

HY

Ocean Industry Standard of the People's
Republic of China

HY/T 096—2007

Test method of seawater dissolved
oxygen analyzer

海水溶解氧测量仪检测方法

(English Translation)

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Foreword

SAC/TC 283 is in charge of this English translation. In case of any doubt about the contents of English translation, the Chinese original shall be considered authoritative.

Annex B to this Standard is normative, while Annexes A, C, D and E are informative.

This standard was proposed by National Center of Ocean Standards and Metrology.

This standard was prepared by Technical Committee SAC/TC 283 (National Technical Committee 283 on Ocean of Standardization Administration of China).

Test method of seawater dissolved oxygen analyzer

1 Scope

This standard specifies the test items, test equipment, test environmental conditions, test methods of the seawater dissolved oxygen (DO) analyzer (hereinafter referred to as the instrument) and writing requirements for test reports.

This standard is applicable to the test of instruments used for determination of DO in ocean, coastal seawater and estuarine water.

2 Normative References

The following normative documents contain provisions which, through reference in this text, constitute provisions of this standard. For dated references, subsequent amendments (excluding corrections), or revisions, of any of these publications do not apply to this standard. However, parties to agreements based on this standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies.

GB 17378.4 *The Specification for Marine Monitoring Part 4: Seawater Analysis*

HY 016.2 *The Basic Method of Environmental Test for Oceanographic Instruments Low Temperature Test*

HY 016.3 *The Basic Method of Environmental Test for Oceanographic Instruments Low Temperature Storage Test*

HY 016.4 *The Basic Method of Environmental Test for Oceanographic Instruments High Temperature Test*

HY 016.5 *The Basic Method of Environmental Test for Oceanographic Instruments High Temperature Storage Test*

HY 016.8 *The Basic Method of Environmental Test for Oceanographic Instruments Alternate Humidity Test*

HY 016.11 *The Basic Method of Environmental Test for Oceanographic Instruments Vibration Test*

HY 016.12 *The Basic Method of Environmental Test for Oceanographic Instruments Shock Test*

HY 016.13 *The Basic Method of Environmental Test for Oceanographic Instruments Bump Test*

HY 016.14 *The Basic Method of Environmental Test for Oceanographic Instruments*

*Inclination and Rolling-pitching Test*HY 016.15 *The Basic Method of Environmental Test for Oceanographic Instruments*
Hydrostatic Pressure Test

3 Terms and definitions

3.1 DO of seawater

The gaseous oxygen dissolved in seawater, the unit is expressed in mL/L or mg/L
[HY/T 008 – 1992, terms 04-020]

3.2 DO analyzer for seawater

for use in oceanographic survey to determine the DO in seawater

[HY/T 008 – 1992, terms 04-021]

4 Technical requirements

4.1 Appearance

The appearance requirements of the instrument are as follows:

- a) The shells of the instruments and the paint layer and clad layer of the surface shall be uniform in color, smooth and firm, without obvious abrasion, rust corrosion, leakage, crack and blistering;
- b) The electrode leader of the instrument shall be connected reliably, and the fasteners and connectors shall not be loosened;
- c) The inner cavity of the electrode shall be filled with electrolyte without bubbles, and electrode film shall be intact.

4.2 Metrological performance

The metrological performance requirements of the instrument are as follows:

- a) Measurement range: (N.D. ~20)mg/L, (N.D. is an abbreviation for no detection);
- b) Indication error: $\pm 0.5\text{mg/L}$ or $\pm 5\%$ of reading value;
- c) Repeatability: $\pm 0.2\text{mg/L}$.

5 Test item

The test items of the instrument are as follows:

- a) Appearance inspection;
- b) The test items of metrological performance are the tests of indication error, repeatability and detection limit;
- c) Environmental adaptability test.

6 Test equipment

Refer to Table 1 for test equipment for metrological performance of instrument:

Table 1 Test equipment for metrological performance of instrument

S/N	Equipment name	Technical indicators
1	thermostatic seawater bath	The fluctuation range of the temperature is $\leq 0.05^{\circ}\text{C}$, and the constant temperature range is $(5-35)^{\circ}\text{C}$
2	sample water	Seawater in ocean and anaerobic water. Refer to Annex A for the preparation of seawater in ocean and anaerobic water
3	Second chronograph	Division value: 0.1s
4	Precision thermometer	Measurement range: $(0-50)^{\circ}\text{C}$; minimum division value: 0.01°C
5	aerator	Porosity
Note: Unless otherwise specified, the reagents used in this standard are analytically pure (Grade AR), and the water is deionized water or equivalent pure water.		

