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THE DISSOLVED OXYGEN DETERMINATION METHOD IS 120 YEARS OLD IN MEMORIAM LAJOS WINKLER (1863–1939) AND REZSŐ MAUCHA (1882–1964)

B. ENTZ

H-8237 Tihany, Váralja u. 3/a.

The measurement of dissolved oxygen is a convenient method of measuring production and decomposition in bodies of water. The Winkler Titration method was devised and modified by the Hungarian scientist LAJOS WINKLER (1863–1939). The young 25 year old chemist recognized the importance of dissolved oxygen in aquatic life and developed a simple oxidation-reduction reaction routinely performed by aquatic biologists. The relatively new oxygen-sensitive electrodes facilitate continuous measurement and broadened our knowledge in all aquatic ecosystems. The main problem with most oxygen probes is that the delicate membrane over the electrode must be replaced frequently. Today the oxygen-sensitive electrode is regularly calibrated with the fundamental WINKLER method. WINKLER's student, REZSŐ MAUCHA became his partner and together they developed a semi-micro field method to measure O_2 in the late 1920's. MAUCHA a founding member of the International Society of Limnology (SIL) became a leading limnologist. His star diagram is used to visually compare the ionic composition of bodies of water both qualitatively and quantitatively. Ahead of his time (before phosphorus was measured in water) he classified the productivity of Hungarian lakes based on the oxygen produced by algae. He broadened the three connecting biological activities – production, consumption and decomposition with the concept of supply and accumulation.

Key words: LAJOS WINKLER, REZSŐ MAUCHA, dissolved oxygen

The importance of dissolved O_2 for aquatic life was already well known quite a long time ago. As such, it is evident that for limnological work the knowledge of the presence and particularly the amount of dissolved oxygen in water bodies is of fundamental value. Still, the determination of free O_2 in water was a tedious and difficult process up to the 1880's.

In 1886, a Hungarian chemist named LAJOS WINKLER (Fig. 1) worked out a new method to solve this problem and published his results in 1888 (WINKLER 1888*a–e*). The new and simple method was a real breakthrough in the determination of free O_2 in water. The principle of WINKLER's method is as follows: As a result of dissolving a small amount of solid NaOH together with some $MnCl_2$ crystals in the studied sample of the water, a solution of $Mn^{II}(OH)_2$ comes into being. In the presence of free O_2 in the water sample, an equivalent amount of $Mn^{II}(OH)_2$

will be oxidized to $Mn^{II}(OH)_3$ and a precipitate of this matter will be formed. The yellowish brown precipitate is ready to settle. This precipitate is quite stable. After acidifying the sample with H_2SO_4 or H_3PO_4 and adding some KI crystals, an amount of free I_2, which is equivalent to the dissolved oxygen originally present in the sample, is liberated. Using a starch solution as an indicator, this can be titrated with an adequate solution of $Na_2S_2O_3$. Accordingly, the exact amount of dissolved oxygen present in the studied water sample can easily be calculated in mg/l.

At first WINKLER used 1000 ml samples for the experiments he published in 1888. After modifying and improving his original technique, WINKLER reduced the volume of the sample to 100 ml. An important requirement to achieve correct results was to always use glass vessels with polished glass stoppers to avoid air bubbles during the determination by closing the samples before the $Mn^{II}(OH)_3$ is formed. Even the glass vessels used in this work were constructed by WINKLER.

The results were so persuading and correct that the WINKLER method became widespread over the world in a very short time. This method to determine O_2 in water was used in its original form almost everywhere exclusively for several decades. In addition, it is used even nowadays for the calibration of the electrodes of modern electrometric field equipment.

Similarly, this method is used to measure the primary production of water plants and the consumption of aquatic animals or bacteria in sewage waters, etc.

A disadvantage of the method is that the final titration has to be done in the laboratory because of the necessary equipment. Consequently, when doing field work, the prepared samples containing $Mn^{II}(OH)_3$ have to be transported as fast as possible, but no longer than within 3 hours in well closed vessels, to the laboratory for further work.

His student REZSŐ MAUCHA (Fig. 1) continued work in the field of water chemistry together with WINKLER (DVIHALLY 1963). They developed many semi-micro and field methods (MAUCHA 1929, 1931). With the experience gained from working with WINKLER, MAUCHA became not only a water chemist but a distinguished Hungarian limnologist. He developed the "MAUCHA star-diagram" method which was a valuable clear approach to comparing the main chemical components of waters (MAUCHA 1933). He attempted to classify natural waters based on chemistry and productivity. MAUCHA considered algae to be the most important constructive organic material builder organisms in waters. The photosynthetic activity of algae is the main source of oxygen in the aquatic environment.

To solve this problem, REZSŐ MAUCHA, developed a semi-micro field method in the end of the 1920's and published his results in 1932 (MAUCHA 1932). By his method, only small samples of 10 ml calibrated test tubes have to be used. So-called dropping pipettes – calibrated by 2.5 ml volume – are used for titration.

