International Council for the
Exploration of the Sea

C.M. 1962
Hydrographical Committee
N No. 79

THE WINKLER OXYGEN ESTIMATION - HOW DOES IT WORK?

by

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(Summary version)

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Chemists, whether they work with sea water, fresh water, tap water or polluted waters, always come to attention when the subject turns to the measurement of dissolved oxygen. The interest stems from the background chemistry of the Winkler estimation, which is something of a mystery. Practical details are well enough known and if judiciously observed, especially with regard to the standardization procedure, the analysis is foolproof. Equations given by Jacobsen, Robinson and Thompson in the official method sponsored by the 'Association d'Oceanographie Physique' and repeated in Dr. Barnes' recent book are essentially as follows:-

1) $Mn^{++} + 2\ OH^{-} \rightarrow Mn(OH)_2$

2) $2\ Mn(OH)_2 + O_2 \rightarrow 2\ MnO(OH)_2$

These equations convey the impression that oxygen gas is adsorbed or absorbed by manganous hydroxide. Consequently one would expect gas-solid laws to apply and the reaction to be slow, poly-molecular and perhaps only poorly stoichiometric. The oxygen-manganese equivalence was determined for well aerated sea water treated with progressively increasing amounts of manganese chloride. Figure 1 shows the reacting quantities of manganese and oxygen. The relationship is nearly linear from the origin to the level of complete oxygen removal. One atom of oxygen is equivalent to two atoms of manganese. This means that in the equations quoted above the valency change for manganese is wrong. It also suggests that the reaction is chemical. The oxygen taking part is not undissociated but is active in some way, presumably <u>via</u> the hydroxyl ion.

To test the effect of pH, an alkaline-iodide reagent was prepared using sodium carbonate and from this and the usual hydroxide reagent progressive mixtures of carbonate-iodide and hydroxide-iodide reagents were tested. Figure 2 shows that at least 30% hydroxide, i.e. $pH > 11$, must be present for complete oxygen fixation. This test also confirms that carbonate interference is unlikely in natural waters and that a large amount of carbonate can be tolerated in the alkali-iodide reagent.

The chemical reactions therefore involve the oxidation of manganous (Mn^{++}) to the manganic (Mn^{+++}) state - not Mn^{++++} as the first equations claim, and the oxygen in solution under alkaline conditions is in equilibrium with the hydroxyl ion, and thus if not actually ionic will for practical purposes behave as an ion rather than as a gas. The oxidation potential for the oxygen half-reaction is -0.5 volts.

3) $2\ OH^{-} \rightleftharpoons \frac{1}{2}\ O_2 + H_2O + 2\ e^{-}$

In theory, any reductant with a potential more positive than this should promote the reduction of molecular oxygen. The potentials for various manganese ions in alkaline solution are

4) $Mn(OH)_2 + OH^{-} \rightleftharpoons Mn(OH)_3 + e^{-}$ + 0.40 volts

5) $MnO_4^{-2} \rightleftharpoons MnO_4^{-} + e^{-}$ - 0.54 "

6) $MnO_2 + 4\,OH^- \rightleftharpoons MnO_4^- + 2\,H_2O + 3\,e^-$ -0.57 volts

7) $MnO_2 + 4\,OH^- \rightleftharpoons MnO_4^{-2} + 2\,H_2O + 2\,e^-$ -0.58 "

Clearly, only reaction 4) conforms with this requirement. Ferrous salts have been used in place of manganese in a modified Winkler estimation. The half reaction shows that the potential is suitable.

8) $Fe(OH)_2 + OH^- \rightleftharpoons Fe(OH)_3 + e^-$ $+0.56$ volts

However, manganese is preferred for the ordinary analysis because ferrous salts in neutral solution are rapidly oxided in air, but the manganous salts are stable.

A general statement of the Winkler reaction with the correct oxygen-manganese equivalence is found in equation 9) obtained by combining equations 3) and 4).

9) $4\,Mn(OH)_2 + 2\,H_2O + O_2 \rightarrow 4\,Mn(OH)_3$

and this is essentially the equation proposed by Winkler in 1888.