7 Test environmental condition

The test environmental condition requirements of the instrument are as follows:

- Ambient temperature: $(20 \pm 5)^{\circ}\text{C}$;
- Relative humidity is less than 80%;
- There shall be no electromagnetic interference that affects the normal operation of the instrument;
- The power supply is AC $(220 \pm 22)\text{V}$, $(50 \pm 2.5)\text{Hz}$.

8 Test method

8.1 Appearance inspection

According to the requirements of 4.1, visual and tactile inspection are used to inspect the appearance of the instrument.

8.2 Metrological performance test

8.2.1 Indication error test

The test methods for indication error of DO are as follows:

- Temperature spots of saturated DO water: 10°C , 20°C and 30°C .
- The test procedures are as follows:
 - At the ambient temperature of $(20 \pm 5)^{\circ}\text{C}$, calibrate the instrument correctly according to the standard operation procedure (SOP) of the instrument.
 - The water temperature of thermostatic seawater bath shall be adjusted to about 10°C , 20°C and 30°C , respectively, and the saturated DO water shall be prepared according to the requirements of Annex A.
 - The DO of saturated DO water at different temperature spots shall be measured by the instruments, and each temperature spot shall be measured repeatedly for 3 times, and the average value shall be calculated as the measurement value of the instrument. At the same time, three bottles of seawater samples shall be taken, and

Winkler method of seawater samples shall be used to analyze DO according to Annex B. The average value shall be calculated as the standard DO of seawater sample;
4) Calculate the oxygen indication error measured by the sensor according to formula (1):

$$\Delta A_j = A_{jp} - A_{js} \dots \dots \dots (1)$$

Wherein:

ΔA_j – indication error of DO measurement of the instrument on the jth DO test point;
(mg/L);

A_{jp} – arithmetic mean value of DO measurement of the instrument on the jth DO test point; (mg/L);

A_{js} – standard DO value on the jth DO test point; (mg/L).

ΔA_j shall meet the requirements in 4.2.

8.2.2 Repeatability test

At the ambient temperature of $(20 \pm 5)^\circ \text{C}$, continuously measure the DO value of the saturated DO water according to the operation rules of the instrument. The measurement times shall be no less than 6.

Calculate the repeatability of the instrument according to formula (2):

$$\sigma = [\sum_{i=1}^n (A_i - A_p)^2 / (n-1)]^{1/2} \dots \dots \dots (2)$$

Wherein:

σ – experimental standard deviation of measurement results of DO in saturated DO water; (mg/L);

A_i – the ith measurement value of DO; (mg/L);

A_p – arithmetic mean value of DO measurement; (mg/L);

n – measurement times of DO.

8.2.3 Detection limit test

At the ambient temperature of $(20 \pm 5)^\circ \text{C}$, continuously measure the DO value of the anaerobic water according to the operation rules of the instrument. The measurement times shall be no less than 10.

Calculate the experimental standard deviation of measurement results of the instrument according to formula (3):

$$\sigma = [\sum_{i=1}^n (A_i - A_p)^2 / (n-1)]^{1/2} \dots \dots \dots (3)$$

Wherein:

σ – experimental standard deviation of measurement results of DO in anaerobic

water; (mg/L);

A_i – the i th mass concentration measurement value of DO in anaerobic water; (mg/L);

A_p – arithmetic mean value of mass concentration measurement results of DO in anaerobic water; (mg/L);

n – measurement times.

Calculate the detection limit of the instrument according to formula (4):

$$D.L = 2\sqrt{2} \cdot t \cdot \sigma \dots\dots\dots (4)$$

Wherein:

$D.L$ – detection limit of the instrument; (mg/L);

t – probability.

Note: Refer to t – distribution table in Annex C for the selection of probability.

8.3 Environmental adaptability test

8.3.1 Environmental test

The specific environmental test items are determined according to the environmental conditions of the instrument. The environmental test methods of the instrument see table 2.

Table 2 Environmental Test Method of Instrument

S/N	Environmental test item	Environmental test method
1	Low Temperature Storage Test	According to HY 016. 3
2	Low Temperature Test	According to HY 016. 2
3	High Temperature Storage Test	According to HY 016. 5
4	High Temperature Test	According to HY 016. 4
5	Shock Test	According to HY 016. 12
6	Inclination and Rolling-pitching Test	According to HY 016. 14
7	Bump Test	According to HY 016. 13
8	Vibration Test	According to HY 016. 11
9	Alternate Humidity Test	According to HY 016. 8
10	Hydrostatic Pressure Test	According to HY 016. 15

8.3.2 Verification test of metrological performance

After the environmental test, the metrological performance shall be tested again as specified in 8.2.

