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THE CHEMICAL AND THE ELECTROCHEMICAL DETERMINATION OF MOLECULARLY DISSOLVED OXYGEN IN INLAND WATERS

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molekular gelösten Sauerstoffes der Binnengewässer.

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I. Preface

[p. 1] Since Winkler's first publication in 1888, on his iodometric method of determination of dissolved oxygen in water, numerous authors tried to [p. 2] conquer the inadequacies with which the original method is affected under special conditions. Modifications of the method were pursued for three reasons. First to eliminate the error through reduction and oxidation. Secondly, to simplify the method, and thirdly to remodel the analysis of very small water quantities. Already it has become a difficult task to sort out, from the abundance of analytical suggestions, a particular method for adoption, especially because chemical methods have been developed as well which bind the oxygen in iron hydroxide or in another manner with the approved O_2-fixation, but which disregard the manganic hydroxide entirely.

A good and brief summary on the many methods developed for determination of oxygen has been given in the recently published work by Liebknecht, Tödt and Kahan (1953). Compare also Maucha (1932) and Ohle (1936). But for a few exceptions, the several recommended procedures are based on the original Winkler method. His principle as well as his precision, makes Winkler's method an exemplary limnological procedure. It is desirable to fix the material which has to be analyzed on the spot of sampling. The real analytical treatment of the samples can then be done more satisfactorily under favourable conditions. This great advantage of the Winkler method is therefore its utilization in the examination of surface water. Under this provision one can eliminate colorimetric and pipette methods which require immediate further processing of individual water samples. In addition, it should be remarked that such methods may be very advantageous under certain conditions with physiological laboratory processes. The following discourse, however, deals with the analysis of natural surface waters.

The volumetric analytical process of the original Winkler method should, in my opinion, be retained because it produces greater precision in a wide range of oxygen concentrations than colorimetric methods. It requires, moreover, only an insignificant amount of apparatus. Consequently, I have thoroughly and methodically checked the Winkler method in various waters and worked out a correction method which gives dependable quantitative O_2 results in every case. The chlorine difference method (Ohle, 1936, 1952) can indeed extensively be used with success, but it has the disadvantage that several reagents have to be added separately from one another under repeated opening and shutting [p. 3] of the O_2 bottles.

It seemed inviting to develop a method in which the effect of reduction on iodine which is brought on by organic matter is titrimetrically determined in parallel samples, and also in which the effect of oxidation on dissolved potassium iodide is cancelled out, as Winkler (1904) has already suggested. Such a correction method is therefore to be preferred, because the Redox reactions produced by a similar component, which came in effect with the Winkler method, namely by iodine and iodide. In addition to this, a rapid quantitative method is especially desired for the determination of oxygen in limnological procedures, even when by its application one has to work with a certain margin of error because one cannot analyze an immeasurable amount of water sample quantitatively. Rather, it must be limited to a characteristic process closest to the rapid process with which the nature of the water is investigated. These investigations cannot in all cases be done on grounds of water temperatures, since regions of the lakes, ponds and streams distinguished by oxygen minima are not also systematically recognized by their temperatures from the other water regions.

In the following chapter the oxygen method will be explained in its currently recommended form for water investigation.

II. The rapid electrochemical process for the determination of oxygen in water.

Owing to the publication of Kolkwitz (1941) concerning biological investigations with the flat screen and oxygen "sounder", the attention of the limnologist is for the first time drawn to an electrical measuring device which was recommended by Tödt more than ten years ago. With this device, dissolved oxygen in water as well as in plant saps (Kolkwitz, 1942) can be detected immediately. By those uncertain early experiments, the influence of the electrolyte and the temperature was, of course, not considered. Its meaning was determined by Tödt (1942a) who initiated this electrochemical technique. It was therefore necessary to determine the efficiency of individual factors which influence the electrical measurement before the method could be applied in quantitative research (Ohle, 1953).

1. The oxygen "sounder"

The construction of the oxygen sounder (Tödt, 1942b) is very simple. It consists only of two metal electrodes which are connected to a microammeter by means of a two-core cable. For waterproof and pressure resistant connections [p. 4] of the electrodes with the rubber cable, the probe is made out of plexiglas (Fig. 1). For use in deep waters it is recommended that the cable be wound on a hand winch (Fig. 2) to which the ammeter is connected so that no slipring contact is required, and thus contact trouble is avoided.

2. The formation of residual currents

The principle of the electrochemical oxygen determination rests on a so-called residual current measurement by means of a galvanic element, and this operates without an external source of current. The element is made of a rare metal and a base metal. In the analyses by Todt and Kolkwitz already mentioned, platinum and cadmium metals were used. In the last few years gold and zinc electrodes have definitely proven to be better. The strength of the residual current, that is the depolarization current which originates below the actual decomposition voltage, is measured by means of an ammeter. [p. 5] The electrochemical process is as follows. The hydrogen which collects primarily on the surface of the gold cathode is oxydized by the dissolved oxygen in the water. The electrode is thus depolarized. An equivalent amount of zinc goes into solution, so that electrons flow via the ammeter to the cathode. The current intensity is therefore equivalent to the oxygen concentration of the water, within certain limits. Further details can be found in my work concerning electrochemical oxygen determination (Ohle, 1953).

3. The oxygen-residual current relation

Electron transport from the cathode to the anode takes place through the water with the aid of dissolved electrolyte and is therefore dependant on the specific conductivity of the water. A certain oxygen concentration gives a significantly smaller current intensity in electrolyte-poor water than in electrolyte-rich water. It is therefore necessary to make up separate calibration curves for the different types of water. In order to be able to read the small as well as the large residual currents on the same instrument, it is equipped with a rotation resistor connected in parallel in the circuit with a changeable shunt in the shape of a ringscale. The greater accuracy thus obtained in reading the instrument may be explained in the following example.

An electrolyte-poor water ($10^6 k_{18} = 50$) gave with a gold disc cathode at an oxygen concentration of 10 mg/L of water and at 15° C, a residual current of 160×10^{-6}A. When the ammeter received a shunt of 180 ohms, the needle deflected 12.3 scale units, but with 280 ohms the deflection was 17.8 scale units. Electrolyte-rich water ($10^6 k_{18} = 320$) gave, under similar circumstances, the same needle deflections as when the ammeter had a shunt of 180 ohms. In spite of the changes in ammeter-needle deflections inflicted by adjustment of different shunts, the current intensity remains unchanged. When the shunt has a small resistance, then 1 scale unit indicates a large microampere value (e.g. 22.6×10^{-6}A with 100 ohms) and vice versa (e.g. 8.5×10^{-6}A with 300 ohms). These relationships are shown in Fig. 3 for the gold disc electrode which I used. The ammeter has its own resistance of 2600 ohms. The proportionally small electrolyte enrichment which develops during summer in the hypolimnion of the lakes is without importance in the electrochemical oxygen determinations. This is also true for very eutrophic lakes, so that calibration values which already have [p. 6] been determined for such waters can be applied to all water zones during the whole year.

[p. 7] The curve shown in Fig. 4 taken with a gold disc electrode of 0.45 cm^2 area at 15°C, indicates the prevailing relation between oxygen concentration of the water and the residual current for the Large Plöner Lake, which averages during the total circulation of its water masses a specific conductivity of about $330 = 10^6 k_{18}$ with an SBV = 2.25 m. eq./L. The size of the zinc anode, which was about 5 cm^2, is unimportant. The working surface of the gold electrode on the other hand, has a deciding influence on the strength of the residual current. The greater the amount of hydrogen which can be depolarized on the cathode, the more electrons will flow through the measuring system. The calibration curve thus obtained inclines to the ordinate. That means that the strength of the residual current is not in ideal proportion to the oxygen concentration obtained by the iodine-difference method. It is therefore apparent that the electrolyte conductivity of the water at higher oxygen concentrations is not sufficient for the relatively strong electron transport. Accordingly, very small gold cathodes with a small surface area of but a few square millimeters produce rectilinear curves as long as the specific conductivity is more than $350 = 10^6 k_{18}$ (corresponding to an electrolyte strength of about 260 mg/L).

[p. 8] A suitable example for such calibration series is found in Fig. 5, which has been made for tellurian or ground water. One could decide from this result that it would be advisable to work only with very small gold electrodes, because rectilinear calibration curves are, of course, superior to the curved ones. But unfortunately, with the decrease in size of the cathodes another process becomes significant, namely the lime encrustation of the gold surface. This process is in close relation to the forming of the depolarization current itself, on account of the hydrogen released on the cathode surface which is oxidized in the presence of dissolved oxygen. This develops an abundance of hydroxyl ions which in their turn lead to carbonate precipitation (compare the diagrammatic presentation of the cathode lime encrustation as a result of the residual current, in my publication of 1953, p. 107).

The heavier the lime film is on the rare metal electrode, the more the residual current is weakened. The platinum cathodes formerly used in the oxygen sounder encrusted easier than the currently used gold electrodes and were rendered useless for those reasons. Not only is the nature of the metal responsible for the intensity of the resulting lime precipitation on the cathode, but so also is the surface structure of the electrode metals which, at least until now, cannot be brought back to their original state. The gold cathode, which served as well for the formulation of the calibration curve of the Large Plöner Lake (see Fig. 4), can be employed without hesitation for an SBV (an alkalinity) of 2.5 m. eq./L. Of course one has to bear in mind that the total available bicarbonate does not act on the electrode. Decisive for the "fatigue" of the cathode is by far the concentration of calcium bicarbonate, while magnesium ions, of which most are coupled to bicarbonate ions as well, remain without importance. To the lime rich north German waters corresponds the indicated SBV boundary of 2.5 m. eq./L with an amount of $Ca(HCO_3)_2$ of about 2.2 m.eq./L. The ratio of concentration of Ca:Mg is here generally 1:6 or 1:8. Compared with the gold disc electrode, a smaller wire electrode will very quickly indicate the encrustation effect in very lime poor waters. In water of the Great Plöner Lake (SBV = 2.26) the current decrease within 30 minutes is up to 16 per cent of the initial current intensity (Fig. 6). This effect is understandable because the lime film will decrease the active size of the cathode.

The faster the electrode coating reduces the magnitude of the active contact surface, the smaller will be the surface of the electrode. The small wire electrodes cannot be used for the analysis [p. 9] of lime rich water as a result of these properties. One has to use here the disc-shaped or similarly shaped gold cathodes and definitely the one of medium size of about .5 cm^2 surface area, regardless of the roughness of the metal.

The curvalinear calibration curves must, therefore, at least until later, be regarded as invincible factors. It was possible, on the other hand, to work throughout with wire cathodes in electrolyte-poor waters. Of course without these, one cannot obtain rectilinear calibration curves since the low electrolyte value of the water of higher oxygen concentrations interferes by dampening the electron transport. A downgrade develops from specific conductivity 100 = $10^6 k_{18}$, and the depolarization current is therefore not proportional with the O_2 concentration of the water. The calibration curves are curved strongly in contrast with the rectilinear ones which are obtained in electrolyte-rich water by means of the same small cathode (see Fig. 5). Because of this, the small wire electrodes do not have any special advantages for the examination of electrolyte-poor water. With regard to the striving for uniformity of measuring apparatus, at the present state of constructive development of the oxygen sounder, the gold disc electrode of medium size is in general recommended.

Finally, of the factors which influence the residual current intensity, the effect of water velocity is an important consideration.

