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Organic Chemical Properties of Water

Main element of organic compounds is carbon. Although the organic matter can be divided into various groups such as proteins, lipids, carbohydrates, and tests exist to determine the concentrations of the various compounds, it is usually sufficient to consider only the overall concentration of the organic content. Tests include the BOD, COD and TOC.

Biochemical Oxygen Demand (BOD)

The BOD_5 is the amount of dissolved oxygen used by micro-organisms as they break down material at 20^0C over a five day period. It measures the readily biodegradable organic carbon. Clean waters have BOD_5 values of <1mg/l. Rivers are considered polluted if BOD_5 >5mg/l.

The BOD_5 is set at 5 days and may not be long enough to determine the BOD ultimate which is set arbitrarily at 20 days. The BOD of municipal wastewater ranges from about 150mg/l to 1,000mg/l while for industrial wastewater (food industries) the value may be several thousand.

Chemical Oxygen Demand (COD)

This test determines the amount of oxygen needed to chemically oxidise the organics. A strong chemical oxidising agent is used rather than using micro-organisms as in the BOD test. This oxidising agent is potassium dichromate in an acid solution. COD is attractive since is takes about two hours only.

Total Organic Carbon (TOC)

The TOC test measures all carbon as CO_2 in mg/l and, therefore, the inorganic carbon (HCO_3, CO_2, CO_3) must be removed prior to the test. The TOC is a simple instrumental test and there are many analysers available commercially.

The Periodic Table

Group → / Period ↓	1	2	3		4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc		22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y		40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	* *	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
				*	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
				* *	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

Theoretical Relationship between TOC and COD

The TOC measures the mass of carbon per litre of water whilst the COD measures the mass of oxygen for chemical oxidation. For the breakdown of glucose:

$$C_6H_{12}O_6 + 6O_2 \leftrightarrows 6CO_2 + 6H_2O$$

$C_6H_{12}O_6$	$6O_2$	$6CO_2$
(C) 12 x 6 = 72 (H) 1 x 12 = 12 (O) 16 x 6 = 96 72 + 12 + 96 = 180	(O) 32 x 6 = 192	(C) 12 x 6 = 72

COD = 192
TOC = 72

Example:

A wastewater is analysed and is shown to contain 100mg/l of ethylene glycol ($C_2H_6O_2$) and 120 mg/l of phenol (C_6H_6O). Determine the COD and TOC.

Ethylene glycol

$$2C_2H_6O_2 + 5O_2 = 4CO_2 + 6H_2O$$

$2C_2H_6O_2$	$5O_2$	$4CO_2$
(C) 24 x 2 = 48 (H) 6 x 2 = 12 (O) 32 x 2 = 64 48 + 12 + 64 = 124	(O) 32 x 5 = 160	(C) 12 x 4 = 48

$$COD = \frac{160}{124} \times 100\ \frac{mg}{l} = 129.03\ \frac{mg}{l}$$

$$TOC = \frac{48}{124} \times 100\ \frac{mg}{l} = 38.71\ \frac{mg}{l}$$

Phenol

C_6H_6O	+	$7O_2$	=	$6CO_2$	+	$3H_2O$
(C) 13 x 6 = 72 (H) 1 x 6 = 6 (O) 16 x 1 = 16 72 + 6 + 16 = 94		(O) 32 x 7 = 224		(C) 12 x 6 = 72		

