

CHEMICAL OXYGEN DEMAND (COD)
EPA Method 410.4 (Colorimetric, Automated; Manual)

Table 1. Summary of Contract Required Detection Limits, Holding Times, and Preservation for Chemical Oxygen Demand (COD)

Analytical Parameter	Contract Required Detection Limit (CRDL)	Technical and Contract Holding Times	Preservation
Chemical Oxygen Demand (COD)	5.0 mg/L	Technical: 28 days from collection; Contract: 26 days from receipt at laboratory	H ₂ SO ₄ to pH <2, Cool to 4EC ±2EC

Homogenize samples, as necessary, to obtain aliquots of representative suspended solids. Qualify results where suspended solids content may affect accuracy.

If samples display a blue-green color after digestion, the quantity of reagents necessary for digestion has been exceeded. Dilute and redigest samples displaying this characteristic.

Data Calculations and Reporting Units:

Calculate the sample results according to Section 8 of EPA Method 410.4.

Report sample results in concentration units of milligram per liter (mg/L) of COD. Report COD concentrations that are less than 10 mg/L to 2 significant figures, and COD concentrations that are greater than or equal to 10 mg/L to 3 significant figures.

For rounding results, adhere to the following rules:

- a) If the number following those to be retained is less than 5, round down;
- b) If the number following those to be retained is greater than 5, round up; or
- c) If the number following the last digit to be retained is equal to 5, round down if the digit is even, or round up if the digit is odd.

All records of analysis and calculations must be legible and sufficient to recalculate all sample concentrations and QC results. Include an example calculation in the data package.

Table 2. Summary of Calibration Procedures for Chemical Oxygen Demand (COD) by EPA Method 410.4

Calibration Element	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration (minimum blank + 5 points) (ICAL) ^a	Daily	$r \geq 0.995$	<ol style="list-style-type: none"> 1. Terminate analysis 2. Recalibrate and verify before sample analysis
Initial Calibration Verification (ICV) (Separate source from ICAL standards)	Daily, prior to sample analysis, immediately following ICAL	$\pm 10\%$ from expected concentration	<ol style="list-style-type: none"> 1. Reprep ICV and, reanalyze all associated samples 2. Identify and document problem 3. Recalibrate and reanalyze reprepared ICV and all associated samples, if necessary
Continuing Calibration Verification (CCV)	Before sample analysis; after every 10 samples and end of run	$\pm 10\%$ from expected concentration	<ol style="list-style-type: none"> 1. Recalibrate and verify 2. Reanalyze samples back to last good CCV
Calibration Blank Verification (ICB, CCB)	After ICV and CCVs	$< \text{CRDL}$	<ol style="list-style-type: none"> 1. Terminate analysis 2. Identify and document the problem 3. Recalibrate, verify and reanalyze all associated samples
CRDL Verification Standard ($< 2X \text{ CRDL}$)	After initial CCV	$\pm 20\%$ from expected concentration	<ol style="list-style-type: none"> 1. Reprep and reanalyze standard 2. Recalibrate and verify

^a ICAL range 3 to 900 mg/L.

Dilute and reanalyze samples with COD concentrations exceeding the range of the calibration curve. Results for such reanalyses should fall within the mid-range of the calibration curve. Report results and submit documentation for both analyses.

Table 3. Summary of Internal Quality Control Procedures for Chemical Oxygen Demand (COD) by EPA 410.4

QC Element	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB) ^a	One per Batch or SDG ^b (1 per 20 samples minimum)	< CRDL	<ol style="list-style-type: none"> 1. If lowest sample concentration is more than 10X the blank conc., no action 2. If samples are non-detected, no action 3. If detected sample concentrations are less than 10X blank conc., all associated samples must be prepared again with another method blank and reanalyzed
Duplicate Sample (DUP)	One per batch or SDG (1 per 20 samples minimum)	RPD <20% for samples >5X CRDL; ± CRDL for samples <5X CRDL	<ol style="list-style-type: none"> 1. Flag associated data with an "*"
Matrix Spike (MS) ^d	One per batch or SDG (1 per 20 samples minimum)	± 15% from expected value ^c	<ol style="list-style-type: none"> 1. Flag associated data with an "N"
One Set of Demand Reference Samples (2 conc. levels)	One set per batch or SDG (1 per 20 samples minimum)	± 15% from expected concentration	<ol style="list-style-type: none"> 1. Terminate analysis 2. Identify and document the problem 3. Reanalyze all associated samples

^a The LCS and MB must be treated identically to the samples.

^b SDG - Sample Delivery Group - each case of field samples received; or each 20 field samples within a case; or each 14 calendar day period during which field samples in a case are received.

^c An exception to this rule is granted in situations where the sample concentration exceeds the spike

concentration by a factor of 4. In such an event, the data shall be reported unflagged.

^d Use potassium hydrogen phthalate (KHP) as a matrix spike compound.