It is evident that the renewal the microfilm of hydrogen and hydrogen ions which form on the gold electrode surface will influence the depolarization current decisively. It can flow only and indeed in full strength when the rate of renewal of the microfilm, related to a given level of oxygen concentration is maintained by constant water movement.

[p. 11] In laboratory experiments this requirement is easily achieved by the use of a stirrer. When one does not shy away from intricate apparatus one gets the same effect when the oxygen sounder together with a "diving" motor is let down in the water. The simplest and most satisfactory method for limnological purposes is the motion of the submerged sinker obtained by shaking the rubber cable. It gives reproducible results, just as was concluded in comparing results obtained in waters up to 70 meters (230 feet) deep.

Water temperature is also to be considered as a factor influencing the residual current. [p. 12] The strength of the depolarization current rises with temperature since primarily the conductivity of the ions points to this relationship and secondly because the speed of diffusion of oxygen molecules on the cathode surface changes in a similar manner with temperature. The relation between residual current intensity and temperature is linear over the span of oxygen concentrations appearing in natural waters. As an illustration of the temperature-residual current relationship, a test series was worked out with lake water in which the oxygen contents was artificially lowered with nitrogen (Fig. 8). During the tests, the O_2 concentration of the water rose, as chemical analyses done at short intervals indicated, from 3.80 mg./L gradually to 5.65 mg./L. If the temperature had remained at 17.2°C throughout, then scale unit values corresponding to oxygen concentrations would have formed a rectilinear relationship.

Table I. Temperature coefficients of the residual current values in percentage of the measuring value (taken at 15°C)

t°C	0	2	4	6	8
3	+45.5	+44.0	+42.5	+41.0	+39.5
4	+38.1	+36.8	+35.6	+34.5	+33.5
5	+32.5	+31.5	+30.6	+29.7	+28.8
6	+28.0	+27.2	+26.4	+25.6	+24.8
7	+24.1	+23.3	+22.6	+21.9	+21.2
8	+20.5	+19.8	+19.1	+18.5	+17.8
9	+17.2	+16.5	+15.9	+15.3	+14.7
10	+14.1	+13.5	+12.9	+12.3	+11.7
11	+11.1	+10.5	+ 9.9	+ 9.3	+ 8.7
12	+ 8.1	+ 7.5	+ 7.0	+ 6.4	+ 5.8
13	+ 5.3	+ 4.7	+ 4.1	+ 3.6	+ 3.0
14	+ 2.5	+ 2.0	+ 1.5	+ 1.0	+ 0.5
15	± 0.0	- 0.5	- 1.0	- 1.5	- 2.0
16	- 2.5	- 3.0	- 3.5	- 4.0	- 4.5
17	- 5.0	- 5.5	- 6.0	- 6.5	- 7.0
18	- 7.5	- 7.9	- 8.3	- 8.7	- 9.1
19	- 9.5	-10.0	-10.4	-10.8	-11.2
20	-11.6	-12.0	-12.4	-12.8	-13.2

Table I (cont'd.)

t°C	0	2	4	6	8
21	-13.6	-14.0	-14.3	-14.7	-15.0
22	-15.3	-15.7	-16.0	-16.3	-16.6
23	-17.0	-17.3	-17.6	-17.9	-18.2
24	-18.5	-18.8	-19.1	-19.4	-19.7
25	-20.0	-20.3	-20.6	-20.9	-21.1

[p. 13] However, the temperature was allowed to rise from 2.5 to 33.5°C. Consequently, the residual current became much stronger, which is shown by the solid curve and which is caused by the difference of oxygen concentrations.

When the measured residual current intensities are to be related on a calibration curve by determination of the real oxygen concentration, recorded at certain temperatures as in this case at 15°C, then the recorded scale units of the ammeter or the corresponding microampere values have to be corrected for the calibration temperature. For simplification of this transformation the temperature coefficients of the residual current have been put together in Table I, in percentage of the measuring value. Then each observed value, in microamperes or scale units, can be corrected for temperature difference. If, for instance, at a water temperature of 19.2°C a needle deflection of 18.5 scale units is observed on the ammeter, then this value, as the correction table shows, is to be decreased by 10% to 16.6. One can read for this value the equivalent oxygen concentration from a calibration curve which is valid for water of similar electrolyte concentrations. Temperature readings are also of special importance for electrochemical oxygen determination. For work in deeper lakes, the thermistor has proved to be very useful, as Mortimer and Moore (1953) discussed extensively in their series of papers. Within a short time it is possible with this apparatus to take long series of temperatures and with greater accuracy. In shallow water the use of the thermistor is also advantageous, although it may be replaced in these instances with a reversing-thermometer.

4. The use of the oxygen sounder

Concurrent with the taking of temperature measurements electrochemical oxygen determinations are made by means of the oxygen sounder. For this purpose the electrodes must first be cleaned. They are daubed with concentrated acetic acid or 10% hydrochloric acid and thus freed of their lime films. The electrodes are then dipped into water for 5 to 10 minutes, preferably in the water to be examined, until the acid has rinsed off entirely and the electrode surfaces have been "soaked in". With constant shaking of the marked cable, the oxygen sounder is lowered into the different water zones and the deflection of the ammeter needle is observed, after which the electrical shunt of the ammeter [p. 14] is adjusted so that the needle deflection for the surface water equals about 22 to 23 scale units (total range of the ammeter = 25 scale units). Therewith the measurements are ended. For rough determination of the layers of the oxygen-poor regions of a body of water no further manipulations are required. Such measurements could give sufficient information for many practical purposes.

These measurements provide an important insight into the condition of the individual water zones, so that further physiographic and biological examinations are considerably aided. It is quite possible to determine the O_2 concentration of the water by means of the apparatus with a precision of ±5%. For this purpose Table I provides the scale units with the temperature correction. Provided a calibration curve is available from laboratory results, oxygen values are readily obtained.

[p. 15] Figure 9 shows oxygen values obtained in this manner in layers of the Large Plöner Lake. It shows the individual chemically determined oxygen concentration as well as the temperature.

The disadvantage of this method is that for all bodies of water or at least for all water types, special calibration curves have to be prepared. In many cases another method proves adequate, in the following descriptive explanation, for use with the oxygen sounder, in which calibration value is determined in every series of examinations.

Although the formation of the residual current does not experience any disturbing influences from reducing substances which are very obvious with the chemical method, the effect of reducing substances must be considered when the oxygen content of the water is to be determined with greater precision. A combined method of the electrochemical and the chemical method is therefore offered. A large amount of individual measurement is done within the shortest time by means of the oxygen sounder. The taking of water samples remains limited to the most important water zones, on grounds of the described electrochemical analysis. The analytical results which have been obtained by chemical methods serve for the calibration of the scale values and residual current values which have been determined <u>in situ</u> with the oxygen sounder for identical water regions. This combination method will be clarified by means of an examination of the lake, in this case, the Plöner Lake (Fig.10).

[p. 16] The temperature arrangement in layers which is determined with the thermistor, gave a stable picture. The thermocline was situated between 11 and 12 meters (36.1 and 39.4 feet). The oxygen sounder showed for the epilimnion the high O_2 concentrations to be expected and their marked decrease from 10.5 meters (34.4 feet) downward. Total absence of molecularly dissolved oxygen was shown in the hypolimnion from 13.5 meters (44.3 feet) to the the mud bottom. The scale units observed on the ammeter (see Table II) are supplied with the temperature corrections according to Table I.

Water samples for chemical oxygen determination were taken only from 1, 10 and 12 meter depths. The O_2 concentration of these three layers was 9.2, 7.0 and 2.0 mg/L. These concentrations were, together with the corresponding residual current or scale units, recorded in a coordinate system and in this way the curve of Fig. 11 was obtained. From this curve one can reproduce, for every residual current value, the corresponding oxygen concentration of the water (Table II). The electrochemical oxygen analysis of water, by means of the oxygen sounder, leads in this way to quantitative results. [p. 17] Of course one must take the temperature corrections and the calibration of the electrical measurement value as "trouble for bargaining".

Table II. Reference lake examination.

Depth in m.	mg O_2/L Winkler	t°C.	oxygen sounder			
			scale units of ammeter	% t° - correction	scale units (SU) after t° - corr.	mg O_2/L according to SU
0	-	15.2	17.6	- 0.5	17.5	9.2
1	9.24	15.2	17.6	- 0.5	17.5	9.2
3	-	15.1	17.5	- 0.3	17.5	9.2
5	-	15.0	17.4	± 0.0	17.4	9.1
6	-	15.0	17.0	± 0.0	17.0	8.8
7	-	15.0	16.8	± 0.0	16.8	8.7
8	-	15.0	16.2	± 0.0	16.2	8.3
9	-	15.0	15.0	± 0.0	15.0	7.5
10	7.04	14.9	14.2	± 0.3	14.2	7.0
10.5	-	14.8	12.5	+ 0.5	12.6	6.1
11	-	13.2	10.3	+ 4.7	10.8	5.1
11.5	-	12.5	8.1	+ 6.7	8.6	4.0
12	2.02	9.6	4.1	+15.3	4.7	2.0
12.5	-	9.0	2.0	+17.2	2.3	1.0
13	-	8.7	0.6	+18.1	0.7	0.3
13.5	-	8.4	0.0	-	0.0	0.0
14	-	8.0	0.0	-	0.0	0.0
15	-	7.7	0.0	-	0.0	0.0
16	-	7.7	0.0	-	0.0	0.0
20	-	7.7	0.0	-	0.0	0.0
23	-	7.6	0.0	-	0.0	0.0

When individual waters are frequently examined the drawing up of calibration curves is recommended for continual reference. When the combination method is applied the oxygen sounder proves itself extremely well in extensive water examinations.

First of all this method gives <u>in situ</u> valuable insight into the general water situation. Secondly, only a few samples have to be taken by the chemical oxygen determination method. Nevertheless oxygen distribution is comprehended without much effort. Thirdly, no errors will be introduced by reducing water in the residual current measurements. Fourth, oxidizing substances also, insofar as they occur in natural waters, remain without influence. Quantitative O_2 determination, by means of the oxygen sounder, is limited in alkaline waters (with an SBV = 2.5) by the lime deposits on the cathode, which henceforth probably can be eliminated by further improvement of the apparatus. The use of the apparatus for semi-quantitative or qualitative oxygen determinations is always possible, however, especially in probing for oxygen-poor water zones even if the SBV = 5 m. eq./L. When the specific conductivity of water is under 100 = $10^6 k_{18}$, then the intensity of the residual current changes only slightly. With low electrolyte content the change is yet more apparent, particularly when the oxygen concentration is in the neighbourhood of its saturation point. Therefore, in electrolyte-poor water the sensitivity of the quantitative O_2 determinations decreases and does not reach the degree of accuracy available in electrolyte-rich waters of ±5 per cent of the actual oxygen concentration.

The calibration of the residual current has to be followed with a satisfactory chemical method. This is true for all of the described combination methods since in its application, where reducing substances are present, water is analyzed and is used as a basis for the utilization of subsequent measurements with the oxygen sounder. Aside from these special considerations of the electrochemical oxygen determination, it appeared necessary to confirm and if necessary to improve some of the different chemical methods for quantitative comprehension of oxygen molecules dissolved in water.

III. The chemical determination of dissolved oxygen in water.

Foregoing this representation it is the aim of the Method Committee of the I.V.L.to recommend those methods which from thoroughly controlled examinations as well as from practical use have already proved themselves valuable and which therefore are recommended for general use.