9 Test Report

The test report shall report each test result accurately, clearly, definitely and objectively, and include the following information:

a) The title name is "Test Report";

- b) Name and address of test institution and test place;
- c) Unique identification of the test report and on each page, which shall ensure that the page is identified as the part of the test report, and clear identification indicating the end of the test report;
- d) Customer's name and address;
- e) Tested instrument name, model/specification, manufacturing number and manufacturing unit;
- f) Technical documents for test;
- g) Name, post, signature or effective identification of approver of test report;
- h) Description and state of the tested instrument;
- i) Name of the standard instrument, model/specification and technical indicators used by the test; Certificate No.:
- j) Test time, place and environmental conditions;
- k) Test results;
- l) Signature of tester and checker;

The test record format see Annex D.

The test report format see Annex E.

Annex A
(Informative)

Preparation methods of sample water and saturated DO water

A.1 Preparation method of saturated DO water

The seawater with 2/3 container shall be injected into a thermostatic seawater bath. The temperature of the seawater shall be adjusted to the required temperature, and the water sample shall be stirred for more than 60min.

Within appropriate speed, the stirrer should continually blow bubbles, the amount of which should not be too much.

If the stirring range of the stirrer is not large enough, the aerator (air pump) can be added to the water for continuous blow bubbles. After the bath temperature is stable for about 10 min, the standard DO value shall be determined by the Winkler method (see Annex B).

A.2 Preparation method of anaerobic water

The anaerobic water can be prepared with 5% of Na₂S₂O₃ solution and CuSO₄ as the catalyst.

Annex B
(Normative)

Iodimetric Analysis Method of Seawater DO

B.1 Applicable scope

This method is applicable to the determination of DO in the ocean water, coastal seawater, river water and estuarine water.

B.2 Principle

Reaction of DO in the sample with freshly precipitated manganese(II) hydroxide [formed by the addition of sodium or potassium hydroxide to manganese(II) sulphate]. Acidification, and oxidation of iodide by the higher valency manganese compound so formed, liberating an equivalent quantity of iodine. Determination of the quantity of iodine liberated by titration with sodium thiosulphate.

B.3 Reagents and preparation methods

B.3.1 Unless otherwise specified, the reagents used are analytically pure, and the water is deionized water or equivalent pure water.

B.3.2 Manganese chloride solution

Weigh manganese chloride ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$) of 210g, to dissolve in water, and diluted to 500 mL

B.3.3 Alkaline potassium iodide solution

250g NaOH is weighted to dissolve in 250mL water when stirring. After cooling, 75g KI is added, then diluted to 500mL, then stored in a stoppered, brown glass flask.

B.3.4 Sulfuric acid solution: 1+1

When stirring, 50mL H_2SO_4 ($\rho=1.84 \text{ g/mL}$) shall be carefully added to 50mL water, and mixed, then stored in a reagent bottle.

B.3.5 Sulfuric acid solution: 1+8

When stirring, 10mL H_2SO_4 ($\rho=1.84 \text{ g/mL}$) shall be carefully added 80mL water, and mixed, then stored in a reagent bottle.

B.3.6 Starch solution: 5g/L

B.3.7 Potassium iodide (KI): Chemically pure

B.3.8 Potassium iodate standard solution

3.567g KIO_3 (guaranteed reagent, and pre-dried at 120°C for 2h, then cooled in a drying vessel) is weighted to dissolve in water. Then dilute to 1000 mL volumetric flask. Mix and place it in the dark. The validation is one month. Withdraw 10.00mL

and dilute with water to 100ml in a volumetric flask, to get the solution concentration of 0.0100mol/L.

B.3.9 Sodium thiosulfate standard solution

25g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ is weighted to dissolve it with freshly boiled and cooled water, and the sodium carbonate of about 2g is added to dilute to 10L. Mix and place it in the dark, to get the solution concentration of 0.01mol/L.

