

Chemical Oxygen Demand

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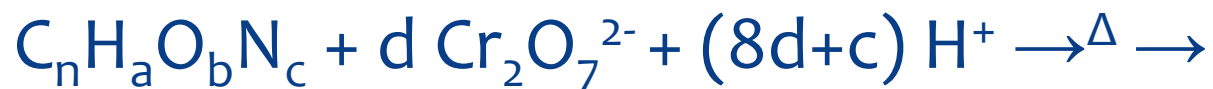
Used to measure the organic strength of wastewaters

Same principle as BOD but different execution.

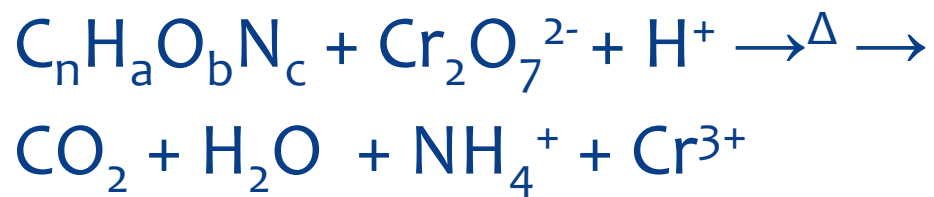
Rather than biologically decompose/oxidize organic waste, we chemically decompose/oxidize organic waste.

It all begins with...

...a balanced equation!

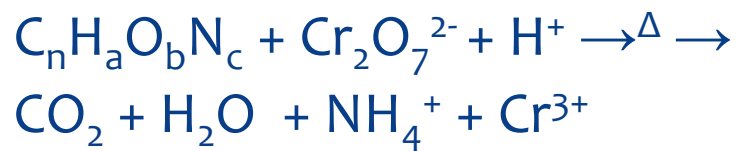


Ignore the stoichiometry for the moment



Notice the similarities!

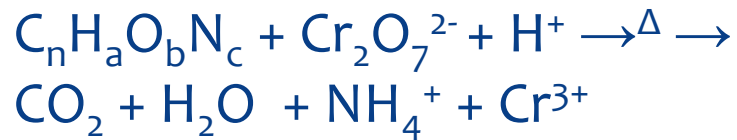
The differences



NH_4^+ instead of NH_3 . Why?

It's in acid. NH_3 is a base. In acid, it gets protonated.

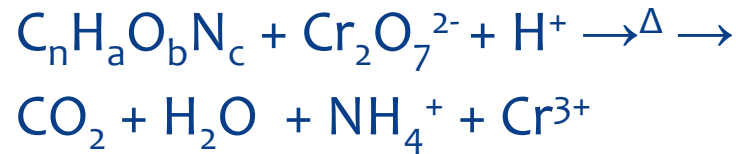
The differences



$\text{Cr}_2\text{O}_7^{2-}$ and acid with heat instead of bacteria and oxygen in a warm, dark place.

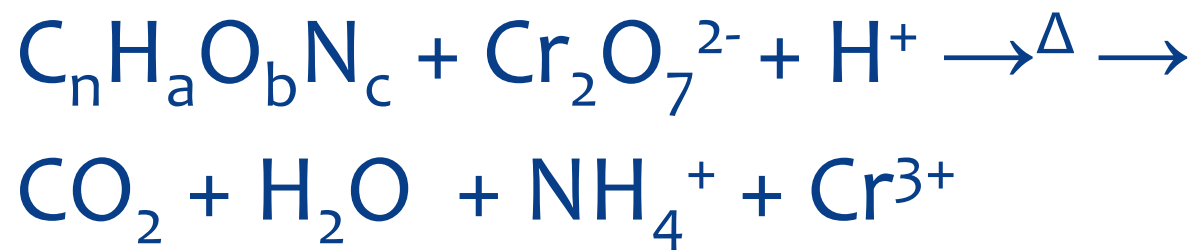
Other than that, they are really the identical process.

The differences



In COD test, for example, both glucose and lignin is oxidized.
Therefore, COD > BOD

Where's the O in equation?

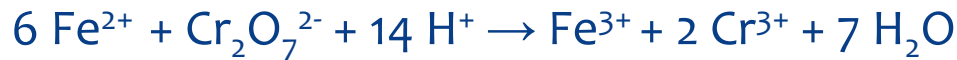


It's in the dichromate ($\text{Cr}_2\text{O}_7^{2-}$).

