D.P.H. Class.

Water Analysis (concluded).

Oxygen absorbed from Permanganate (Tidy figure).

Sewage Analysis.

250.0.57033.

Water Analysis.

Oxygen absorbed from permanganate, or Tidy figure.

When a water is mixed with potassium permanganate in acid solution, a certain amount of oxygen is taken up from the permanganate by oxidisable matter in the sample. Very pure waters absorb little oxygen whereas those polluted with animal or vegetable organic matter absorb considerable quantities. Although not a reliable index per se of either the quality or the quantity of organic matter present yet the determination is of value inasmuch as the amount of oxidisable matter varies in different waters and the figure for the oxygen absorbed, when taken in conjunction with the other figures of the analysis or compared with the results of previous determinations on the same water, may yield valuable information.

Certain inorganic constituents of a water such as nitrites, ferrous salts and sulphides also absorb oxygen from permanganate but their action in this respect is, for practical purposes instantaneous whereas organic matter is more slowly oxidised. If inorganic reducing substances are known to be present they can be removed by boiling with dilute sulphuric acid for 20 minutes before proceeding with the test.

The conditions of the test vary in different laboratories as regards the temperature and period of incubation. Some chemists use a temperature of 27°C, (80°F.), others 98°F. or even 212°F., and the period of incubation varies from about 15 minutes to 4 hours. It is important therefore for purposes of comparison, to decide on the temperature and period to be adopted in all these permanganate estimations, to retain them as constant conditions of the test, and to state the conditions in the report of the analysis. For class purposes room temperature and a period of contact of 1 hour are convenient conditions for a water.

The Test.

250 cc. H_2O + 10 cc. $KMnO_4$/cc.=0.1 mgm + 10cc 25% H_2SO_4
Later + K.I.

Two stoppered 400 cc. flasks are needed. To one are added 250 cc. of the water sample, 10 cc. of potassium permanganate solution of such strength that 1 cc. = 0.1 mgm. of available oxygen and 10 cc. of 25 per cent. sulphuric acid. To the other flask are added 250 cc. of distilled water and the same quantities of the reagents as in the first flask. The flasks are stoppered and kept at the chosen temperature for the chosen period in the darkness. It is found that light increases the oxygen used up. The flasks are examined from time to time and if the permanganate has been greatly decolourized an additional measured quantity of that solution should be added. At the end of the period a few ccs. of potassium iodide solution are added to each flask. The iodide is decomposed by the permanganate with the liberation of an amount of iodine equivalent to the amount of potassium permanganate left unchanged. The iodine is now titrated in each flask by means of a solution of sodium thiosulphate using starch as the indicator. The thiosulphate solution used is a dilute one and is not of carefully prepared standard strength. Thiosulphate solution keeps badly and it is best to standardise it with each test by the titration of the control flask which contains a known quantity of a standard permanganate solution mixed with a distilled water which should have no power of absorbing oxygen.

Calculation.

Supposing that 30.2 c.c. of the thiosulphate solution are used to decolourize the iodine set free by the 10 c.c. of standard permanganate in the second flask and that 26.5 c.c. are required for the flask containing the 250 c.c. of the water sample.
Then 30.2 c.c. thiosulphate = 10 c.c. standard permanganate

= 1.0 mgm. available oxygen.

Now the amount of permanganate used up is that amount which is equivalent to the difference between the figures of the two thiosulphate titrations, i.e. 30.2 - 26.5 c.c.

Since 30.2 c.c. thiosulphate $\equiv$ 1.0 mgm. of oxygen

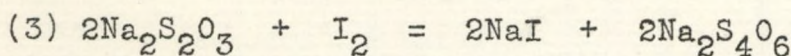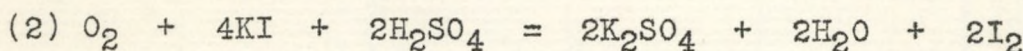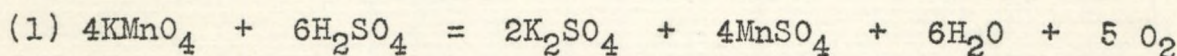$\therefore$ 30.2-26.5 c.c. or 3.7 c.c. $\equiv \dfrac{1.0 \times 3.7}{30.2}$ mgm. of oxygen

But this was used up by 250 c.c. of water

$\therefore$ 100 c.c. of water use up $\dfrac{100 \times 1.0 \times 3.7}{250 \times 30.2}$ mgm. oxygen

$$= 0.049 \text{ mgm. oxygen}$$

or Oxygen used up by permanganate is 0.049 parts per 100,000.

The reactions in this test are:-

(1) $4KMnO_4 + 6H_2SO_4 = 2K_2SO_4 + 4MnSO_4 + 6H_2O + 5 O_2$

(2) $O_2 + 4KI + 2H_2SO_4 = 2K_2SO_4 + 2H_2O + 2I_2$

(3) $2Na_2S_2O_3 + I_2 = 2NaI + 2Na_2S_4O_6$

Interpretation.

