ADVANCEDTECHNOLOGY

pH Measurements in the Presence of Organic Materials

Specific solutions for typical problems when measuring nonaqueous solutions

By Jane Stevens

With the wide range of organic constituents of solutions that require a pH measurement, there are several techniques that can be used to understand and overcome the problems of measuring nonaqueous solutions.

Typical complaints include unstable readings, long response time and errors. These symptoms are indicative of high sample resistance, bulb dehydration, contamination and large, unstable junction potentials. Also, these problems are usually encountered by those trying to measure solutions with a large amount of organic material such as oils, alcohols, acetone or monomers. Small amounts of organics may be present and cause no problems with the threshold amount in the solution varying dependent on the particular chemical.

Common Problems and Solutions

The high resistance (low conductivity) of some organic compounds can cause unstable readings and noise. This would not be a problem in a highly buffered system. To eliminate this problem, analyzers may use an electrode with a low glass resistance, such as a Thermo Scientific Orion ROSS Ultra 8172BNUWP or Orion 9162BN.

When measuring samples with a high amount of sodium ion and pH above 12, sodium error can occur. If sodium error becomes a problem, then a routine pH electrode such as Orion 9104BN should be used and a small amount of soluble, inert salt like quaternary ammonium salt should be added to the sample. This will increase the conductance of the solution and result in a stable response. Adding salt will affect the activity of the hydrogen ion, causing a small shift in pH; however, this would be a small error when compared to the instability problem or sodium error.

Slow response and instability are often results of dehydration of the pH glass bulb. For a pH bulb to function, the surface of the glass must be properly wetted or hydrated. Hydrogen ion must be absorbed onto the surfaces of the glass bulb for it to have pH sensitivity. In a nonaqueous solution, the bulb dehydrates, resulting in slow response. Samples with high resistances can benefit from any Orion ROSS Ultra pH electrode or Orion 9162BN low-resistance glass combination Ag/AgCl electrode to give faster response times.

When working in viscous solutions, carryover of solution on the electrodes can cause contamination of the samples. To avoid this, the electrode should be rinsed well between measurements with a solvent that will dissolve the sample material from the electrode. A Sure-Flow flushable electrode makes cleaning and preparing for the next measurement simpler by washing the junction and electrode bulb with the filling solution itself.

Glass surfaces should not be rubbed for two reasons—dehydration of the bulb and buildup of static electricity on the glass. This static will need to be discharged before the electrode will stabilize properly. Traces of this rinse solution should be removed with a volatile solvent like acetone. A brief resoaking in a pH buffer may be necessary to restore a fast electrode response. For very dirty electrodes, an oil and grease cleaning solution such as Orion 900024 may be used to dissolve the coating on the glass. After a major cleaning and reconditioning in pH buffer, a recalibration is needed for accurate results.

A major source of confusion and error comes with the selection of buffers for nonaqueous pH measurement. Because of differences in hydrogen activity, direct quantitative comparisons are difficult to make between nonaqueous samples and aqueous buffers. The pH values, however, can be used as relative measurements to determine where pH adjustments should be made to a solution or to compare the pH of similar solvents.

Ideally, samples and buffers should have similar backgrounds. The development of pH scales for nonaqueous solutions is a formidable task since every material would have to be characterized. Some work has been done by the National Institute of Standards and Technology with methanol and ethanol mixtures.

Adjusting the Filling Solution

Large, unstable liquid junction potentials that cause slow, unstable responses are problems that sometimes occur when measuring samples with a high concentration of the nonaqueous solutions portion, especially if the sample and reference electrode solution are immiscible. To minimize this problem, the filling solution should be adjusted to provide compatibility with the sample. The ability to alter the filling solution depends on the type of electrode utilized.

One of the benefits of the ROSS electrode technology is its ability to change the electrode-filling solution to better suit the sample requirements. For all Orion ROSS and ROSS Ultra glass refillable electrodes, using a filling solution of a methanol and deionized water saturated with potassium chloride salt (KCl) is recommended. The Sure-Flow junction electrode style will also minimize the junction potential issues because the flow, and thus ion mobility, is better than with a ceramic junction.

Two points to consider when selecting a reference system are the internal reference element and the material of the electrode body. Epoxy body electrodes should not be used in certain solvents, particularly in highly polar organic solvents. In cases where damage of the epoxy body is possible, a glass electrode should be used. Organic solvents should not come in contact with the reference within the electrode.