For measuring purposes, a much diluted $Na_2S_2O_3$ solution has to be added drop by drop to the sample.

To calculate the volume of one drop and its $Na_2S_2O_3$ content, even the numbers of drops within the 2.5 milliliter pipette have to be counted.

In this way, the volume of titration liquids as well as the oxygen concentration of the water body studied can be calculated in milligrams/liter.

Of course, the achieved results can be accepted only until the first decimal value, taking into consideration that small changes within the decimal of the oxygen concentration in the field – caused by biological activities and water currents – may happen and have no significance.

Besides the simplicity of the method, an advantage of the semi-micro method when working in the field is that the knowledge of the exact total volume of the water sample within the test tube is unimportant.

The fundamental work of these two hydrochemists and, at the same time, hydrobiologists, made possible the fast and exact determination of dissolved oxygen in freshwater.

Professor LAJOS WINKLER (1863–1939), was a student of the famous professor KÁROLY THAN, the founder of scientific chemistry in Hungary. As a student, WINKLER was already interested in the solubility of gases in water.

At the age of 25, he succeeded in working out the reported well-known method of O_2 determination in fresh water. As a scientist, WINKLER was a very diligent extremely talented but humble person, a well-honoured professor, and a beloved head of his family.

Professor REZSŐ MAUCHA (1882–1962) was a student and co-worker of WINKLER. He was not only a hydrochemist but also hydrobiologist. As such, he performed excellent works regarding production, consumption accumulation, and decomposition in aquatic ecosystems. Together with WINKLER, he worked out several other methods to determine other dissolved gases and several other solid components in water.

To demonstrate the proportions of the most characteristic cations (Na^+, K^+, Ca^{++}, and Mg^{++}, furthermore those of the anions as CO_3, HCO_3, Cl, and SO_4), MAUCHA constructed a special star diagram (Fig. 2). He used 8 axes intersecting each other at angles of 22.5 degrees. An octagon is formed by marking these axes at the same distances from the centre and binding these points together. The surface of the segments among the axes represents percentages of the main ions in question.

Accordingly, the percentage of the present component in question, the marked points on the axes are at different distances from the centre. Therefore, a so-called star diagram is the result. The surface of the right half of the star represents the presence of the different anions, and those of the left side represent the cations of the water sample.

MAUCHA even adapted his presentation to demonstrate the quantities of the components involved.

This method makes it possible to visualy compare different water bodies according to their ionic composition both qualitatively as well as quantitatively by taking fresh water samples.

As vice president of Societies Internationalis Limnologorum (SIL), MAUCHA reported several results of Hungarian hydrobiological studies in international scientific periodicals and wrote a book in the series Binnengewässer in 1934. He was an excellent scientist, a helpful colleague, and he had a charming personality. In 1922, AUGUST THIENEMANN (German), L. MINDER, R. KOLKWITZ, H. UTERMÖHL, R. MAUCHA, EINAR NAUMANN, H. JARNEFELT, F. RUTTNER, C. WESENBERG-LUND, and W. M. RYLOW founded SIL, which is today a world wide society for aquatic biologists and boasts many thousands of members. The concept of production biology has been introduced in limnology by EINAR NAUMANN, a Swedish scientist. The concept of the three connecting biological activities – production, consumption, and decomposition – was introduced by THIENEMANN in 1931. These three fundamental processes were completed with the concept of supply and accumulation by MAUCHA.

Professor MAUCHA classified the Hungarian shallow lakes according to their productivity. A standard unit of productivity in his system was the WINKLER unit, when the phytoplankton living one liter lake water at 27.7°C produced 22.42×10^{-9}

Fig. 1. LAJOS WINKLER (left) and REZSŐ MAUCHA (right)

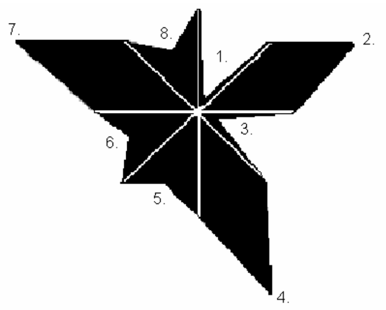

Fig. 2. Star-diagram of Lake Velencei 1928 (Original form of Maucha star–diagram, redrawn from the figure of WOYNAROVICH)

cm^3 oxygen. Later, the MAUCHA type oligotroph and eutroph types of productivity were not enough to determine many scores of productivity of lakes. In most lakes there is a direct relationship between the concentration of the total phosphorous (TP) and the maximum crop of phytoplankton. Based on this finding, the Canadian VOLLENWEIDER classified lakes according to their TP content. The concept of MAUCHA is today regularly used in fishpond limnology and his results are regularly cited in limnology textbooks.

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