The individual procedures should be written so that they can be used without further reference to other publications.

1. The Winkler method of oxygen determination

The method for oxygen determination is now, as before, the original titrimetric method by Winkler (1888) and it is the base for the limnological oxygen method. Special attention should be paid to the suggestions for improvement of the author's methods, among which are those recommended by Winkler himself, especially for limnological purposes. These recommendations were advanced on the occasion of the Budapest I.V.L.Congress in 1930 (Winkler, 1931).

The 100-120 ml. sample volumes are considered best from the experience of both Winkler and the present author. However, one can use 30 ml. bottles under difficult transportation conditions and procure satisfactory analytical results when diluted thiosulfate or micro burettes are used for the iodine titration (Kalle, 1939). The bottles have to be weighed with distilled water at room temperature. Also the ones which are commercially available with the volume showing on the bottom should be checked for the accuracy of the figures. If one decides to use an aliquot of the bottle contents for iodometric titrations, then the careful weighing of the bottle volume can be disregarded and if necessary one can repeat the titration with a second part of the same sample.

It seems essential to know what temperature changes may have affected the bottled sample so that an error correction may be incorporated into the oxygen determination. When the reagents for the fixation of oxygen are added immediately after obtaining the sample, then an increase or decrease of the volume is of little importance unless small air bubbles are taken up which can be avoided by wrapping the samples in wet cloths. Following the preliminary treatment of the samples (e.g. in order to make the reducing matter harmless) a rise in temperature may occur and the resulting expansion of the sample volume may lead to a reduction in the amount of oxygen in the bottles. If the temperature of the sample <u>in situ</u> was 4.0°C and it warmed up to, as an extreme example, 18.0°C, then the volume increase would be 0.14%.

The original oxygen concentration decreases about the same amount, before the fixation with chemical reagents. For example, if there were 9.0 mg O_2/L dissolved in the water initially, then after the rise in temperature 8.95 mg O_2/L would remain. When the errors in analysis which originate in this way are proportionally small, then by appropriate insulation these errors will be kept as small as possible. Over and above this, a rise in temperature of the water naturally leads to loss of oxygen when the oxygen concentration nears its point of saturation. If, in the above mentioned example at 4.0°C the oxygen concentration is 4.14 mg O_2/L, this amount is maintained at 18°C, 0.56 mg O_2/L below saturation.

An original oxygen concentration of 11.10 mg/L (2.04 mg/L below saturation) under the same temperature conditions leads to an over-saturation of 1.54 mg O_2/L. Oxygen can then readily be released out of the water as a gas, so that no exact analytical result can be procured.

The so-called correction methods for the original Winkler procedure are especially vulnerable to this danger and indeed all the more so the longer the treatment, which is necessary for the oxidation of interfering reduction substances, may last. For this reason, among others, the brominating method [p. 20] (Alsterberg, 1926) is affected by considerable disadvantages and it is difficult to keep the water temperature constant for a total of 24 hours, which is prescribed as the reaction time of the bromine. Analysis of the water sample should be completed without delay, as is attempted when carrying out the chlorine-difference method. In addition to this the iodine-difference method should be discussed (see No. 2).

The taking and analysis of water samples is simplified when conical ground-glass stoppered bottles are used (Ohle, 1936). There are also the small amounts of liquid which are displaced from the sample on addition of the reagents, the stopper being replaced in a fashion so as to exclude any air bubbles from the bottle. The bevelled ground-glass stoppered bottles produced by laboratory supply houses are not too good in use, as the edge of the bevelled surface chips easily.

The filling of the bottle has to be carried out in such a manner that the water being sampled is lead via a rubber, glass or plastic tube to the bottom of the bottle and at least three times the volume of the bottle overflows. It can then be certain that no trace of the water which has been in contact with the air will remain in the bottle.

For these and other gas-analytical examinations only the first half of the contents of the sampling apparatus should be used (for instance, the Ruttner scoop or the Friedinger bucket) as the remainder of the water would have come into contact with the air. The fixing of the dissolved oxygen takes place according to Winkler's original directions wherein the water sample is treated with a manganous chloride solution and sodium hydroxide containing potassium iodide. The dissolving of the precipitate is attained with hydrochloric acid or sulphuric acid. For iron-rich water is recommended the Alsterberg (1926) sirupy phosphoric acid.

Later Winkler (1931) suggested using sodium bisulfate solution. It was quite apparent that acids were difficult to handle in the field. Kalle (1939) also points to this convenience for sea investigation. Sodium bisulfate when compared with the strong acids has another advantage in that it can be carried along as the dry salt where it can be dissolved in the field with distilled water or even filtered surface water from the lake to be examined. Of course under these provisions [p. 21] not too much is demanded for the exactness of the oxygen determination. This also applies in the case of the direct addition to the 100 ml. sample bottle of 0.5 g manganous chloride tablets (Merck), as well as for 0.6 g sodium hydroxide and 1 g crystallized potassium iodide. It should be clear that in many cases only such a method can be applied and then correspondingly more accuracy has to be exercised.

The Winkler reaction proceeds according to the following equations:

$$MnSO_4 + 2\ NaOH = Mn(OH)_2 + Na_2SO_4$$

$$2Mn(OH)_2 + O_2 = 2MnO(OH)_2$$

The decisive change occurs then in acid solution by oxidation of the potassium iodide to iodine:

$$MnO(OH)_2 + 4NaHSO_4 + 2KI = I_2 + MnSO_4 + 2Na_2SO_4 + K_2SO_4 + 3H_2O$$

One molecule of oxygen corresponds thus with two molecules of iodine and since the oxygen is divalent and the iodine monovalent, an equivalent of O_2 leads to an elimination of an equivalent of iodine.

It has been customary to bring the hydroxide precipitate into solution by acidification only after it has completely settled, as Winkler intended. But the longer the apparent reducing or oxidizing impurities in the water act on the aqueous manganic oxides, the more will the manganic concentration differ from the actual O_2 value equivalents. In a similar manner these substances have an intensified influence on the iodine which appears in the acid solution, if one delays the titration. When one wants to undertake the oxygen determination according to Winkler's original method, with water containing nitric or ferrous iron, it is therefore necessary to restrict the action periods of the reagents to a minimum. After a series of tests, it was concluded that the chemical bonding of the dissolved oxygen has ended after a maximum of 15 seconds (Table III). It is thus not necessary to wait for the precipitate to settle, but it is possible to add the sodium bisulfate solution after the above-mentioned short period during which the water sample is to be shaken rather vigorously. It is best to wait 10 minutes before carrying on with further treatment. In this way one reduces the error, which is apparent by impurities, considerably. However this method is employed in very few cases for moving water examinations, since the technical provisions for completing the oxygen determinations on the spot are not offered. The disturbing impurities have to be made harmless in another way.

[p. 22] The titration of the liberated iodine is undertaken with sodium thiosulfate solution the titre of which is related to the oxygen concentration of the sample. For example: 0.5-0.20 mg O_2/L (corresponding with 1.55 19 g to 6.2076 g $Na_2S_2O_3 \cdot 5H_2O$/L). Starch solution serves as an indicator which, by addition of a little formalin, is kept free of putrefaction. Another approved solution is the Polyviol M 05/14 preparation which is produced by the Wacker firm (Munchen 22, Prinzregentenstrasze 22). This shows a dark red coloration with iodine. The 1% watery solution is stable without further additives and the color change from red to colorless is very easy to recognize. The thiosulfate is protected from the influence of CO_2 by the addition of sodium hydroxide as was suggested by Hahn and Windisch (1922).

Table III. Comparison of mg O_2/L determined with and without sedimentation of the manganese dioxyhydrates

Groundwater		Dist. H_2O		Pond water	
30-45 min*	10-15 sec*	30-45 min*	10-15 sec*	30-45 min*	10-15 sec*
1.91	1.92	6.24	6.22	8.86	8.86
1.92	1.92	6.26	6.24	8.83	8.84
1.94	1.91	6.22	6.24	8.82	8.82
1.89	1.89	6.25	6.22	8.84	8.86
1.94	1.93	6.24	6.26	8.86	8.88

*Waiting period from the addition of sodium hydroxide until the acidification.

It is made bactericidal by isobutyl alcohol (Winkler, 1931). Solutions of more than half a year old which contained these preservatives showed no alteration in their titres. The standardization of the thiosulfate solution can be accomplished in several ways, for instance with potassium bio-iodate after Than (1877) or after Tulkowsky (1868, quote after Treadwell, 1927) or by the use of potassium dichromate which in my opinion serves the purpose very well. By repeated crystallization it can be kept very clean and by drying at 130°C it can be kept completely free of water. Of this salt so treated and cooled in a dessicator, for example, 1.5314 g are dissolved in distilled water and made up to 1 litre. One ml of this titrimetric standard corresponds with 0.2499 mg O_2. Five ml of the solution are put into a 100 ml glass stoppered bottle with about 1 g crystallized potassium iodide, 30 ml distilled water and 5 ml concentrated sodium disulfate solution. After a waiting period of 20 minutes, during which the flask should be placed in the dark, it is titrated in the presence of starch or polyviol. If the titre of the thiosulfate solution for example is 0.20 mg O_2/ml, then there will be 6.25 ml used [p. 23] in the titration. Three titrations should be done in sequence.

Table IV. Saturation table for molecularly dissolved oxygen as mg O_2/L in clean water, in contact with the atmosphere with 20.93 vol. % O_2 at 760 Torr. (Torricelli) total pressure with inclusion of the pressure of the saturated water vapor (according to measurements by Fox, 1907).

t°C	0	1	2	3	4	5	6	7	8	9
0	14.64	14.60	14.56	14.52	14.48	14.44	14.40	14.36	14.32	14.28
1	14.24	14.20	14.16	14.12	14.08	14.04	14.01	13.97	13.93	13.89
2	13.85	13.81	13.78	13.74	13.71	13.67	13.63	13.60	13.56	13.53
3	13.49	13.45	13.42	13.38	13.35	13.31	13.28	13.24	13.21	13.17
4	13.14	13.11	13.07	13.04	13.01	12.97	12.94	12.91	12.88	12.84
5	12.81	12.78	12.74	12.71	12.68	12.64	12.61	12.58	12.55	12.52
6	12.48	12.45	12.42	12.39	12.36	12.33	12.30	12.27	12.24	12.21
7	12.18	12.15	12.12	12.09	12.06	12.03	12.01	11.98	11.95	11.92
8	11.89	11.86	11.84	11.81	11.78	11.75	11.73	11.70	11.67	11.65
9	11.62	11.59	11.57	11.54	11.51	11.48	11.46	11.43	11.40	11.38
10	11.35	11.32	11.30	11.27	11.25	11.22	11.20	11.17	11.15	11.12

Table IV. (cont'd.)