COD errors

The most common COD errors are due to oxidation of inorganic species.

Dichromate is a powerful oxidant – it will oxidize not only almost all organics but many metals and non-metal ions:



INORGANIC INTERFERENCES

- Chloride Interference



- Prevention:



- Nitrite Interference:

- Nitrite is oxidized to nitrate and this interference can be overcome by the addition of sulfamic acid to the dichromate solution. However, significant amounts of nitrite seldom occur in wastes or in natural waters. This also holds true for other possible interferences such as ferrous iron and sulfides.

COD

- * Disadvantages:

- * Do not differentiate between the biologically oxidizable and inert substances
- * Do not indicate the rate of reaction

- * Advantages:

- * Short time required for evaluation

COD vs. BOD

They purport to measure the same thing – but they will never agree.

Biggest error in BOD?

BOD tends to err on the low side due to humus (“inedible” organic waste).

Biggest error in COD?

COD tends to err on the high side due to oxidation of inorganic species.

Using COD

COD is again a relative measure: higher COD = dirtier water.

COD can be used with BOD – they are not a replacement for each other.

History of COD test

- * Oxidants used
 - * Permanganate
 - * Oxidation highly variable wrt various compounds
 - * Oxygen consumed values are always less than BOD₅
 - * Ceric sulfate
 - * Potassium iodide
 - * **Potassium dichromate**
 - * **Capable of oxidizing a wide variety of org. Matter**
 - * **Solution must be acidic**
 - * **Elevated temperature**

**TABLE 2.
Major Oxidants Other than $K_2Cr_2O_7$ and $Mn_2(SO_4)_3$ Used in COD Determinations**

Oxidant	Advantages	Disadvantages
$KMnO_4$	<ul style="list-style-type: none"> • Stable for several months, MnO_2 must be excluded • Is used in acidic, neutral and basic media • Manganese is a non-hazardous metal 	<ul style="list-style-type: none"> • Relatively slow-acting and is not quantitative • Results may depend upon sample size • Does not oxidize volatile acids or amino acids • Incomplete oxidation of many organic compounds • Unstable in solution: Forms MnO_2 precipitate which catalyzes reagent decomposition.
$Ce(SO_4)_2$	<ul style="list-style-type: none"> • More complete oxidation of organic compounds than $KMnO_4$ • More stable than $KMnO_4$ 	<ul style="list-style-type: none"> • Incomplete oxidation of many organic compounds • Poor reproducibility • Photometric measurement at 320 nm where incompletely oxidized organic compounds interfere • Relatively expensive
$K_2S_2O_8$	<ul style="list-style-type: none"> • Oxidizes many organic nitrogen-containing compounds more completely than other oxidants • Widely used with TOC instrumentation 	<ul style="list-style-type: none"> • Requires elaborate equipment • More labor intensive • Relatively unstable
KIO_3	<ul style="list-style-type: none"> • Strong oxidant 	<ul style="list-style-type: none"> • Difficult to use • Questionable accuracy
O_2	<ul style="list-style-type: none"> • Oxygen consumption measured directly 	<ul style="list-style-type: none"> • Elaborate equipment required

The oxidants described in Table 2 have a number of limitations which are eliminated when $K_2Cr_2O_7$ are used as an oxidant.

Potassium dichromate limitations

- * Low molecular weight fatty acids are not oxidized unless a catalyst is present
 - * Silver catalyst
- * Aromatic hydrocarbons and pyridine are not oxidized at all

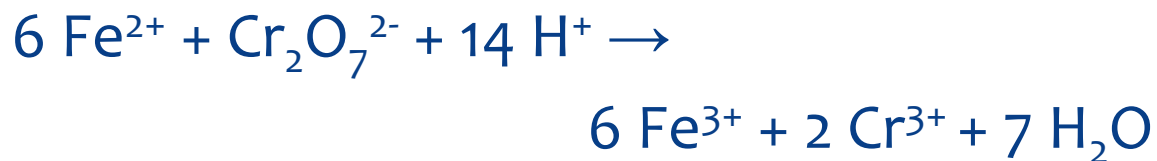
How to test for COD...

How would you test for COD?

You need to monitor either the disappearance of dichromate or the appearance of Cr^{3+}

Excess dichromate

Dichromate can be reduced inorganically to Cr^{3+} using Fe^{2+}



To Conduct the test:

Take x mL of the waste water sample to be tested. Add an equal amount of $\text{K}_2\text{Cr}_2\text{O}_7$ solution to the sample and a sample of distilled water (the blank).

