A Standard Method for the Measurement of Photoelectrochemical Oxygen Demand in Drinking Water

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Introduction

The use of a commercial photoelectrochemical chemical oxygen demand analyzer, the PeCOD, is gaining significant interest in the drinking water industry. The instrument enables rapid (5~10 min), low level (down to~0.5 mg/L) detection of oxygen demand without the use of hazardous potassium dichromate. For the drinking water industry this means rapid determination of oxygen demand, which can be used as a natural organic matter surrogate, much like the more common parameters of total and dissolved organic carbon and UV absorbance. However, unlike these parameters, oxygen demand can give an indication of the oxidative state of compounds.

Mechanism of Photoeletrochemical Oxygen Demand

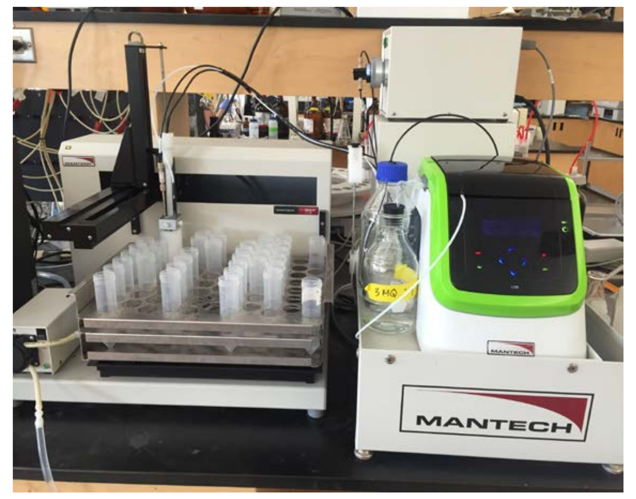

Figure 1. PeCOD L100 autosampler analyzer (Center for Water Resources Studies, Dalhousie University)

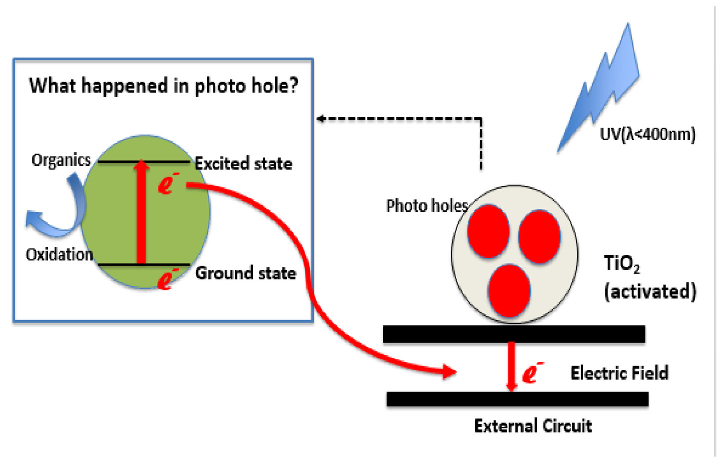

Figure 2. A schematic diagram of photoelectrocatalytic oxidation process with TIO2 (Shujie F. A presentation in 17th Canadian National Drinking Water Conference)

Material and Methods

Reagent	Parameter
Calibration	Prepared from sorbitol
Electrolyte	Prepared from lithium nitrate
Sodium hydroxide	Concentration at 0.01 N, 0.1 N and 1 N

Material	Parameter
Sample Vials	50 mL
Macropippet	1-10 mL
Racks	Suitable for sample vials

Prime lines
- Use deionized water to rinse the lines for influent and effluent port
- Check pump state by volume detection

Calibration
- Prepare Electrolyte and Blank solution
- Use macropippete and a 50 mL vial to take 21mL calibrant(sorbitol) and do a triplicate test
- Check the state of analyzer and sensor based on parameters in feedback file

Standard Curve
- Prepare calibrant standard solution at different concentration
- Use macropippete and a 50 mL vial to take 21mL each standard solution and do a triplicate test
- One blank is added along with 3 triplicate to ensure the right working state of analyzer and rinse the lines for residues

Sampling
- Neutralize samples to recommended detection pH range for acid preserved water
- Use macropippete and a 50 mL vial to take 21mL water and do a triplicate test
- Record 3 individual Chemical Oxygen Demand results for each sample and an average number, check if the deviation among 3 results is less than 0.5 mg/L which ensures the reliability of data

Figure 3. Material and operating procedure of autosampler PeCOD analyzer

Results and Discussion

MDL testing

Mean Concentration—mg/L			
2.0	2.1	2.3	2.1
1.6	1.8	2.3	MDL: 0.73
2.3	2.1	2.3	
Blank:0.0	Blank:0.0	Blank:0.0	

Figure 4. Method Detection Limit testing with pure sorbitol reagent.

