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Title: Determination of dissolved oxygen in water with Leukoberbelin-Blue I.
A quick Winkler method.

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Translated by Lorna Heller

1. Introduction

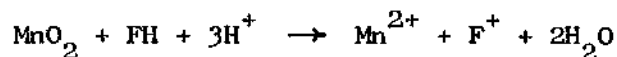
The reaction of Mn(II) with water-dissolved oxygen, to a higher manganese hydroxide in an alkaline medium, as with the longstanding classic Winkler method, is the first step in the method described here. The assumption for faultless results by the conventional and modified Winkler method is clean water, which contains no organic substances by Mn(III) or Mn(IV). In many cases, however, eg. in river and lake-water tests, it can be seen with the naked eye that after some time the originally brown-coloured precipitate of manganese hydroxide becomes more and more colourless. The time which elapses before the precipitate of manganese hydroxide has settled is sufficient to allow a part of the freshly precipitated and very active higher manganese hydroxide to react with the organic content of the water. The consequences of this are false measurements. The reaction $O_2 + Mn(OH)_2 \rightarrow$ higher manganese hydroxide comes to an end quantitatively in a few seconds and with it ends the basic reaction of the oxygen determination. Any continuing contact of the higher manganese hydroxide with the organic material in the water is detrimental and is only necessary so far because the manganese hydroxide must settle for the continuation of the further steps of the method.

2. Theoretical Part

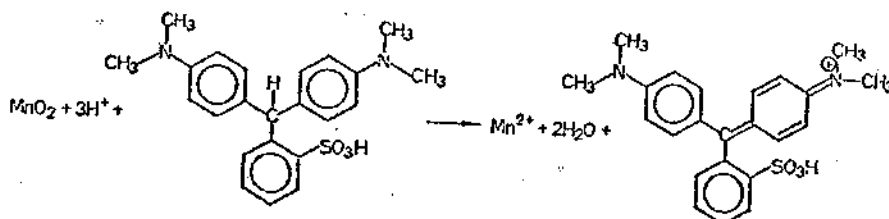
Leuko-bases of triphenylmethane colouring substances are oxidised in the space of a few seconds in an acidic medium by Mn(III) or Mn(IV) to coloured cations. The extinction of solutions of colouring matter so obtained is consequently also a measure for the determination of the oxygen content. The leuko-bases of indigo-carmin and the o-toluidine have hitherto been used in similar methods. These reactants are, however, either unstable themselves or do not form stable colouring substances. This is also true of leuko-malachite green used for the determination of manganese, as described in the literature, which besides is not soluble in water (1, 2, 4).

Further triarylmethane-derivatives have been examined as reagents for the determination of Mn(VII) (3).

We have succeeded, through the synthesis of the leuko-base of a triphenylmethane substance, in removing these troublesome factors. We have obtained a new reagent, which is suitable for the determination of the oxygen content of a water specimen. $Mn(OH)_2$ reacts in a well known way to form higher manganese hydroxides, characterized here by MnO_2 . The leuko-base (FH) of the colouring substance is oxidised quantitatively to the colouring substance (F⁺) in this way.



The reagent Leukoberbelin-Blue I (FH) used by us, is 2-(bis-(4-dimethylaminophenyl) methyl) benzene sulphonic acid. Thus the reaction is comprised as follows:



3. Synthesis of Leukoberbelin-Blue I¹

25g (25ml, 0.21M) freshly distilled N-dimethylaniline and 21g (ca. 0.1M) 2-formylbenzol sulphonic acid (sodium salt) are reflux-condensed with 30ml 2N H₂SO₄ for 24 hours. Then they are cooled, neutralised with 4N NaOH, and the excess N-dimethylaniline is driven off with steam. After cooling, the crystal sludge is rigorously vacuum filtered and washed with a few millilitres of water. The still damp substance is recrystallised from methanol. Particularly pure preparations are obtained if the acetone solution of the leuko-base is filtered through a silica gel column. Should, after some time (several weeks), a surface blue-colouring occur on the crystals, the substance can be repurified by filtration through silica gel.