Standardization of sodium thiosulfate standard solution:

10.00mL standard KIO_3 solution (B.3.8) flow into the iodine flask along with the inner wall. The inner wall of the flask is rinsed with a little water, and add 0.5g potassium iodide (B.3.7) into the 1.0mL sulfuric acid solution (B.3.5) along the inner wall. Plug the stopper, mix it gently, seal it with a little water, and place it in the dark for 2 min. Gently unscrew the stopper, add 50mL water along the inner wall. When shaking, the solution is titrated with sodium thiosulfate solution (B.3.9) until the solution reaches pale straw color. 1mL starch solution (B.3.6) is added. Continue to titrate until decoloration, then repeate titration until the difference value of two titration readings is less than 0.05mL. Calculate its concentration according to formula (1):

$$C(\text{Na}_2\text{S}_2\text{O}_3) = \frac{10.00 \times 0.010}{V(\text{Na}_2\text{S}_2\text{O}_3)} \dots\dots\dots (\text{B.1})$$

Where

$c(\text{Na}_2\text{S}_2\text{O}_3)$ - concentration of sodium thiosulfate standard solution; (mol/L);

$V(\text{Na}_2\text{S}_2\text{O}_3)$ - volume of sodium thiosulfate standard solution; (mL).

B.4 Instrument and equipment used in iodometric method

The instrument and equipment used in iodometric method are as follows:

- Water sample bottle: The volume is about 250mL, and the cork is tapered. The grinding mouth must be tight, and the volume must be calibrated to 0.01mL;
- Glass tube: Diameter: (5~6)mm; length: 12cm;
- Latex tube: The diameter is the same as that of the glass tube; and the length is (20~30)cm;
- Burette of D0: 25mL; scale division: 0.05mL
- Magnetic stirrer: The rotational speed can be adjusted to (150~400)r/min;
- Glass magnetic rotor: The diameter is about (3~5)mm, and the length is 25mm;
- Conical flask: 250mL;

- Iodine flask: 250mL;
- Measuring cylinder: 100mL;
- Beaker: 500mL, 1000mL;
- Bi-join ball;
- Reagent bottle: 500mL, 5 bottles; Brown, 10mL, 2500mL;
- Quantitative liquid feeder: 5mL, 4 feeders;
- Transfer pipette: 20mL;
- Regular instruments and equipments of laboratory.

B.5 Analytical procedures

B.5.1 Fixing of water sample

After opening the water sample bottle, the manganese chloride solution of 1.0mL (B.3.2) and alkaline potassium iodide solution (B3.3) of 1.0mL shall be injected immediately by the quantitative liquid feeder with the tube tip inserted below the surface. Replace the stopper carefully to avoid the inclusion of air bubbles, press the stopper and turn the bottle upside down no less than 20 times.

B.5.2 Determination procedures

B.5.2.1 After the sample is fixed about for 1h or is completed precipitation, open the stopper, and 1.0mL sulfuric acid solution (B.3.4) shall be injected immediately by the quantitative liquid feeder. Stuff the stopper up, turn the sample upside down repeatedly until the precipitation is dissolved completely.

B.5.2.2 Allow the solution fully mixed for 5min, carefully open the stopper, and all water samples are transferred into the conical flask. Put a stirring rotor along the inner wall gently, and place the conical flask on the titration table.

B.5.2.3 After the burette of DO is full of the standardized sodium thiosulfate standard solution (B.3.9), turn on the magnetic stirrer for titration. When the solution is pale straw color, add 1mL starch solution (B.3.6), and continue to titrate until decoloration.

B.5.2.4 Calculate DO mass concentration in water samples according to formula (2):

$$\rho_{O_2} = \frac{c \times V \times f_1 \times 8}{V_1} \dots\dots\dots (B.2)$$

Wherein:

ρ_{O_2} — mass concentration of DO in the water samples; (mg/L);

V — volume of sodium thiosulfate solution during titrating the sample; (mL);

C — concentration of the sodium hyposulfite solution; (mol/L);

V_1 – volume of all or partially fixed water sample used for titration; (mL);

$f_1 = \frac{V_1}{V_2 - 2}$ Of which V_2 is the total volume (volume of water sample bottle) of fixed water sample; and the unit is mL; 2 is the volume of the reagents (3.2 and 3.3), and the unit is mL.

B.6 Attentions

B.6.1 Keep up the speed when the titration towards the end, otherwise the decoloration is not sharp. If the solution turns amaranth, which indicates that the starch solution is deteriorated, and it shall be re-prepared.

B.6.2 If the oxidizing substances in the water sample forms iodine, the result will be higher than the real value. If the reducing substances consumes iodine, the result will be lower than the real value.

Note: This method is quoted from GB/T 17378.4 Specification for Marine Monitoring – Part 4: Seawater Analysis.