It is again very important to take the Tidy figure in conjunction with the other figures of the analysis. Also the source of the water should be known since harmless vegetable organic matter may give a high figure. The following figures may be taken as a rough guide:-

	Great Purity	Satisfactory	Suspicious	Bad
Upland water (peaty)	0.10	0.30	0.40	>0.40
Not peaty	0.05	0.10	0.15	>0.20

Sewage and Sewage Effluents.

The objects of water purification and of sewage purification are entirely different from one another. In water purification the main purpose is to destroy pathogenic organisms or to reduce them to a safe concentration. In sewage purification the purpose is not the destruction of micro-organisms but the alteration of those characters which would have a deleterious effect on the river or other mass of water destined to receive the sewage. If an untreated sewage is allowed to enter a river in quantity, fish and other animal life as well as green plants tend to die and the stream silts up. It is to prevent these changes occurring that sewage purification is undertaken. There are two main harmful characters of crude sewage:-

(1) the suspended solids
(2) the Biochemical Oxygen Demand [B.O.D.]

The Suspended Solids.

Sewage contains solids in solution and also in suspension. It is the latter which must first be considered. In amount they may be 40.0 or more parts per 100,000 and consist in large measure of organic matter although inorganic particles are also present. These suspended solids if not removed, tend to settle to the bed of the stream, so silting it up particularly in relatively stagnant stretches and backwaters. Furthermore this organic matter readily takes up the oxygen dissolved in the stream with the result that in the bed of stream chiefly anaerobic microbic action takes place producing foul odours of putrefaction. The early stages of sewage purification are effectual in lessening the amount of suspended solids.

Biochemical Oxygen Demand.

Crude sewage usually contains no oxygen dissolved in it whereas good river water or tap water may be saturated with oxygen dissolved from the atmosphere. If crude sewage is allowed to stand exposed to the air it absorbs gaseous oxygen with avidity but this oxygen actually goes into combination with the organic matter in the sewage and cannot be demonstrated as dissolved molecular oxygen. That this absorption occurs can be demonstrated in a number of ways, for example, by showing that crude sewage contains no nitrate but that after exposure to air for a week or two this form of oxidised nitrogen is present in considerable quantity. This capacity of sewage to take up molecular oxygen which then enters into combination with the oxidisable matter is called the Biochemical Oxygen Demand. The word 'biochemical' is used because the oxygen uptake is actually a phenomenon brought about by the bacteria present in the sewage and does not occur to the same extent in sterilised sewage. The importance of the B.O.D. lies in the fact that a crude sewage entering a stream will take out of the stream the oxygen dissolved therein with the result that fish and green plants will die and the river will become foul and putrid.

The later stages of sewage purification effect a lessening of the B.O.D. by oxidising the sewage to an adequate extent.

Analysis.

Suspended Solids.

A tared Gooch crucible with a bed of asbestos as the filter medium, is prepared. A known volume of a uniform sample of sewage - say 50 to 300 c.cs. depending on the strength of the sample - is filtered through the crucible, if necessary with the help of a vacuum pump. The retained matter is washed with a little distilled water after which the crucible is dried at 105°C. and reweighed. The increase in weight represents the amount of suspended solid in the volume of the sample filtered and the result is expressed as parts per 100,000.

Biochemical Oxygen Demand.

The procedure which determines this in the laboratory is sometimes known as the Rideal-Stewart figure. It consists in the chemical determination of the oxygen dissolved in a dilution of the sewage or effluent at the beginning and the end of a period of five days. The steps in the test are:-

(1) Dilution of the Sewage or Effluent.

Sewage contains little or no oxygen dissolved in it so the first step is the dilution of the sewage with well aerated tap water, so that dissolved oxygen shall be present.

The dilution required depends on the nature of the sample:-

Good sewage effluents	1 in 5
Poor effluents	1 in 10
Tank liquor or crude sewage	1 in 50 or more.

Supposing a good effluent is to be examined: into a large flask place 200 c.cs. of the effluent and then 800 c.cs. of tap water so making a dilution of 1 in 5.   Shake the flask to mix thoroughly and to saturate the mixture with dissolved oxygen.

(2) Bottling.

Two bottles with well-fitting glass stoppers and of about 300 c.cs. capacity are needed.   The volume of the bottles when stoppered is measured by means of a graduated cylinder.   Both bottles are filled to the very top with the diluted effluent and allowed to stand on the bench for about ten minutes during which time they are tapped occasionally to allow any air bubbles to rise to the surface.   Throughout this time the bottles are left open.   Then the stoppers are inserted and allowed to sink into position.   In this way no air bubbles are included.   Label the bottles A and B.

