Aqua Diagnostic Pty Ltd
White Paper – PeCOD^{TM} COD Technique

1.0   INTRODUCTION

Understanding the level of organic pollutants and their potential environmental impact in water streams and discharges is critically important to the health of our water ways and for the optimal management of waste water treatment plants.

A number of standard tests, specifically Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) have been developed to estimate the oxygen demand of an aqueous sample via oxidative degradation of the organic material present in the sample. Due to a range of drawbacks, the currently available techniques have failed to completely satisfy the market demands for sensitive, reliable, real-time, automated measurement of organic pollutant levels in both laboratory based and on-line analysers.

Aqua Diagnostic Pty Ltd ("Aqua Diagnostic") has developed a new technique for determining COD that addresses recognised key problems while maintaining a very strong correlation with the standard approved COD test. This paper considers Aqua Diagnostic's technology (trademarked PECOD™) that utilises a unique approach in which the extent of electron transfer (COD) is quantified directly and simply at a TiO_2 nanoparticle film electrode during photo-catalytic degradation of organic material.

2.0   OXYGEN DEMAND IN WATER

At present, two standard analytical methodologies, BOD, where oxidation is carried out biochemically via heterotrophic microorganisms and COD, where the oxidation is carried out chemically via strong oxidising agents such as dichromate, are in widespread use for the determination of the oxygen demand of waters and waste waters.

2.1   Limitations of the Standard BOD and COD Methodologies

Despite their widespread use to estimate oxygen demand, both BOD and COD methodologies have technological limitations.

BOD is a complicated and time consuming procedure (5 days) and has limited linear working range and questionable accuracy. Interpretation of BOD results is also difficult since the results tend to be specific to the body of water in question, depend on the specific pollutants in the sample and the nature of microbial seeds used in the test. In addition, the BOD method cannot be used to assess the oxygen demand for many heavily polluted water bodies because of inhibitory and/or toxic effects from polluting species.

The COD method is more rapid and less variable than the BOD method. Thus it is the preferred method for assessing the oxygen demand of organic pollutants in heavily polluted water bodies and, as such, is the national standard for organic pollution evaluation in many countries, e.g., Japan and China. Despite this, the method has drawbacks. It requires a time consuming (2-4 hr) reflux process for complete oxidation of the organic material and requires expensive (e.g. Ag_2SO_4), corrosive (e.g. concentrated H_2SO_4) and highly toxic; e.g., (Hg(II) and Cr(VI)) reagents. The latter reagents are of particular environmental concern. It should be noted that the Cr(VI) method has been abandoned in Japan for this reason.

3.0   PeCOD™ COD ANALYSIS

The patent pending PeCOD™ technology provides a unique nanotechnology-based photoelectrochemical technique to determine dissolved COD in natural and waste-water 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.

3.1   Background of Photo-catalytic Degradation of Organic Materials

In recent years the application of photo-catalytic processes that are based on nano-particle metal oxides has been used to great effect in the oxidative degradation of organic compounds.

The photo-catalytic degradation of organics is initiated through the photo-generation of electron/hole pairs within a semiconductor catalyst (TiO_2). Illumination of TiO_2, with photons whose energy is equal to or greater than the band-gap energy (E_g), will result in promotion of an electron from the valence band to the conduction band. This leaves an electronic charge carrier (e_{cb}^-) in the conduction band and a positive photo-hole (h_{vb}^+) in the valence band (see Fig. 1).
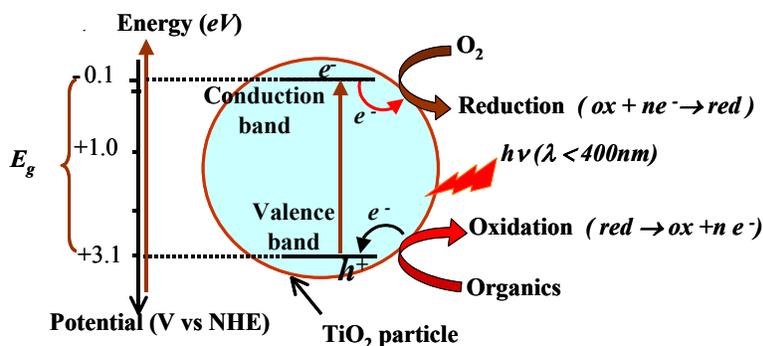

