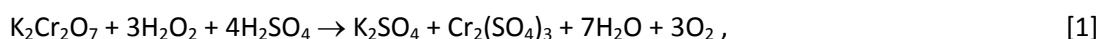


Peroxide Interference in the PeCOD[®] and Dichromate Methods for COD

A. BACKGROUND:

Some industrial cleaning processes, and some COD reduction processes in wastewater treatment, use the powerful oxidant Hydrogen Peroxide, H₂O₂. Residual H₂O₂ may persevere in the wastewater until the point where it is analysed for COD for regulatory compliance prior to discharge. Some users of the Dichromate method for COD measurement (COD_{Cr}) report that they have observed measurement interference when wastewater samples contain hydrogen peroxide (H₂O₂). These users have observed spuriously high COD_{Cr} COD readings associated with residual H₂O₂ in wastewater samples. In light of these reports Aqua Diagnostic has undertaken a brief study to quantify the extent to which residual H₂O₂ may interfere with both the conventional COD_{Cr} method, and with our new PeCOD[®] method, of COD measurement.

The scientific literature contains at least two articles directly addressing H₂O₂ interference in the COD_{Cr} method. Talinli and Anderson, (*Water Research* **26**, 1, 107-110, 1992), report a +25 % error in COD_{Cr} due to H₂O₂ interference; i.e., each 1 mg/L of H₂O₂ present contributes a spurious +0.25 mg/L to the COD_{Cr} reading. Kang, *et al.*, (*Water Research*, **33**, 5, 1247-1251, 1999), in a more thorough study, report a H₂O₂ interference rate of 45-50%. They further report that this rate of interference is in accord with the stoichiometry of the equation



in which each mg/L of H₂O₂ gives rise to a contribution of 0.47 mg/L to the COD_{Cr} reading through its reduction of Cr⁶⁺ to Cr³⁺. Equation [1] reflects that although H₂O₂ is normally a powerful *oxidant*, when it is in the presence of the even more powerful oxidant, the dichromate ion, Cr₂O₇²⁻, H₂O₂ behaves as a *reductant* and is itself oxidised, thereby contributing positively (and spuriously) to the COD_{Cr} reading.

B. AIM:

The present study aims to:

- confirm the rate of H₂O₂ interference reported in the literature, by running COD_{Cr} tests using both Hach LR (0-150 mg/L COD) and Hach HR (0-1500 mg/L COD) dichromate closed reflux vials, spiked with varying levels of H₂O₂;
- assess the rate of H₂O₂ interference in the PeCOD[®] method by analysing samples spiked with varying levels of H₂O₂.

C. RESULTS FOR COD_{Cr} LR (0-150 mg/L COD) VIALS:

Four standard solutions were prepared in duplicate as tabulated below and were analysed using Hach LR closed reflux vials to give the following COD_{Cr} results:

Sample Solution		COD _{Cr} LR Reading		
COD as sorbitol (mg/L)	H ₂ O ₂ (mg/L)	sample #1 (mg/L)	sample #2 (mg/L)	Mean (mg/L)
60	0	64	63	64
60	20	74	71	73
60	50	88	89	89
60	100	113	114	114

As illustrated in the results plotted in Figure 1 below, the H₂O₂ interference rate for the COD_{Cr} method when using LR vials is ~50 %, i.e. a spurious contribution to the COD_{Cr} reading of 0.5 mg/L COD for each 1 mg/L H₂O₂ present. This is in good agreement with the value reported by Kang, *et al.* (1999), 45-50%, and with the theoretical stoichiometric value, 47%.

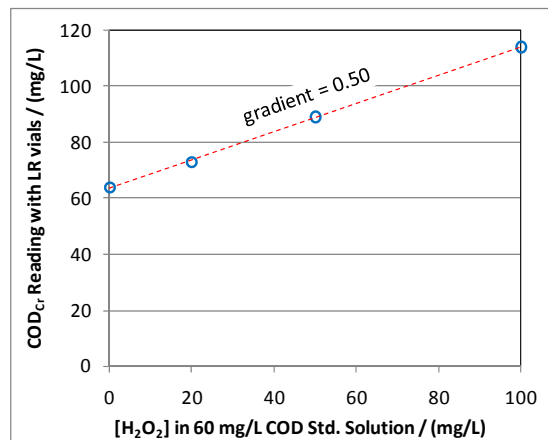


Figure 1. Interference in COD_{Cr} COD reading when using LR COD vials (0-150 mg/L COD) due to presence of H₂O₂.

D. RESULTS FOR COD_{Cr} HR (0-1500 mg/L COD) VIALS:

Four standard solutions were prepared in duplicate as tabulated below and were analysed using Hach HR closed reflux vials to give the following COD_{Cr} results:

Sample Solution		COD _{Cr} HR Reading		
COD as sorbitol (mg/L)	H ₂ O ₂ (mg/L)	sample #1 (mg/L)	sample #2 (mg/L)	Mean (mg/L)
600	0	602	603	603
600	20	682	669	676
600	50	826	790	808
600	100	1025	1014	1020

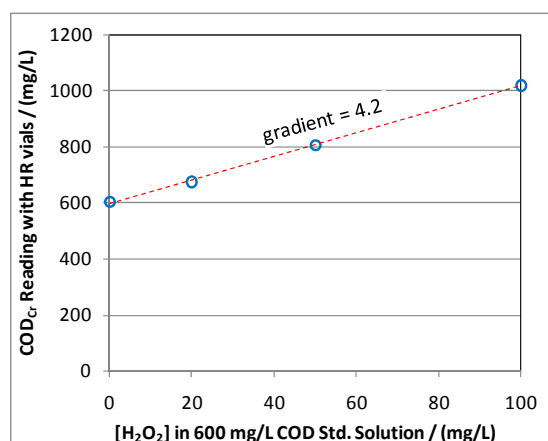


Figure 2. Interference in COD_{Cr} COD reading when using HR COD vials (0-1500 mg/L COD) due to presence of H₂O₂.

