Application of photoelectrochemical chemical oxygen demand to drinking water

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This study investigated the use of a photoelectrochemical chemical oxygen demand (peCOD) analyzer for the detection of natural organic matter (NOM) from four drinking water treatment plants in Nova Scotia, Canada. This novel method was investigated because it can measure NOM within 5 minutes and does not require hazardous reagents. As an initial research step, eight model organic compounds were used to demonstrate instrument feasibility. The study found that peCOD could accurately detect oxygen demand based on theoretical chemistry concepts (i.e., theoretical oxygen demand). The next step in the study evaluated NOM removal in practice. Specifically, a drinking water–plant survey found that the removal of NOM, as measured by peCOD, was approximately 3.5 times greater than the removal using traditional NOM surrogates—e.g., total organic carbon (TOC). This expanded scale in resolution highlighted the instrument’s ability to provide detailed information on treatment performance that was often more subtle with traditional NOM techniques.

Photoelectrochemical chemical oxygen demand (peCOD) analysis is a novel method to rapidly determine chemical oxygen demand (COD) without the use of harmful chemicals (i.e., potassium dichromate, sulfuric acid, silver sulfate, mercuric sulfate). The hypothesis of this study was that peCOD as measured using a commercial COD analyzer1 could provide analysis of NOM removal that would be applicable to the drinking water industry. To address this hypothesis, the study was structured into the following research tasks: (1) evaluate the ability to detect and quantify COD from model organic compounds (e.g., amino acids and carboxylic acids) in a concentration range relevant for drinking water; (2) compare peCOD analysis with traditional NOM detection techniques (e.g., TOC analysis); and (3) evaluate peCOD concentration range in source water and during subsequent treatment from surface water treatment plants in Nova Scotia, Canada. Because COD is a measure of oxidizable organic matter, relationships between peCOD and traditional NOM surrogates were also studied.

MATERIALS AND METHODS

Samples were analyzed for peCOD using a commercial COD analyzer1 with an autosampler2 and associated automation software.3 This method has a manufacturer-reported calculated method detection limit of 0.5 mg/L and sample analysis time ranging from 5 to 10 minutes. To measure COD, the analyzer measures the current generated from the photocatalytic oxidation of organic matter using a titanium dioxide catalyst irradiated with ultraviolet light from a light-emitting diode.

Samples were measured after a single point calibration with 20 mg/L COD calibrant4 and calibration verification with calibrant standards of 20, 15, 10, 5, 3, 1, 0.5, and 0.25 mg/L for model organic compounds and of 20, 15, 10, 5, 3, and 1 mg/L for surface waters. The system was operated with a sample-to-electrolyte ratio of 3:1 in which the electrolyte is used to determine the background photocurrent generated by the oxidation of water. Calibration was accepted when the ratio of COD to charge generated was between 0.02 and 0.06 COD/μC, the terminal photocurrent generated was > 90% of the 20 μA baseline, and the $R^2$ of the calibration verification was ≥ 0.99. A ratio of COD to charge generated in this range ensured that the charge generated from the oxidation reaction was adequate for the expected calibrant concentration (20 mg/L). A terminal photocurrent near the baseline photocurrent ensured that the calibrant was oxidized completely.

Model organic compounds. Three amino acids (tyrosine, tryptophan, phenylalanine), three carboxylic acids (sodium acetate, sodium oxalate and sodium formate), and two reference standards (potassium hydrogen phthalate [KHP] and caffeine) were used as model organic compounds. Carboxylic acids and amino acids are found in natural waters and can make up 8% and 2–3% of COD in natural waters, respectively (Langlais et al, 1991). KHP is commonly used as a reference standard for TOC determination, and caffeine is commonly used as a marker for human contamination.

Surface waters. Samples were collected from four surface water treatment plants in Nova Scotia, Canada.
Treatment trains included one biofiltration plant, one ultrafiltration/nanofiltration membrane plant, and two conventional filtration plants. Samples included raw water, prefiltered water, filtered water, and finished water.

RESULTS AND DISCUSSION

Correlation between peCOD and theoretical oxygen demand (ThOD). Model organic compounds were used to determine peCOD correlation to ThOD. A value of unity demonstrated that peCOD was a complete predictor of ThOD. Model compound peCOD measurements showed reasonable correlation (value of unity contained in the 95% confidence interval), with ThOD with the exception of reference standards and oxalate.

Model compounds. peCOD was detectable at TOC concentrations characteristic of raw and treated surface water in Nova Scotia. Predictable peCOD-to-TOC ratios based on the stoichiometry of the oxidation reaction (i.e., molecular ratio of oxygen to carbon) were achievable when peCOD was an accurate predictor of ThOD.

Surface and treated waters. Reductions in peCOD over the course of treatment at all utilities mirrored reductions in TOC and dissolved organic carbon (DOC), demonstrating the ability of peCOD to function as a treatment performance indicator and NOM surrogate. As shown in Figure 1, the DOC in Pockwock Lake (biofiltration) was reduced from 2.71 to 1.66 mg/L, or a total of 1.05 mg/L, from raw to finished water. Comparatively, the peCOD reduction from raw to finished water was much greater at 3.6 mg/L. This expanded scale of resolution noted with peCOD could allow for easier detection of subtle changes in treatment performance and subsequent water quality. This expanded scale could be important for biofiltration monitoring because the biodegradable fraction of DOC is typically in the μg/L range. For example, reduction in DOC across the biofilter was 0.26 mg C/L, whereas peCOD reduction was 1.5 mg/L.

Overall, further work would be required for other water matrices. For example, although not an issue for the waters investigated in this study, Zhang and Zhao (2008) found peCOD was sensitive to chloride concentrations above 26.6 mg/L, but that measurement error could be reduced to acceptable levels (i.e., < 5%) with a chloride-to-organics ratio smaller than 5:1. As an initial study, however, the current work provides evidence for development of peCOD as a useful drinking water NOM surrogate.

CONCLUSION

This article demonstrates the potential for photoelectrochemical determination of COD in the drinking water industry. Analysis of model organic compounds was reproducible and followed a predictable trend with ThOD and TOC for most compounds. Analysis of four raw and treated surface waters showed that peCOD removal followed a trend that was similar to other NOM surrogate parameters such as TOC and DOC. When compared with other surrogate parameters, peCOD had an expanded scale of resolution, highlighting its ability to provide information on treatment performance even when NOM removal is small. Given the need for rapid response time in treatment-plant performance analysis, it is conceivable that this tool could be accepted for inline analysis or for analysis of water treatment processes that require more understanding of NOM removal and/or transformation, such as biofiltration and advanced oxidation.

FOOTNOTES

1PeCOD® L100 AssayPlus™ analyzer, Mantech Inc., Guelph, Ont., Canada.
2AutoMax™ 73 autosampler, Mantech Inc., Guelph, Ont., Canada.
3PC-Titrate™ software, Mantech Inc., Guelph, Ont., Canada.
4Blue range (< 25 mg/L) calibrant, Mantech Inc., Guelph, Ont., Canada.

REFERENCES


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