

En Chem, Inc.

Quality Assurance Document

SET No: 1

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WCM-40
REVISION NO. 4
APRIL 2000
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ANALYTICAL METHOD

TITLE: Chemical Oxygen Demand, Colorimetric, Manual (Vial-Mid)
DEPARTMENT: Inorganic - Wet Chemistry
APPLICATION: Surface and Ground Waters, Domestic and Industrial Wastes
REFERENCE: EPA manual 600 4-79-020, March 1983, Method 410.4.

PROCEDURE SUMMARY:

Blanks and standards are sealed in tubes that are heated in an oven in the presence of dichromate at 150°C. After two hours, the tubes are removed, cooled and measured spectrophotometrically at 600 nm.

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SAMPLE HANDLING AND PRESERVATION:

Samples are collected in glass bottles and preserved with H₂SO₄ to a pH of 2 and cooled to 4° C.
Holding Time = 28 days.

INTERFERENCES:

Chlorides are quantitatively oxidized by dichromate and represent a positive interference. Mercuric sulfate is added to the digestion tubes to complex the chlorides.

APPARATUS AND MATERIALS:

10 mL sealed OIC standard level ampules which contain all reagents for the test
Mechanical ampule sealer capable of providing strong consistent seals
Oven capable of maintaining 150°C ± 2° C
Hach Spectrophotometer DR2000
Volumetric flasks: 50 mL, 1000 mL
Adjustable pipettor
Wire racks
Insulated gloves

REAGENTS:

Deionized (D.I.) water
Potassium acid phthalate

Prepare COD Stock Standard, 1.0 mg/L

Add 0.8503 grams of potassium acid phthalate to a 1 liter volumetric flask and dilute to the mark. (Shelf life = 1 year).

Prepare Calibration Standards

Prepare a series of standards using the stock standard as follows:

Milliliters of COD Solution	Standard Concentration when Diluted in 50 mL Volumetric Flasks
<u>1 mL = 1.0 mg COD</u>	<u>mg COD/liter</u>
0.00	0.0
1.00	20.0
3.00	60.0
5.00	100
10.0	200
25.0	500
45.0	900

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Optimum concentration: 40-900 mg/L
Reporting Limit: EQL = 50 mg/L

PROCEDURE:

1. Unseal the OIC ampules.
2. Carefully pipet 2.5 mL sample using a calibrated adjustable pipettor into each ampule such that it forms a layer on top of the reagents contained in the ampule.

NOTE: Samples containing particulates should be roughly homogenized and milled in a blender or similar device before adding the sample to the ampule.

3. Carefully seal the ampule. It is recommended that a mechanical ampule sealer be used which is designed to form a strong, consistent seal. During digestion, the reagents and sample are raised to a point just below boiling. Improperly sealed ampules may leak or break. Ampules should be checked for leakage by running top of ampule over paper towels.

4. Thoroughly mix the contents of the sealed ampule by shaking.

CAUTION: The ampule will get very hot during mixing. It is recommended that ampules be mixed either in racks or with the use of insulated gloves. Eye protection MUST be worn.

5. Place the ampule in the oven at $150^{\circ}\text{C} \pm 2^{\circ}\text{C}$ for 2 hours.
6. Invert ampule once to mix contents after removing from oven and allow to cool to room temperature. If rapid cooling is desired, the ampules may be placed in a water bath. If, however, certain samples form crystals, discontinue the rapid cooling and allow these samples to cool slowly in the room air.
7. Allow any suspended precipitate to settle for 10 minutes.
8. Set up the Hach DR2000 spectrophotometer. The 150 mg/L standard should be used as a procedural blank to zero the spectrophotometer. After zeroing, use the remaining standards to prepare a procedural curve. Read the absorbance of each ampule on the spectrophotometer at 600 nm wavelength. By use of the standard curve, the absorbance is converted graphically into mg/L\COD.

Quality Control

Correlation Coefficient (r-value)

The correlation coefficient, the measure of linearity of a standard curve, must be 0.995 or greater. If the value is less than 0.995 recalibrate the instrument.

Initial Calibration Verification (ICV)

The ICV must be analyzed immediately after calibration and meet the rejection criteria of $\pm 10\%$ of the true value. Recalibrate if the ICV fails. The concentration of the ICV should be near the mid-point of the calibration curve. Use 500 mg/L made from a different source than the calibration standards (25mL to 50mL volumetric).

