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978-1-107-49473-2 - The Chemical Examination of Water, Sewage, Foods: And Other Substances: Second @ Enlarged Edition

J. E. Purvis and T. R. Hodgson

Excerpt

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CHAPTER I

WATER—SEWAGE—SEWAGE EFFLUENTS—RIVER- WATER AND SEWAGE—SEA-WATER AND SEWAGE —WORKS EFFLUENTS

WATER

CHEMICALLY pure water does not occur in nature. All water supplies are obtained ultimately from rain water, which contains various substances, both organic and inorganic, dissolved by the water during its passage through the air, soil, subsoil, etc.; and, it may be, by contamination with sewage material and trade wastes.

An analysis of water is undertaken with the object of estimating these impurities and of deciding whether the water is of sufficient purity to be used for domestic purposes. The value of this analysis depends on the accuracy of the results, and, in a large measure, on careful and proper sampling.

Method of sampling. The sample should be collected in a "Winchester Quart," having a ground glass stopper. Stone jars should not be used, and care should be taken to see that the bottle has not been previously used for storing ammonia and ammonium salts. Before collecting the sample, the bottle should be well rinsed at least three times with the water.

If the sample is to be taken from a stream, the bottle should be completely immersed in the stream, as near the centre as possible, and care should be taken not to disturb any mud.

If the sample is to be taken from a well, at least ten gallons should be allowed to run to waste before filling the bottle, and the water should then be allowed to flow directly into the bottle; in no case should a funnel be used.

When the sample is to be collected from a tap, at least ten gallons should be allowed to run to waste; and the sample should then be collected directly from the tap.

When a sample of water is submitted for analysis, the largest possible amount of information regarding it should be forwarded at the same time. In order to assist the analyst in

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arriving at his opinion, information on the following points is essential and should always be supplied: (a) risk of pollution; (b) nature of the surface and subsoil, *e.g.* clay, chalk, gravel, sand, etc.; (c) if the water comes from a well the approximate depth of the well.

Physical characters. A careful preliminary examination of a water is of great importance.

(a) Test the water with blue and red litmus papers, and notice if the reaction is acid or alkaline. Most drinking waters are slightly alkaline or neutral in reaction. Peaty waters and waters from upland surfaces are often acid, as well as waters from chemical works and breweries. Waters which are contaminated with sewage are usually alkaline. Waters which contain carbon dioxide give a slightly acid reaction.

(b) Warm a portion in a test-tube and notice if any smell is produced. Polluted water may give off sulphuretted hydrogen.

(c) Place a portion in a two-foot glass tube and examine it downwards in a good light. Notice if it is clear and bright or turbid. Pure water has a bluish tinge; polluted waters may be yellow or brown; peaty waters and upland surface waters are usually coloured yellow or brown.

(d) Allow a portion of the water to stand for an hour or two in a conical shaped tube, and collect the sediment. Mount a little of the sediment on a glass slide, and examine it carefully with a microscope to see if it is mineral matter, such as sand or chalk or oxide of iron; or vegetable matter, such as vegetable cells, starch granules, cotton or linen or silk fibre, yeasts, moulds, bacteria, diatoms and other water organisms; or animal refuse such as worms, insects, hairs, fish scales, animal fibre, etc.

(e) Also notice if it is well ærated, by shaking a portion of it in a glass bottle and noticing the liberation of gas bubbles.

Free and saline ammonia

Solutions required:

Nessler's solution. Weigh out

- 35 grams of potassium iodide,
- 13 grams of mercuric chloride,
- 120 grams of caustic potash,

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Excerpt

[More information](#)

1]

WATER

3

dissolve each separately in water, and gradually add the potassium iodide solution to the solution of mercuric chloride, a precipitate of mercuric iodide appears at first which is afterwards redissolved in the excess of potassium iodide; the caustic potash solution is then added gradually; and, afterwards, a saturated solution of mercuric chloride drop by drop, until a very slight precipitate, which will not redissolve, is formed. The whole is then finally made up to 1000 c.c. and allowed to stand until the precipitate settles; the solution should always be kept in contact with the precipitate.

Ammonium chloride solution (strong): weigh out 3.147 grams of pure dry ammonium chloride, dissolve it in water and make up to 1000 c.c.

Ammonium chloride solution (dilute): measure out 10 c.c. of the strong ammonium chloride solution and add ammonia-free distilled water to 1000 c.c. 1 c.c. of this solution = 0.00001 gram of ammonia.

Estimation of free and saline ammonia. The most convenient apparatus for this determination is a 1500 c.c. round-bottomed distilling flask, with a ground glass stopper, having a fused-in delivery tube, bent at right angles, this delivery tube is fitted into a double surface condenser.

