COLORIMETRIC METHOD FOR ESTIMATION OF DISSOLVED OXYGEN IN THE FIELD

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The suitability of the Winkler method for the estimation of oxygen dissolved in water is well established (*Standard Methods of Water Analysis*, 1936; Fox & Wingfield, 1938). Its usefulness in the field, however, is limited by the fact that it is necessary either to titrate the iodine solutions in the field, or to carry back to the laboratory numerous samples of water. Moreover, the titration of iodine solutions necessitates the frequent standardization of the sodium thiosulphate solution. With the modification of the Winkler method described here, the oxygen content of water can be estimated quickly and easily in the field without bulky apparatus. As no standard solutions are required the method is particularly useful when estimations are made only occasionally.

This adaptation of the Winkler method takes advantage of the fact that chloroform removes iodine from solution in water and gives with it a brilliant purple colour. The eye is more sensitive to the purple colour of iodine solutions in chloroform than to the brown colour of iodine in water, so that chloroform solutions of iodine equivalent to 1·0 and 1·2 c.c. oxygen/l. are distinguishable in comparator tubes, whereas similar solutions in water are not. The purple colour unfortunately fades perceptibly after some days, so that it is not profitable to make up standards of chloroform-iodine solutions. To overcome this difficulty glass comparator disks have been made which match the colour of our chloroform extracts from appropriate Winkler samples.[1] Two disks have been made, one (A) covering the range 0–2·0 c.c. oxygen/l. (0, 0·4, 0·8, 1·0, 1·2, 1·4, 1·6, 1·8, 2·0) and the other (B) covering 1·8–4·4 c.c./l. (1·8, 2·0, 2·2, 2·4, 2·8, 3·2, 3·6, 4·0, 4·4).

The disks were made in the following way. A series of water samples was made up of different oxygen concentrations ranging from 8 to 0 c.c./l. To each sample Winkler reagents were added in the same proportions as are used in the actual estimations (i.e. for each 100 c.c. of water, 2 c.c. of a solution containing 10 g. potassium iodide and 34 g. sodium hydroxide per 100 c.c., 0·4 c.c. 40 % manganous chloride solution, and 0·4 c.c. sulphuric acid). Some of each iodine solution was titrated and its oxygen equivalent calculated, taking into account the volume and oxygen content of the reagents. Another 10 c.c. of the iodine solution were shaken for 30 sec. with 10 c.c. chloroform and the resulting solution of iodine in chloroform matched with coloured glass against the sky. No difficulties were experienced in

[1] The disks and the Lovibond Comparator in which they are used are obtainable from Tintometer, Ltd., Milford, Salisbury.

making glass disks to cover a range of oxygen tensions of 0–4·4 c.c./l., but above this the "brilliancy" of the solution introduces technical difficulties. It was afterwards found that when the water sample contained more than 4·4 c.c./l. its oxygen equivalent could be estimated sufficiently accurately by shaking 5 c.c. (instead of 10 c.c.) of the iodine solution with 10 c.c. of chloroform, comparing the colour with disk B, and multiplying the reading by 2. Oxygen contents lower than 4·4 c.c./l. cannot, however, be estimated accurately by diluting similarly and comparing with disk A, readings obtained in this way being too low.

It is important to notice that the coloured glass disks match the colour of the iodine-chloroform solution in equilibrium with Winkler-iodine solution of known oxygen equivalent. When using the disks it is, therefore, necessary always to use the same proportions of Winkler reagents, as the partition coefficient of iodine in chloroform and water varies with the amount of potassium iodide present.

METHOD

The sample of water is transferred to a bottle of about 100 c.c. capacity, the usual precautions to avoid contact with air being taken. If the water contains dissolved organic matter, it is treated with Rideal-Stewart reagents (*Standard Methods of Water Analysis*, 1936). 2 c.c. of a solution containing 10 g. potassium iodide and 34 g. sodium hydroxide per 100 c.c. are run into the bottom of the bottle. 0·4 c.c. 40% manganous chloride solution is then added and the mixture shaken. When the precipitate has settled, 0·4 c.c. concentrated sulphuric acid or *o*-phosphoric acid is added.

If the water contains less than 4 c.c. oxygen/l., 10 c.c. of the resulting iodine solution are poured into a 25 c.c. stoppered measuring cylinder and an equal volume of chloroform is added. The mixture is shaken for 30 sec. and then transferred to a comparator tube supplied with the disk. When the chloroform has separated out from the water, its colour is compared with that of disk A (0–2·0 c.c./l.) or B (1·8–4·4 c.c./l.) in the comparator. If the water contains more than 4·4 c.c. oxygen/l., 5 c.c. of the iodine solution are shaken with 10 c.c. chloroform, the resulting iodine-chloroform solution is compared with disk B, and the reading is multiplied by 2.

