Application Note AN-P1

Antimony Electrode pH Sensors

Occasionally, pH sensors are supplied with an antimony process electrode. Usually these sensors are used in applications where a glass process electrode has a short service life, such as in hydrofluoric acid. Due to inherent problems, special care must be taken when using a pH sensor with an antimony electrode.

Analyzing the electrochemical activity of the electrode reveals that the antimony reacts with water to form an oxide with a release of hydrogen ions:

$$2Sb + 3H_2O \Leftrightarrow Sb_2O_3 + 6H^+ + 6e^-$$

(Eº = 0.144 volts)

The electrode is sensitive to pH changes because hydrogen ions (H+) participate in the reaction.

Usage Conditions

Many conditions associated with using an antimony electrode pH sensor should be evaluated before it is put into service:

1. The electrode potential is only linear between 3 and 8 pH. The electrode should not be used for applications outside this range.

2. The electrode output is affected by the presence of other oxidizing or reducing agents in the solution being measured.

3. Trace amounts (in ppm) of copper, tin, lead, and some other metals less commonly found will interfere with the electrochemical activity of the antimony electrode and "poison" it. The result is no sensitivity to pH, which can occur in a matter of minutes after contact with the solution.

4. The electrode is temperature sensitive. The temperature coefficient varies from 1 to 3 mV per °C, increasing with pH. By comparison, a glass process electrode is much less sensitive, having a temperature coefficient of about 0.4 mV per °C.

NOTE: The antimony electrode does not have symmetry with reference electrodes (in conventional pH sensors) making temperature compensation necessary but difficult. With the patented GLI Differential Electrode Technique of measurement this problem is largely eliminated. The antimony electrode is used as the Standard Electrode as well as the active process electrode.

5. The antimony electrode tends to foul itself with oxide deposits that occur in the chemical reaction on its surface. This problem is not as prevalent between 3 and 6 pH as the acidic solution helps dissolve the oxide. Polishing the electrode tip with fine emery paper is the recommended cleaning method. Since antimony is highly toxic, caution should be used during cleaning!

6. The electrode output is affected by the varying flow rate of the solution being measured. Reproducible readings can only be attained when the flow rate is constant.

7. The potential of an antimony electrode is sensitive to the oxygen content of the solution. Oxygen is necessary for electrode operation, and oxygen concentration should be constant for optimum results.

8. Calibration of pH sensors with an antimony process electrode is difficult. Buffers should not contain oxalates, tartrates or citrates. Commercially available buffers have known inaccuracies. Hach pH 7 buffer and pH 4 buffer are recommended for calibration.

Because of application problems associated with antimony electrodes, they should only be used when process conditions, such as the presence of hydrofluoric acid, dictate their use. Also, the process must be able to tolerate the use of an antimony electrode.

Hydrofluoric Acid Applications

The presence of fluoride in a process doesn't always suggest the use of an antimony electrode. Fluoride ions (F^-) do not attack glass. Only molecular hydrofluoric acid (HF) etches the glass. If the process is 6 pH or higher, there will be very little HF present. The fluoride will be in ionic form:

$$HF + OH^- \Rightarrow H_2O + F^-$$

If the process always remains above 6 pH, a pH sensor with a glass process electrode may be used. During an accidental low pH condition, the glass would be attacked at a rate dependent upon the actual pH and temperature.

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