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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 the National Technical Committee 283 on Ocean of Standardization Administration of China (SAC/TC 283).

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 analyzer (hereinafter referred to as the instrument) and requirements for the compilation of test reports. This standard is applicable to the test of instruments used for determination of dissolved oxygen in ocean, coastal seawater and estuarine water in the production and use.

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 InstrumentsHigh Temperature Test*

HY 016.5 *The Basic Method of Environmental Test for Oceanographic InstrumentsHigh 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 seawater dissolved oxygen

the gaseous oxygen dissolved in seawater, which is expressed in ml of oxygen/L or mg of oxygen/L

[HY/T 008 - 1992, terms 04-020]

3.2 seawater dissolved oxygen analyzer

instruments for the determination of dissolved oxygen in seawater for oceanographic survey

[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 supported by electrolyte, without bubbles, and covered film shall be intact.

4.2 Metrological performance

The metrological performance requirements of the instrument are as follows:

a) Measurement range: (0～20)mg/L;

b) Indication error: ±0.5mg/L or ±5% of reading;

c) Repeatability: ±0.2mg/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	Constant temperature seawater tank	The fluctuation range of the temperature is no more than 0.05℃, and the constant temperature range is (5-35) ℃
2	Test 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) ℃; minimum division value: 0.01℃
5	Bubbler	Porosity
Note: Unless otherwise specified, the reagents used in this standardare 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:

a) Ambient temperature: (20±5) ℃;

b) Relative humidity is less than 80%;

c) There should be no electromagnetic interference that affects the normal operation of the instrument;

d) The power supply is AC (220±22) V, (50±2.5) 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 dissolved oxygen are as follows:

a) Temperature spots of saturated dissolved oxygen water: 10° C, 20° C and 30° C.

b) The test procedures are as follows:

1) At the ambient temperature of (20±5)° C, calibrate the instrument correctly according to the operation rules of the instrument.

2) The water temperature of the constant temperature seawater tank is adjusted to 10° C, 20° C and 30° C, respectively, and the saturated dissolved oxygen water is prepared according to the requirements of Annex A.

3) The dissolved oxygen value of saturated dissolved oxygen water at different

temperature spots is measured by the instruments, of which each temperature spot is measured for 3 times, and the average value is taken as the measurement value of dissolved oxygen of the instrument. At the same time, three bottles of seawater samples are taken in parallel, and iodometric analysis method of seawater dissolved oxygen is used to analyze dissolved oxygen. Refer to Annex B for the iodimetric analysis method of seawater dissolved oxygen. The average value is taken as the standard dissolved oxygen value of water sample;

4) Calculate the oxygen indication error measured by the sensor according to formula (1):

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

Wherein:

ΔA_j – indication error of dissolved oxygen measurement of the instrument on the jth dissolved oxygen test point; unit: mg/L;

A_{jp} – arithmetic mean value of dissolved oxygen measurement of the instrument on the jth dissolved oxygen test point; unit: mg/L;

A_{js} – standard dissolved oxygen value on the jth dissolved oxygen test point; unit: mg/L.

8.2.2 Repeatability test

At the ambient temperature of (20±5)° C, continuously measure the dissolved oxygen value of the saturated dissolved oxygen water according to the operation rules of the instrument. The measurement times should be no less than 6.

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

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

Wherein:

σ – experimental standard deviation of measurement results of dissolved oxygen in saturated dissolved oxygen water; unit: mg/L;

A_i – the ith measurement value of dissolved oxygen; unit: mg/L;

A_p – arithmetic mean value of dissolved oxygen measurement; unit: mg/L;

n – measurement times of dissolved oxygen.

8.2.3 Detection limit test

At the ambient temperature of (20±5)° C, continuously measure the dissolved oxygen 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):

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

Wherein:

σ – experimental standard deviation of measurement results of dissolved oxygen in anaerobic water; unit: mg/L;

A_i – the ith mass concentration measurement value of dissolved oxygen in anaerobic water; unit: mg/L;

A_P – arithmetic mean value of mass concentration measurement results of dissolved oxygen in anaerobic water; unit: mg/L;

n – measurement times.