t°C	0	1	2	3	4	5	6	7	8	9
11	11.10	11.08	11.05	11.03	11.00	10.98	10.96	10.93	10.91	10.88
12	10.86	10.84	10.81	10.79	10.76	10.74	10.72	10.69	10.67	10.64
13	10.62	10.60	10.57	10.55	10.53	10.50	10.48	10.46	10.44	10.41
14	10.39	10.37	10.35	10.33	10.31	10.28	10.26	10.24	10.22	10.20
15	10.18	10.16	10.14	10.12	10.10	10.07	10.05	10.03	10.01	9.99
16	9.97	9.95	9.93	9.91	9.89	9.86	9.84	9.82	9.80	9.78
17	9.76	9.74	9.72	9.70	9.68	9.66	9.64	9.62	9.60	9.58
18	9.56	9.54	9.52	9.50	9.48	9.46	9.45	9.43	9.41	9.39
19	9.37	9.35	9.33	9.32	9.30	9.28	9.26	9.24	9.23	9.21
20	9.19	9.17	9.16	9.14	9.12	9.10	9.09	9.07	9.05	9.04
21	9.02	9.00	8.99	8.97	8.95	8.93	8.92	8.90	8.88	8.87
22	8.85	8.83	8.82	8.80	8.78	8.76	8.75	8.73	8.71	8.70
23	8.68	8.66	8.65	8.63	8.62	8.60	8.58	8.57	8.55	8.54
24	8.52	8.50	8.49	8.47	8.46	8.44	8.43	8.41	8.40	8.38
25	8.37	8.35	8.34	8.32	8.31	8.29	8.28	8.26	8.25	8.23
26	8.22	8.21	8.19	8.18	8.16	8.15	8.14	8.12	8.11	8.09
27	8.08	8.07	8.05	8.04	8.02	8.01	8.00	7.98	7.97	7.95
28	7.94	7.93	7.91	7.90	7.88	7.87	7.86	7.84	7.83	7.81
29	7.80	7.79	7.77	7.76	7.75	7.73	7.72	7.71	7.70	7.68
30	7.67	-	-	-	-	-	-	-	-	-

Another way of adjustment of the titre of the thiosulfate solution is provided by using oxygen saturated water, which is prepared by half hour aerations (Moggio and Burland, 1951), during [p. 24] which the temperature and the atmospheric pressure are carefully considered. The result of the chemical oxygen determination with this water is compared with the theoretical saturation value corresponding to the same physical conditions. In this way the titre of the thiosulfate solution is compiled. Clifford (1953) proceeded similarly, whereby he used as a basis a well shaken and aerated water sample of the lake concerned as a standard for 100% O_2 saturation. However, actually in these two procedures the quantitatively satisfactory standardization of the thiosulfate solution is not accomplished since another factor comes into action, namely, the decrease of the saturation concentration of the oxygen by ions, colloids and gasses present in the water (Ohle, 1952). But as a reference quantity for the examination of one and the same water, the titre value obtained with this method can prove itself entirely true, even if this does not correspond in chemical ways unconditionally with the actual titre and cannot be applied to other waters. It remains an important limnological problem, in a theoretical respect, to investigate more closely the influence of the impurities on the solubility of oxygen in water. We know first of all that the O_2 saturation point of inland waters can be reached a few tenth of a mg sooner than the saturation table of Fox indicates (Table IV) which, however, for clarification of this problem shall be taken as underground for calculation of the O_2 saturation percentage (Ohle, 1952). Especially the decrease of oxygen solubility produced by dissolved sodium chloride in the water was examined by Fox as also later by Whipple and Whipple (1911). Their calculated correction value in mg O_2/L for 100 mg Cl (corresponding 164.9 mg NaCl per litre of water is shown in the following table.

Table V. Decrease of oxygen saturation concentrations of salt and brackish water in mg O_2/L per 100 mg Cl/L at temperatures from 0 to 39 °C.

units t°C tens	0	1	2	3	4	5	6	7	8	9
0	0.017	0.016	0.015	0.015	0.014	0.014	0.014	0.013	0.013	0.012
10	0.012	0.011	0.011	0.011	0.101	0.010	0.010	0.010	0.009	0.009
20	0.009	0.009	0.009	0.008	0.008	0.008	0.008	0.008	0.008	0.008
30	0.007	0.007	0.007	0.007	0.007	0.007	0.007	0.007	0.006	0.006

In regard also to the unit of measurement of oxygen data, uniformity is desired. Data in cm^3 are waived and instead units in mg/L are adopted. Not even millimol data is more advantageous for the utilization of the analyses. (compare Czensny, 1943a; Ohle, 1953).

For the sake of completeness conversion factors are mentioned whereby the oxygen volumes are related to 0°C and 760 Torricelli: 1 cm^3O_2 = 1.429 mg O_2/L; 1 mg O_2 = 0.70 cm^3O_2; 1 mmol O_2 = 16.0 mg O_2 = 11.2 cm^3O_2. Since the O_2 saturation values are related to the pressure of 760 Torr., they must be recalculated with low barometer readings, the values of which are obtained in the simplest way by means of the formula of approximation of Maucha (1932) and Minder (1941).

$$\log B = \log 760 - \frac{h}{18421(1+0.004t)}$$

B = medium local barometer press.
h = latitude of the water in meters
t = medium temperature of the air

For the medium local pressure, B, calculated in this way which is valid for the altitude of the water concerned, provides the oxygen saturation value (O_2'') from which, for a definite temperature taken from Table IV (O_2') in mg/L, is applied the formula contracted from Henry's Law which signifies the tension of the saturated water vapour.

$$O_2'' = \frac{B - f}{760 - f} O_2'$$

The value of f is for different temperatures shown in the following table.

Table VI. Pressure (in Torr.) of the saturated water/vapor in relation to the temperature (0 to 39°C) (After D'Ans and Lax, 1949)

units t°C tens	0	1	2	3	4	5	6	7	8	9
0	4.58	4.93	5.29	5.69	6.10	6.54	7.01	7.51	8.05	8.61
10	9.21	9.84	10.52	11.23	11.99	12.79	13.63	14.53	15.48	16.48
20	17.54	18.65	19.83	21.07	22.38	23.76	25.21	26.74	28.35	30.04
30	31.82	33.70	35.66	37.73	39.90	42.18	44.56	47.07	49.69	52.44

For the examination of mountain lakes the publication by Minder (1941) gives a thorough foundation. In relation to the hydrostatic pressure and its meaning with apparent O_2 supersaturated water, the reader is referred to Ohle (1952). [p. 26] The oxygen contents of the analytical reagents are yet to be considered.

From 0.5 ml of manganous sulfate (or manganous chloride) solution and the sodium hydroxide containing potassium iodide 0.004 mg O_2 is introduced into the sample bottle as long as the reagents have been freshly prepared with boiled distilled water.

Shortly after preparation of reagents, the O_2 concentration rises slightly. I found repeatedly after several days or weeks that old reagents contained a constant O_2 concentration of 0.007 mg/ml (Fig. 12). Consequently, the oxygen concentration of the water, since 100 ml bottles were used, was found to be too high by 0.07 mg O_2/L. This correction value is to be employed in general. One may settle for 0.004 mg O_2/L when, as mentioned, freshly made up reagents are at one's disposal. This is actually seldom the case. With the sodium bisulfate solution about 0.001 mg O_2 with the prescribed 3 ml, as well as 0.003 mg O_2 (Fig. 14) is introduced into the bottle and bound with the manganese hydroxide, but only then, when the addition follows without the former precipitation of the hydroxide. Otherwise the oxygen concentration of the bisulfate does not come into play.

[p. 26] Reagents

1. Manganous sulfate solution:

   100 g $MnSO_4 \cdot 4\ H_2O$ +
   200 ml boiled distilled water (or a solution of the same concentration of $MnCl_2 \cdot 4\ H_2O$)
   Filter

2. Sodium hydroxide containing potassium iodide:

   100 g NaOH +
   200 ml boiled distilled water +
   50 g KI

[p. 27] 3. Sodium bisulfate solution:

   500 g $NaHSO_4 \cdot H_2O$ +
   400 ml boiled distilled water
   Filter

4. Phosphoric acid:

   89% sirupy solution

5. Sodium thiosulfate solution:

   Concentration depending on demand, e.g.
   1.5519 g $Na_2S_2O_3 \cdot 5\ H_2O$ (adequate for .05 mg O_2/L
   or 6.2076 g $Na_2S_2O_3 \cdot 5\ H_2O$ (adequate for .20 mg O_2/L
   Standardization as described in the text.
   It is clear therefore that the thiosulfate does not necessarily have to be weighed out very accurately.

6. Starch solution:

1 g soluble starch with H_2O is stirred into a paste and transferred into 100 ml of hot distilled water + 0.5 ml of 40% formalin (or Polyviol solution which is mixed as the starch solution, but without the formalin)

The use of the reagents.

In the prescribed sensitivities 100 to 120 ml sample bottles are used. One releases each time 0.5 ml manganous sulfate and 0.5 ml of the potassium reagents by means of a small mouth pipette of which the tip should be held to about 1 cm under the miniscus of the bottle contents. After the precipitation of the hydroxide sediment which, in the stoppered and shaken bottle, will generally be reached within 10 minutes, 3.0 ml of the bisulfate is added. The iodometric titration can then follow after a waiting period of 10 minutes. Starch solution (1 ml) or Polyviol solution (2 ml) is used as indicator. When concerned with iron-rich water one does not dissolve the hydroxide sediment with bisulfate but with 3.0 ml sirupy phosphoric acid. When it is possible to work the samples immediately, as for instance in the laboratory, the errors which arise through impurities can be minimized considerably when one does <u>not</u> wait for the precipitation of the hydroxide sediment. But one adds immediately after the 10 to 15 seconds period of shaking, bisulfate or phosphoric acid. In this case the volume of the water sample has to be corrected, firstly for the added amounts of manganous sulfate and sodium hydroxide, and secondly for the amounts of phosphoric acid or bisulfate. The value for the oxygen concentration which has been obtained by means of titration has to be reduced by 0.07 mg O_2/L for the Winkler reagents and where the process has been employed without precipitation, 0.03 mg O_2/L for the bisulfate solution has to be subtracted.

When one examines extremely oxygen-poor water and water laden with reducing matter, such as water from the Hypolimnion of highly eutrophic lakes, then the amount of oxygen which has been added with the reagents will often not be indicated. Then the corrections are of course not applied.

[p. 28] 2. The iodine-difference method

a) Elaboration of the process

A whole series of correction methods has been developed for the original Winkler method to eliminate reducing or oxidizing materials. One should recall the preliminary treatment of water samples with potassium permanganate or bromine or calcium chloride or with sodium azide.

It was essential to work with the different method when it concerned manganous-rich deep water lakes, whereby manganic quantities can be detected. These were apparent with a preliminary oxidizing treatment (Ohle, 1936). The former methods are not entirely satisfactory. They are connected with troublesome or unmanageable errors. However, Winkler (1904) produced a correction method in which he used an iodine solution. The advantage of this method is that the water samples are not treated with various reagents. Winkler detected by back titration with thiosulfate that water could trap iodine after addition of potassium iodide, phosphoric acid and N/100 iodine solution.

For the oxygen determination of waters which contain sulfate and in which iodine is used for the oxidation of sulfite ions, Haase (1932) advised the treatment of samples with an iodine solution of known titre and the addition of an equivalent amount of thiosulfate solution. One should then proceed with the hydroxide precipitation as is described in the Winkler method. However it appears that errors occur due to the reduction of the manganese dioxide hydrates caused by the formed tetrathionate. These errors have to be eliminated since the acidification follows as soon as possible.

Skopinzew and Owtschinnikowa (1933) agreed that Winkler's correction method with iodine is superior compared with other methods for pre-oxidation. These authors point out that the preliminary treatment with permanganate (Rideal and Stewart) shows an oxygen concentration which is always too insignificant. This is also the case with the Alsterberg bromine method (Ohle, 1936). The iodine sample of Winkler gives practically uniform results in slightly polluted waters.