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There are many recommended procedures for the estimation of dissolved oxygen in sea water based on Winkler's original technique of 1888. For example, the method of the 'Association d'Oceanographie Physique' (Jacobsen et al 1950) gives full practical details and if the pitfalls involved in standardization are avoided, successful analyses should be well within the grasp of even a beginner in chemistry. Nevertheless the background chemistry of the technique is something of a mystery. Equations are quoted (ibid) which purport to describe the reactions involved,

$$Mn^{++} + 2\ OH^{-} \rightarrow Mn(OH)_2$$

$$2\ Mn(OH)_2 + O_2 \rightarrow 2\ MnO(OH)_2$$

$$Mn(OH)_2 + 2\ H^{+} \rightarrow Mn^{++} + 2\ H_2O$$

$$MnO(OH)_2 + 4\ H^{+} + 3\ I^{-} \rightarrow Mn^{++} + I_3^{-} + 3\ H_2O$$

yet in practice the quantities of reagents used bear no relation to these equations.

A full investigation of the technique is outwith the scope of a fisheries laboratory but two simple experiments have produced results which indicate the direction of the further research needed.

The equations quoted and the usual accompanying text create the impression that the reaction occurs between dissolved but undissociated oxygen gas and the adsorbing or absorbing solid, manganous hydroxide. Consequently one would expect gas/solid laws to apply and the reaction would be slow, polymolecular and perhaps only poorly stoichiometric. The newness of the precipitate and other aspects of its dispersion would determine how great an excess of manganese hydroxide would be required for complete oxygen fixation.

Clearly the first step was to determine the oxygen-manganese equivalence.

Manganase concentration

Observing all the usual basic practical requirements, increasing amounts of manganese chloride solution (Reagent A) were added to well-oxygenated sea water in similar calibrated glass bottles (ca 160 ml capacity); all other treatments were standard. Manganese (Mn) was determined gravimetrically in Reagent A as pyrophosphate. In Fig. 1 the reacting quantities of Mn(mg) are given with the corresponding amounts of oxygen (mg) found by titration. The oxygen-manganese relationship is almost linear from the origin to the level of complete oxygen removal (mean 1.745 mg O_2 per sample). Expressed as atoms, 1 atom of oxygen is equivalent to 2 atoms of manganese for practically the whole range. The equations given above which require 1 atom oxygen to 1 atom manganese are clearly wrong. The required amount of Reagent A is about 0.14 ml and 0.2 ml would suffice for any sea-water oxygen sample.

The oxygen-manganese equivalence follows a simple chemical relationship except when the residual oxygen concentration is very low, when, presumably because of the settling of the precipitate, the manganese reactions are slightly less efficient.

Alkalinity

The Winkler reaction takes place in a highly alkaline medium (pH about 12). The precise state of oxygen in solution under these conditions is a matter of considerable complexity. Certainly, oxygen will not behave as the undissociated gaseous molecule but will be in equilibrium with the hydroxyl ion and thus dissolved oxygen if not necessarily ionic itself will for practical purposes behave as an ion rather than as a gas.

Closely bound up with alkalinity is the presence in the sea water of metals precipitated by hydroxide and also carbon dioxide. Winkler expressed concern about interference due to carbon dioxide (or carbonate) and recommended additional reagents. Also the alkali-iodide solution (reagent B) absorbs carbon dioxide on exposure to air and thus may deteriorate. What are the limits of carbon dioxide interference and what hydroxide concentration is required?

Two alkaline-iodide solutions were prepared, reagent B with 4 N sodium hydroxide and reagent B' with the equivalent 4 N sodium carbonate final concentrations. Next, a set of reagents was made by varying the combination of these two. Oxygen was determined in well aerated sea water with results as summarized in Fig. 2. It was noted that the usual flocculent buff to brownish-buff precipitate became less flocculent and nearly white with increased carbonate. The settled precipitates of the latter after several days in the dark changed to black, granular material.

The graph indicates that oxygen fixation was complete so long as at least 30% sodium hydroxide or not more than 70% sodium carbonate was present.