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

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

Wherein:

$D.L$ – detection limit of the instrument; unit: 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 the method specified in HY 016.3
2	Low Temperature Test	According to the method specified in HY 016.2
3	High Temperature Storage Test	According to the method specified in HY 016.5
4	High Temperature Test	According to the method specified in HY 016.4
5	Shock Test	According to the method specified in HY 016.12
6	Inclination and Rolling-pitching Test	According to the method specified in HY 016.14
7	Bump Test	According to the method specified in HY 016.13
8	Vibration Test	According to the method specified in HY 016.11
9	Alternate Humidity Test	According to the method specified in HY 016.8

10	Hydrostatic Pressure Test	According to the method specified in 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 Method of Test Water and Saturated Dissolved Oxygen Water

A.1 Preparation method of saturated dissolved oxygen water

The seawater with a volume of about 2/3 is injected into a constant temperature seawater tank. The temperature of the seawater is adjusted to the required temperature, and the stirrer is started to stir the water sample for more than 60min. The stirring speed is appropriate which can make the water continuously blow bubbles, and not overflow a large amount of constant temperature water bath. If the stirring range of the stirrer is not large enough, the bubbler (air pump) can be added to the water for continuous bubbling. After the stability is about 10 min, the standard dissolved oxygen value is determined by the iodometric method (the iodimetric analysis method of seawater dissolved oxygen see Annex B).

A.2 Preparation method of anaerobic water

The anaerobic water can be prepared with 5% of sodium sulfite (Na_2SO_3) solution and moderate cupric sulfate ($CuSO_4$) as the catalyst.

Annex B

(Normative)

Iodimetric Analysis Method of Seawater Dissolved Oxygen

B.1 Applicable scope

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

B.2 Method and principle

The dissolved oxygen reacts with oxygen with manganese chloride and sodium hydroxide dissolved in the water sample, which generates high-price manganese brown precipitate. After the dissolution of acid dosing, the free iodine which is equivalent to the dissolved oxygen content is released in the presence of iodine ions, then the free iodine is titrated with sodium thiosulfate standard solution, and the dissolved oxygen content can be converted.

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 ($MnCl_2.4H_2O$) of 210g, to dissolve in water, and diluted to 500 mL.

B.3.3 Alkaline potassium iodide solution

The sodium hydroxide (NaOH) of 250g is weighted to dissolve in 250mL water under stirring. After cooling, potassium iodide (KI) of 75g is added to dilute to 500mL, then fill the brown reagent bottle with rubber plug.

B.3.4 Sulfuric acid solution: 1+1

Under stirring, the concentrated sulfuric acid (H_2SO_4, p=1.84 g/mL) of 50mL is carefully added to water with the same volume, and mixed, then fill the brown reagent bottle.

B.3.5 Sulfuric acid solution: 1+8

Under stirring, the 10mL of concentrated sulfuric acid (H_2SO_4, p=1.84 g/mL) is carefully added to water of 80mL, and mixed, then fill the brown reagent bottle.

B.3.6 Starch solution: 5g/L

B.3.7 Potassium iodide (KI): Chemically pure

B.3.8 Potassium iodate standard solution

The potassium iodate (KIO_3, guaranteed reagent, and pre-dried at 120° C for 2h, then

cooled in the silica gel drier) of 3.567g is weighted, to dissolve in water. The full amount is transferred in a volumetric flask with 1000mL, and the water is added to the marking. Mix it, and place in the shade. The valid period is one month. The amount of 10.00mL is weighted and diluted with water to 100mL. The solution concentration is 0.0100mol/L.

B.3.9 Sodium thiosulfate standard solution

The sodium thiosulfate (Na2S2O3•5H2O) of 25g is weighted to dissolve it with boiling water, and the sodium carbonate of about 2g is added to dilute to 10L. Mix it, and place in the shade. The solution concentration is 0.01mol/L.

Concentration calibration of sodium thiosulfate standard solution:

The potassium iodate standard solution (B.3.8) of 10.00mL is weighted to flow into the iodine flask along with the wall. The bottle wall is rinsed with a small amount of water, and add potassium iodide (B.3.7) is added to inject into the 1.0mL sulfuric acid solution (B.3.5) of 1.0mL along the wall. Plug the cork, mix it gently, add a little water, then seal it, and place in the dark for 2 min. Gently unscrew the cork, add the water of 50mL along the wall. Under constant shaking, the solution is titrated with sodium thiosulfate solution (B.3.9) until the solution is faint yellow. The starch solution (B.3.6) of 1mL is added to the solution. Continue to titrate until the blue of the solution has faded out, then conduct the repeated calibration, until the difference of two titration readings is less than 0.05mL. Calculate its concentration according to formula (1):

$$C(Na_2S_2O_3)=\frac{10.00\times 0.010}{V(Na_2S_2O_3)} \quad \text{(B.1)}$$

Wherein:

$c(Na_2S_2O_3)$ - concentration of sodium thiosulfate standard solution; unit: mol/L;

$V(Na_2S_2O_3)$ - volume of sodium thiosulfate standard solution; unit: 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 corrected;
- Glass tube: Diameter: (5～6)mm; length: 12cm;
- Latex tube: The diameter is same as the glass tube; and the length is (20～30)cm;
- Burette of dissolved oxygen: 25mL; scale division: 0.05mL

- Electromagnetic 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;
- Erlenmeyer flask: 250mL;
- Iodine flask: 250mL;
- Measuring cylinder: 100mL;
- Beaker: 500mL, 1000mL;
- Duplex ball pump;
- Reagent bottle: 500mL, 5 pieces; Brown, 10mL, 2500mL;
- Quantitative liquid core filler: 5mL, 4 pieces;
- Transfer pipette: 20mL;
- Regular instrument and equipment of conventional laboratory.

B.5 Analytical procedure

B.5.1 Fixation 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 core filler (tube tip inserted level). Stuff the cork up (no bubble in the bottle), hold down the cork and turn the bottle upside down not less than 20 times.

B.5.2 Determination procedures

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

B.5.2.2 After standing for 5min, carefully open the dissolved oxygen cork, and all water samples treated in the water sample bottle are moved into the conical flask. Put a stirring rotor along the bottle wall gently, and place the conical flask on the titration table.

B.5.2.3 After the burette of dissolved oxygen is full of the calibrated sodium thiosulfate standard solution (B.3.9), turn on the electromagnetic stirrer for titration. When the solution is faint yellow, add the starch solution (B.3.6) of 1mL, and continue to titrate until the blue has faded out.

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

$$\rho 0_2 = \frac{c \times V \times f_1 \times 8}{V_1} \quad \text{.....(B.2)}$$

Wherein:

ρO_2– mass concentration of dissolved oxygen in the water samples; unit: mg/L;

V – volume of sodium thiosulfate solution during titrating the sample; unit: mL;

C – concentration of the sodium hyposulfite solution; unit: mol/L;

V_1 – volume of all or partially fixed water sample used for titration; unit: 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 Precautions

B.6.1 When the titration is close to the end point, the speed should not be too slow, otherwise, the end point discoloration is not sharp. If the solution is amaranth before the end point, which indicates that the starch solution is deteriorated, and it should be re-prepared.

B.6.2 The oxidizing substances in the water sample will separate iodine out, and produce positive interference, and the reducing substances will consume iodine, and produce negative interference.

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

Annex C

(Informative)

t – Distribution Table

Refer to Table C.1 for t – distribution table used by the probability calculation.

Table C.1 t – Distribution Table

v / n	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 Dissolved Oxygen Analyzer

Inspection unit								
Instrument model				manufacturing No.				
Standard instruments used								
Test place				Test date				
Environmental conditions		Temperature and humidity						
Appearance inspection situation								
Solution temperature ℃	Standard value mg/L	Instrument indication mg/L						Indication error mg/L
		1		2		3	Average value	
Solution temperature ℃	Standard value mg/L	Instrument indication mg/L						experimental standard deviation mg/L
		1	2	3	4	5	6	Average value	
Solution temperature ℃	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		

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Table D.2 Environmental Test Record Format of Dissolved Oxygen Analyzer

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

Room temperature Relative humidity

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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 _____

Approved by (Signature)

(Stamp for Test)

Name (Roman type)

Post

Address: Postal code: Fax: Tel.:

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 ℃	Standard value mg/L	Instrument indication mg/L				Indication error mg/L
		1	2	3	Average value	

Solution temperature ℃	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 ℃	Standard value mg/L	Instrument indication mg/L						experimental standard deviation mg/L
		1	2	3	4	5	6	Average value	

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Figure E.2Inside page format of test results for metrological performance 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 place and its environmental conditions Place: Temperature: Relative humidity: (Other):			
Environmental adaptability test results			

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Figure E.3 Inside page format of test results for environmental adaptability of test report