- The method detection limit is shown in Figure 4. It was determined at a target calibrant(sorbitol) concentration of 2 mg/L.
- The final MDL is 0.73 mg/L.

Matrix Spike testing

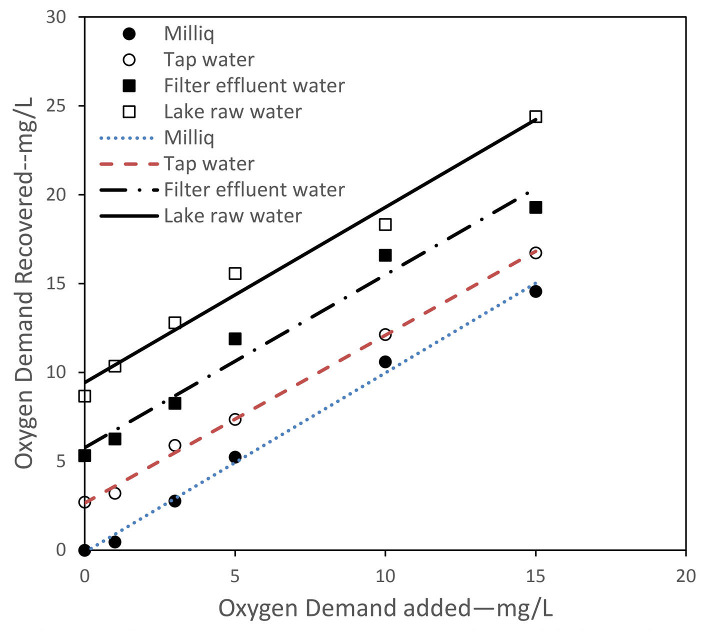

Figure 5. Oxygen Demand Recovery tests for sorbitol powder spiked with real Matrix

- Photoelectrochemical oxygen demand is a composite analyte, representing complexed organic compounds in water.
- The black circles(blue line) stand for recoveries of standard samples which maintained good linear.
- The recoveries of three different real matrices also maintained good linear, and slopes fitted with standard one(blue line). It means PeCOD method is reliable as a drinking water detector.

pH interference testing

pH	Oxygen Demand-mg/L
5.85[a]	4.5±0.1
5.81[a]	4.8±0.1
5.01[b]	4.6±0.1
7.02[b]	4.4±0.1
7.44[b]	4.8±0.2
8.02[b]	4.5±0.2
8.61[b]	4.5±0.1
9.00[b]	3.7±0.1

Figure 6. Oxygen Demand Recovery tests of sorbitol reagent at various pH; a: unadjusted pH, b: pH adjusted by acid and base.

- pH 5~8.61 did not interfere tests. pH 9 caused a low bias.

Preservative/Holding time testing

Hold time	Preservative			
	None	Sulfuric Acid	Nitric Acid	Phosphoric Acid
0 hours	4.8±0.1	4.6±0.2	4.8±0.1	0.0±0.0
24 hours	4.5±0.1	4.3±0.2	4.6±0.2	0.0±0.0
48 hours	4.8±0.1	4.6±0.2	4.3±0.1	0.0±0.0
7 days	4.6±0.2	4.5±0.2	4.6±0.2	0.0±0.0

Figure 7. Hold time and preservative tests for pure sorbitol reagent.

Matrix	Hold time (day)	Oxygen demand Recovery rate(%)	
		None	Sulfuric Acid
Surface Water	1	97.2±0.9	102.0±1.0
	2	95.3±2.8	99.0±3.0
	7	85.0±1.9	99.0±2.0
	14	74.8±2.8	101.0±2.0
Treated Water A	1	98.6±2.9	95.6±1.4
	2	104.3±1.4	94.4±2.8
	7	88.6±1.4	97.2±1.4
	14	77.1±1.4	97.2±1.4
Treated Water B	1	102.0±2.0	102.0±2.1
	2	96.0±4.0	100.0±2.1
	7	80.0±2.0	95.8±4.2
	14	72.0±6.0	97.9±4.2

Figure 8. Hold time and preservative tests for real matrix.

