

Real-time Trace Level Monitoring of Chemical Oxygen Demand (COD) in Seawater by PeCOD™ COD Analyser

Keywords: Seawater; Chemical Oxygen Demand (COD), Cooling systems

Abstract

The use of seawater in cooling towers is a commonly used practice providing significant cost savings. However, until now, monitoring of seawater discharge has been limited due to the presence of high chloride concentrations. The PeCOD™ COD analyser is capable of measuring levels of COD in seawater discharge that would breach environmental discharge requirements, with a saline concentration of up to 35,000 mg/L (35 ‰), at a rate that is significantly quicker, more sensitive and which is innocuous compared to the toxic standard dichromate method test for COD.

Introduction

Seawater is typically used in cooling towers to cool the condenser. By using seawater for cooling the condenser, a significant saving of energy used for generation of cooling can be achieved. However, the usage and discharge of seawater requires monitoring to avoid associated environmental concerns. COD is an index of water pollution by organics and is a bellwether parameter for seawater quality discharge.

Various methods differing in oxidizing agent, acidity, catalyst and temperature have been reported to measure COD. The dichromate method oxidises almost all organic compounds and is widely used as a standard method for measurement of COD. However, the oxidising ability of dichromate is so high that chloride ions present in a sample are easily oxidized to chlorine. To suppress this interfering reaction, mercury is used for samples containing chloride up to 1,000 mg/L. Both dichromate and mercury are hazardous to the environment and it is not desirable that routine methods utilize significant amounts of such substances¹. Seawater concentrations of chloride can be as high as 21,000 mg/L (35,000 mg/L as NaCl). With significant dilutions of sample sufficient to bring

the chloride concentration in range, the dichromate method will struggle with sensitivity, in addition to still possessing the requirement for the addition of hazardous substances for suppression of chloride oxidation to achieve an accurate COD determination.

The Aqua Diagnostic PeCOD System

Aqua Diagnostic has developed a new, rapid, sensitive and green alternative to measuring COD employing recently developed photoactive TiO₂ nanomaterials combined with photocatalytic technologies. The standard method is currently the dichromate COD test. However, this dated method is slow, limited in sensitivity and (as noted) requires the addition of toxic chemicals (i.e. mercury) to eliminate interferences such as chloride.

Based on the oxidative degradation principle, the innovative aspects of the PeCOD™ method lie in the novel approach to generate and quantify the useful analytical signals⁴ with a sensitivity and speed far greater than any standard method (minutes compared to hours and µg/L compared to > 10 mg/L).

System Performance

To meet the seawater testing requirements, the PeCOD™ system must provide adequate sensitivity and be able to measure COD in seawater samples up to 35,000 mg/L salinity. The oxidation rate of chloride via titanium dioxide is known to be much slower than the oxidation of organics³. Previous studies have shown that inorganic interferences such as Cl⁻ to the organically derived COD were mainly manifested at low organic carbon levels, but were masked in the presence of higher concentrations of organic^{3,4}. The photooxidation behaviour of Cl⁻ in the absence of organics is very different to its behaviour in the presence of organics. In particular, it has been

proposed that the oxidation of organics dominates the initial oxidation process even when the Cl⁻ concentration is high. By exploiting the slower kinetics of chloride oxidation the PeCOD™ system can measure COD down to 1 mg/L in a seawater sample that has been diluted by a factor of 1:50. This leaves an in-cell concentration of 420 mg/L chloride (salinity 700 mg/L). To comply with regulatory requirements the PeCOD™ system could alarm users when seawater discharges contain COD above permitted levels. Table 1 describes analytical figures of merit for the PeCOD™ system for high chloride applications, while Figure 1 shows the standard calibration curve for COD in a 420 mg/L chloride background.

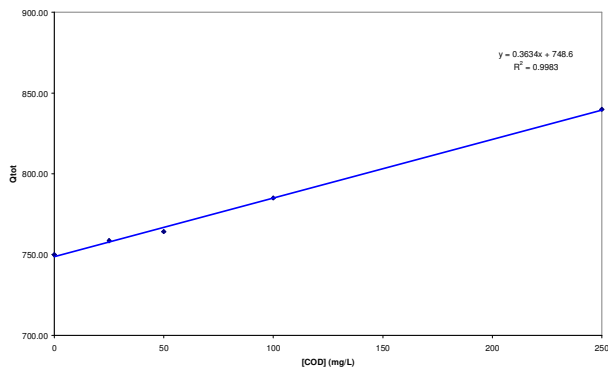


Figure 1 - Calibration showing linear relationship between COD in a saline background and charge response for standards ranging from 1-250 mg/L.