The Russian authors stated that the results with sewage water were too high. Dissolved oxygen has to be present in order to use this procedure with the iodine sample. This does not seem to be the case at all under natural conditions. Thus an iodine consumption is detected in the titration of the parallel sample. The results of the oxygen [p. 29] determination are not to be corrected, since no iodine reduction occurred in the main sample. If the actual iodine reduction of the water _is_ considered, then there is a ficticious amount of oxygen. The modification of the Winkler method, which has been suggested by Winkler himself, is affected by this defect.

Skopinzew and Mitjagina (1939) were first to add a certain amount of iodine to the water sample. Haase (1932) proceeded similarly but the Russians did not disturb the remaining iodine excess. This was preserved and its value was determined in a parallel sample.

The main sample and the parallel sample both receive the same amount of iodine, for instance 2 to 4 ml 0.01N iodine solution in a saturated sodium chloride solution and, after 5 minutes, each sample receives 1 ml potassium iodide in sodium hydroxide (Skopinzew and Mitjagina, 1939). This is followed with the addition of 1 ml manganous chloride or manganese sulfate solution in the main sample and 1 ml distilled water in the parallel sample. Completion of the usual procedure is carried out as soon as the hydroxide precipitation in the main sample has settled. Both samples have to be treated in a similar manner.

Independently from the publications I mentioned, Adams, Barnett and Keller (1943) developed a preliminary treatment with iodine which differs from the method by Skopinzew in that the iodine is not added separately but together with the sodium hydroxide - potassium iodide solution. Although the method is simplified in this manner, it cannot be recommended because it is impossible to deliver with a pipette the highly concentrated sodium or potassium hydroxide in an absolute quantity. This is necessary, however, in regard to the added iodine. The separate addition of iodine is therefore preferable and a necessity when the treatment of the water samples cannot be completed at the sampling point.

The correction method by Skopinzew does not give reproducible results for oxygen determination when the water is polluted, and the reaction time is not exactly measured (example in Table VII). In this case the following method was employed. A main sample bottle and a parallel sample bottle were filled with water from the Klinker River. Both received 1.0 ml iodine reagent (4.0 mg iodine and 80 mg potassium iodide in a saturated sodium chloride solution). They were stoppered and shaken. The main sample then received 0.5 ml sodium hydroxide - potassium iodide and [p. 30] 0.5 ml $MnSO_4$ solution. The parallel sample received only sodium hydroxide.

Table VII. The influence of time on the oxidation of iodine and hypoiodide in very polluted water. (Klinker River, Plön, 1953)

Waiting period in min. from addition of sodium hydroxide to acidification	ml. thiosulfate for 1000 ml water		Apparent mg O_2/L	Difference mg O_2/L
	Main sample	Parallel sample		
5	47.1	6.2	7.89	-
10	47.2	5.2	8.10	+ 0.21
20	47.3	5.1	8.14	+ 0.25
30	47.2	4.5	8.24	+ 0.35
45	47.1	3.9	8.34	+ 0.45
60	47.2	3.8	8.38	+ 0.49
120	47.3	3.5	8.45	+ 0.56
180	47.3	2.2	8.70	+ 0.81

A waiting period of 5 to 180 minutes followed as Table VII indicates. Then 3.0 ml concentrated sodium bisulfate solution was added to the main sample and almost simultaneously 3.5 ml of the same solution to the parallel sample. This was followed after 10 minutes with the thiosulfate titration. The results were remarkable. The longer the standing time of the hydroxide precipitation, the higher the value for the oxygen concentration. This was particularly the case in waters which contained much reducing matter, as for instance the Klinker River, while this phenomenon was not so apparent in cleaner waters and indistinguishable in distilled water.

From the beginning it was established that the increase in these data was not the result of an actual increase of oxygen concentration since the main sample produced approximately the same titration results (Table VII). That was to be expected because the water was kept in a glass tub under liquid parafin during the sample taking. Thus the temperature remained almost constant throughout. The increase of the determined values was a result of the iodine reduction in the parallel samples, which increased with the waiting period. The difference between the titration results of the main samples and their corresponding parallel samples increased proportionally.

For the transformation of the amount of I_2, which is found in 10.0 ml iodine reagent, 9.6 ml of thiosulfate solution was used up in distilled [p. 31] water which had been acidified with $NaHSO_4$. The first parallel sample of Klinker River water which was left for 5 minutes in alkaline medium took up so much HOI or I for the oxidation of reducing matter (probably inorganic) that for back titration only another 6.2 ml thiosulfate had to be used. With the rest of the parallel samples the amount of hypoiodide or iodine decreased steadily up to acidification. After 3 hours the hydrogen-iodine combination required only 2.2 ml of thiosulfate solution (Table VII). The following facts account for the reaction in which the iodine reduces steadily in the parallel samples. The prophylactically delivered iodine in the water samples yields hypoiodide ions in alkaline solutions.

$$I_2 + Na^{\cdot}OH' = H^{\cdot}OI' + Na^{\cdot}I'$$

The hopoiodide oxidizes the reducing matter which is present in the water much more than iodine. But in the main sample this oxidation process is prevented by the voluminous hydroxide precipitation, because the colloid and suspensoid are carried along. The oxidation of inorganic reducing substances has then already ended. The intensive oxidation process carries on in the parallel samples until the bisulfate is added. Cleaner waters react differently and this is now obvious. As an extreme example, a test with distilled water was carried out and the results are shown in Table VIII.

Table VIII. Testing the iodine difference method in distilled water

Waiting period in min. from addition of sodium hydroxide to acidification	ml thiosulfate solution for 1000 ml water		mg O_2/L
	Main sample	Parallel sample	
5	50.0	11.3	7.47
10	49.9	11.4	7.43
20	49.8	11.3	7.43
30	50.0	11.4	7.45
45	49.7	11.4	7.39
60	49.9	11.3	7.45
120	49.8	11.3	7.43

This distilled water was treated in the same way as the samples from the Klinker River and the amount of thiosulfate used for the parallel samples was almost the same for each sample, regardless of whether the sodium bisulfate was added after 5 minutes or after 2 hours. [p.32] In addition it can be mentioned that the values for the oxygen concentration are identical for the Winkler method and the iodine difference method. That is why the Skopinzew correction method is not adaptable for water which is rich in organic matter.

The method described by Adams et al. can only be employed when the water samples can be processed right away and on the spot, right up to acidification. It is rather difficult to do this when the samples have to be transported.

Ellis, Westfall and Ellis (1948, page 14/15) remarked that the method which had been developed by Adams et al. was useless for the determination of oxygen in sewage water and other very polluted waters. Many organic substances use molecularly dissolved oxygen and at a higher pH, as for instance pH 11; they have a reducing action on the intermediate products of the Winkler reactions. This pronounced reduction process in the parallel samples is of special importance, because hydroxide precipitation does not occur. The difference between main and parallel sample is apparent only when the water carries much organic matter. But this difference is also apparent in waters which do not contain as much reducing matter.

The Little Uklei Lake (group II of the water [p. 33] color categories, Ohle, 1934, p. 602) is electrolyte-poor and mildly humic. The Large Plöner Lake (group I in water color) is electrolyte-rich. In Table IX surface water was used for both cases. I wanted then to overcome the difficulties when I also discovered a rather heavy hydroxide precipitation in the parallel samples using aluminum sulfate, aluminum hydroxide and other additives. This was without result. The oxidation in the main and parallel samples can be controlled when one starts with the acidification immediately after the addition of sodium hydroxide. These two stages can be done in a laboratory or at least under favourable working conditions. One adds only 1.0 ml of the iodine reagent to all the bottles on the spot of sampling. For this purpose a pipette is used with a stopcock (Fig. 13) which delivers exactly 1 ml. The iodine has to be added with the greatest accuracy. The tip of the pipette is so long that it reaches to the bottom of the sample bottle. This pipette makes it possible to treat the samples without difficulty in a small boat.

Table IX.

Waiting period in min. from addition of sodium hydroxide to acidification	ml thiosulfate solution for 1000 ml water		Apparent mg O_2/L	Difference mg O_2/L
	Main sample	Parallel sample		
		I. Little Uklei Lake		
5	50.0	8.1	8.73	–
10	50.0	7.6	8.22	+ 0.09
20	50.1	7.4	8.28	+ 0.15
45	50.1	7.1	8.34	+ 0.21
		II. Large Plöner Lake		
5	76.1	8.3	13.60	–
19	76.2	8.1	13.22	+ 0.06
20	76.2	8.0	13.24	+ 0.08
45	76.2	7.8	13.27	+ 0.11

b) Procedure for the iodine-difference method

Two glass stoppered sample bottles are selected with a volume of about 100 ml. The water which has to be sampled is siphoned into the bottles with rubber tubing and care has to be taken to let the bottles over flow three times their volume. The siphon should be held very close to the bottom of the bottle. Both sample bottles receive simultaneously 1.0 ml iodine reagent. This is released on the bottom of the bottle by means of a stopcock pipette and the bottles are stoppered and shaken. If the brown iodine color disappears another 1 ml of the iodine reagent has to be added. In most cases 1 ml of the iodine reagent (4.0 mg I_2/ml) is sufficient.

After the iodine has been added the samples are wrapped in moist cloths or placed in water and thus kept in darkness until they can be completed. To avoid error in oxygen determinations, especially when working with sewage water, every main sample and its parallel sample should be treated with the iodine almost simultaneously.

[p. 34] The main sample receives then 0.5 ml sodium hydroxide - potassium iodide and 0.5 ml manganous sulfate and the bottles are stoppered and shaken for about 10 to 15 seconds. Then before the precipitation settles, 3.0 ml sodium bisulfate is added. The bottle remains stoppered for about 10 minutes after which its contents are transferred into a 200 ml Erlenmeyer flask. Add 1 ml starch or 2 ml Polyviol solution and titrate with thiosulfate.

The parallel sample does not receive manganous sulfate but its volume has to be equal to that of the main sample and thus 3.5 ml has to be added instead of 3.0 ml sodium bisulfate. Further treatment is similar to that of the main sample. It is desirable to complete the main and parallel sample immediately after each other.

Reagents

1. Iodine - stock solution:

   5 g Iodine + 100 g KI + 80 ml boiled H_2O, giving a total volume of about 114 ml. 1 ml contains approximately 44 mg I_2 and 0.88 g KI.

[p. 35]

2. Iodine reagent:

   10.0 ml iodine stock solution + 100 ml saturated NaCl solution. 1 ml contains approximately 4.0 mg I_2 and 80 mg KI. For the preparation of the saturated sodium chloride solution one uses 35 g NaCl per 100 ml boiled distilled water. This solution is filtered as far as possible before it is used for the iodine reagent.

3. Sodium hydroxide - potassium iodide:

   100 g NaOH + 200 ml boiled H_2O + 50 g KI.

4. Manganous sulfate solution:
   100 g $MnSO_4 \cdot 4H_2O$ + 200 ml boiled H_2O.
   Filter

5. Sodium bisulfate solution:

   250 g $NaHSO_4 \cdot H_2O$ + 200 ml boiled H_2O.
   Filter

6. Starch solution:

   1 g soluble starch + H_2O. Stir this into a paste and add it to 100 ml hot H_2O. Add 0.5 ml of 40% formalin when the solution is cool.