It is necessary first to free the apparatus from ammonia; and, in order to do this, 200 c.c. of distilled water and about one gram of solid sodium carbonate, which has been fused in a platinum dish to drive off any ammonium salts, are placed in the distilling flask and boiled; the distillate is collected in a Nessler cylinder, and the boiling continued until the distillate gives no colour with 2 c.c. of the Nessler solution. As soon as the apparatus has been freed from ammonia, 500 c.c. of the sample are added to the contents of the distilling flask and the boiling continued; the distillate being collected in Nessler cylinders, 50 c.c. at a time; to the contents of each cylinder, 2 c.c. of the Nessler solution are added and the colour obtained is compared with the standard colours.

Standard colours are obtained by placing known quantities of the dilute ammonium chloride solution (*e.g.* 0.5 c.c., 1.0 c.c., 1.5 c.c., etc.) in a Nessler cylinder, filling up to the mark with distilled water free from ammonia, and adding 2 c.c. of the

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Excerpt

[More information](#)

4

WATER

[CH.

Nessler solution. In some cases it may be found that the colour obtained with the first glass of the distillate is too deep to be compared with a standard solution, the contents of the glass are therefore diluted to 250 c.c. and then compared with the standard; or an aliquot portion may be taken and diluted with ammonia-free water to 50 c.c. and then compared with the standard. The amount of ammonia obtained in the distillation is calculated from the known strength of the dilute ammonia solution.

In this process the sodium carbonate decomposes any ammonium salts in the water, and the ammonia so obtained, together with any free ammonia in the water, passes over and is collected in the distillate. Ammonia is one of the first products of the decomposition of animal matter and its presence in water in very large quantities must be looked upon with suspicion; but it must be remembered that ammonium salts are not in themselves harmful and their presence in water does not necessarily render the sample unfit for drinking purposes.

Albuminoid ammonia

Solution required:

Alkaline permanganate solution. Weigh out

8 grams of potassium permanganate,
200 grams of caustic potash,

dissolve these together in about 1200 c.c. of distilled water and evaporate the solution to about 900 c.c., add 200 c.c. of distilled water and again evaporate the solution to 1000 c.c.; the solution, which will be found to be free from ammonia, is kept in a glass stoppered bottle.

Estimation of albuminoid ammonia. To the remainder of the water in the distilling flask, after the estimation of free and saline ammonia, add 50 c.c. of the alkaline permanganate solution, which has been previously heated to boiling, and continue the boiling; the ammonia is estimated colorimetrically as before.

The nitrogen in organic combination (as urea, uric acid, indol, skatol, and other proteid substances) is oxidized by the action of the alkaline solution of permanganate to ammonia.

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Excerpt

[More information](#)

1]

WATER

5

The amount of ammonia obtained is, therefore, a measure of the organically combined nitrogen present in the sample.

Estimation of total solid matter

Measure out 100 c.c. of the sample into a weighed platinum dish, and evaporate it to dryness on a water bath; then place the dish in a water oven at 100° C. for three hours; cool in a desiccator and weigh; the increase in weight represents the total solid matter in 100 c.c. of the water. Each mgm (= 0.001 of a gram) of solid matter represents one part per 100,000.

Chlorine as chlorides*Solutions required:*

Silver nitrate solution. Weigh out 2.4 grams of pure dry silver nitrate, and dissolve it in distilled water and make up to 1000 c.c. 1 c.c. of this solution = 0.0005 gram of chlorine; or when working on 50 c.c. 1 c.c. = 1 part of chlorine per 100,000.

Potassium chromate solution. Weigh out 10 grams of potassium chromate, free from chloride, and dissolve it in 100 c.c. of distilled water.

Estimation of chlorine as chlorides. Place 50 c.c. of water in a porcelain dish; add three drops of the potassium chromate solution, and run in the silver nitrate solution from a burette, with constant stirring, until a slight but permanent red brown colour is obtained; then read off the number of c.c. of silver nitrate solution used. The silver nitrate precipitates the chlorine present in the water, as silver chloride; and, as soon as all the chloride is precipitated, a reddish insoluble compound of silver chromate is formed.

Oxygen absorbed from potassium permanganate solution*(1) Solutions required:*

Potassium permanganate solution. Weigh out 0.395 gram of pure potassium permanganate; dissolve it in distilled water and make up to 1000 c.c. 1 c.c. of this solution = 0.0001 gram of available oxygen.

Oxalic acid solution. Weigh out 0.7875 gram of crystallized

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[More information](#)

6

WATER

[CH.

oxalic acid; dissolve it in distilled water and make up to 1000 c.c. 1 c.c. of this solution = 1 c.c. of the permanganate solution.

Sulphuric acid solution. Measure out 33 c.c. of pure concentrated sulphuric acid, and add it gradually, with constant stirring, to 66 c.c. of distilled water; allow it to cool; to the cold solution add, drop by drop, potassium permanganate solution until a faint pink colour remains after keeping the solution at 80° F. for four hours.