If changes in filling solution become necessary, a ROSS reference electrode or a double-junction electrode should be used. ROSS electrodes allow a mixture of water and methanol or other alcohols with KCl to be used as an outer fill solution. If drift is due to a large junction potential, the filling solution should be altered.

The following points should be considered when selecting the appropriate filling solution: the solvent should be electrically conductive, not react with the electrode body and should minimize the liquid junction potential formed with the sample solution. A mixture of methanol and water saturated with KCl is often used.

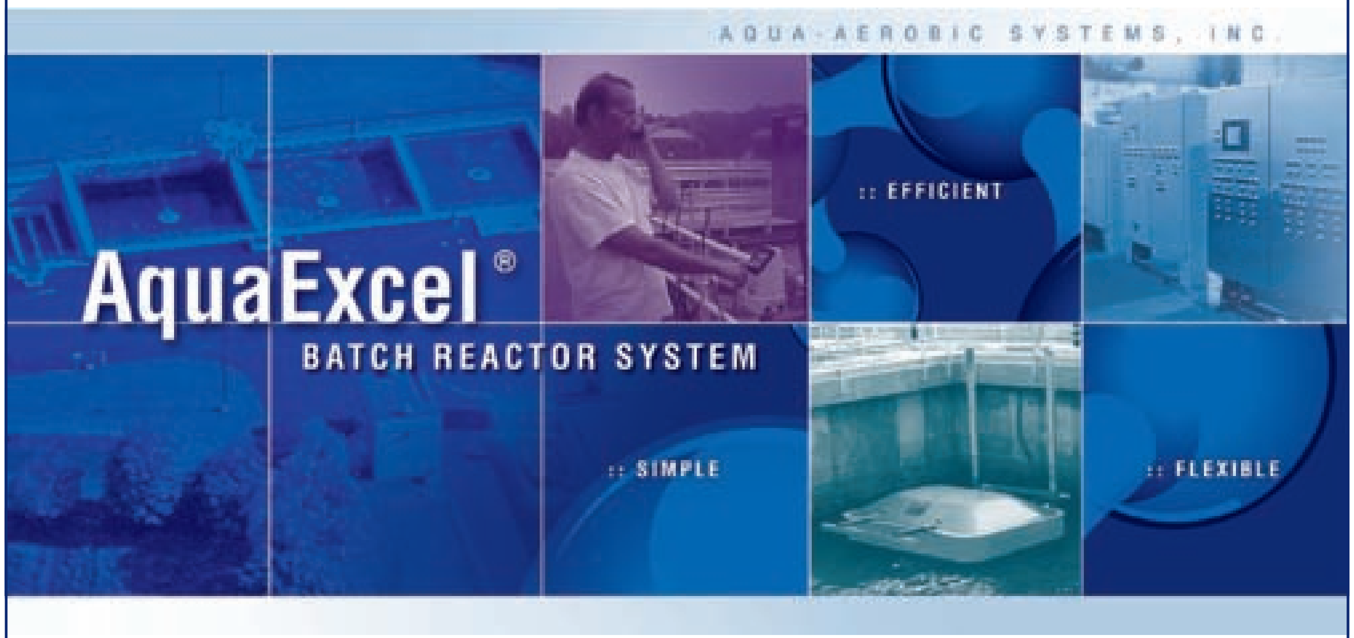

TABLE 1. Undiluted toothpaste samples using an Orion ROSS Ultra 8172BNWP electrode.	pH measured
Run 1	6.77
Run 2	6.75
Run 3	6.76
Run 4	6.73
Run 5	6.72
Average pH	**6.75**
Standard of deviation	**0.0207**
Coefficient of variation	**0.31%**

There has been some recent information in the European press about the effects of organics of shower gels and fragrances on water systems, as well as other organic waste products from various sources. Because pH information is needed for process control, reproducibility is the key to understanding if a system is in control or something has perturbed it.

Table 1 is intended to serve as an example of pH measurement with some organic constituents and the reproducibility that can be obtained with the proper direct measurement system for the sample matrix. The data for a viscous sample containing water, as well as several organic compounds using a ROSS Ultra Sure-Flow electrode, is listed in the table. The sample was an undiluted children's toothpaste gel. WWD

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