7. Polyviol solution:

   1 g Polyviol M 05/14 + H_2O. Stir this into a paste and add it to 100 ml hot H_2O.

8. Sodium thiosulfate solution:

For example, 6.2076 g $Na_2S_2O_3 \cdot 5H_2O$ (this corresponds with 0.20 mg O_2/ml) and boiled H_2O + 1 ml NaOH (20%) + 10 ml isobutyl alcohol. Make this up to 1000 ml with boiled H_2O.

9. Potassium dichromate solution:

With reference to the preparation and use of this solution for the standardization of the sodium thiosulfate solutions refer to the directions for the original Winkler method which are described after Table III of this paper.

Calculation of the results.

One requires, for example, 5.28 ml thiosulfate solution (titre = 0.196 mg O_2/ml) for the main sample and 0.74 ml for its parallel sample. The last value has to be subtracted from the main sample (5.28 - 0.74 = 4.54 ml) without consideration of the volume of the parallel sample. The volume of the main sample bottle is 116.4 ml. Subtract from this the amount of delivered reagents: 1.0 (iodine reagent) + 0.5 (KI + NaOH) + 0.5 ($MnSO_4$) + 3.0 ($NaHSO_4$) = 5.0 ml. The amount of water in the sample is then 111.4 ml. Consequently 40.75 ml thiosulfate solution were necessary for 1000 ml water. This corresponds with an oxygen concentration of 40.75 X 0.196 = 7.99 mg O_2/L. The following amount has to be subtracted since with the reagents a quantity of oxygen has been added to the sample: 0.015 or 0.02 (iodine reagent, when [p. 36] only 1 ml per bottle has been added) + 0.07 (NaOH and $MnSO_4$) + 0.03 ($NaHSO_4$) = 0.12 mg O_2/L. The result is then: 7.99 - 0.12 = 7.87 mg O_2/L. It is in general sufficient to round off to the nearest tenth of a mg (Ohle, 1952), except where less than 1.0 mg is found.

Results of the analysis of the iodine difference method (I△ method) and some remarks.

This method is suitable for limnological examinations of water whether eutrophic or oligotrophic, humic or humic-free, polluted or clean. The method produces perfect oxygen values. When the water contains NO_2 ions, simulating an oxygen concentration which is too high when the original Winkler method is employed, then the following equation results:

$$2HNO_2 + 2HCl + 2KI = I_2 + 2NO + 2KCl + 2H_2O$$

When additional oxygen is also introduced as for instance in the titration with thiosulfate, and the NO oxidizes to N_2O_3 etc., then this cycle is already introduced in the I△ method by the iodine reagent which contains in sufficient amounts not only iodine but also potassium iodide. One can therefore disregard the "nitrite error" in the developed difference between main and parallel sample.

The values for domestic waste water are according to the original Winkler method, 0.57 and 0.52 mg O_2/L, and according to the I△ method only, 0.15 and 0.14 mg O_2/L. The nitrite concentration of these waste waters was 0.44 mg $N(NO_2)$/L. The reduction of sulfite ions can prevent the original Winkler method from being used in a cellulose industry or elsewhere, because the iodine is transformed into HI.

$$\mathrm{Na_2SO_3 + I_2 + H_2O = Na_2SO_4 + 2HI}$$

This can be compensated for by the use of the I△method with the parallel sample. A water which contains 10 mg $\mathrm{Na_2SO_3}$/L showed an oxygen concentration of 8.0 mg/L when the I△method was employed. The Winkler method indicated without preliminary treatment only 7.3 mg $\mathrm{O_2}$/L.

All kinds of possible errors are prevented when the I△method is used. We consider here errors caused by hydrogen sulfide, sulfide, ferrous and ferric iron as also an organic matter and reducing and oxidizing substances. The iodometric $\mathrm{O_2}$ determination with preliminary iodine addition produces in sewage water 1.6 mg $\mathrm{O_2}$/L more than the method without preliminary treatment.

It is not always possible to use the original Winkler method for the $\mathrm{O_2}$ determination of surface water of eutrophic lakes, when exact values have to be obtained. The $\mathrm{O_2}$ values which have been obtained with the unmodified method are often a few tenths of a milligram less than the values obtained with the I△method. An example of these differences is shown in Table X. This table has been compiled with surface water of the Large Plöner Lake. The $\mathrm{O_2}$ concentration of the waters has been lowered gradually with addition of nitrogen from a cylinder. The question was whether a higher concentration of divalent manganese, which occurs in the deep waters of many lakes, would interfere in the I△ method.

Table X. Comparison of the original Winkler method with the iodine difference method (results in mg $\mathrm{O_2}$/L).

Original Winkler method	13.08	8.76	6.76	2.56	2.29	2.00	1.30	1.16	0.59	0.34
I △ method	13.35	9.00	6.96	2.76	2.40	2.17	1.42	1.28	0.80	0.54

It was possible that the strong alkaline manganous hydroxide solution which was apparent in the parallel samples would absorb the oxygen. Primarily, Mn(II)-ions appear often along with $\mathrm{O_2}$ in the higher zones of the hypolimnion. This is also the case in the lakes of Holstein. Secondly, it may also be possible that this divalent manganese is transformed into quadri-valent manganese when the water is treated with iodine and hypoiodite. In both cases the "imaginary value" of the parallel samples is too high and thus one simulates an oxygen concentration which is too low, as an effect of forming the difference between the parallel and the main sample.

For this reason I examined several waters which contained a manganese concentration up to 5 mg Mn/L. It was proven that neither the manganese oxidation nor the forming of manganese dioxyhydrate were of any importance. The manganese concentration which can be found in natural waters is obviously too small for a formation of manganese dioxyhydrate. Manganese oxidation occurs in the small small quantity with the addition of hypo-iodite and iodine as is the case in the main samples after forming of the manganese hydroxide precipitate. Thus the iodine difference method has proved to be valuable for the examination of all kinds of waters.

I am grateful for the advice given by Professor Thieneman, Dr. Mortimer and Dr. Rodhe which assisted in the completion of this work. I also wish to thank my technical assistant, Mr. Dieterich, for his cooperation.

Summary (Translated)

On grounds of many years of experience and under consideration of the newest methodical improvements, directions are provided for the determination of the molecularly dissolved oxygen in waters. For quick limnological determination of oxygen, an electrochemical method is recommended which operates by means of an "oxygen sounder". Based on Winkler's original method, which is described in a similar manner, the iodine difference method has been developed. This method tends to give the most exact oxygen determination in all types of water and its general use is explained for limnological examinations. The work procedures of these methods is described, the error margin is shown on the basis of analyses and the compilation of the final oxygen values is carried out with the use of the added supporting tables.

Summary (English)

The chemical and electrochemical determination of oxygen molecularly dissolved in fresh water

The aim of this paper is two-fold: (1) to develop an electrochemical technique (the "oxygen sounder") for rapid exploration of oxygen distribution in a body of water, and (2) to recommend procedures, based on Winkler's technique and its modifications, designed to give true and precise estimates in waters of all types, including those contaminated with oxidizing or reducing substances of various kinds, and yet to be sufficiently simple for use in the field.

Based on a method employed by Tödt (1942), the oxygen sounder consists of two electrodes, one of gold and one of zinc, mounted in a Perspex holder (Fig. 1), and lowered into the water on a two-core cable which connects the electrodes to a micro-ammeter, which is mounted directly on the cable drum (Fig. 2). When immersed in natural waters these electrodes form an electrolytic cell, and the resultant current which passes through the micro-ammeter is controlled mainly by the depolarizing effect of dissolved oxygen, but also by the electrical conductivity and temperature of the water, by the size of the cathode, the degree of stirring around the electrodes and, in very hard waters, by the amount of calcium carbonate precipitate which forms on the electrodes. The presence of reducing substances and of oxidizing substances encountered in natural waters has no effect. The mechanics of these processes are discussed.

In practice, when working in waters of different conductivity, it is necessary to provide a shunt to vary the sensitivity of the micro-ammeter, and to prepare a calibration curve for each type of water. Such a curve for the Large Plöner Lake, using a gold foil electrode of 0.45 cm^2 and a zinc electrode of about 5 cm^2 area, is given in Figure 4, and shows the relationship at 15°C between the micro-ammeter reading and dissolved oxygen. The latter was determined by the iodine difference method. The flattening of

the curve at high oxygen concentrations is interpreted as the failure of the available electrolyte to keep pace with the increased electron transport at high oxygen concentrations. Smaller electrodes provide straighter curves (Figure 5), but are not recommended for the investigation of hard waters because the washing effect of calcium carbonate precipitation increases as the gold electrode area is decreased. In this respect, gold was found to be superior to platinum originally used, but even with gold the surface condition of the metal appears to play a part, and it is difficult to prepare electrodes which behave identically. Electrodes of the area mentioned above can be used without trouble in waters of alkalinity up to 2.5 m. eq./L. Gold wire can be used in soft waters, but because of the low conductivity the current-oxygen curves become very non-linear (Fig. 7) and foil electrodes of medium size are to be generally recommended.

Depolarization and the resultant current clearly depend on the degree of stirring around the electrodes, and in the laboratory it is usual to provide a stirrer. In the field instrument described here it has been found sufficient to stir by jerking the cable up and down while taking a reading.

Correction for the effect of temperature can be made by using Table I [p. 12], which gives the percentage correction to convert a current reading at temperature t° to that temperature (15°C) for which the calibration curves have been prepared.

In the field the first step is to determine the temperatures at the depths to be investigated. This may be conveniently done with the thermistor thermometer described by Mortimer and Moore (1953) in the preceding publication in this series. The electrodes are then washed free of encrusting calcium carbonate by brushing with conc. acetic acid or 10% hydrochloric acid, and then left hanging in the water for 5 to 10 minutes to remove the acid. With the electrodes in surface water, the shunt is adjusted until the micro-ammeter reads about 90% of full scale deflection (f.s.d. = 25 in the instrument used). The electrodes are then lowered to the depths required and each reading is taken while jerking the cable sharply up and down. Where only a rough indication of oxygen distribution is required, this is all that need be done. But if a calibration curve has already been prepared for the water concerned, then the readings, after correction to 15°C by means of Table I, will give an estimate of dissolved oxygen to ±5% accuracy in waters of electrical conductivity of more than $100 = 10^6 K_{18}$ and alkalinity of less than 2.5 milli-equivalents per litre. In waters of lower conductivity, and also in harder waters, the oxygen sounder will still give useful results, but the accuracy is less. An example of the application of a calibration curve to an actual set of readings is given by Fig. 9 [p. 14].

Another method of arriving at quantitative results without the use of a calibration curve is the "combined" method, of which Table II [p. 16] provides an example. Having obtained a set of micro-ammeter and temperature readings at the required depths, water samples are then taken at a few selected depths for chemical determination of dissolved oxygen, preferably by the iodine-difference technique described below, and the results are then used to calibrate the temperature-corrected current readings.

After discussing sources of error using the original Winkler procedure, the author gives the description of the reagents [p. 26]. Sodium hydrogen sulphate is recommended, especially under field conditions, as a more convenient reagent than strong acids. As an alternative to starch "Polyviol" indicator M 05/14 marketed by Messrs. Wacker, Munchen 22, Prinzregentenstrasze 22, Germany, may be used. The thiosulphate solution should be protected against the effects of CO_2 by NaOH solution and against bacterial decomposition by isobutyl alcohol. The solution is standardized by any of the common procedures, among which the use of potassium dichromate is preferred by the author [p. 22]. "Oxygen"-bottles of 100 to 120 ml capacity with the stoppers ground to a point are recommended. The whole content of the bottles or part of which may be titrated.

