

ORP Sensors – Are They Really the Best Thing “After the Sliced Bread”?

Letter to the Editor of Water Online by Vadim Malkov, PhD, Hach

There have been many publications lately that claim universal appeal of the ORP sensors and their applicability across the board. This concerns me, because the authors sometimes forget to mention some well-known practical limitations of the method, let alone the realities of water treatment applications potentially influencing the sensor performance. This is why I'd like to set the record straight and provide a balanced account of what the ORP method and sensors are good for and where may be not be appropriate. I am doing this only because the misunderstanding of this method may cause confusion among the engineering companies specifying analytical equipment for water utilities and this, in turn, causes potential misapplication of this technology and failed end-user expectations.

The ORP method that stands for Oxidation-Reduction Potential bears in its name the implication that it is applicable only for monitoring the chemical reactions with not just exchange of electrons, but accompanied with change in oxidation degree of some ions, molecules, or atoms in such processes (redox reactions). Therefore, such chemical reactions are accompanied by change in redox potential of the solution and this is what ORP sensors detect – change in the potential, not concentration of specific molecules, atoms, or ions. Can this change be correlated to the shift in concentration of the species of interest? Of course; however, we must always be cognizant of the cost of such correlation and the factors affecting its accuracy.

It is a given and well-known fact that accuracy of the ORP method and sensors built upon it is dependent on such common factors as temperature and pH of the solution to name just a few. If the temperature influence may be compensated relatively easily, the pH provides a noticeable interference and must be either controlled or its swings must be compensated by multiple sensors and some mathematical algorithm. The algorithm may be as simple or as complex as the matrix where the measurement takes place, because the pH may influence the oxidants and reducers in a different manner. Let's add another known interference to the ORP measurement – activity of the ions in the solution, which is correlated with total dissolved solids (TDS) and may be called the matrix effect. However, this interference may depend on the nature of such solids and therefore such influence may be quantitatively different based upon the water sample composition.

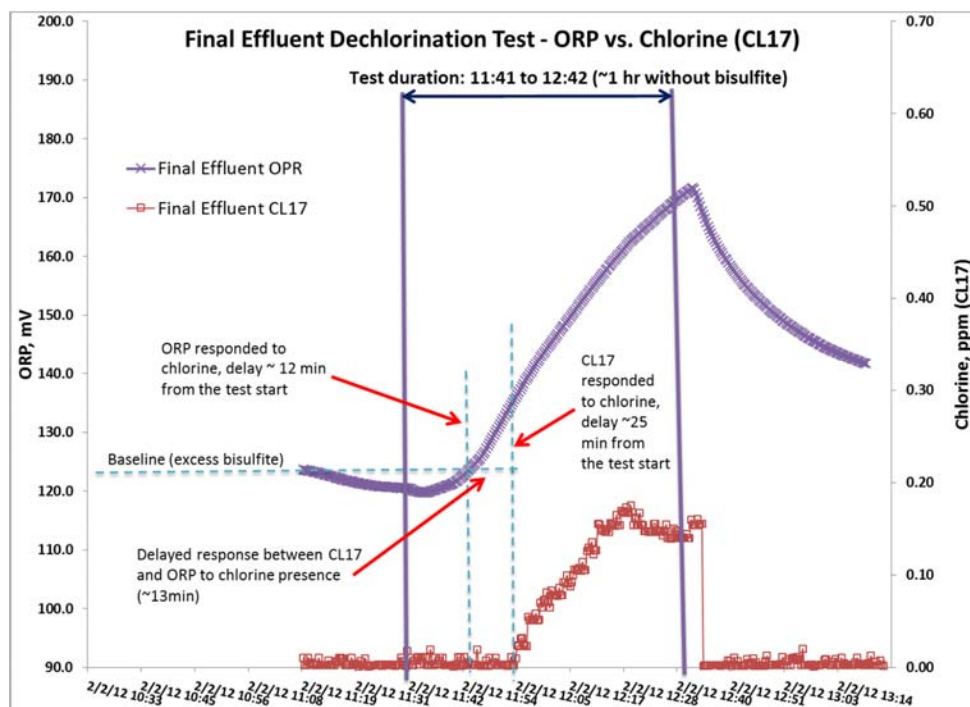
Thus, we can conclude that the best use of the ORP technology is in stable water matrices where major interferences are under control. The best example of such matrix is cooling water that is prepared with corrosion control in mind and therefore has most of the constituents under tight control. Therefore, it makes sense that in cooling water one can correlate ORP of the water with concentration of the oxidizing disinfectant with acceptable degree of accuracy. There are other examples of such stable samples and they may be combined under the umbrella of industrial water applications – the applications when the matrix is tightly controlled to achieve specific goals and the only variable is the redox reaction.

