# TECHNICAL BULLETIN

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This technical bulletin describes the peCOD technology and method; a unique nanotechnology-based photoelectrochemical technique to determine dissolved COD in natural and wastewater samples in a simple, rapid, direct and absolute fashion. The peCOD approach utilizes photocurrent (charge) originating from oxidizing organic species contained in the sample to quantify COD.

The core of peCOD technology is the sensor, which consists of a UV-activated nano-particulate TiO2 (titanium dioxide) photocatalyst coupled to an external circuit. When a sample analysis is initiated, the sample is introduced into a microcell containing the sensor. The TiO2 is irradiated by UV light, and a potential bias is applied. The UV light creates a photo hole in the TiO2 sensor which is a very powerful oxidizing agent (+3.1 V) that will readily lead to the transfer of electrons from organic species in the cell. TiO2 has a much higher oxidizing power compared to dichromate (the chemical potential of dichromate is only E° = 1.6V), meaning that TiO2 is better able to break the bonds contained within difficult organic compounds and liberate electrons. Since dichromate has less energy available to perform this function, the method relies on additional help in the form of heat, pressure, and sulfuric acid. It is because of this increased oxidizing power that peCOD is better able to measure certain organics such as nicotinic acid, benzene, diethylamine, and others.

By applying an appropriate potential bias to the system, liberated electrons are forced to pass into the external circuit where the reduction of oxygen (or other species) takes place. The charge is monitored, and this gives a direct measure of the oxidation of organic compounds. The measured charge, Q, is simply the total amount of electron transfer that results from the degradation of all compounds in the sample. Given that one oxygen molecule is equivalent to 4 transferred electrons, the measured Q value can be easily converted into an equivalent O2 concentration (or oxygen demand) value.

The figures to the right and below illustrate the processes involved in photocurrent generation, the core of PeCOD® technology.

$$+ \; O_2 \; \rightarrow \; CO_2 + H_2O + NH_3 + e\text{-}$$

PeCOD measures generation of e-
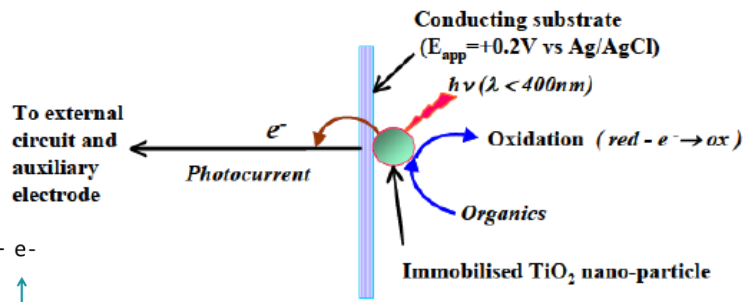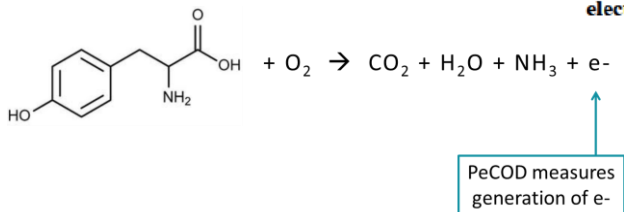
The photocurrent (I_{work}) generated by the peCOD oxidation reaction is captured and plotted against time, as seen in the diagram below. The oxidation continues until the change in output current reaches a termination criterion (near 0.01 uA/s). The output current at the point of termination (I_{term}) is recorded. The curve generated by the photocurrent is then integrated, above the I_{term} level, to determine the total charge generated by the oxidation of the sample (Q_{net}). The charge generated by an oxidation of Blank solution (Q_{blank}) is subtracted from the Q_{net}, then multiplied by a constant (k) to attain the sample COD value. The k constant is determined by the M value attained through calibration, and the dilution ratio of the sample/electrolyte mixture specific to the peCOD range being used.
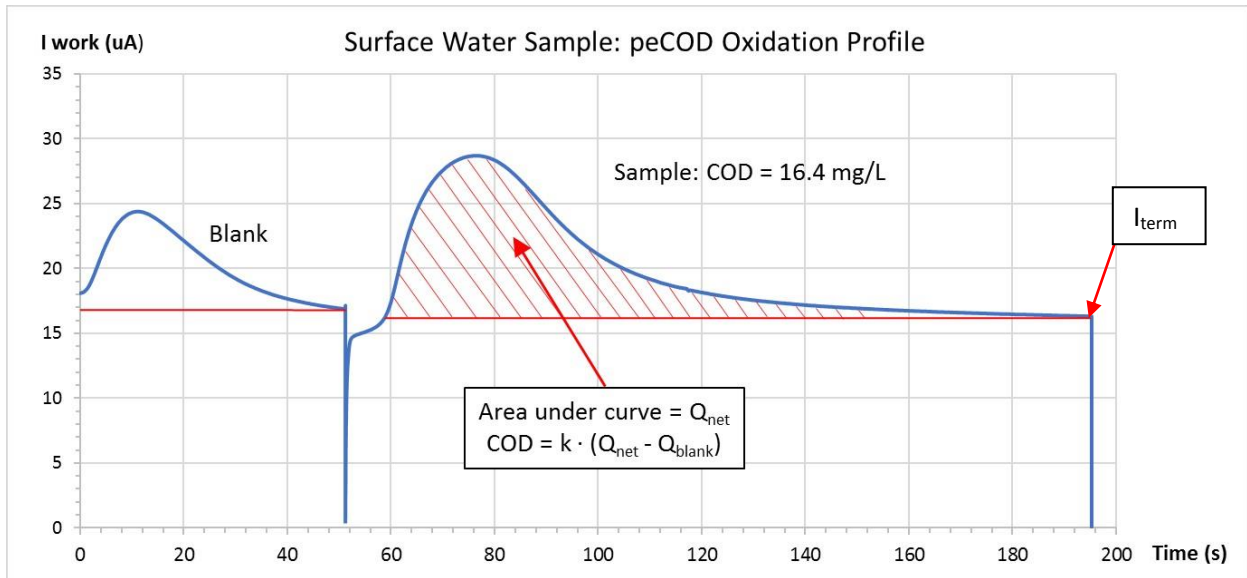
$$COD \left(\frac{mg}{L} O_2\right) = k \cdot (Q_{net} - Q_{blank}) \qquad k = M_{Cal} \cdot D.F.$$

Example for Adv. Blue Range: $\qquad COD = [0.0376 \cdot 1.333] \cdot (412.89 - 84.95) = 16.4 \frac{mg}{L} O_2$

Q_{net} – Charge generated by sample oxidation; calculated as area between photocurrent curve and I_{term}

Q_{blank} – Charge generated by blank oxidation; calculated as area between photocurrent curve and I_{term}

k – Constant determined through calibration; applied to each sample calculation

M_{Cal} – Ratio of generated charge to expected COD; set by daily calibration with range-specific standard

D.F. – Range specific dilution factor to account for electrolyte reagent addition