$$COD = \frac{224}{94} \times 120\ \frac{mg}{l} = 285.96\ \frac{mg}{l}$$

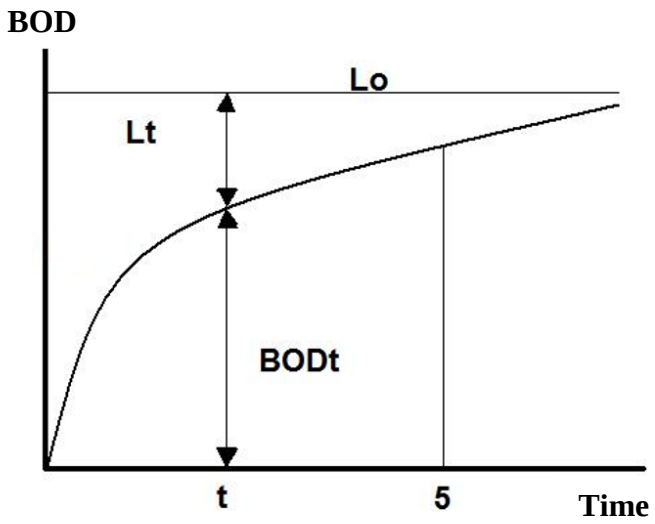
$$TOC = \frac{72}{94} \times 120\ \frac{mg}{l} = 91.91\ \frac{mg}{l}$$

So the Totals;

COD = 129.03 + 285.96 = **414.99 mg/l**
TOC = 38.71 + 91.91 = **130.62 mg/l**

Past and Future Oxygen Demand

As stated the BOD test measures the oxygen already consumed by bacteria whilst oxidising organic matter under aerobic conditions. BOD for a particular time period can, therefore, be considered to be the amount of oxygen consumed by the bacteria up to that particular time. At any time the amount of organic matter remaining has a future oxygen demand (Lt) which may be considered to be a 'future BOD' demand.



It may be proved that;

$$\boldsymbol{BOD_5 = BOD_{ult}\left(1 - e^{-k_1 t}\right)}$$

Where;

BOD_{ult} is the ultimate BOD demand

k_1 is the deoxygenation rate coefficient

Example:

If a wastewater has a deoxygenation rate coefficient of 0.15/day, determine the ultimate BOD if the 5 day BOD is 615mg/l. Determine the BOD_2 and BOD_{10} values.

$$\boldsymbol{BOD_5 = BOD_{ult}\left(1 - e^{-k_1 t}\right)}$$

Therefore;

1. BOD_{ult}

$$BOD_{ult} = \frac{BOD_5}{(1 - e^{-k_1 t})} = \frac{615}{(1 - e^{-0.15\times5})} = \frac{615}{(1 - e^{-0.75})} = \frac{615}{0.528} = 1165$$

$$\boldsymbol{BOD_{ult} = 1165\ \frac{mg}{l}}$$

2. BOD_2

$$BOD_2 = BOD_{ult}\left(1 - e^{-k_1\times2}\right)$$

$$BOD_2 = 1165(1 - e^{-0.15\times2}) = 1165(0.259) = 302$$

$$\boldsymbol{BOD_2 = 302\ \frac{mg}{l}}$$

3. BOD_{10}

$$BOD_{10} = BOD_{ult}\left(1 - e^{-k_1\times10}\right)$$

$$BOD_{10} = 1165(1 - e^{-0.15\times10}) = 1165(0.777) = 905$$

$$\boldsymbol{BOD_{10} = 905\ \frac{mg}{l}}$$

Determination of BOD

The traditional BOD test is conducted in standard 300 ml bottles. The test for the 5 day BOD of a water sample involves taking two DO measurements when the test begins at time t = 0 and a second measurement at t = 5, after the sample has been incubated in the dark for 5 days at 20°C. The BOD_5 is simply the difference between the two DO measurements.

Clean surface water usually has a BOD_5 of about 1mg/l. BOD_5>10mg/l indicate usually the presence of sewage pollution.

When measuring the BOD_5 of sewage it is necessary to first dilute the sample in the BOD bottle. Domestic sewage generally has a BOD_5 value of about 200mg/l. If the sample was not diluted, all the DO would be quickly depleted and it would, therefore, be impossible to obtain a DO reading on the 5th day.

Mass balance concept

BOD_{conc} x VOL_{conc} = BOD_{sol} x VOL_{sol}
BOD_{conc} = BOD of concentrate
BOD_{sol} = BOD of solution