Yield: 29.4 g (71.6%)

Formula: C₂₃H₂₆N₂O₃S Mwt. 410,54

λ_{max} of the colouring substance 623 nm

Furthermore, the N-dimethylaniline and N-phenylmorpholin are converted with formylbenzol-2,4-disulphonic acid (sodium salt) by the above method. Both products of the synthesis are also useful as reagents, but more difficult to produce purely.

4. Behaviour of Leukoberbelin-Blue I and its associated colouring substances

The pure substance of Leukoberbelin-Blue I, when stored in the dark, can be kept for several weeks, during which time it slowly forms the associated colouring matter. The aqueous solution of the leuko-base, with a few drops of NH₄OH solution added, is stable for over a year. The extinction of the colouring substance Berbelin-Blue I formed in the reaction is not altered in the acetate buffer. The analysis can consequently take

¹ Available through: Mecron GmbH, 1 Berlin 41, Haupstr. 76.

place of the sampling, while the measuring of the colouring matter formed can still be undertaken days later in another place. The colouring matter has a molar extinction coefficient of $\epsilon = 110,000$.

5. Apparatus and chemicals

For the determination of the dissolved oxygen, several syringes (polyethylene) with 7 cm long, sharp cannules and the glass vessel (ca 100 ml) shown in fig. 1 are necessary. In one ground opening a suitable stopper (brass) is fitted, sealed with silicone grease, which has in the bottom a packing of silicone rubber (packing rubber for gas chromatography, made by Perkin and Elmer). This packing is pierced from above with the injection tubule and the reagents injected. The details of this sealing which is easy to make, can be inferred from the figure. In the glass vessel there is a magnetic stirrer, which can be driven by a magnetic motor. For field-work a stirrer can be made with the help of a clockwork motor and a second magnetic stirrer secured on top, which is independent of electricity. Because of the short time necessary for stirring, a single winding of the spring is sufficient for each analysis. According to the quantity of oxygen expected various concentrations of the leuko-base solution can be employed. The $MnCl_2$ and $NaOH$ solutions used hitherto for the Winkler method can be adapted, although then both substances are present in a large but not disturbingly large excess. The advantage in the use of these concentrated solutions is their own small oxygen content. The following solutions were used by us for the determination of oxygen.

1. 40 g $MnCl_2 \cdot 4H_2O$ are made up to 100 ml with boiled de-ionised or distilled water.
2. 10 g $NaOH$ are made up in the same way to 100 ml.
3. 25 g CH_3COOH are made up in the same way to 100 ml.
4. 4 g Leukoberbelin-Blue I are mixed with ca 80 ml boiled water, 0.3 ml conc. NH_4OH are added and made up to 100 ml. In darkness this solution can be kept for longer than 6 months.

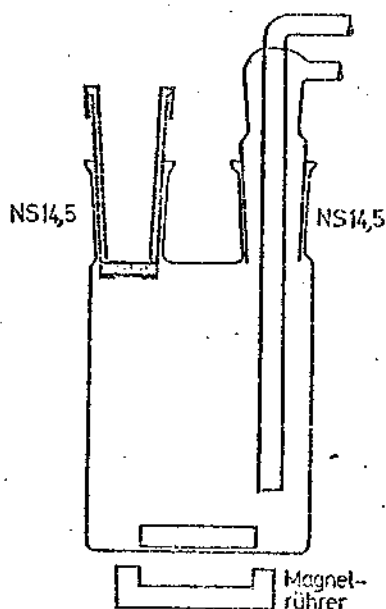


Fig 1. Reaction vessel for the oxygen determination.