The amount of carbonate ($CO_3^{=}$) tolerated is thus 84 mg in addition to 4 mg (Harvey, 1955) present in the sea water. Clearly there is no concern about interference due to natural carbonates in sea water. With regard to the deterioration of reagent B in air, satisfactory performance is obtainable with 70% of the hydroxide neutralised with carbon dioxide but for safety perhaps 50% should be regarded as a working limit.

No measurements were made but it is likely that the pH at the limiting carbonate concentration would be about 11 to 11.5. To generate such a pH change using 4 N sodium hydroxide in absence of carbonate would need quantities of 0.1 ml or less which would involve considerable mechanical difficulty if carbonate interference is to be completely avoided. Further experiments using dilute carbonate-free hydroxide solutions are pending.

Conclusion

The above evidence is sufficient to indicate the main course of the reaction. Each atom of oxygen, probably via a complex hydroxyl ion, reacts with two atoms of manganese under suitable oxidation-reduction conditions which require a pH of above about 11 in the usual treated sea-water sample.

The Winkler estimation may be broken down into half reactions whose oxidations potentials are known. (Conventions according to Latimer, 1938).

$Mn\,Cl_2 \rightleftharpoons Mn^{++} + 2\,Cl^-$ (in the reagent solution)

$Mn^{++} + 2\,OH^- \rightarrow Mn(OH)_2$ (precipitation)

1) $2\,OH^- \rightleftharpoons {}^1/2\ O_2 + H_2O + 2\,e^-$ (at pH 12, − 0.5 volts)

2) $Mn(OH)_2 + OH^- \rightleftharpoons Mn(OH)_3 + e^-$

(at alkaline pH, + 0.40 volts)

Therefore, in theory, any reductant with a potential for the ion-electron half-reaction more positive than -0.5 volts should promote the reduction of molecular oxygen. Ferrous salts provide a suitable potential and have been used in a modified Winkler estimation.

$$Fe(OH)_2 + OH^- \rightleftharpoons Fe(OH)_3 + e^- \quad (+\ 0.56 \text{ volts})$$

However, ferrous iron is readily oxidised in neutral solution on exposure to air so manganese is more convenient for ordinary analyses.

It can be seen that other manganese reactions in alkaline solution do not meet the requirement regarding potential.

$$MnO_4^{-2} \rightleftharpoons MnO_4^{-1} + e^- \quad (-0.54 \text{ volts})$$

$$Mn_2 + 4\,OH^- \rightleftharpoons MnO_4^- + 2\,H_2O + 3\,e^- \quad (-0.57 \text{ volts})$$

$$MnO_2 + 4\,OH^- \rightleftharpoons MnO_4^= + 2\,H_2O + 2\,e^- \quad (-0.58 \text{ volts})$$

A general statement of the chemistry of the Winkler estimation may be derived by combining equations 1 and 2 to give 3 which shows the correct oxygen-manganese equivalence,

$$3)\quad 4\,Mn(OH)_2 + 2\,H_2O + O_2 \rightarrow 4\,Mn(OH)_3$$

and this is essentially the equation suggested by Winkler in 1888.

More detailed electrochemical evaluation of the Winkler process may well be justified as this would enable the precise conditions for oxygen fixation to be defined so that measures to exclude or reduce interference in contaminated waters may be logically undertaken. It would also be useful to know what sort of substances can not be tolerated in the oxygen analysis.

Reagents

Reagent A. Manganese chloride, hydrate, analytical reagent grade, 400 g, is dissolved in distilled water and the volume adjusted to 1 litre.

Reagent B. (a) A solution of 10 g, potassium iodide, analytical reagent grade, is made up to 500 ml.

(b) A solution of 160 g, sodium hydroxide, analytical grade is made up to 500 ml and cooled.

Mix equal volumes of (a) and (b) as required.

Reagent B'. (a) As (a) Reagent B.

(b) A solution of 212 g sodium carbonate anhydrous, analytical reagent grade, is made up to 500 ml and cooled. Mix equal volumes of (a) and (b) as required.

