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MEASUREMENT OF BASIC WATER POLLUTION PARAMETERS AND THEIR INTERPRETATION

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Measurement of Basic Water Pollution Parameters and their Interpretation

The basic parameters may be listed as

1. pH
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3. Suspended Solids
4. Dissolved Oxygen
5. B.O.D. (Biochemical Oxygen Demand)
6. 4 hour Permanganate Value $\left(\frac{N}{10}\right)$
7. C.O.D. (Chemical Oxygen Demand)
8. T.O.C. (Total Organic Carbon)
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10. Total Organic Nitrogen
11. Total Oxidised Nitrogen
12. Free and Saline Ammonia

Of these the parameters Nos. 4 - 8 are the ones of importance.

Dissolved Oxygen

Air is only slighly soluble in water and only~20.9% of air is oxygen. The dissolved oxygen content of water varies:

(i) inversely with salinity
(ii) directly with pressure
(iii) inversely with temperature

Normally the pressure effect can be ignored. At $0^{o}C$ and 100 mg/l' Cl the saturation concentration of dissolved oxygen in water is about 14.0 mg/l,

at $10^{o}C$	11.0 mg/l
at $20^{o}C$	9.0 mg/l
at $30^{o}C$	7.5 mg/l

On this small amount of dissolved oxygen depends all the aquatic life of a normal stream. The addition of easily bio-degradable organic material to the water (pollution) leads to an increased activity among the bacteria and other micro-organisms which are able to use the added complex organic chemicals as food sources. These micro-organisms are aerobic i.e. they require oxygen dissolved in the water to support their metabolic reactions.

Hence a stimulated activity in these organisms can lead quickly to a depletion in the dissolved oxygen content of the water, to the death of all normal aquatic life, and to complete deoxygenation which is characterised by the emission of hydrogen sulphide.

The rate of reoxygenation of a partially deoxygenated water is proportional to the oxygen deficiency and described by the first order equation.(1)

$$\frac{d\rho_B}{dt} = k'_2 (C_s - C_B) = \frac{k'_L \cdot A.}{V} (C_s - C_B)$$

Where C_s - saturation value of the dissolved oxygen

C_B - bulk dissolved oxygen concentration

k'_2 reaeration coefficient (T^{-1})

k'_L reaeration coefficient (Masstransfer units LT^{-1})

k_2 increases with temperature according to the expression

$$k_2 (T^{o} C) = k_2 (20^{o} C) \; 1.024^{(T-20)}$$

Hence, although the solubility of air in water decreases with increase of temperature the rate of reaeration increases.

The Biochemical Oxygen Demand Test ($B.O.D._5$)

When readily degradable organic matter (sewage) is discharged to a stream a natural process of self-purification is initiated. All surface waters contain bacteria and other microorganisms which are capable of attacking the complex chemicals of pollution and utilizing them as sources of energy and of new cellular material. These microoganisms are essentially 'aerobic' in that they require oxygen, dissolved in water, in order to carry on their metabolic processes. As this dissolved oxygen is used by the aerobic bacteria the limited amount available at any one time in water is decreased. The decrease in dissolved oxygen as a result of bacterial activity is directly related to the amount of pollution added.

Basically the Biochemical Oxygen Demand (B.O.D.) is an attempt to utilize this natural phenemenom to quantify water pollution.(2,3). The B.O.D. is a measure of the dissolved oxygen required by purifying organisms in a definite volume of liquid in order to break down the available organic material.

If a quantity of polluted water is placed in a stoppered, air-tight bottle the concentration of dissolved oxygen will decrease according to a first-order equation until, after about 20 days, the action will have effectively ceased. This total drop in the dissolved oxygen is commonly referred to as the Ultimate Oxygen Demand (U.O.D.) but, naturally, the period of the test is far too long for normal laboratory practice. For this reason a standard time for the B.O.D. test of 5-days has been selected and this period is often indicated by the subscript to the letters B.O.D. $_{(5)}$.

Biological activity increases with temperature and therefore the higher the temperature of the test the more dissolved oxygen will be used up in five days. To enable results to be reproducible and comparable a standard temperature of 20°C is always used.

For the same reasons, i.e. those of reproducibility and comparability if it is necessary to dilute the original sample because of its excessive organic strength then a standard dilution water containing prescribed concentrations of ferric chloride, calcium chlroide, magnesium sulphate and a buffered phosphate solution is used.

The B.O.D. is therefore an attempt to simulate the natural decomposition of organic wastes through aerobic microbial action under standard conditions and for a standard time.