The precipitate of hydroxydes is allowed to settle for about 10 minutes and the sodium hydrogen sulphate solution is added. If the water contains a lot of iron, phosphoric acid is used. If it is possible or desirable to proceed with the titration immediately after sampling, the disturbing effect of other substances in the sample can be reduced if the precipitate is not allowed to settle and if the acid is added immediately after 10 to 15 seconds strong shaking. Corrections for the oxygen content of the reagents must be introduced [p. 26].

Among the numerous modifications which have been proposed to correct for the presence of oxidizing and reducing substances in the sample the author has selected the iodine-difference method for accuracy and simplicity as well and has carried out thorough investigations, on which suggested improvements are based. The reagents required for this method are listed on page 34. The following procedure is given:

Two 100 ml "oxygen" bottles are filled from the same sample. To both is added exactly 1.00 ml of the iodine reagent by means of a pipette with tap (Fig. 13). If, in extreme cases, this iodine should disappear, a further 1.00 ml is added. Both samples are then kept wrapped in wet cloths or under water in the dark until the next step can be taken. It is important, especially in highly polluted samples, that the duration of the iodine treatment should be the same, within a few minutes, for each bottle of the pair.

To one of the pair (the "main" bottle) is then added 0.5 ml of each of the Winkler reagents; the stopper is replaced and the bottle briskly shaken for 10 to 15 seconds. Then 3 ml of the sodium hydrogen sulphate reagent is immediately added, and the stopper replaced, before the precipitate begins to settle. After standing for 10 minutes the contents are titrated in a 200 ml conical flask after the addition of 1 ml starch or 2 ml Polyviol indicator. The "parallel" bottle of the pair is treated identically, except that it receives no manganous sulphate reagent, but in this case 3.5 instead of 3.0 ml of sodium hydrogen sulphate reagent are added. The treatment and titration of the parallel bottle should follow closely on that of the main bottle, in order that the duration of the various redox reactions involved shall be approximately the same for each.

The principle of the iodine-difference method will be clear from the foregoing outline of procedure. Any substances which would have reacted with the iodine in an unmodified Winkler determination will do so with the iodine initially added to both the main and the parallel sample. The iodine equivalent to oxygen is liberated in the main sample only, and, if the reaction times are the same, the difference in titre between the two bottles will be equivalent to the dissolved oxygen originally present plus that added in the reagents. But the author has found that to avoid errors, the samples must be acidified as described above before the precipitate is allowed to settle in the main bottle. In polluted water it was found that, in the main bottle, a good deal of particulate matter was carried down with the precipitate, and that its reducing effect on the iodine and hypoiodite formed <u>in situ</u> was thereby much diminished; while in the parallel bottle with no precipitate, the reducing effect continued unabated. Therefore the longer the interval elapsing between the formation of the precipitate and its acidification, the greater the error (see Table VII, p. 30). An example to illustrate calculation follows:

The volumes of thiosulphate used (titre = 0.196 mg O_2/ml) for the main and parallel bottles were 5.28 and 0.74 ml respectively. The difference (4.54 ml) may be taken without considering the volume of the parallel bottle. The volume of the main bottle was 116.4 ml from which the volumes of added reagents must be subtracted: these volumes in ml were (reagents named in brackets): 1 (iodine reagent), 0.5 (KI + NaOH), 0.5 ($MnSO_4$), 3.0 ($NaHSO_4$), total 5.0 ml. This leaves 111.4 ml, and the concentration works out at 0.196 · (4.54 · 1000)/ 111.4 = 7.99 mg O_2/L. From this must be deducted the oxygen added in the reagents (named in brackets as follows: 0.02 (iodine reagent), 0.07(NaOH + $MnSO_4$), 0.03 ($NaHSO_4$), total 0.12 mg O_2/L. The final result is therefore 7.87 mg O_2/L.

It is recommended for limnological work that oxygen results should be rounded off to the nearest 0.1 mg O_2/L, except where less than 1.0 mg is found.

Results obtained by using the iodine-difference method are compared with those obtained by the original Winkler procedure. (See Table X, p. 37.)

[p. 42]

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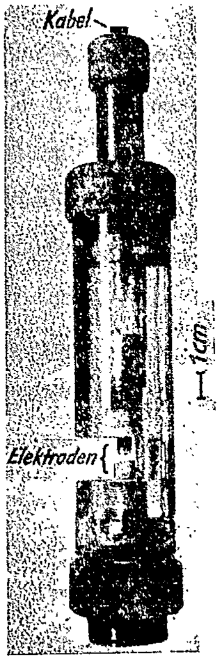

Fig. 1. Probe of the oxygen sounder with electrodes and cable connection. (Material: plexiglas with brass couplings.)

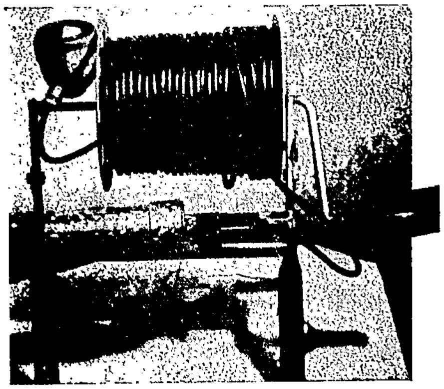

Fig. 2. Complete instrument for electrochemical oxygen determination in water. (Winch with 70 meter [230 ft.] long two-core rubber cable; micro-ammeter which revolves with the winch; oxygen sounder during transport protected in metal cover.)

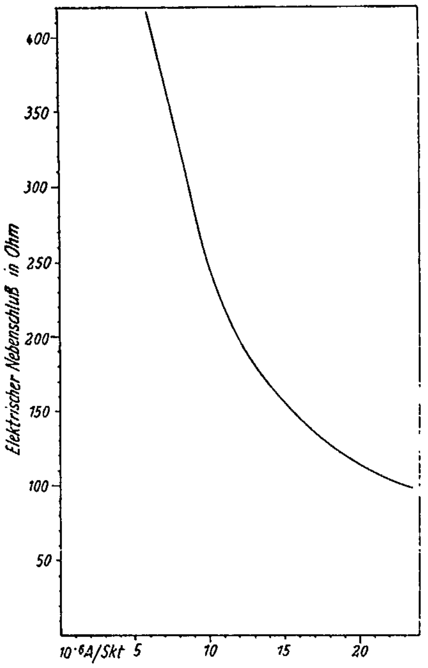

Fig. 3. Change of micro-ampere valve per scale unit with adjustment of the electrical shunt, administered on the rotating resistor of the ammeter.

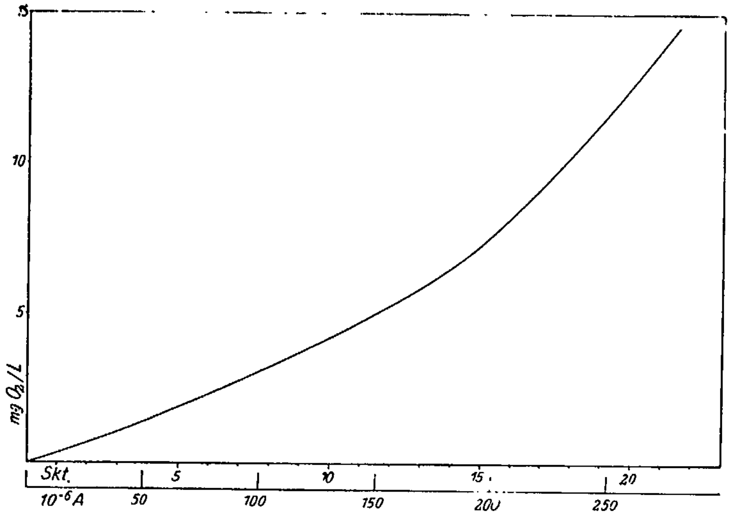

Fig. 4. Calibration curve of the oxygen sounder for the Large Plöner Lake (30-3-1953), drawn at 15.0°C with the use of a gold-disc cathode of 0.45 cm^2 area; shunt = 180 ohms; abscissa = scale unit of the ammeter (or micro-ampere). Chemical procedure = iodine-difference method.

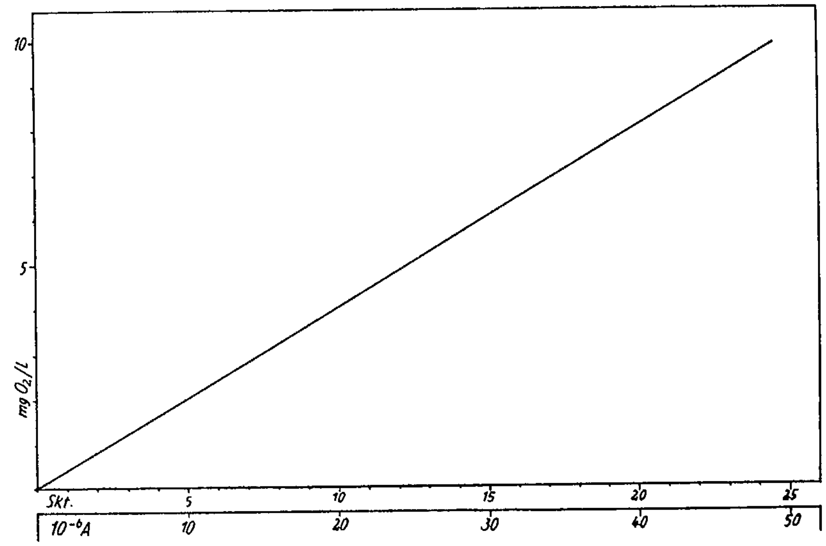

Fig. 5. Calibration curve of the oxygen sounder for Plöner ground water (10^6k_{18}= 965, SBV = 4.41 m. eq./L), taken at 15°C by means of a gold-wire cathode of about 2.7 mm^2 surface area. Abscissa = scale units of the ammeter (or micro-ampere). Ordinate = mg O_2/L.

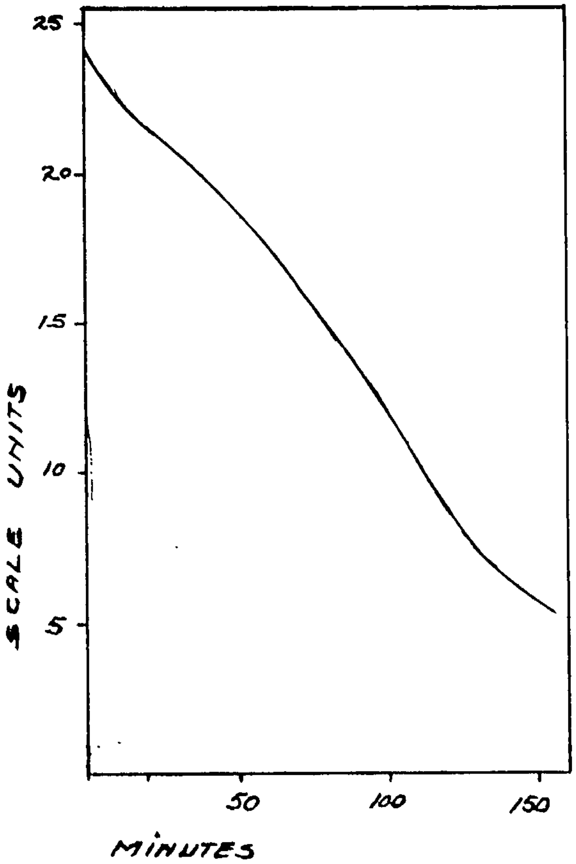

Fig. 6. Fast decrease of residual current intensity in Plöner Lake water (10^6k_{18} = 324 = 2.26 m. eq./L) with the use of the smallest cathode. (Ordinate = scale units of the ammeter; abscissa = duration of experiments in minutes.)