- The standard samples can be persevered with sulfuric acid and nitric acid in 7 days.
- Real matrices can be preserved in 2 days without acid. But the PeCOD concentration decreased over 20% after 14 days without preservatives,

Chloride/Thiosulfate interference testing

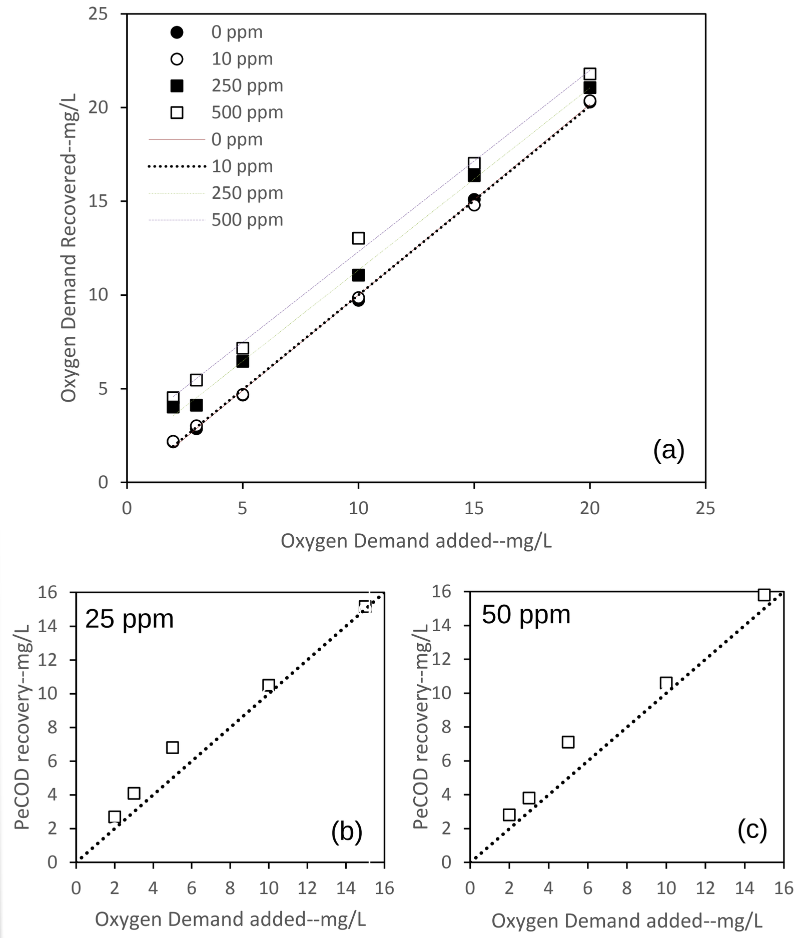

Figure 9. (a) Oxygen demand recovery with various Cl-; (b) effect of COD:Cl- at 25 ppm Cl-; (c) effect of COD:Cl- at 50 ppm Cl-

- Chloride can react with strong oxidants, thus is an important interference for both PeCOD and COD tests.
- Figure 9(a) indicates 10 ppm Cl- did not interfere PeCOD tests, but 250 and 500 ppm Cl- caused a high bias.
- Figure 9(b) and (c) illustrates the additional organic potentially diminished Cl interference. At 25 ppm Cl-, recovery reached over 90% when ratio of Cl- to COD smaller than 2.5, while ratio was below 5 for 50 ppm Cl-.

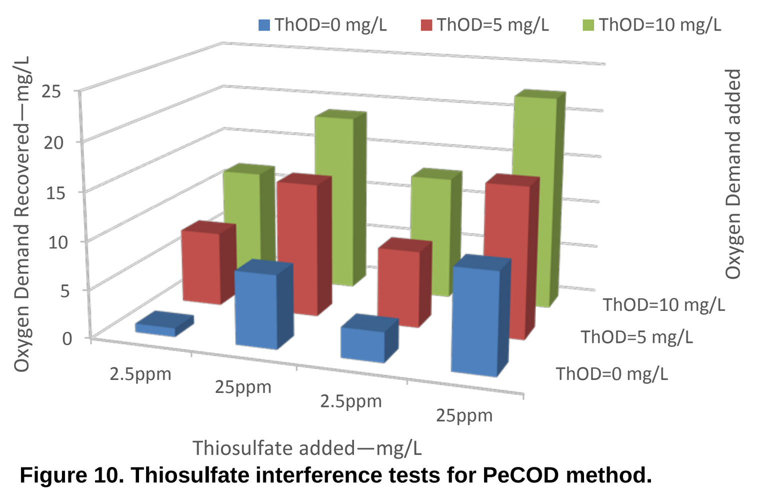

Figure 10. Thiosulfate interference tests for PeCOD method.