6. Method of determination of Oxygen

The water sample is flushed through the vessel shown in Fig. 1, where, by repeated brief raising of the stopper the vessel becomes free of air. After several minutes, when the vessel has been rinsed free of the air which has been in contact with the water, the inflow of water is stopped up. With the help of the syringe (a separate one is necessary for each solution) are then injected one after the other through the silicone rubber membrane. 0.5 ml of solution 1 and 0.5 ml of solution 2, are given a quick stir with the magnetic stirrer and after ca. 20 secs 0.5 ml of solution 3 and 1 ml solution 4 are injected and mixed. Thus is the critical part of the determination of oxygen completed. Now the necessary aliquot for the filling of the cuvettes is removed with a pipette and the extinction measured photometrically. The blue-tinted solution, depending on the oxygen content can, however, also be transferred and be measured after a few days have elapsed. These conditions are particularly advantageous for field-work. The silicone rubber stopper is then rinsed, the remains from the previous analysis are poured out of the glass vessel, the stopper is replaced and the vessel is flushed with the next water sample to be measured. The named quantities of reagent are sufficient for oxygen contents up to 15 mg O₂/l when using a 100 ml reaction vessel.

7. Evaluation

The solution of the blue colouring matter obtained is measured in a photometer with filter 618 nm (Elco II, made by Zeiss) against water. The following cuvettes are necessary:

Range 0-50 µg O₂/l cuvettes with path lengths of d = 5 cm

Range 50-250 µg O₂/l cuvettes with path lengths of d = 1 cm

Range 250-2,500 µg O₂/l cuvettes with path lengths of d = 0.1 cm

Range 2.5-15 mg O₂/l the solution of colouring matter obtained is diluted 1:10, then path length d = 0.1 cm

By raising the amount of the leuko-base and giving the corresponding dilution of the colouring matter solution formed still higher oxygen contents can be measured. We have obtained our calibration curve with Mn(IV) suspensions (German Standard Method G2) as we were not successful in manufacturing pure aqueous oxygen solutions with O₂ concentrations < 300 µg O₂/l.

The quantitative reaction of dissolved oxygen with Mn²⁺ in an alkaline medium is the basis of all Winkler methods, both classical and all modified methods. In spite of this the roundabout way via higher manganese hydroxide to find the calibration curve cannot be satisfactory. A treatment constant of $\omega = 312$ is obtained from the calibration curve. In this way the oxygen content per litre of water shows itself.

$$a) \text{ Extinction} \times 312 = \mu\text{g O}_2/\text{l}$$

If one bears in mind the dilution of the sample by the added reagents, one obtains

$$\text{b) Extinction} \times 312 \cdot \frac{V+a}{V} = \mu\text{g O}_2/\text{l}$$

Both V and a are in opposition to other Winkler methods and can be implicated in the treatment constants. V is found from the size of the reaction vessel and ought to lie around 100 ml (magnet stirrer in vessel). a is the constant from the treatments and amounts to 2.5 ml. For the case V = 100 ml the simplified formula is obtained:

$$\text{c) Extinction} \times 320 = \mu\text{g O}_2/\text{l}$$

Given $V \approx 100$ ml, the corrected treatment constant must be reckoned from b) separately for the reaction vessel used. If less exact results are required then the analysis solutions can also be compared with colour standards. For the range 2.5 - 15 mg O₂/l the result must be multiplied by 10 on account of the dilution.

For the range 1 - 10 mg O₂/l, single measurements by this method vary by 4% from the German Standard Method G2 in which pure water is used. The application of this method of oxygen determination in the presence of strongly reducing substances such as eg. Fe²⁺ in conjunction with a semi-automatic arrangement working by a different method, which is also suitable for fieldwork, is still being worked on. The method is also feasible with sea-water. The determination of ozone and H₂O₂ with leuco-bases of triphenylmethane colouring substances is to be published in a later paper.

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Notice

Please note that these translations were produced to assist the scientific staff of the FBA (Freshwater Biological Association) in their research. These translations were done by scientific staff with relevant language skills and not by professional translators.