Accuracy of method

The consistency of the method was tested by filling six bottles from the same sample of water and estimating the oxygen content colorimetrically. The chloroform extracts from the six bottles were indistinguishable. Chloroform extracts were made over a period of 4 days and gave the same result, although the sky against which the colours were matched varied from grey to blue and white. This was done for samples of water containing 6·8, 5·2, 3·2 and 1·0 c.c./l.

Estimations were also made of the oxygen content of fifty-nine samples of water by both the colorimetric method and by titration with sodium thiosulphate in the usual way. Regarding the titration figure as correct (actually, of course, this is itself subject to variation), within the range of 2·0–8·0 c.c./l. the absolute error of

the colorimetric method rose with rising oxygen concentration, but the percentage error remained approximately constant. Treating the percentage error as a normally distributed variable, the standard deviation was found to be $\pm 3{\cdot}26\,\%$. This means that 68 % of all determinations made with disk B may be expected to be within $3\frac{1}{4}\,\%$, and 95 % within $6\frac{1}{2}\,\%$ of the titration value. Eight of the fifty-nine estimations came within the range of disk A; the figures were within 10 % of the titration values. In nineteen cases out of twenty, therefore, the oxygen content of water can be estimated to within half the difference between adjacent figures on the disks. We consider this satisfactory for ordinary purposes.

Use of the syringe pipette with the colorimetric method

The construction and use of a syringe pipette for the determination of oxygen in natural waters has been described recently by one of us (Whitney, 1938). The syringe pipette is used for taking the sample of water and treating it with Winkler reagents. The iodine solution is then titrated by connecting the pipette with a special burette filled with standard sodium thiosulphate solution. The same pipette can be used with the colorimetric method. The iodine solution is not titrated, but is shaken with chloroform in the pipette. The chloroform-iodine solution is then ejected from the pipette for comparison with the standard disks. The estimation can be completed in 5 or 6 min.

It is necessary to describe here certain constructional details of the syringe pipette which are particularly relevant to the colorimetric method. The special burette is not, of course, required. The head-screw of the syringe pipette is removed by screwing it out of the sleeve. The movements of the plunger for adjusting the capacity of the pipette and for drawing in the reagents are now controlled by the spring-loaded nut on the side-limb (see Fig. 1 *a*, Whitney, 1938). When the plunger is pulled backwards by the tension of the spring, the flange of the metal head of the plunger bears against the nut. The flange is cut away at one part of its circumference, so that, by rotating the plunger head, the plunger is no longer retained by the nut, but can be pushed to and fro in the bore of the barrel. By this arrangement chloroform can be drawn quickly into the pipette after the Winkler-iodine solution has been obtained, and the chloroform-iodine solution can be rapidly ejected for comparison with the disk.

In the ordinary Winkler method about 2 c.c. of reagents are added for each 100 c.c. of water sample. Each 10 c.c. of the iodine solution will therefore contain the iodine equivalent of the oxygen which was present in 9·8 c.c. of the water sample. In order that our colour disks may be used with the syringe pipette, it is necessary to arrange that the pipette shall take in 9·8 c.c. of water. The iodine solution obtained from this sample is then equivalent to 10 c.c. of the iodine solution which would be obtained by the application of the ordinary Winkler method to the same water sample.[1]

[1] The error due to the oxygen content of the reagents is larger in the syringe pipette method than in the ordinary Winkler method. The difference is not taken into account as we do not consider it significant.

The procedure in an analysis is as follows:

(1) The cannula of the pipette is fitted into place (see Fig. 1 *b*, Whitney, 1938). The head-screw of the syringe pipette having been removed, the nut on the side-limb is adjusted so that the total capacity of the pipette is 10·1 c.c. The graduations on the barrel of the pipette are sufficiently accurate for this purpose. This setting allows 9·8 c.c. water to be taken in, for the dead space of the pipette (0·3 c.c.) is filled with manganous chloride solution.

(2) The sample is taken and treated with the reagents as described in Whitney (1938), but the reagents are drawn in with the nut on the side-limb and not with the head-screw.

(3) The volume of iodine solution in the pipette after the completion of (2) is 10·4 c.c., since 0·3 c.c. of reagents are added by turning the nut on the side-limb.

If the iodine solution is comparatively weak, 10 c.c. of chloroform are drawn in (using the graduations on the barrel) after the plunger head has been rotated free of the retaining nut. The volume of chloroform is measured by the graduations on the barrel.

If the iodine solution is strong, half of it (5·2 c.c.) is ejected before drawing in the 10 c.c. of chloroform. In this case the disk reading is doubled to give the oxygen content of the water sample.

(4) The plunger is now allowed to come right back against the sleeve, air being drawn into the barrel. The pipette is shaken for 30 sec. It is convenient while shaking to remove the cannula and place a finger over the open bore of the ground-glass mount of the pipette.

(5) The chloroform solution is ejected into a comparator tube for comparison with the disks.

SUMMARY

A modification of the Winkler method is described with which the oxygen content of water can be determined quickly and without standard solutions.

REFERENCES

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