- Thiosulfate is used for quenching chlorination in drinking water treatment and monitoring. It can react with strong oxidants, so also needs to be concerned for PeCOD test.
- Figure 10 shows thiosulfate increased oxygen demand at both 5 and 10 ppm. In addition, the aggregate impact existed during consecutive detection.

Application for real matrix

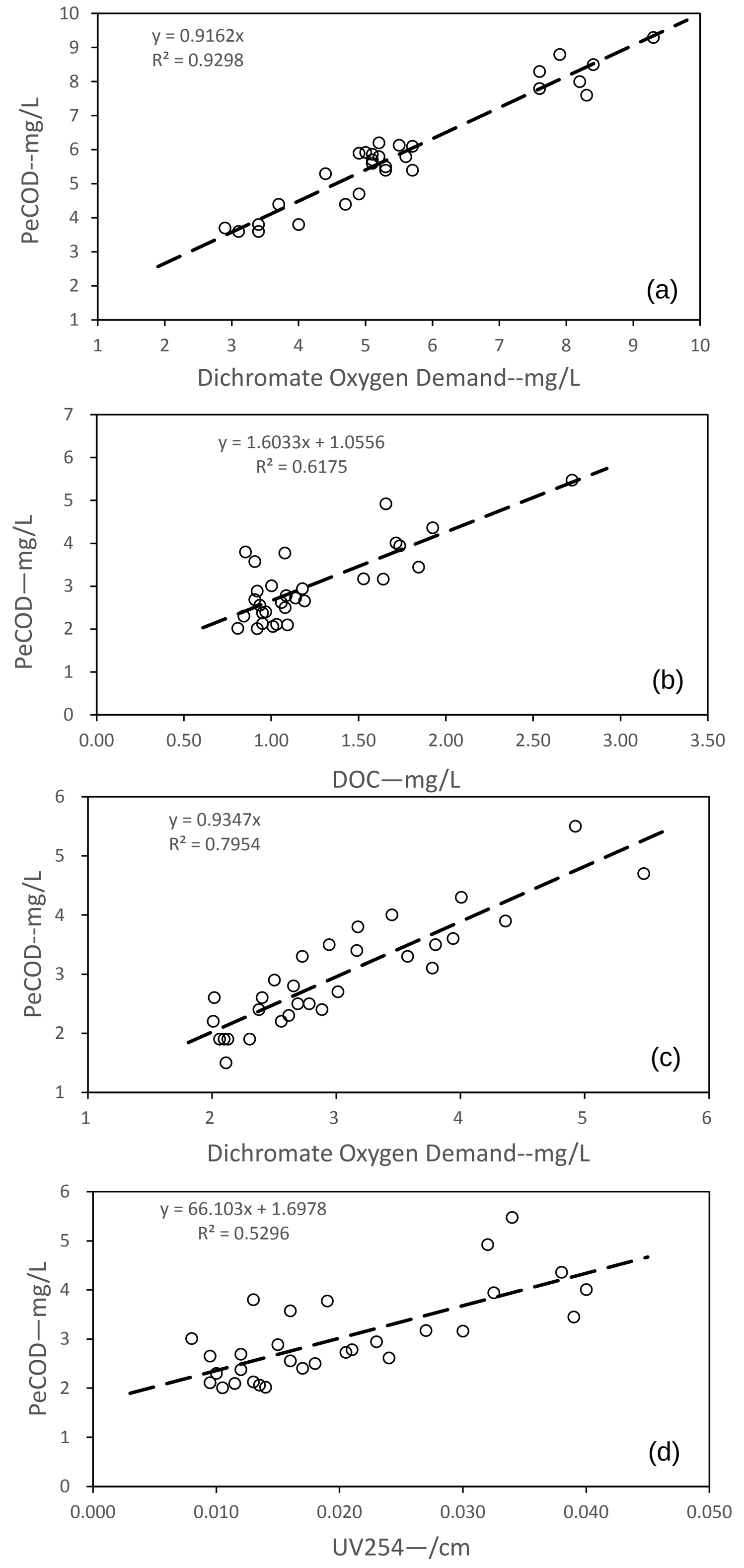

Figure 11. (a) PeCOD vs COD for biofiltration water; (b) PeCOD vs DOC (c)PeCOD vs COD (d) PeCOD vs UV 254 for distribution system water.