Estimation of the oxygen absorbed. Into each of two conical flasks, of about 800 c.c. capacity, pour a small quantity of concentrated sulphuric acid and thoroughly rinse, taking care that the sulphuric acid comes in contact with the whole of the inside of the flask; wash out the flasks thoroughly first with tap water and afterwards with distilled water.

Into one flask measure out 250 c.c. of the sample; into the other flask 250 c.c. of distilled water; and to each add 10 c.c. of the potassium permanganate solution from a pipette, and 10 c.c. of the sulphuric acid solution; raise the temperature to 80° F. and maintain it at this temperature for four hours; if, at any time, the pink colour disappears a further quantity of 10 c.c. of the potassium permanganate solution must be added. At the end of four hours titrate the solution in each flask with the oxalic acid solution; the difference in the two titrations multiplied by 0.0001 will give the amount of oxygen absorbed by 250 c.c. of the sample.

(2) *Potassium iodide and sodium thiosulphate method.*

Solutions required:

Standard solution of potassium perman- } prepared as
ganate. } described

Dilute sulphuric acid solution. } above.

Potassium iodide solution; 10 grams of KI are dissolved in 1000 c.c. of water.

Standard sodium thiosulphate solution; 1 gram of pure recrystallized sodium thiosulphate is dissolved in 1000 c.c. of water.

Starch solution; 1 gram of pure potato starch is mixed into a smooth paste with a small quantity of water; and 200 c.c. of boiling water are then carefully added with constant stirring and the solution allowed to cool.

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Excerpt

[More information](#)

1]

WATER

7

The process. The actual determination is carried out exactly as described above, except that after standing for four hours at 80° F. a few drops of the potassium iodide solution are added to each flask, when a brown solution will be obtained owing to the reaction of the potassium iodide with the excess of potassium permanganate and the liberation of free iodine; the standard solution of sodium thiosulphate is then run in from a burette with constant shaking until a straw yellow colour is obtained; a few drops of starch solution are then added, producing a deep blue colour, and the titration with the thiosulphate solution continued until the blue colour is discharged.

Example. A blank experiment required 34 c.c. of the thio-sulphate solution, and 250 c.c. of a water required 31.3 c.c. $400 \times 0.001 \times \frac{34 - 31.3}{34} = 0.032$ parts of oxygen absorbed per 100,000 parts of water.

The purer natural waters, as a rule, contain only very small quantities of oxidizable organic substances of vegetable origin; this process, therefore, is a measure of the oxidizable organic substances of animal origin in the water.

With a view of coming to a provisional conclusion more rapidly than can possibly be done in all bacteriological tests, and to a certain extent with chemical tests, Sir A. C. Houston, in his 5th Report (1911) and 7th Report (1913) to the London Metropolitan Water Board, made a considerable number of detailed experiments to correlate the oxygen absorbed from potassium permanganate in *five minutes*, as compared with that absorbed in three hours, both at 80° F. He found that, taking the arbitrary figure 0.1 per 100,000 as the basis for objecting to a water in a three hours' test, the comparable figure for the five minutes' test was somewhat less than 0.038, the ratios varying slightly with different waters. When a water is appreciably worse than 0.1 in the three hours' test, the five minutes' test will be usually above 0.038; and when a water is appreciably better than 0.1 in the three hours' test, the five minutes' test may be nearly always trusted not to exceed 0.038. Dr Houston states that since April, 1910, the figure 0.038 has been adopted for the five minutes' test, and if on

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[More information](#)

the examination of a sample of water, the results reach or exceed this amount, a telephone communication is sent at once to the district concerned. The five minutes' method is of little use when the waters are very good, but when they are unsatisfactory, the parallelism between the two sets of results is very striking, although, of course, the *actual* results differ in the two cases.

Nitrogen as Nitrates

Estimation of nitrogen as nitrates. Nitrogen occurring as nitrates is determined by one of several methods:

- (a) Gasometric method.
- (b) Colorimetric method.
- (c) Ammonia method.
- (d) Indigo method.
- (e) Titanous Chloride method.

(a) *Gasometric method.* The residue from the determination of the total solid matter is dissolved in the smallest possible quantity of water, the sides of the dish being well scrubbed with a rubber-tipped glass rod; the solution is then poured into the cup of a Crum's nitrometer, filled with mercury and standing in a dish containing mercury, the tap is carefully opened and the solution allowed to run into the nitrometer; an equal volume of concentrated sulphuric acid is then poured into the cup and allowed to flow into the nitrometer in its turn, care being taken that no air is admitted; the bottom of the tube is closed with the thumb and the whole tube removed from the dish and well shaken, at an angle of 45° so that the mercury comes in contact with the mixture at the top of the tube; from time to time during the shaking the tube is replaced in the dish and the thumb removed to release the pressure; when the whole of the nitrate is decomposed the volume of gas obtained (nitric oxide) is noted, together with the temperature and pressure, and the volume is reduced to normal temperature and pressure. From the volume of the gas thus obtained the weight of nitrogen as nitrate in 100 c.c. of the water is calculated. The nitrogen present as nitrate is converted by the action of the sulphuric acid and mercury into nitric oxide (NO).