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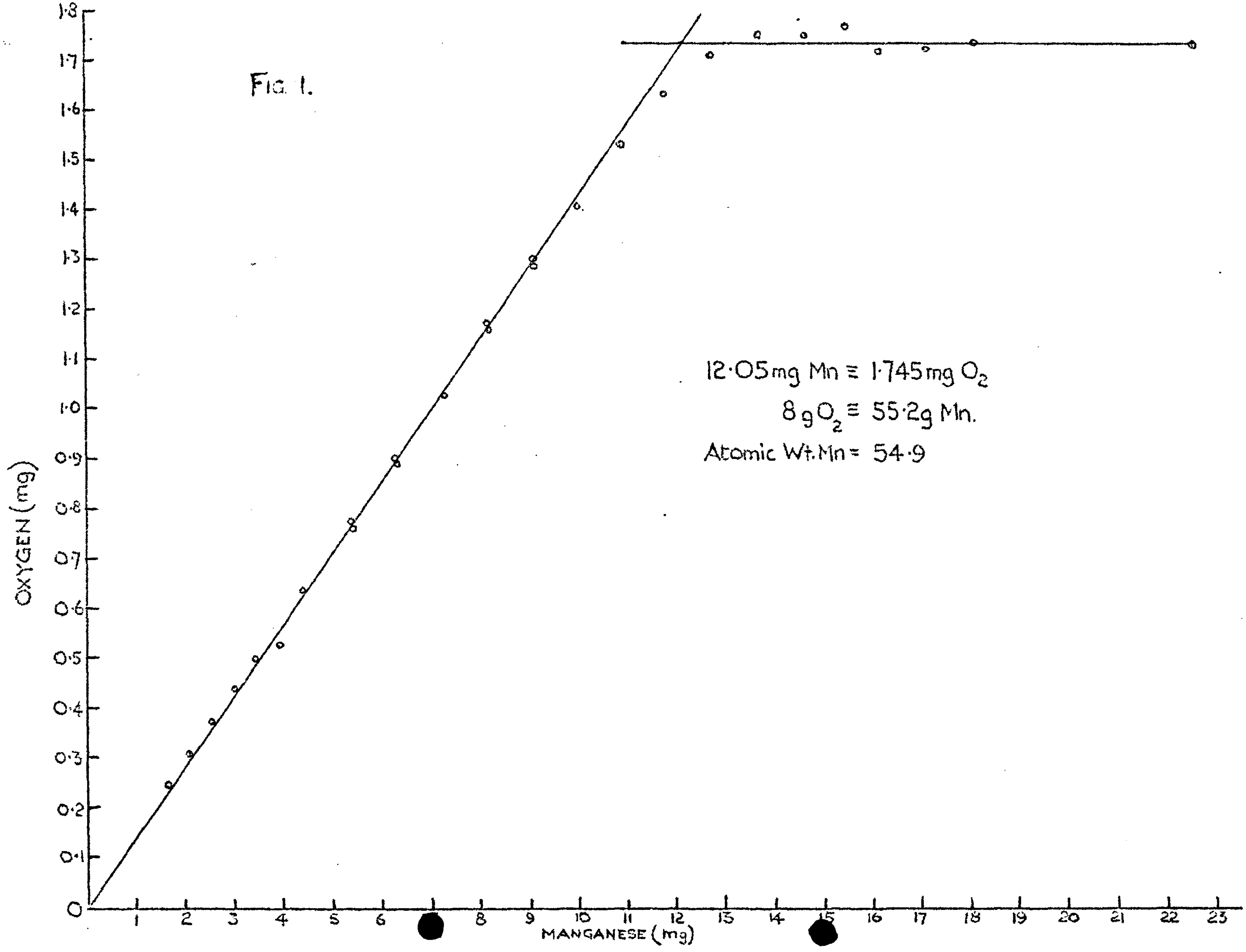

FIG. 1.

$12{\cdot}05\,\mathrm{mg\ Mn} \equiv 1{\cdot}745\,\mathrm{mg\ O_2}$

$8\,\mathrm{g\ O_2} \equiv 55{\cdot}2\,\mathrm{g\ Mn.}$

Atomic Wt. Mn = 54·9

FIG. 2.

HYDROXIDE AND CARBONATE REAGENTS