Figure 1.   *Schematic energy band diagram of the photo-catalytic degradation processes*

In order to achieve chemically useful photocatalysis, recombination of the electron-hole pair must be suppressed. This is typically achieved by "trapping" these species with surface adsorbates leading to surface redox processes. Photo-hole "traps" can include organic compounds, water, and the hydroxide ion – all of which are readily oxidised. The photoelectrons, on the other hand, are typically "trapped" by molecular oxygen, which is reduced to peroxide or water.

The photo-hole is a very powerful oxidising agent (+3.1 V) that will readily lead to the transfer of an electron from a species adsorbed to the solid semi-conductor. It is important to note that the two half-reactions shown in Figure 1 must take place separately in two different areas on the same particle via multiple chemical steps.

3.2   The Innovative PeCOD™ COD Technique

The PeCOD™ technology utilises photo-electrochemical current (or charge) generated from photo-electrochemical degradation of organic compounds as the analytical signal.

The photo-catalytic degradation efficiency at TiO_2 depends on the degree of the recombination of photoelectrons and holes. With traditional TiO_2 photocatalysis

systems, this relies on how rapidly the photoelectrons and holes are consumed by the adsorbed species. Nearly every report described to date requires the photo-excited electron to be "trapped" by an adsorbed species on the semi-conducting surface.

In the PeCOD™ approach the photoelectrons are "trapped" by electrochemical means. A TiO_2 nanoparticle film electrode is used as the working electrode in a three-electrode photo-electrochemical cell. By applying an appropriate potential bias to the working electrode, it becomes more favourable for the photoelectron to be transferred to the working electrode rather than to the adsorbed O_2. The photoelectrons are subsequently forced to pass into the external circuit and to the auxiliary electrode, where the reduction of oxygen (or other species) takes place (see Fig. 2). The photocurrent (or charge) is monitored and this gives a <u>direct</u> measure of the oxidation of organic compounds.

Separation of the two half-reactions by imposing an electrochemical potential suppresses the recombination of photoelectrons and holes and enhances the degradation efficiency. A further advantage of the approach is that the rate of degradation is independent of O_2 concentration since the rate of reduction at the auxiliary electrode will never be the rate-limiting step of the overall degradation process.
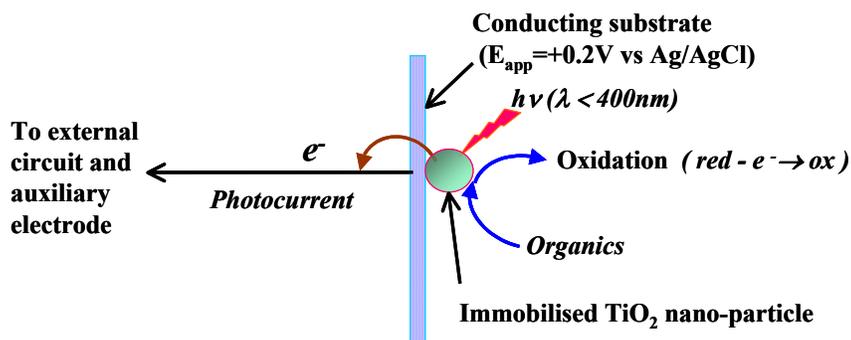

Figure. 2. *Schematic of the photo-electrocatalytic processes involved in the analytical signal generation.*

3.3   Quantification of analytical signal

The photo-electrochemical system described above can be used for two different degradation models – either exhaustive or non-exhaustive degradation.

