TECHNICAL BULLETIN

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Subject: Differences between PeCOD COD and Dichromate COD

Chemical Oxygen Demand (COD) results may differ when measured via the PeCOD® COD method versus the traditional dichromate COD method for certain sample matrices. There are various reasons for this difference, outlined below.

Reasons why PeCOD may measure LOWER than dichromate:

1. **Solids** - PeCOD does not measure solids. Samples should be filtered/settled prior to analyzing dichromate in order to obtain a true correlation between soluble COD results. Filter can be up to 50um pore size.

2. **Insoluble Organics** (even if not visible) - may be particles that do not completely settle out or pass through a filter. If not fully dissolved, PeCOD may not measure.

3. **Large macromolecules present in sample** - some large compounds, even if not visible, may not be fully measured by PeCOD. These may include cellulose, protein, fat, yeasts, etc. These are long-chain compounds that UV light and titanium dioxide alone cannot break down and/or solubilize to make available for oxidation in a 10 minute test. Dichromate has the help of concentrated acid, catalysts, high heat and time to do this.

4. **Sample pH** - Samples should be close to neutral when analyzing via PeCOD. At minimum the sample should be within pH 4-10, but ideal between 7-9. If samples have been preserved in acid, they should be neutralized prior to analysis to avoid a low reading (as well as damage to the sensor).

5. **Interferences** - chloride may suppress a PeCOD reading while inflating a dichromate reading. High concentrations of ammonia, or the presence of ferrous iron, silver, chromate or other heavy metals can cause a low PeCOD reading. This can be confirmed with multiple pre-dilutions and checking for recovery.

6. **Peroxide** - greatly inflates dichromate COD readings while it does not interfere with PeCOD measurements. Note that certain wastewater treatment procedures may introduce interferences, eg. chlorination, nitrification, and even hydrogen peroxide is sometimes used.

7. **Sampling** - representative sampling is important, especially for samples with high TSS/solids present.

8. **Time Delays** - it is best to analyze samples via PeCOD and dichromate on the same day to limit uncertainties due to sample degradation.

9. **Method differences with respect to theoretical COD** - the theoretical COD of any organic compound can be calculated, but the true recovery will not always be 100%. COD is not measuring a specific compound and is therefore not an exact science. Different organics will recover to different degrees for different measurement techniques. While PeCOD usually recovers the difficult organics more efficiently than dichromate, there may be some that are underestimated by PeCOD or overestimated by dichromate.

10. **Inaccuracies in technique/method limitations** - dichromate has high uncertaintly levels, especially when there is chloride present and/or you are looking at low CODs. Published methods often report high RSDs for the dichromate method. The detection limit for dichromate is also cited at 50ppm. With PeCOD, it is important to ensure that the correct range is selected for the COD concentration being measured to ensure measurements are within detection limits.

11. **PeCOD/sensor is not fully hydrated** – Ensure that at least 2 calibrations are run before analyzing samples and that the Iterm is within specified values.

Reasons why PeCOD may measure HIGHER than dichromate:

1. **Titanium Dioxide** (See #9 Above) – TiO_2 has an oxidation potential of ~3.2V while dichromate is only 1.6V. This means that TiO_2 is a stronger oxidant and often times will oxidize difficult organics more efficiently than dichromate. As discussed above, PeCOD may also overestimate some organics as well. PeCOD reads many aromatics and some carboxylic acids falsely high, plus dichromate reads some carboxylic acids low. This may contribute to some of the higher readings on PeCOD.

2. **Interferences** - sulfide and sulfite are positive interferences for PeCOD, causing high readings.

3. **Sampling** - See #7 above.

4. **Time Delays** - See #8 above.