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Excerpt

[More information](#)

1]

WATER

9

(b) Colorimetric method. Solutions required:

Phenol-sulphuric acid solution; weigh out 24 grams of pure phenol; dissolve it in 12 c.c. of distilled water and add 148 c.c. of pure concentrated sulphuric acid; heat the mixture on the water bath in a round bottomed flask for six hours; allow it to cool and preserve it in a tightly stoppered bottle.

Potassium nitrate solution; weigh out 0.722 gram of pure fused potassium nitrate; dissolve it in distilled water and make up to 1000 c.c. 1 c.c. of this solution = 0.0001 gram of nitrogen.

Place 25 c.c. of the water in a glass or porcelain dish and evaporate it to dryness on the water bath. 5 c.c. of the standard potassium nitrate solution are evaporated in another similar dish.

To each dish, when dry, 2 c.c. of phenol-sulphuric acid are added, and the contents of each dish thoroughly mixed with a glass rod while standing on the water bath; the contents are then washed with dilute ammonia solution into Nessler cylinders; excess of ammonia is added to each solution to the 50 c.c. mark. A deep yellow colour will appear in the standard solution and also in the water if nitrates are present; these colours are compared and the volume of the darker coloured solution equal in tint to 50 c.c. of the paler solution is noted. From this the amount of nitrate in 25 c.c. of the water is calculated, as 5 c.c. of the standard potassium nitrate solution, containing 0.0001 gram of nitrogen, were taken. When phenol-sulphuric acid acts upon a nitrate, picric acid is formed, and this with ammonia forms ammonium picrate, which has a deep yellow colour, clearly visible in even very dilute solutions.

The estimation of nitrates by this method shows a serious error in the presence of chlorine as chlorides, even when the chlorides are present in small quantities; and in order to overcome this error, Frederick (*Analyst*, 1919, XLIV, 281) proposes the following method, which is not affected by the presence of chlorides.

Solutions required:

Potassium nitrate solution containing 1.4434 grams of potassium nitrate in 1000 c.c.; 25 c.c. of this solution will contain 0.005 gram of nitrogen as nitrates; 10 c.c. of this solution are

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Excerpt

[More information](#)

10

WATER

[CH.

diluted to 100 c.c., and the resulting solution will contain 0.001 gram of nitrogen as nitrate in 25 c.c.

Phenol-sulphonic-sulphuric acid mixture. 4 grams of phenol are mixed with 4 c.c. of ammonia-free distilled water, 100 c.c. of pure sulphuric acid are then added and the mixture is heated for 6 hours at 80° to 85° C., cooled and made up to 500 c.c.; 300 c.c. of pure sulphuric acid are then mixed with 200 c.c. of ammonia-free water and added to the phenol-sulphonic acid solution, giving 1000 c.c. of the reagent.

The method. 25 c.c. of the sample are placed in a round-bottomed porcelain basin and 25 c.c. of the standard potassium nitrate solution are placed in a similar basin, 2 c.c. of the phenol-sulphonic-sulphuric acid mixture are added to each and thoroughly stirred with a glass rod. The basins are placed on a water bath and the contents are evaporated until no more water is expelled; during the evaporation, the liquid is occasionally stirred with a glass rod; the sides of the basin are washed with a very small quantity of water and the contents of the basin are again evaporated on the water bath, the residue is taken up with water and again evaporated; the final residue is taken up with water and washed into measuring glasses, the volume being brought up to about 95 c.c., 3 c.c. of ammonia (specific gravity 0.880) are then added and the volume is brought up to 100 c.c. with water. The colour in each glass is proportionate to the quantity of nitrate present. It is claimed that by this method the nitrogen as nitrates is accurately estimated, even in the presence of 100 parts of chlorine per 100,000, and further that the purity of the colours obtained is such that the matching with the standard solution is considerably simplified.

(c) *Ammonia method. Preparation of copper-zinc couple.* A small piece of zinc foil is immersed in a solution of copper sulphate containing 3 per cent. of the dissolved crystallized salt; a deposit of copper is left upon the zinc; the deposition of the copper should not be allowed to proceed too far, otherwise it will not adhere firmly to the zinc; the couple is well washed with distilled water.

250 c.c. of the sample are made acid with 0.5 gram of crystallized oxalic acid; the wet couple is added; the whole