Table 1 – Analytical Figures of Merit and System Requirements

Linear Instrument Range (mg COD/L)	0-300
Chloride Tolerance Range (mg NaCl/L)	0- 35,000
Calibration Equation	$Q_{net} = 0.3634[COD] + 748$ $R^2 = 0.99$
Sample throughput	Up to 7 analyses hr ⁻¹
Sample Volume	10 µL analyses ⁻¹
Supporting Electrolyte	2M NaNO ₃

Real Sample Analysis and Validation

A sugar refinery employing seawater in their cooling water was used as a trial site to monitor COD in a high chloride matrix. Grab samples were collected and analysed for COD using the PeCOD™ COD analyser and externally measured for COD by the dichromate

Conclusions

method and for BOD₅. The results are presented in Table 2.

Table 2 – Results for oxygen demand measurements taken at a Sugar Refinery

Sample	Spiked concentration*	BOD*	PeCOD™ *	COD*
A	Sea water blank	2	3.8	633
B	11.2	6	9.6	260
C	22.4	16	22.1	47
D	33.6	22.7	33.5	163
E	44.9	29	41.4	77

* Expected COD concentration (mg/L) after blank correction

* Concentrations reported as mg/L post blank correction

As can be seen in Table 2 the standard dichromate COD method was unable to accurately measure COD in such a high chloride background and subsequently struggled to produce any meaningful relationships with the expected spiked concentration. Figure 2 shows the correlation between the estimated spiked concentration and the concentration obtained by the PeCOD™ COD analyser.

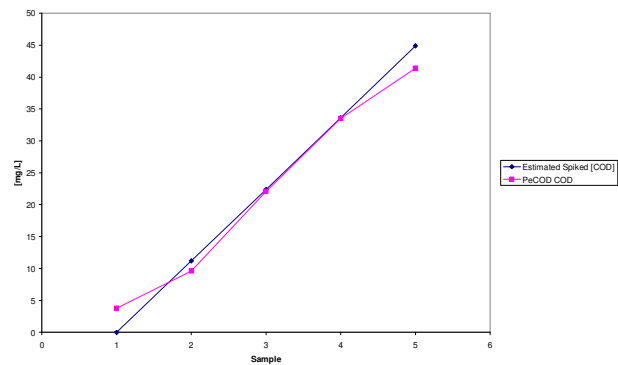


Figure 2 – Comparative concentration data at a Sugar Refinery for estimated spiked concentration of COD and PeCOD™ COD analysis

The correlation was validated by statistical analysis via a paired t-test and regression analysis performed at the critical $\alpha = 0.05$ level. The t-test showed no significant difference between the estimated spiked concentration and the PeCOD™ COD results ($t = 3.18$, $P = 0.18$) implying a good relationship. A regression analysis showed a significant linear relationship ($F = 254$, $P = 0.0005$, $r = 0.99$) implying there is a significant correlation between estimated spike concentration and the PeCOD™ COD results.

The use of seawater in cooling towers is a common application in today's society. However, the chloride content in seawater has limited monitoring of water pollution in seawater discharges by any of the standard methods currently available. The rapid monitoring of COD in seawater discharge presents an opportunity for users to both comply with regulatory standards and control process costs by eliminating the unwanted discharge of processing chemicals.

The PeCOD™ system provides the ability to accurately monitor COD in seawater in real time without the need for toxic chemical use.

References

- (1.) Sato, H.; Ishikawa, T.; Sato, T.; Yokoyama, Y., Determination of Low-Range COD with Cr(VI)-Cr(III)-Hg(II) for Samples of High Concentration Chloride, *Analytical Sciences*, **2001**, 17, 1569-1570.
- (2.) Zhang, S.; Zhao, H.; Jiang, D.; John, R., Photoelectrochemical determination of chemical oxygen demand based on an exhaustive degradation model in a thin-layer cell, *Analytica Chimica Acta*, **2004**, 514, 89-97.
- (3.) Zhao, H. Water Analysis, Patent No. PCT/AU2006001132 2005.
- (4.) Belkin, S.; Brenner, A.; Abeliovich, A., Effect of Inorganic Constituents on Chemical Oxygen Demand - II. Organic Carbon to Halogen Ratios Determine Halogen Interference, *Water Research*, **1992**, 26, 1583-1588.