Initial Calibration Blank (ICB)

The ICB must be analyzed after the ICV. The absolute value must be $\leq \text{EQL}$. Recalibrate if it fails.

Continuing Calibration Verification (CCV)

The CCV is analyzed after every 10 samples. Rejection criteria is $\pm 10\%$ of true value. If the CCV fails, the problem must be corrected and the previous 10 samples between the CCV and last CCB must be reanalyzed. Concentration of the CCV should be near the mid-point of the calibration curve.

Continuing Calibration Blank (CCB)

The CCB is analyzed after every CCV. The absolute value must be $\leq \text{EQL}$. If the CCB fails, the problem must be corrected and the previous 10 samples between the last CCB and the CCV must be reanalyzed.

Laboratory Control Sample (LCS)

The LCS is carried through all preparation procedures (approx. 500 mg/L), and analyzed for each matrix type with a frequency of 5%. See current QC Charts for control ranges. In cases where the LCS is outside of acceptable ranges all samples prepared in that batch must be reprepared and reanalyzed.

Method Blank (MB)

A MB is carried through all prep procedures and analyzed with a frequency of 5%. Rejection criteria is $< \text{LOD}$. Other criteria may apply, such as regulatory limit and the analyte concentration in the samples.

ACCURACY

One matrix spike and matrix spike duplicate are analyzed for each group of samples that are similar in matrix at a frequency of 5%. Both QC samples must be calculated for accuracy. See current QC charts for control range.

$$\text{Spike Percent Recovery} = \frac{\text{SSR} - \text{SR}}{\text{SA}}$$

SSR = Spike Sample Result

SR = Sample Result

SA = Spike Added

If both spike recoveries are outside of the specified control limit, the corresponding parent sample is to be post-spiked and the reported result shall be flagged with a [N] qualifier. The control limits for a post-spike are 75-125%. If the post-spike recovery is out-of-control, dilute the corresponding sample and perform a post-spike on the diluted aliquot of sample. Dilute appropriately until an acceptable recovery is obtained. If only the matrix spike OR the matrix

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spike duplicate are out of control for accuracy, then the corresponding parent sample is flagged with a [MS qualifier.

If the analyte of interest is greater than the linear range, dilute appropriately and post-spike the sample; however, a [N qualifier is not required. Also, if the analyte of interest is greater than 4x the level of the spike concentration, accuracy calculations are not necessary. Spike with 1.0 mL 300ppm standard and 1.5 mL of sample.

Calculation:
$$\frac{(2.5) (\text{spike value}) - (1.5) (\text{sample value})}{200\text{ppm}}$$

If there is insufficient sample volume to perform a matrix spike and a matrix spike duplicate a LCS and an LCS DUP must be used in its place.

PRECISION

Matrix spike duplicate samples are analyzed 1 per batch or at a frequency of 5%, for samples that are similar in matrix.

For matrix spike duplicate samples, relative percent difference (RPD) is used to calculate compliance. See current QC charts for control limits.

Calculation:

$$\text{RPD} = \frac{\text{MS} - \text{MSD}}{(\text{MS} + \text{MSD})/2} \times 100$$

MS = Method Spike Value
MSD = Method Spike Duplicate Value

If the RPD is outside of the acceptable control limits, the reported sample result is to be qualified with an [* flag.

Sample Result Calculations:

Aqueous Sample Calculation:

Enter the standard curve into a calculator with linear regression program. Enter the absorbance of the samples to obtain the total mg of sample.

$$\text{COD mg/L} = \frac{2.5}{A} \times B \times C$$

Where:
A = mL sample used
B = dilution factor, if any
C = mg COD from Standard Curve

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SAFETY:

The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Laboratory staff should observe all safety procedures as outlined in the Laboratory Health and Safety Manual. Staff should consult Materials Safety Data Sheets (MSDS) for information on specific chemicals.

POLLUTION PREVENTION and WASTE MANAGEMENT:

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Laboratory staff should order and prepare only those quantities of reagents that will be used prior to the expiration date. Other appropriate measures to minimize waste generation should be brought to the attention of laboratory management. All laboratory waste shall be handled as directed by the Laboratory Waste Management Plan and Hazardous Waste Contingency Plan.