(3) Treatment of Bottle B.

This is allowed to stand untouched for a period of 5 days at 18°C. For research work this temperature is secured by special methods but for demonstration purposes room temperature will give a good result.   During this period of 5 days dissolved oxygen will be taken up by the liquid in Bottle B after which the oxygen left unused is determined by a procedure identical with that which is employed for Bottle A at the beginning of the 5 day period.

(4) Treatment of Bottle A.

(a) Remove the stopper carefully.
    Add 1 c.c. of strong sulphuric acid followed by a few drops of the potassium permanganate solution provided.   Insert the stopper carefully and mix.

[N.B.   These reagents are for the purpose of oxidising any reducing substances such as nitrites, sulphides or iron salts, which otherwise would interfere with the later reactions.]

Allow to stand for 20 minutes.   Should the colour of the permanganate disappear, a few more drops of the permanganate must be added. A definite pink colour must remain throughout the 20 mins.

(b) Unstopper, add about 2 c.cs. of the given solution of potassium oxalate, restopper, mix and allow to stand for some minutes till the permanganate colour has quite disappeared.   An extra amount of oxalate may be needed if a large amount of permanganate remains.

[N.B.   The oxalate in the presence of the acid originally added destroys the permanganate.   This must be done for otherwise the later reactions do not take place.]

(c) Unstopper, add 2 c.cs. of the solution of manganous chloride followed by 5 c.cs. of the solution of potassium iodide and caustic potash.   If no precipitate forms, add more of the second solution.   Stopper, mix, and set aside in darkness for ten minutes, occasionally inverting the bottle.
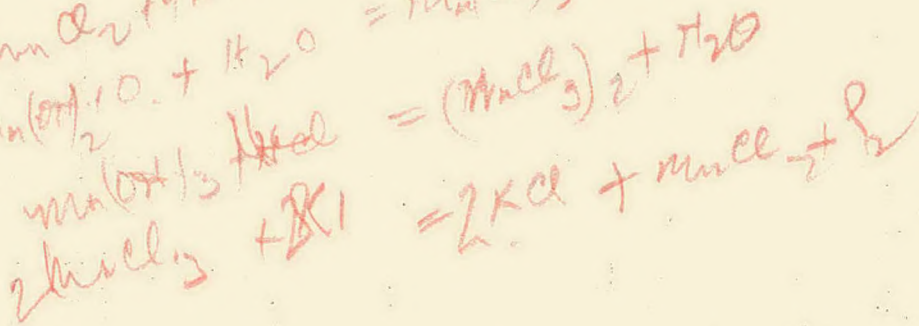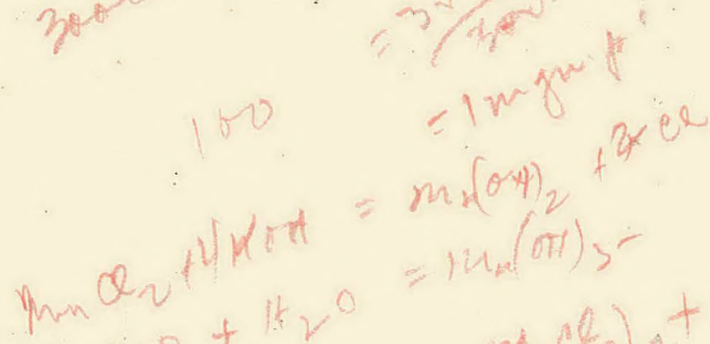
(d) Add about 5 c.cs. of strong hydrochloric acid to a flask (about 400 c.cs.) and pour the contents of the bottle into the flask. A clear solution, yellow from liberated iodine, results. This iodine is now titrated in the usual way with a standard solution of sodium thiosulphate which is conveniently of such a strength that 1 c.c. = 0.25 mgm. of oxygen.

Calculation.

e.g. 12 c.cs. of thiosulphate used. Capacity of bottle 300 c.cs.

Then there are 12 x 0.25 mgms. oxygen in 300 c.cs.

     ∴   4 x 0.25   "   "   "   100 c.cs.

     or   1.0 mgms. per 100 c.cs.
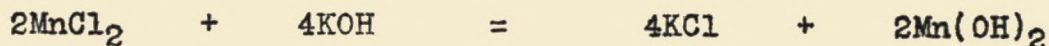
     or   1.0 parts per 100,000

Bottle B at the end of 5 days is treated throughout by the same procedure. Supposing that at the end of this period it is found that the amount of oxygen left is 0.6 parts per 100,000. It is clear that 0.4, i.e. the difference between the figures at the beginning and end of the 5 days is the amount used up.

But it must be remembered that the effluent was diluted to 1 in 5 and therefore 0.4 must be multiplied by the dilution to give the amount of oxygen actually used up by the sewage effluent itself.