- Figure 11(a) shows a high correlation(R squared=0.912) between PeCOD and COD for biofiltration effluents.
- For distribution system water, COD and PeCOD also fitted well in Figure 11(c). But the relationship between PeCOD and DOC or UV254 were not that high, which was led by different detecting mechanism.
- Though different detectors may give different information, PeCOD provides a new understanding for drinking water detection.

Analysis based on photocurrent and fluorescence excitation-emission matrix

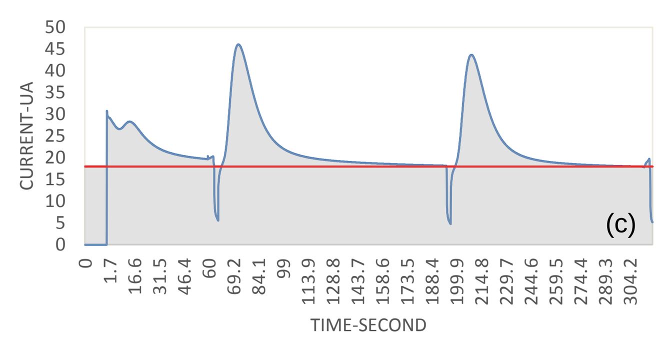

Figure 12. Dynamic profiles of photocurrent on (a)calibration; (b)blank; (c)sorbitol(20 mg/L)

PeCOD analysis is displayed by dynamic photocurrent as shown in Figure 12. Red line is baseline, thus the integrating area above determines oxygen demand.

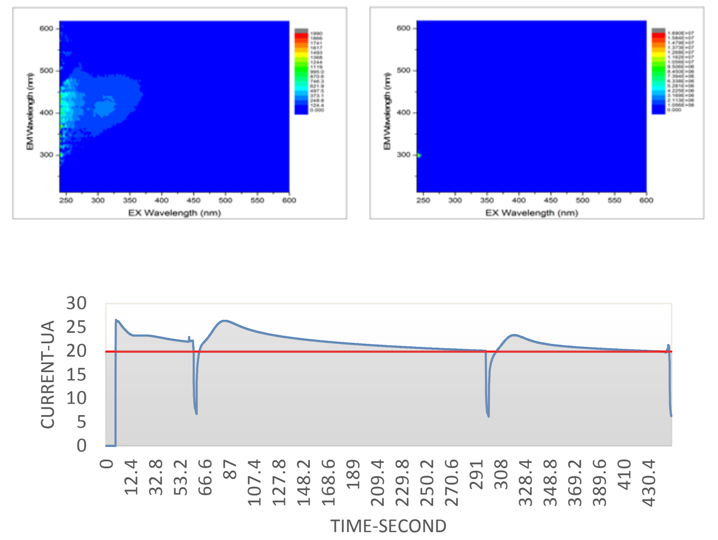

Figure 13. Comparison between Fluorescence excitation-emission matrix and photocurrent profile for tap water.

Figure 13 indicates the comparison between PeCOD and FEEM. By comparing 2 FEEM graphs, one was before PeCOD test the other was after, nearly all fluorescent compounds were oxidized.

Conclusions

- MDL is 0.73 mg/L and PeCOD analyzer works well with reagent grade water..
- Water samples can be kept in 2 days without preservation. Sulfuric acid and Nitric acid can preserve samples in 14 days.
- High concentration of Chloride(>250 ppm) interferes oxygen demand, but additional organic can diminish the effect. Thiosulfate is another interfering factor and aggregate impact exists.
- Dynamic photocurrent profiles represent oxidation state and is useful for mechanism research.

If you missed my poster session but you still have questions please contact me at: shujie.fu@dal.ca or come find me. I'll be here all week!