THE COMPARISON OF PHOTOELECTROCHEMICAL CHEMICAL OXYGEN DEMAND TO TRADITIONAL METHODS FOR MEASURING NATURAL ORGANIC MATTER (NOM) IN SOURCE WATER

Justin Dickerman, MANTECH Inc.*

Robert Menegotto, MANTECH Inc.

*MANTECH Inc., 5473 Highway 6 North
Guelph, Ontario N1H 6J2
jdickerman@mantech-inc.com

Natural organic matter (NOM) is a complex mixture of organic compounds that are the products of various decomposition and metabolic reactions in the source water and its surrounding watershed. The presence of NOM directly affects drinking water treatment processes; in many source waters NOM can vary greatly both in concentration and specific composition and therefore must be consistently monitored. Some NOM compounds are known to react with commonly used disinfectants to produce disinfection by-products (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAA) that are thought to be carcinogenic. NOM may also promote biological growth in distribution systems and increase levels of complex heavy metals and adsorbed organic pollutants.

Routine NOM monitoring is typically conducted using surrogates such as total organic carbon (TOC), dissolved organic carbon (DOC), ultraviolet absorbance at 254 nm (UV254) and specific ultraviolet absorbance at 254 nm (SUVA). These surrogates are used in drinking water treatment for their ease of use and rapid feedback. However, these parameters may not provide adequate information on treatment performance and NOM removal in some cases. Specifically, UV254 and SUVA rely on aromaticity, which is not a chemical feature of many organic compounds such as sugars. TOC and DOC measure carbon content, but do not provide information on the electron-donating capacity of organic compounds. For example, glucose and benzene, which have the same carbon content, have different electron-donating capacity.

Chemical oxygen demand (COD) is a measure of the amount of oxygen required to chemically oxidize organic species. COD is not often used for drinking water due to the harmful chemicals used in the dichromate method, the long analysis time, and relatively low precision below 50 mg/L. The traditional dichromate COD method (Standard Methods 5220) involves digestion of organic matter at high temperatures with sulfuric acid, dichromate, and a catalyst for 2 to 3 hours, followed by indirect determination of COD through unreacted dichromate.

The PeCOD® COD method is a new nanotechnology-based photoelectrochemical technique for rapidly determining dissolved COD in natural and wastewater samples. It utilizes the charge originating from oxidizing organic species contained in the sample to measure COD, and therefore generates an accurate measurement of reactive compounds. The PeCOD® method eliminates the need for hazardous chemicals and has potential for source water treatment monitoring. The high oxidation potential of the PeCOD® can measure and characterize organics that may not be detected by TOC or UV254, providing a better understanding of NOM removal and DBP formation. As a source monitoring tool, the PeCOD® provides a greater magnitude of change due to increases in NOM when compared to TOC or UV254, allowing operators to make confident decisions on changes in treatment techniques in response to increased NOM events.

Dalhousie University completed a study in 2014 using the PeCOD® to monitor NOM at four surface water treatment plants (*Stoddart & Gagnon 2014*). It was found that the removal of PeCOD® COD across a biofilter follows a similar trend to TOC and DOC. Additionally, the PeCOD® had an expanded scale of resolution, highlighting its ability to detect reactive organic species. PeCOD® results are particularly useful prior to biofiltration because COD can distinguish between compounds with the same number of carbon atoms at different oxidation states. The PeCOD® oxidation method is currently scheduled for a full-scale source water monitoring project at Halifax Water's Lake Major Plant. A location known to have variable NOM that isn't currently measured by TOC or UV254. Dalhousie is currently testing the hypothesis that PeCOD® correlates with ATP generated from biological redox reactions during the biofiltration process.

The University of Massachusetts began a project comparing PeCOD® to traditional monitoring techniques in characterizing NOM in surface water influent to a pilot treatment plant. The first stage of this project focuses on event detection capabilities of PeCOD®, TOC, UV254, and SUVA, while also establishing baseline values for each of the parameters. Initial findings show the PeCOD giving a response significantly greater in magnitude relative to the baseline in comparison to the other techniques. It has also been identified that TOC, UV254, and SUVA are all impacted greatly by changes in the flow regime of the sampling stream, resulting in false event detections that are not mirrored by the PeCOD® method. The next stages of the project will evaluate the ability of each monitoring technique to detect the changes in residual NOM throughout the treatment train and determine correlations between optimal coagulant dosing and the various parameters. As each of these techniques characterizes NOM in a different manner, multi-parameter correlations will also be evaluated.

ASTM International has recently approved the PeCOD® method as a bulk surrogate measure of NOM in freshwater source waters and treated drinking water. The PeCOD® method was identified as a bulk surrogate measure of NOM compounds and is described as complementary to existing NOM monitoring techniques. The PeCOD® method has also been included in guidelines issued by Health Canada on monitoring of NOM in raw source water, and throughout drinking water treatment and distribution systems.

The speed of this new technique allows for real-time, continuous organic monitoring to ensure constant compliance with regulations. PeCOD® can be used to predict DBP (disinfection by-products) formation, provide a bulk measurement of NOM, and assist in optimizing coagulation. Online units can be used to provide rapid feedback on changing source water quality to guide upstream treatment processes, as well as potentially reduce consumption of raw materials which would result in considerable cost savings.