When the water sample is not as tightly controlled, there is another way to efficiently correlate concentrations of added oxidizer or reducer to the matrix – by applying ORP in a differential manner, before and after addition of the target analyte. However, in some situations there are better alternatives as was implemented in a successful application of differential conductivity measurement for CIP (clean-in-place) processes, when the ORP was evaluated and dismissed¹.

The most important lesson here is to understand the difference between the industrial applications where the water matrix can and, sometimes, must be controlled and municipal applications (DW and WW) where such control is not easily achievable and may be impossible.

There is another aspect diminishing the value of ORP sensors in all applications across the board that is frequently overlooked – the sensor maintenance requirements. It is well known that all electrochemical sensors require calibration, because the core technology is based upon consumption of the electrode material, etc.

However, speaking specifically of the ORP sensors, not everyone knows that their response to increase and decrease of the oxidant is uneven, especially when the matrix influence is significant. The figure below shows results of a test conducted at a WWTP where the response to dechlorinating agent feed was recorded:



¹ "Inductive Conductivity for Control of CIP Processes" - Vadim B. Malkov, Jeff Tocio – *Proceedings of 53th ISA Analytical Division Symposium (April 20-23, 2008), Calgary, Canada, AD2008.S12*

As can be seen from the graphs, there is an advantage in speed of response to increase of the oxidant (chlorine) vs. a regular colorimetric method (Hach CL17); however, there is a very sluggish response of the ORP sensor to decrease of chlorine concentration, while the CL17 responded immediately. This and other factors may greatly reduce accuracy of the ORP correlation to the concentration of target analyte and may require a specific instrumentation setup, additional calibrations, and mathematical algorithms to provide ongoing verification of the sensor performance, as described in this publication².

The advantages potentially provided by the ORP sensors may be easily offset by the sensor fouling, which is not uncommon in WW and raw water (DW intake) applications where implementation of this technology is frequently recommended. There are published evidences that fouling of the ORP sensor may completely erase all advantages in cost and “ease-of-use” and therefore other methods to control raw water pre-oxidation may be recommended³.

To conclude, I would like to reiterate a few main thoughts about implementation of the ORP technology and associated sensors:

- Know your water and avoid ORP technology if the matrix is unstable;
- In order to provide meaningful correlation of ORP with concentration of target analyte, all interfering factors, e.g. pH, temperature, TDS, etc. must be tightly controlled or truly compensated;
- In order to achieve expected performance, ORP technology may need to be implemented in a differential mode, before and after addition of the oxidant/reducer;
- Be aware of maintenance requirements to ensure ORP sensor performance;
- Be aware of sluggish response of the ORP to decrease of oxidant concentration in the sample;
- Based on all the above, scrutinize the suggested use of the ORP technology to understand the advantages and deficiencies, especially if the application is in the municipal water treatment.

² Vadim B. Malkov, David L. Rick "Oxidation/Reduction Measurement" - *US Patent, Pub. No.: US 2012/0298529 A1*, Nov. 29, 2012

³ Vadim Malkov and Mike Sadar, “Control of Iron and Manganese Ozone Removal by Differential Turbidity Measurements” – *Ozone: Science & Engineering*, 2010, Vol.32, Issue 4, p. 286-291