<u>Exhaustive Degradation</u>

When the exhaustive degradation model is employed, 100% of the analyte in the sample is consumed and the charge (Q) can be measured by the integration of photocurrent within the degradation period. The analytical principle can be established using Faraday's Law. 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 for oxidation by O_2, one oxygen molecule is equivalent to 4 electrons, the measured Q value can be easily converted into an equivalent O_2 concentration (or oxygen demand) value.

For exhaustive degradation, the equivalent COD value can therefore be represented as:

$$COD \ (mg \ / \ L \ of \ O_2) = \frac{Q}{4FV} \times 32000 \qquad \textbf{(1)}$$

where F is the Faraday constant and V is the sample volume.

Non-exhaustive Degradation

For non-exhaustive degradation, only a small fraction of available analyte is consumed and its concentration in the bulk solution remains essentially unchanged. When sufficient photo intensity and adequate potential bias are employed, and the overall process is controlled by mass transfer and if we again assume that after photochemical oxidation, the analyte is fully oxidised, then the number of electrons transferred (*n*) during photo-electrochemical degradation is a constant for any given analyte. The limiting photocurrent (*i*$_l$) can, therefore, be used to represent the rate of reaction:

$$i_l = nFA \left(\frac{dN}{dt} \right)_l = nFAk \ C_b \qquad \textbf{(2)}$$

where *A* is electrode area, C_b is the concentrations of analyte in the bulk solution and k is the Mass-Transfer Coefficient.

3.4   Analytical Measurement

The analytical signal generated from the analysis is shown in Figure 3.
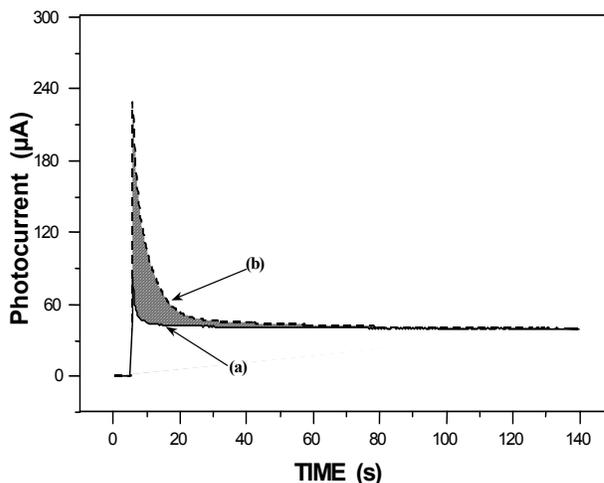

Figure 3.   *Photocurrent response of (a) blank solution and (b) a sample solution containing potassium hydrogen phthalate.*

These are typical photocurrent-time profiles obtained during an exhaustive degradation of potassium hydrogen phthalate (KHP) in the thin-layer photo-electrochemical cell.

Under a constant applied potential of +0.30 V, for the blank (curve a), the photocurrent results purely from the oxidation of water, while photocurrent that is observed from the sample solution containing organics (curve b) consists of two current components, one from photo-electrocatalytic oxidation of organics and the other from the oxidation of water, which is the same as for the blank photocurrent. When all organics in the sample have been consumed, the photocurrent of the sample solution drops to the same level as the blank. Note the short time frame of the analysis.

During a given time period, the charge passed for both blank and the sample solutions can be obtained by integration of photocurrents with time. The net charge that originates from the oxidation of organics can be obtained by subtracting the charge of the blank from the charge of the sample, which is indicated as the shaded area in Figure 3. This net charge can then be used to quantify the COD value of a sample according to Equation 1.

