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ENVIRONMENTAL PROTECTION INDUSTRY STANDARD OF THE PEOPLE'S REPUBLIC OF CHINA

HJ 506-2009

Replacing GB 11913-89

Water Quality - Determination of Dissolved Oxygen - Electrochemical Probe Method

水质 溶解氧的测定 电化学探头法

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Water Quality - Determination of Dissolved Oxygen - Electrochemical Probe Method

1 Scope

This Standard specifies the electrochemical probe method for the determination of dissolved oxygen in water.

This Standard is applicable to the determination of dissolved oxygen in surface water, underground water, domestic sewage, industrial wastewater and saline water.

This Standard can determine dissolved oxygen with a saturation percentage of 0% ~ 100% in water and can also determine supersaturated dissolved oxygen above 100% (20 mg/L).

2 Normative References

The content of this Standard takes the clauses in the following documents as a reference. In terms of reference documents without a specified date, their valid versions are applicable to this Standard.

GB 7489 *Water Quality - Determination of Dissolved Oxygen - Iodometric Method*

ISO 7888 *Water Quality - Determination of Electrical Conductivity*

3 Terms and Definitions

Dissolved Oxygen

Dissolved oxygen refers to molecular oxygen dissolved in water, which is usually recorded as DO, and expressed in milligrams and saturation percentage of oxygen per liter of water. The saturation content of dissolved oxygen is closed related to the partial pressure of oxygen in the air, the air pressure, water temperature and water quality.

4 Method and Principle

The electrochemical probe for dissolved oxygen is a small chamber enclosed by a selective membrane, which contains two metal electrodes and is filled with electrolyte. Oxygen, and a certain amount of other gases and lyophilic substances can penetrate through this membrane, but water and soluble substance ions can hardly penetrate through this membrane. When the probe is immersed in water for the determination of dissolved oxygen, due to the effect of battery or the potential difference between the

type (for example, silver / gold); there should be a temperature compensation device attached to the probe.

6.1.2 Meter: directly display the mass concentration or saturation percentage of dissolved oxygen.

6.2 Magnetic stirrer.

6.3 Electrical conductivity meter: with a measuring range of 2 ~ 100 mS/cm.

6.4 Thermometer: with a minimum division value of 0.5 °C.

6.5 Barometer: with a minimum division value of 10 Pa.

6.6 Dissolved oxygen bottle.

6.7 Commonly used glass instruments in the laboratory.

7 Analytical Procedures

When using the measuring instruments, strictly comply with the instructions of the instruments.

7.1 Calibration

7.1.1 Zero-point check and adjustment

When the mass concentration level of dissolved oxygen being determined is lower than 1 mg/L (or 10% saturation), or when the dissolved oxygen membrane cover or the internally filled electrolyte is replaced, zero-point check and adjustment are required. If the instrument has a zero-point compensation function, then, it is unnecessary to adjust the zero-point.

Zero-point adjustment: immerse the probe into the zero-point check solution (5.3), after the reaction is stable, read the reading; adjust the instrument to the zero point.

7.1.2 Calibration near saturation value

At a certain temperature, aerate the distilled water, so that the oxygen content in the water reaches saturation or approaches saturation. At this temperature, maintain for 15 min; adopt the method specified in GB 7489 to determine the mass concentration of dissolved oxygen.

Immerse the probe in the bottle. The bottle is completely filled with the sample prepared and determined in accordance with the above-mentioned steps. After the probe is stable in the stirred solution for 2 ~ 3 min, adjust the instrument reading to the already-known dissolved oxygen mass concentration of the sample.

10.2 Linearity Check

Before a new instrument is put into use, and after electrode or electrolyte is replaced, the linearity of the instrument shall be checked. Generally speaking, linearity check shall be performed once every 2 months.

Method of linearity check: by determining the concentration of dissolved oxygen in a series of distilled water samples with different concentrations, check the linearity of the instrument. Slowly flow nitrogen bubbles into three to four 250 mL narrow-necked bottles that are completely filled with distilled water, so as to remove oxygen in the water; use the probe to measure the remaining dissolved oxygen content at all times, until the approximate mass concentration of the required dissolved oxygen is obtained, then, immediately stop the nitrogen flow; use GB 7489 to determine the accurate mass concentration of dissolved oxygen in the water.

If there is no significant difference between the dissolved oxygen concentration value determined by the probe method and the iodometric method at the significance level of 5%, then, it is deemed that the response of the probe is linear. Otherwise, the cause for the deviation from linearity shall be found.

10.3 Maintenance and Regeneration of Electrodes

10.3.1 Maintenance of electrodes

At any time, DO NOT touch the active surface of the membrane with your hands.

Electrode and membrane cleaning: if there are pollutants on the membrane and electrode, they would cause measurement errors. Generally speaking, the electrode and membrane shall be cleaned once every 1 ~ 2 weeks. Be careful when cleaning. Put the electrode and membrane in clean water and rinse them; be careful not to damage the membrane.

It is recommended that frequently used electrodes shall be stored in a container with distilled water, so as to maintain the membrane moist. Before use, dried membrane shall be moistened and activated with distilled water.

10.3.2 Regeneration of electrode

When the linearity of an electrode fails, the electrode needs to be regenerated. The regeneration of electrode is performed about once a year.

The regeneration of electrode includes replacement of dissolved oxygen membrane cover and electrolyte, and electrode cleaning.

Every certain time, or when the membrane is damaged and contaminated, it is necessary to replace the dissolved oxygen membrane cover and replenish new filling electrolyte. If the membrane is not damaged or contaminated, it is recommended that

Appendix A

(normative)

Relations between Solubility of Oxygen in Water, and Temperature, Air Pressure and Salinity

The solubility of oxygen in water changes with the temperature at a given air pressure; similarly, it changes with the air pressure at a given temperature. In addition, the solubility of oxygen decrease with the increase of salinity.

A.1 Functional Relations between Oxygen Solubility in Water and Water Temperature and Salinity

A.1.1 Influence of temperature

Table A.1-1 provides the solubility $\rho(\text{O})_s$ of oxygen in pure water under the standard air pressure (101.325 kPa) in the presence of water vapor-saturated air with an oxygen volume fraction of 20.94%, expressed in milligrams of oxygen per liter of pure water.

A.1.2 Influence of salinity

The solubility of oxygen in water decreases with the increase of salinity. When the total salinity is below 35 g/kg, the two are in a linear relation.

Table A.1-1 provides the correction factor $\Delta\rho(\text{O})_s$ of dissolved oxygen in the water when the water temperature is t °C (0 ~ 39 °C, at the interval of 1 °C) and the salt content in the water (calculated as NaCl) changes by 1 g/kg. This correction factor is applicable to sea water or harbor water. Using the above correction value can bring about 1% error to the calculation result of dissolved oxygen in saline water.

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Contact: Wayne Zheng, Sales@ChineseStandard.net

Linkin: <https://www.linkedin.com/in/waynezhengwenrui/>

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