Annex C

(Informative)

 t - Distribution Table t - distribution table used by the probability calculation is given in Table C.1Table C.1 t - Distribution Table

$\begin{matrix} v \\ n \end{matrix}$	0.5	0.6	0.7	0.8	0.9	0.95	0.98	0.99	0.995	0.999
1	1.000	1.376	1.963	3.078	6.3138	12.706	31.821	63.657	127.32	636.69
2	0.816	1.061	1.336	1.886	2.9200	4.3027	6.965	9.9248	14.089	31.589
3	0.765	0.978	1.250	1.638	2.3534	3.1825	4.541	5.8409	7.4533	12.924
4	0.741	0.941	1.190	1.533	2.1318	2.7764	3.747	4.6041	5.5976	8.610
5	0.727	0.920	1.156	1.476	2.0150	2.5706	3.365	4.0321	4.7733	6.869
6	0.718	0.906	1.134	1.440	1.9432	2.4469	3.143	3.7074	4.1368	5.959
7	0.711	0.896	1.119	1.415	1.8946	2.3646	2.998	3.4995	4.0293	5.405
8	0.706	0.889	1.108	1.397	1.8595	2.3060	2.896	3.3354	3.8325	5.041
9	0.703	0.883	1.100	1.383	1.8331	2.2622	2.821	3.2498	3.6897	4.781
10	0.700	0.879	1.093	1.372	1.8125	2.2281	2.764	3.1693	3.5814	4.587
11	0.697	0.876	1.088	1.363	1.7959	2.2010	2.718	3.1058	3.4966	4.437
12	0.695	0.873	1.083	1.356	1.7823	2.1788	2.681	3.0545	3.4284	4.318
13	0.694	0.870	1.079	1.350	1.7709	2.1604	2.650	3.0123	3.3725	4.221
14	0.692	0.868	1.076	1.345	1.7613	2.1448	2.624	2.9768	3.3257	4.140
15	0.691	0.866	1.074	1.341	1.7530	2.1315	2.602	2.9467	3.2860	4.073

Annex D
(Informative)

Test record format

Refer to Table D.1 and Table D.2 for the record format used in the test.

Table D.1 Metrological Performance Test Record Format of D0 Analyzer

Inspection unit									
Instrument model				manufacturing No.					
Standard instruments used									
Test place				Test date					
Environmental conditions		Temperature and humidity							
Appearance inspection situation									
Solution temperature °C	Standard value mg/L	Instrument indication mg/L				Average value	Indication error mg/L		
		1	2	3					
Solution temperature °C	Standard value mg/L	Instrument indication mg/L						Average value	experimental standard deviation mg/L
		1	2	3	4	5	6		
Solution temperature °C	Standard value mg/L	Instrument indication mg/L						Experimental standard deviation mg/L	Detection limit mg/L
		1	2	3	4	5	6		
		7	8	9	10	11	12		

Tested by

Checked by

Table D.2 Environmental Test Record Format of D0 Analyzer

Instrument name		Test item	
Test date		Test basis	
Test condition			
Test situation			

Room temperature

Relative humidity

Tested by

Checked by

MM/DD/YY

Annex E

(Informative)

Test report format

The homepage format of test report see Figure E.1, and the inside page format of test report see Figure E.2 and E.3.

Unit(Institution) Name

Test Report

Certificate Number:

Customer	
Customer Address	
Instrument Designation	
Type/Specification	
Serial Number	
Manufacturing	
Issue date	

(Stamp for Test)	Approved by	(Signature)
	Name	(Roman type)
	Post	

Address:	Postal code:	Fax:	Tel. :
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Figure E.1 Homepage format of test report

Main measuring instruments and equipment used by the test									
Name	Model/specification	Uncertainty or accuracy class or maximum permissible error						Certificate No.	
Test time, place, and its environmental conditions									
Time:					Place:				
Temperature:					Relative humidity:				
Test results									
Solution temperature °C	Standard value mg/L	Instrument indication mg/L				Average value	Indication error mg/L		
		1	2	3					
Solution temperature °C	Standard value mg/L	Instrument indication mg/L					Experimental standard deviation mg/L	Detection limit mg/L	
		1	2	3	4	5			
		6	7	8	9	10			
Solution temperature °C	Standard value mg/L	Instrument indication mg/L							experimental standard deviation mg/L
		1	2	3	4	5	6	Average value	

Tested by

Checked by

Figure E. 2 Inside page format of test results for metrological performance of test report

References:

- [1] GB/T 12763.4-1991 *The specification for oceanographic survey--Observations of chemical parameters in sea water.*
- [2] JJG 291-1999 *Film Electrode Dissolved Oxygen Meter.*
- [3] JJF 1001-1998 *General Terms in Metrology and Their Definitions.*
- [4] JJF 1002-1998 *The Rules for Drafting National Metrological Verification Regulation.*
- [5] JJF 1059-1998 *Evaluation and Expression of Uncertainty in Measurement.*