3.5   Validation of Analytical Principle

<u>Relationship between Net Charge and Concentration</u>

In order to validate the proposed methodology, a range of organic compounds including KHP (which is a standard for testing the standard COD method) were studied. The relationship between the net charge and the concentration of individual organic compounds is given in Figure 4.
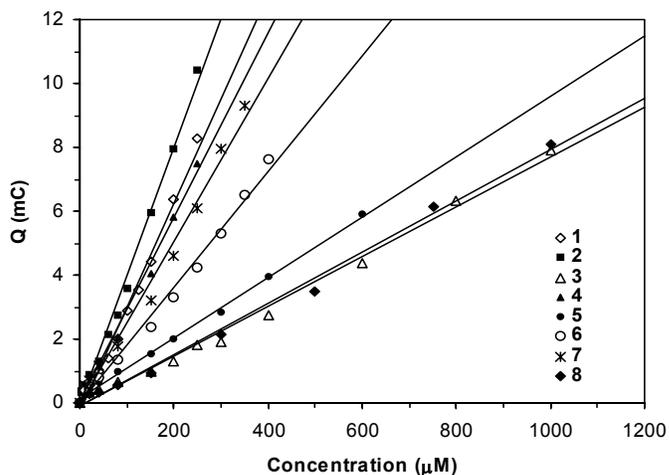

Figure 4: *Validation of analytical principle, showing the quantitative relationship between the net charge and the concentration of organic compounds; . 1: p-chlorophenol; 2: potassium hydrogen phthalate (KHP); 3: methanol; 4: d-glucose; 5: malonic acid; 6: succinic acid; 7: glutaric acid; 8: glycine; 9: mixture of 1 to 8 with equal COD concentration of each.*

It can be seen that for all organic compounds investigated, the net charges obtained are directly proportional to the concentration. The slopes of the curves are found to be directly proportional to the number of electrons transferred to fully oxidize the organic compounds during the oxidative degradation. Consequently, Equation 1 is valid for this type of photo-electrocatalytic degradation process. The results also indicate that the PeCOD™ system is capable of oxidizing different organic compounds uniformly

<u>Relationship to Theoretical Values</u>

Plotting the PeCOD™ values against the theoretical COD values, the line of best fit with the slope=0.9957 and R^2=0.990 was obtained demonstrating that the method measures essentially the theoretical COD values.

<u>Comparison to Standard Dichromate COD Method</u>

The applicability of the proposed principle was further validated using the standard COD method and three different types of synthetic samples.

The COD values obtained from the two methods demonstrated the high correlation between the two sets of COD values (*r=0.995, P= 0.000, n=27*) and the slope of the principle axis of the correlation ellipse of 0.9887. At 99% confidence interval, this slope was between 0.9400 and 1.0400.

Detection Limit, Linear Range and Reproducibility

The detection limit, linear range and reproducibility were also evaluated. It was found that the real detection limit of 0.20 mgL^{-1} COD with linear range up to 360 mgL^{-1} COD can be achieved under the experimental conditions employed. It is noted that the detection limit can be further improved through the use of dilution. The introduction of dilution also has the added benefits of potentially speeding up the analysis time per sample when fast sampling is required. It also acts to reduce the concentration of interfering agents to a level that maintains reliability of results.

The reproducibility was evaluated by performing 17-replicate detections of a sample with the concentration of KHP equivalents to 15.0 mgL^{-1} COD. The relative standard deviation obtained was 0.87%.

It is important to note that for both the exhaustive and non exhaustive degradation, the time required for a single assay will be _less than 5 minutes_ due to the high photo-electrochemical degradation efficiency of the system.

3.6   Interference

The nature of the waters tested using PeCOD™ technology mean that the measurement of total organic pollutants could potentially be inhibited through any interference caused by chloride and phosphatic species, etc. Aqua Diagnostic Pty Ltd has been able to overcome this potential problem through the introduction of a patent pending technique that permits the technology to work effectively, even in the most highly contaminated waters.

4.0   CONCLUSIONS

Aqua Diagnostic Pty Ltd has developed an exciting new technique that addresses many of the problems inherent in the standard methods, while maintaining a very strong correlation with the approved standard COD test. Thus it is able to provide a sensitive real time solution for the Water Monitoring and Treatment Market.

The PeCOD™ COD technique is based on strong fundamental principles, which have been supported by exhaustive experimental results.

If you have any further questions that have not been addressed in this short paper please contact;

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