In this instance it is:-

5 x 0.4 or 2.0 parts per 100,000.

The following equations may be regarded as representing the chemical changes:-

$$2MnCl_2 \quad + \quad 4KOH \quad = \quad 4KCl \quad + \quad 2Mn(OH)_2$$

$$2Mn(OH)_2 \quad + \quad O \quad + \quad H_2O \quad = \quad 2Mn(OH)_3$$

$$2Mn(OH)_3 \quad + \quad 6HCl \quad = \quad 2MnCl_3 \quad + \quad H_2O$$

$$2MnCl_3 \quad + \quad 2KI \quad = \quad 2MnCl_2 \quad + \quad 2KCl \quad + \quad I_2$$
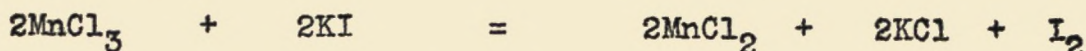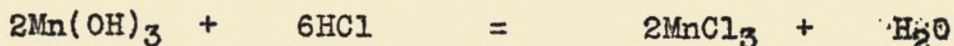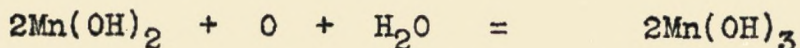
Note. The disadvantage of this test lies chiefly in the fact that 5 days must elapse before a result can be obtained. Nevertheless, the test is of great value in that it endeavours to secure natural conditions in the laboratory. So the temperature of 18°C. was chosen as being near the average of temperatures of diluting streams in this country.

The period of 5 days was chosen because there is a relatively rapid oxygen uptake in the first five days but after this the oxygen absorption becomes very slow.

Royal Commission of Treatment and Disposing of Sewage.

Although there are no legal standards for the degree of purification which must be reached by a sewage effluent, the Commissioners made certain recommendations, based on the tests just described. These recommendations are generally quoted in Courts of Law and in Bills before Parliamentary Committees. The most important points are:-

(1) there should be a <u>general</u> standard which requires that:-

    (a) an effluent must not contain more than 3 parts of suspended
        matter per 100,000.
    (b) the effluent with its suspended matter included must not
        have a higher B.O.D. than 2 parts per 100,000.

(2) if the dilution afforded by the stream is low a more stringent
    standard should be imposed.

(3) if the dilution is great, the general standard may be relaxed or
    suspended altogether, as indicated below:-

Dilution	B.O.D.	Suspended Solids	Sewage Treatment
Less than 1:150	2.0	3.0	Full
150 to 300	omit	6.0	e.g. Chemical Precipitation
300 to 500	omit	15.0	Simple Tanks
Over 500	omit	omit	Screen or Detritus Tank *Grit chamber*

Other Methods of Determining the Strength of a Sewage or Effluent.

    Although the determination of suspended solids and of the B.O.D.
gives so good an indication of the effect which a particular sewage or
effluent is likely to have on the diluting stream, some experts prefer
other methods partly because of the length of time taken to complete
the B.O.D. estimation.

    Practically all the estimations of a water analysis are made by
some analysts. Some attach great significance to the nitrite and
nitrate figures: it is certainly true that nitrite shows that
oxidation is proceeding and that as oxidation continues the nitrate
figure rises and the free and saline ammonia figure diminishes.

    The Tidy figure is used extensively to help determine the
strength of a sewage or the degree of purification of an effluent.
But the time of contact with the permanganate is often 4 hours instead
of the shorter time more usual in a water analysis. The oxygen thus
absorbed may be under 1.0 parts per 100,000 in a good effluent. The
strength of a sewage is sometimes expressed on the figure obtained by
McGowan's formula which is:-

    4.5 (Free Ammonia Nitrogen + Albuminoid Ammonia Nitrogen)

                    + 6.5 (Tidy figure of 4 hours at 27°C.)

Weak Sewage under 50   Strong Sewage over 175.

A formula for the strength of an effluent:-

$$\frac{(Albuminoid\ Ammonia \times 100) + (4\ hour\ Tidy \times 10)}{2}$$

    If this figure is under 10 and the suspended solids are not more
than 3.0 then the effluent is a good one and is not likely to have a
B.O.D. of more than 2.0.

Figures of Analyses

	B.O.D.
Good Filter Effluent	0.5
Standard Effluent	2.0
Average Precipitation Tank Effluent	15.0
Strong Septic Tank Effluent	33.0
Average Sewage	35.0
Strong Sewage	50.0

	Sewage			Good Effluent
F.A.	2.5	to	13.4	1.5
A.A.	0.6	to	1.75	0.15
Tidy (4 hour)	6.5	to	18.0	1.0
Cl	6.6	to	13.6	8.0
Solids in Suspension	26.0	to	42.0	3.0
Nitrates		0.0		2.0 or more

The sewage figures range from weak to very strong.