It is first necessary to decide on a suitable dilution of the origina sample that will result in a decrease of the d.o. content of the water by between 3 and 5 mg/l. The sample is then diluted with the necessary volume of the standard, well-acrated dilution water, placed in a suitable air-tight bottle and the initial dissolved oxygen content determined. After five days in a dark incubator at 20°C the final d.o. content is determined and the B.O.D. is reported as mg/l.

The dark incubator is essential as the water sample may contain photosensitive algae which produce oxygen under the influence of light which would invalidate the whole test.

The B.O.D. test is essentially one of carbonaceous oxidation i.e. the breakdown of organic (carbon containing) molecules to carbon dioxide, water and ammonia. It is not a measure of the dissolved oxygen used by autotrophic bacteria in the oxidation of ammonia to nitrite and nitrate. Until fairly recently it was considered that oxidation of the ammonia to nitrates in the B.O.D. test did not commence until after five days, and hence was of no significance to

the result.

This is now appreciated to be false and under certain conditions[5] i.e. the presence of substantial quantities of the nitrite and nitrat forming bacteria in the original sample together with an initial concentration of ammonia, the oxygen demand of the ammonia oxidisers can be intense and can cause a complete misrepresentation of the carbonaceous oxidation result. For this reason the ammonia oxydising bacteria are normally inhibited in the B.O.D. test by the addition of a small quantity of Allyl Thiourea (A.T.U.)

The microorganisms in the B.O.D. test are also liable to be inhibited by the presence of toxic elements and compounds (lead, hexavalent chromium, cyanide etc). This inhibition will lead to artificially low results which will only be recognised by comparison with the result of chemical oxidation tests.

The B.O.D. test is generally accepted, for all practical purpose to follow 'first-order' kinetics in that the rate of the reactio (bacterial decay of organic matter or uptake of d.o.) is direct proportional to the amount of organic matter remaining.

i.e. $$-\frac{dc}{dt} \propto C \qquad \text{or} \qquad -\frac{dc}{dt} = k'C$$

where C is the concentration of the organic pollutants at the beginning.

If L, the ultimate B.O.D. replaces C then on integration one ob

$$\frac{L_t}{L} = e^{-k't} = 10^{-kt}$$

$$k = \frac{k'}{2.303}$$

where Lt is the B.O.D. remaining at any time t.

If y is the B.O.D. already exerted at time t then

$$y = L - L_t$$

$$y = L(1-10^{-kt})$$

This is the classic form of the B.O.D. equation. k is the rate constant for the reaction and is normally considered to be about 1.0 days $^{-1}$ although higher figures are obtained with many organic compounds, particularly those in industrial wastes.

It might be considered that the ultimate oxygen demand (U.O.D.) should be equal to the amount of oxygen used in the chemical oxidation of a substance. This is not normally so. A glucose solution with a theoretical oxygen demand of 300 mg/l, i.e. the oxygen necessary to convert the glucose entirely to water and carbon dioxide, will normally only give a U.O.D. of between 250 and 280 mg/l. This is a result of the conversion of a proportion of the glucose into fresh bacterial cells instead of directly oxidising it all completely.

The B.O.D. has many disadvantages which include the inaccuracy of the test procedure, the length of the test, the variability of the rate constant, susceptibility to the presence of inhibiting agents and uncertainty as to what exactly is being measured. The test, however, remains the best single parameter of water pollution and of the bio-availability of organic waste. If possible the B.O.D. results should always be compared with those from a chemical oxidation test of the same sample.

Chemical methods of evaluating water pollution

These methods depend upon the chemical oxidation of the complex chemicals of pollution. Chemical oxidation tests are valuable either as a direct measurement of the polluting organic material present or as a check on the validity (absence of inhibiting effects) of the B.O.D. results. Their general weakness is that either they do not oxidise sufficient organic material (4 hours P.V.) or that they oxidise too much. They do not represent a measure of the biodegradable organic material in the water.

Four Hour Permanganate Value Test (N/80)

This test relies upon an acid solution of potassium permanganate to oxidise organic material. It takes place at a standard temperature (27°C), for a standard time (4 hours) and with a standard initial concentration of permanganate $(\frac{N}{80} \simeq \frac{M}{400})$. Its principal value is in its ease of performance and the relatively short period of time necessary compared with the B.O.D. test.

