does not appear and therefore is not recorded. pH 4.01 remains on the screen until CT2 appears.
- (xiii) is amended in that the M button is pressed to convert to pH units – this button has the same function of changing the measuring mode as pH/mV button.

1.9 SAMPLE ANALYSIS

- Analyse for pH as soon as possible after sampling ensuring that pH probe with a temperature sensor.
- Remove electrode from buffer, rinse, blot dry and immerse in sample.
- Stir sample to ensure homogeneity - stir gently to avoid entrainment of carbon dioxide.

1.10 REPORTING OF RESULTS

Report the pH values to the nearest 0.1 pH unit for samples only.

1.11 QUALITY CONTROL STANDARD

Run Q.C. standards with each batch of samples analysed. Measure the pH of the Q.C. standard buffers pH 7.00 and 4.01 (reference temperature 25°C) as outlined in section 1.7. (xiii) and (xv).

1.12 STORAGE OF pH PROBE

The pH probe may be stored in pH 7.00 buffer during the day between use but the protective cap should be half-filled with 3M KCl solution and placed on the electrode overnight or for long periods when not in use. The KCl solution should be replaced regularly.
1.12 REFERENCES

- Sentix Electrode Operating Instructions
- Instruction Manuals for WTW pH 320, 330 and 340 portable pH meter
- Standard Methods, 19th Edition, Section 4500-H+, Page 4-65

2.1.1 Procedural History
(Revision 1 compiled to include details for new WTW 340i meters)

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