After digestion, you titrate both the blank and the waste water sample with an $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ standard solution.

The difference between the 2 titrations is the amount of $\text{Cr}_2\text{O}_7^{2-}$ used in the digestion.

Sample COD problem

A 50 mL waste water sample is collected. 10 mL of 0.25 N $\text{K}_2\text{Cr}_2\text{O}_7$ is added to the water sample and to 50 mL of distilled water. Both samples are heated to 150°C for 2 hours. The samples are allowed to cool for 10 minutes and then titrated with 0.1015 N iron (II) ammonium sulfate. The waste water sample requires 15.36 mL of titrant, while the blank sample requires 23.65 mL to reach a 1,10 phenanthroline endpoint. What is the COD of the waste water sample?

Let's break it down:

A 50 mL waste water sample is collected. 10 mL of 0.25 N $K_2Cr_2O_7$ is added to the water sample and to 50 mL of distilled water. Both samples are heated to 150°C for 2 hours. The samples are allowed to cool for 10 minutes and then titrated with 0.1015 N iron (II) ammonium sulfate. The waste water sample requires 15.36 mL of titrant, while the blank sample requires 23.65 mL to reach a 1,10 phenanthroline endpoint. What is the COD of the waste water sample?

What's going on?

You add dichromate to distilled water AND to your water sample.

What does dichromate do in distilled water?

NOTHING! There's nothing for it to oxidize.

Let's break it down:

A 50 mL waste water sample is collected. 10 mL of 0.25 N $K_2Cr_2O_7$ is added to the water sample and to 50 mL of distilled water. **Both samples are heated to 150°C for 2 hours.** The samples are allowed to cool for 10 minutes and then titrated with 0.1015 N iron (II) ammonium sulfate. The waste water sample requires 15.36 mL of titrant, while the blank sample requires 23.65 mL to reach a 1,10 phenanthroline endpoint. What is the COD of the waste water sample?

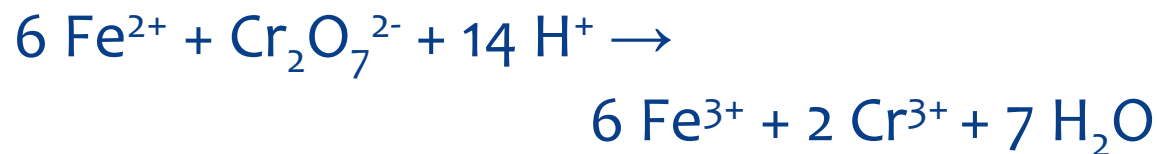
What's going on?

The dichromate is being allowed to react. It is oxidizing organic material!!!

Let's break it down:

A 50 mL waste water sample is collected. 10 mL of 0.25 N $K_2Cr_2O_7$ is added to the water sample and to 50 mL of distilled water. Both samples are heated to $150^\circ C$ for 2 hours. **The samples are allowed to cool for 10 minutes and then titrated with 0.1015 N iron (II) ammonium sulfate.** The waste water sample requires 15.36 mL of titrant, while the blank sample requires 23.65 mL to reach a 1,10 phenanthroline endpoint. What is the COD of the waste water sample?

You can't avoid the stoichiometry



The titration reaction has 6:1 stoichiometry of the Fe^{2+} titrant to the $\text{Cr}_2\text{O}_7^{2-}$.

Titrating the solutions with Fe^{2+} is telling us how much dichromate is left over!

Let's break it down:

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We have different amounts of dichromate in the 2 different samples, does this make sense?

Yes, we reduced some dichromate in the “dirty” sample while the distilled water should have all the dichromate it started with!

The difference between the two samples is the amount of dichromate reduced and, therefore, the amount of organic material oxidized!

Normality

You can express solution concentrations (like the Fe^{2+}) in “normality” instead of “molarity”.

Do we remember what “normality” is?