As illustrated in the results plotted in Figure 2 above, the H₂O₂ interference rate for the COD_{Cr} method when using HR vials is ~420 %, i.e. a spurious contribution to the COD_{Cr} reading of 4.2 mg/L COD for each 1 mg/L H₂O₂ present. This is an order of magnitude greater than the interference values so far reported in the literature, and confirmed by us for Hach LR vials. The difference between the Hach method for LR and HR vials lies mainly in the spectrophotometric determination of the change in the Cr⁶⁺/Cr³⁺ balance in the vial solution after 2 hrs at 150°C. For the LR vials, a UV absorbance peak at 420 nm is used to determine the concentration of Cr⁶⁺ remaining in the solution. For the HR vials, a UV absorbance peak at 620 nm is used to determine the concentration of Cr³⁺ produced. Possibly any residual H₂O₂ interferes with the 620 nm peak absorbance measurement, although it is hard to imagine that there is any residual H₂O₂. Alternatively, the H₂O₂ initially present may interfere with the HR vial reagents in a different way from how it does with the LR reagents. Again, the chemistry of such a process is not obvious. Nevertheless the large interference effect is real.

E. RESULTS FOR PeCOD[®] ANALYSIS:

The first result obtained when analysing COD/H₂O₂ solutions by PeCOD[®] was the observation that H₂O₂ will immediately oxidise the organics present, before there is a chance to present the sample to the instrument for analysis. H₂O₂ is of course a powerful oxidant. We can conclude that an industrial wastewater stream which contains H₂O₂ won't simultaneously contain organics that can be oxidised by it. There must, however, be organic species that cannot be oxidised by H₂O₂. We tested a number of compounds in an effort to identify one resistant to oxidation by H₂O₂ so that we could make up stable COD/H₂O₂ solutions for the PeCOD[®] interference tests.

From our tests, compounds which were *not* resistant to oxidation by H₂O₂ include: sorbitol, KHP, nicotinic acid, lactose, benzoic acid and benzene. Subsequently, having sought guidance from the literature, acetone has been identified as a compound which may be resistant to oxidation by H₂O₂. Any further assessment of H₂O₂ interference in PeCOD analysis should begin with acetone/H₂O₂ standard solutions, however this has not yet been done. Other, less volatile, ketones may also suit.

Having initially failed to find an organic compound resistant to H₂O₂ oxidation, we tested H₂O₂ interference in PeCOD[®] using simple H₂O₂/water/electrolyte solutions. The solutions and the results of their analysis in duplicate are tabulated below:

Sample solution	PeCOD [®] reading, Green range		
	analysis #1 (mg/L)	analysis #2 (mg/L)	Mean (mg/L)
0	1.7	2.4	2.1
40	7.4	6.6	7.0
100	11.4	11.0	11.2
200	17.5	17.4	17.5

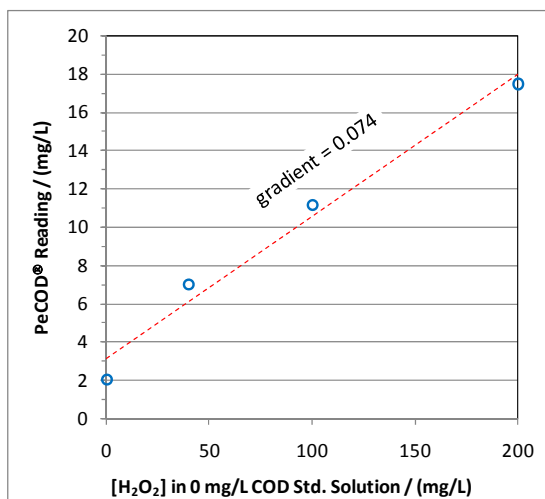


Figure 3. Interference in COD_{Cr} COD reading when using the PeCOD® method, due to presence of H₂O₂.

As illustrated in the results plotted above, the H₂O₂ interference rate for the PeCOD® method is approximately 8 %, i.e. a spurious contribution to the COD_{Cr} reading of 0.08 mg/L COD for each 1 mg/L H₂O₂ present. This is about 1/6th of the magnitude of the interference effect for COD_{Cr} LR vials and only 1/50th of the magnitude of the interference effect for COD_{Cr} HR vials.

CONCLUSION:

The degree of interference by hydrogen peroxide in COD analysis depends sensitively on the method used, and are given here for three such methods tested in our lab:

- COD_{Cr} with LR (0-150 mg/L COD) Hach vials: 45-50 % (in agreement with literature values)
- COD_{Cr} with HR (0-1500 mg/L COD) Hach vials: 420 %
- PeCOD®: 8 %

Aqua Diagnostic will update this report when we have run a similar set of PeCOD® tests on mixtures containing an organic species which is resistant to immediate oxidative attack by H₂O₂.