There are two 4 hour PV tests; one for wastewater and another, utilizing a larger volume of sample and a smaller volume of permanganate, for potable waters. The wastewater test employs 10 ml of 25% sulphuric acid, 50 ml of $\frac{N}{80}$ potassium permanganate together with 100 ml of the sample. The oxidation is usually incomplete so a precise control of the test is essential, but even some results are of limited value (6). The ratio of B.O.D. to 4 hour PV varies from about 4:1 for crude municipal wastewater to 1.6:1 for a well-purified effluent.

Other Permanganate Tests

A 3-minute test employing $\frac{N}{80}$ permanganate is sometimes used to determine the immediate oxygen demand of trade wastes.

The McGowan strength of a wastewater is still sometimes determined using a stronger, $(\frac{N}{8} \simeq \frac{M}{40})$ permanganate solution. The formula

$$\text{Strength of wastewater} = 4.5N + 6.5P$$

is employed where P is the $\frac{N}{8}$ permanganate value and N is the separately determined ammoniacal and organic nitrogen content.

Chemical Oxygen Demand (C.O.D.)

This represents a later development than the 4 hour P.V. test and has now largely superseded it. The C.O.D. relies on the stronger oxidising power of $(\frac{M}{48})$ potassium dichromate solution operating in boiling sulphuric acid. The reaction time is two hours.

In order to assist in the break-down of certain organic molecules such as straight chain aliphatic acids the catalyst silver sulphate is added to the reaction. Despite the presence of the catalyst some compounds possessing a benzene ring structure may exhibit only partial and non-reproducible break-down (7). Pyridine and certain other heterocyclic compounds are not oxidised by this reaction. Ammonia is not oxidised to nitrate although nitrogen in higher oxidation states in some organic compounds will be converted to nitrate.

Chloride ions interfere and may lead to the formation of volatile compounds that will be lost by volatilization. This interference is largely prevented by the addition of mercuric sulphate which supposedly represses all chloride interference up to a concentration of 500 mg/l and permits only slight interference up to 1,000 mg/l. In practise the addition of the mercuric salt does not overcome all chlorion interference.

The normal range of application of the C.O.D. test is from about 50 mg/l to 400 mg/l. There is always an appreciable blank and the tests should always be carried out at least in duplicate.

The C.O.D. test is quick, relatively simple and appreciably reproducible. Its disadvantages result from the indiscriminate oxidation of organic matter. Both glucose and lignin are readily decomposed and consequently there is no differentiation between biodegradable and non-biodegradable compounds. The ratio of C.O.D. to B.O.D. increases with the increasing concentration of biologically resistants organic compounds.

Total Organic Carbon (T.O.C.)

With this test all the organic carbon is oxidised to carbon dioxide which is then quantitatively determined. In the wet method (2) the oxidising agent is acid potassium dichromate solution and the CO_2 is collected in a solution of Barium hydroxide. The carrier gas is air from which CO_2 has been removed by soda-lime. A dry-method is also employed which uses an electric furnace and nitrogen gas to which about 200 mg/l of oxygen is added.

The T.O.C. is rapidly becoming a most popular parameter and there are many different equipments on the market. These frequently incorporate a catalytic furnace operating at about 900° C. The CO_2 produced is determined either by a non-dispersive infra-red analyser or by reductive pyrolysis to methane followed by a flame ionization detector.

Again,with the T.O.C. there is no distinction between biodegradable and non-biodegradable organic material.

Combined Nitrogen Tests

These are the Total Organic Nitrogen, the Albuminoid Nitrogen and the Total Oxidised Nitrogen tests.[2] The organic nitrogen test may be carried out on a sample from which the ammonia and oxidised nitrogen have already been removed and determined; or the oxidised nitrogen may be destroyed and the ammonia included in with the result obtained. Basically, the organic material present is digested at the high temperature produced by a boiling solution of sodium

sulphate in concentrated sulphuric acid. The breakdown of the nitrogenous material is assisted by the presence of selenium and copper sulphate catalysts. Later the ammonia is distilled off from an alkaline solution and determined. Most of the organic material will be recovered as ammonia.

The Albuminoid Nitrogen test produces less meaningful results but is still useful, in some situations, because of its simplicity and because of the short time required. The alkaline permanganate solution used possesses only a limited ability to convert nitrogenous, organic material to ammonia and the results obtained should only be regarded as a guide to the total organic content of the sample.

Total oxidised nitrogen includes both nitrites and nitrates. It is best determi using Devarda's alloy on the residue from the free and saline ammonia determination although the copper/zinc couple method is simple and reliable, if overlong. It is rarely necessary or useful to determine nitrites and nitrates separately.

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