The Reason Why Chlorine-Treated Water and Peroxyacetic Acid Treated Water Register Different Oxidation-Reduction Potential (ORP) Responses

Jonathan Howarth Ph.D
Enviro Tech Chemical Services

To a first approximation, the Oxidation-Reduction Potential (ORP) measured at a platinum electrode in a water system is governed by the Nernst Equation:

$$E = E^o + 2.303 \frac{RT}{zF} Log \frac{[Red]}{[Ox]}$$

Where

E = ORP/mV
E^o = Standard Electode Potential for the Redox Couple
R = Gas molar Constant equal to 8.314 J K^{-1} mol^{-1}
T = temperature in Kelvin (T_K = 273.15 + $T_{°C}$.)
F = Faraday's Constant (the charge per a mole of electrons), equal to 96,480 C mol^{-1} s
z = the number of electron transferred in the half-reaction
[Red] is the molar concentration of the oxidizing agent (the reduced species).
[Ox] is the molar concentration of reducing agent (the oxidized species).

Don't be alarmed by the math, strange constants with even stranger units, or technical terms you may not have heard of before. You don't need to remember any of them, just undertand that the Nernst Equation is theoretical, and predicts that the ORP responds to the logarithm of the concentration of oxidizing agents present. More on this point later.

Now, when peroxyacetic acid is introduced to water, an excess amount of hydrogen peroxide is also introduced. Therefore, the electrical potential measured at the platinum surface is actually the result of 2 redox couples. For simplicity, let's assume that the hydrogen peroxide is the dominant influence the ORP when peroxyacetic acid is introduced to a water system, and that hypchlorous acid is the dominant redox couple when sodium hypochlorite is intoduced to a water system. The two respective half reactions are:

$$H_2O_2 + 2H^+ + 2e^- = 2H_2O \qquad\qquad E^o = 1.766 \text{ V}$$

$$HOCl + H^+ + 2e^- = Cl^- + H_2O \qquad\qquad E^o = 1.482 \text{ V}$$

Since, E^o for H_2O_2 is higher than that for HOCl, intuitatively, we might expect the peroxyacetic acid-treated water would register a higher ORP than that for chlorinated water. However, many factors effect the actual ORP response that are not defined by the Nernst Equation. These include slow electrode kinetics, the pH effect on acid dissociation constants, electrode poisoning, and dissolved oxygen.

Practical ORP Measurement in Agricultural Applications

Measurement of a water system's ORP is simple and it provides the operator with a rapid assessment of its disinfection potential. Unfortunately, as the Nernst Equation indicates, the ORP varies with the <u>logarithm</u> of the concentration of the oxidizing agent. This makes correlation of the ORP to an absolute concentration of oxidizing agent, inaccurate at best, and plain wrong at worst. Instead, the operator should rely on previous experiences or historical measurements without drawing any conclusions as to the concentration of disinfectants present. For example, chlorination has been practiced for decades. Instinctively, and from years of experience, users know that microbiological quality will not be compromised provided an ORP of 650-700 mV is maintained.

Would we expect to measure a similar ORP if a peroxyacetic acid/hydrogen peroxide sanitizer was to be used? Of course not! because of the limitations of the methodology outlined above.

A practical approach to using ORP in a peroxyacetic acid-treated environment would be first to select the desired or target concentration for the treatment program. This would depend on several factors such as the required microbiological performance, the soil-loading on the produce being treated etc, but let's say that we wanted to maintain 40 ppm PAA and to control the dosing using ORP. The user should then start introducing peroxyacetic acid into the water system and measure the concentration using test strip or a test kit. Once the target dose has been reached, discontinue the feed and measure the ORP of the system. It may be far lower than be typically experienced in chlorinated water, but now that we understand the Nernst Equation and its limitations in practical applications, there is no cause for alarm. Set this ORP as the trip point on the ORP controller, telling the pump to turn on when the ORP is below this voltage, and off when it is reached.

At least once per week, and preferably every day, check that the target ORP still corresponds to 40 ppm PAA using a test kit or test stips. If there has been a drift, readjust accordingly. It's also a good idea to clean the ORP probe weekly as fouling is a common cause of ORP errors.

In summary, you <u>can</u> use ORP to control the dosage of peroxyacetic acid solutions into agricultural applications, but you must understand the limitation of the technique and frequently check that the ORP set point still corresponds to the target dose.

5th May 2008