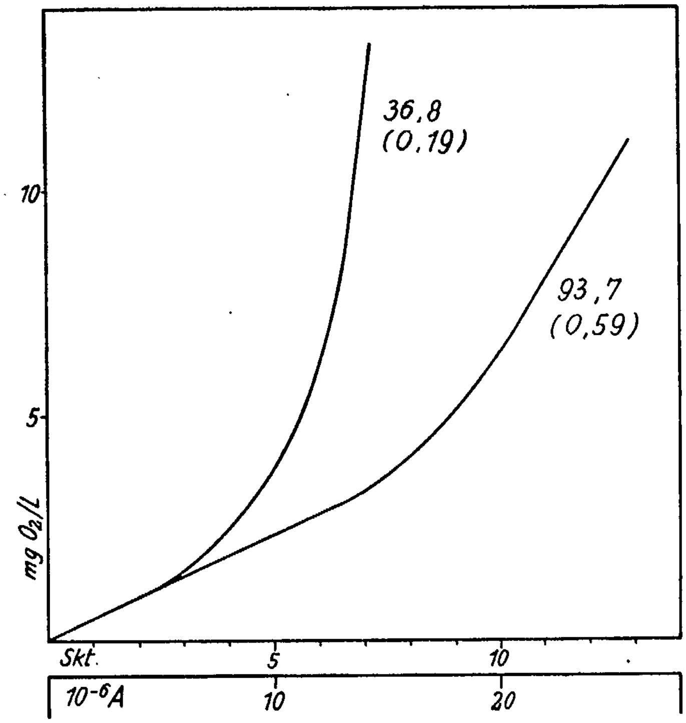

Fig. 7. Calibration curves of the oxygen sounder for electrolyte-poor water ($10^6 k_{18}$ = 36.8 or 93.7 and SBV = 0.19 or 0.59 m. eq./L) drawn at 15.0°C, by means of a wire-shaped gold cathode of approximately 2.7 mm^2 area (ordinate = mg O_2/L; abscissa = scale units of the ammeter [or microampere]).

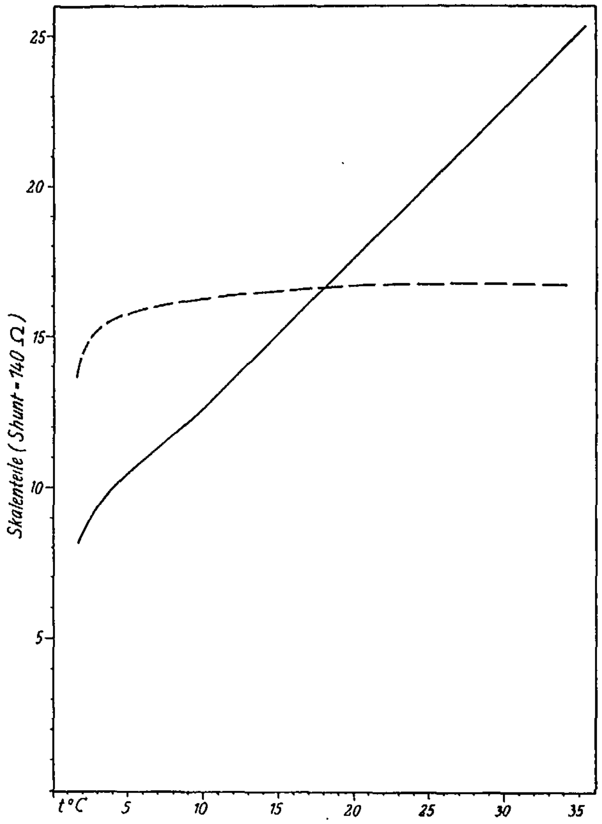

Fig. 8. Temperature relationship of the residual current. The broken curve shows the oxygen concentrations obtained with the chemical method (3.80 to 5.65 mg O_2/L) expressed in residual current values or scale units of the ammeter, and drawn at 17.2°C. The temperature conditioned actual rise in residual current value is represented by the solid curve.

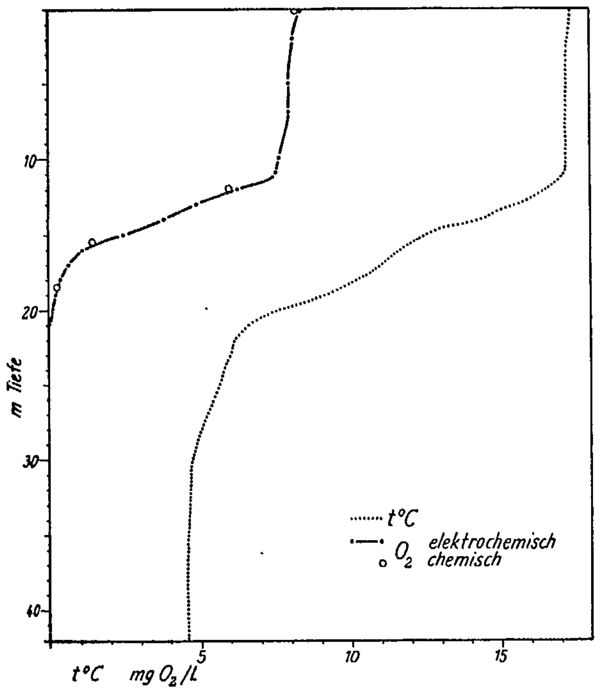

Fig. 9. The arrangement of oxygen layers of the Large Plöner Lake (28-8-1952), ascertained with the oxygen sounder and made up by four chemically determined O_2 values. Temperatures taken with the thermistor (ordinate = depth in meters).

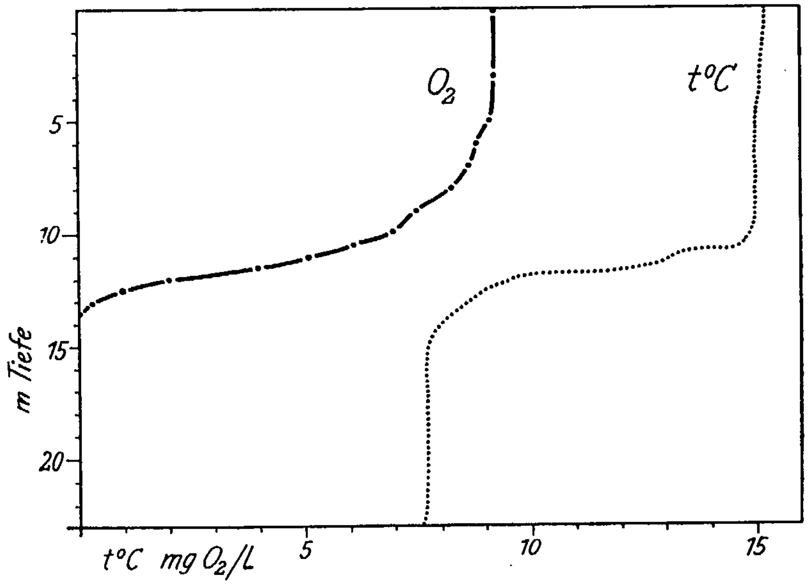

Fig. 10. The distribution of dissolved oxygen of the reference lake, determined by means of the combination method.

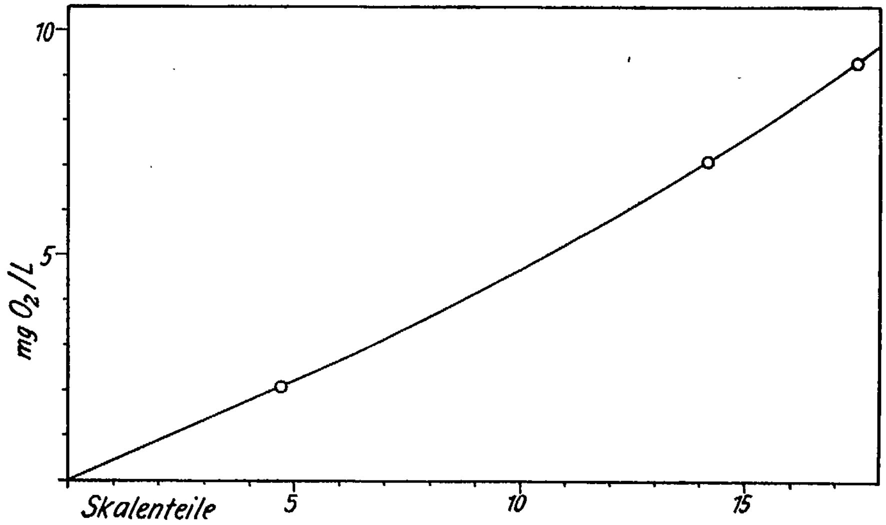

Fig. 11. Accomplishment of the electrochemical combination method. Three oxygen concentrations determined in the reference lake served for the calibration of all the residual current values determined simultaneously with the oxygen sounder.

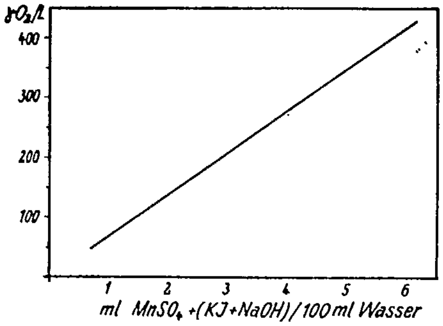

Fig. 12. O_2 concentration of the Winkler reagents, detected by an increasing amount of $MnSO_4$ solution and sodium hydroxide - KI (see Fig. 14).

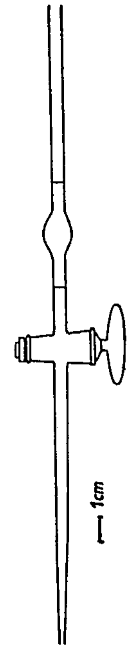

Fig. 13. Stopcock pipette with 1 ml marks for quantitative delivery of the iodine reagent.

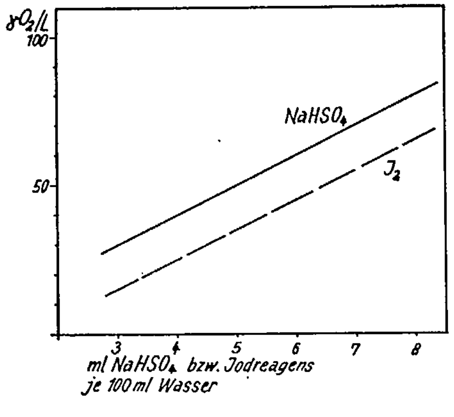

Fig. 14. Oxygen contents of the sodium bisulfate solution and iodine reagent (see legend of Fig. 12). Ml of $NaHSO_4$ or iodine reagent per 100 ml water.