Normality = $\frac{\text{equivalent moles of solute}}{\text{L solution}}$

Using Normality

$$N_1 V_1 = N_2 V_2$$

$$N_{\text{Cr}} V_{\text{Cr}} = N_{\text{Fe}} V_{\text{Fe}}$$

$$N_{\text{Cr}} * 50 \text{ mL} = 0.1015 \text{ N} * 15.36 \text{ mL}$$

$$N_{\text{Cr}} = 3.12 \times 10^{-2} \text{ N } \text{Cr}_2\text{O}_7^{2-}$$

For the reference water:

$$N_1 V_1 = N_2 V_2$$

$$N_{\text{Cr}} V_{\text{Cr}} = N_{\text{Fe}} V_{\text{Fe}}$$

$$N_{\text{Cr}} * 50 \text{ mL} = 0.1015 \text{ N} * 23.65 \text{ mL}$$

$$N_{\text{Cr}} = 4.80 \times 10^{-2} \text{ N Cr}_2\text{O}_7^{2-}$$

What does this mean?

Pure water:

$$N_{\text{Cr}} = 4.80 \times 10^{-2} \text{ N Cr}_2\text{O}_7^{2-}$$

“Dirty” water:

$$N_{\text{Cr}} = 3.12 \times 10^{-2} \text{ N Cr}_2\text{O}_7^{2-}$$

The difference between the two is the amount reduced! Since the volume is the same, you can just subtract:

$$4.80 \times 10^{-2} \text{ N} - 3.12 \times 10^{-2} \text{ N} = 1.68 \times 10^{-2} \text{ N Cr}_2\text{O}_7^{2-} \text{ reduced}$$

Still no “O”

We could express the impurity based strictly on the dichromate used: the more dichromate required, the more organic material that must have been there.

Equivalent oxygen

Instead of reporting the dichromate used, the dichromate is converted into equivalent amount of oxygen, as if you were again “burning” the organic waste as in the BOD process:



(unbalanced)

It's a redox reaction

An equivalent is...

...an electron

How many electrons does O_2 transfer?

FOUR! $O_2 \rightarrow 2 O^{2-}$

So, the “equivalent mass of oxygen” is...

... 8 g/mol $\left[\frac{32 \text{ g } O_2}{\text{mol } O_2} * \frac{1 \text{ mol } O_2}{4 \text{ equiv moles}} \right]$

Convert Normality $\text{Cr}_2\text{O}_7^{2-}$ to $\text{g O}_2/\text{L}$

$$1.68 \times 10^{-2} \text{ N } \text{Cr}_2\text{O}_7^{2-} \text{ reduced} = 1.68 \times 10^{-2} \text{ N } \text{O}_2$$

Normality is always 1:1 stoichiometry

$$\frac{1.68 \times 10^{-2} \text{ equiv moles } \text{O}_2}{\text{L solution}} * \frac{8 \text{ g } \text{O}_2}{\text{equiv mole } \text{O}_2} * \frac{1000 \text{ mg}}{1 \text{ g}} =$$

$$= 134 \text{ mg } \text{O}_2 / \text{L}$$

This is the COD of the original sample.

COD BY DICHROMATE

- Selection of Normality of Dichromate Solution:
- COD is reported in terms of milligrams of oxygen per liter.
- Equivalent weight of oxygen is 8 g. Then,
- **1ml of 1N dichromate = 8 mg oxygen**
- If 1 ml of dichromate is set to 1 mg of oxygen,
- *Then, divide both sides by 8:*
- *N/8 or 0.125 N solution of oxidizing agent (dichromate) should be used.*

The Formula in the Book

You could calculate the COD using the scheme I just outlined. Your book reduces this to a single formula that is often usable:

$$\text{COD (mg/L)} = \frac{8000 (\text{mL blank} - \text{mL sample}) [\text{Fe}^{2+}]}{\text{mL sample}}$$

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A 50 mL waste water sample is collected. 10 mL of 0.25 N $K_2Cr_2O_7$ is added to the water sample and 50 mL of distilled water. Both samples are heated to $150^\circ C$ for 2 hours. The samples are allowed to cool for 10 minutes and then titrated with 0.1015 N iron (II) ammonium sulfate. The waste water sample requires 15.36 mL of titrant, while the blank sample requires 23.65 mL to reach a 1,10 phenanthroline endpoint. What is the COD of the waste water sample?

$$\text{COD (mg/L)} = \frac{8000 (\text{mL blank} - \text{mL sample}) [\text{Fe}^{2+}]}{\text{mL sample}}$$

$$\text{COD (mg/L)} = \frac{8000 (23.65 - 15.36 \text{ mL}) [0.1015 \text{ M}]}{50 \text{ mL}}$$

$$\text{COD} = 135 \text{ mg/L}$$