Technical Note for GS Dissolved Oxygen Sensor KDS-25 Series

Specialty Division
of
Japan Storage Battery Co., Ltd.
(Kyoto City , Japan)

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1. Introduction

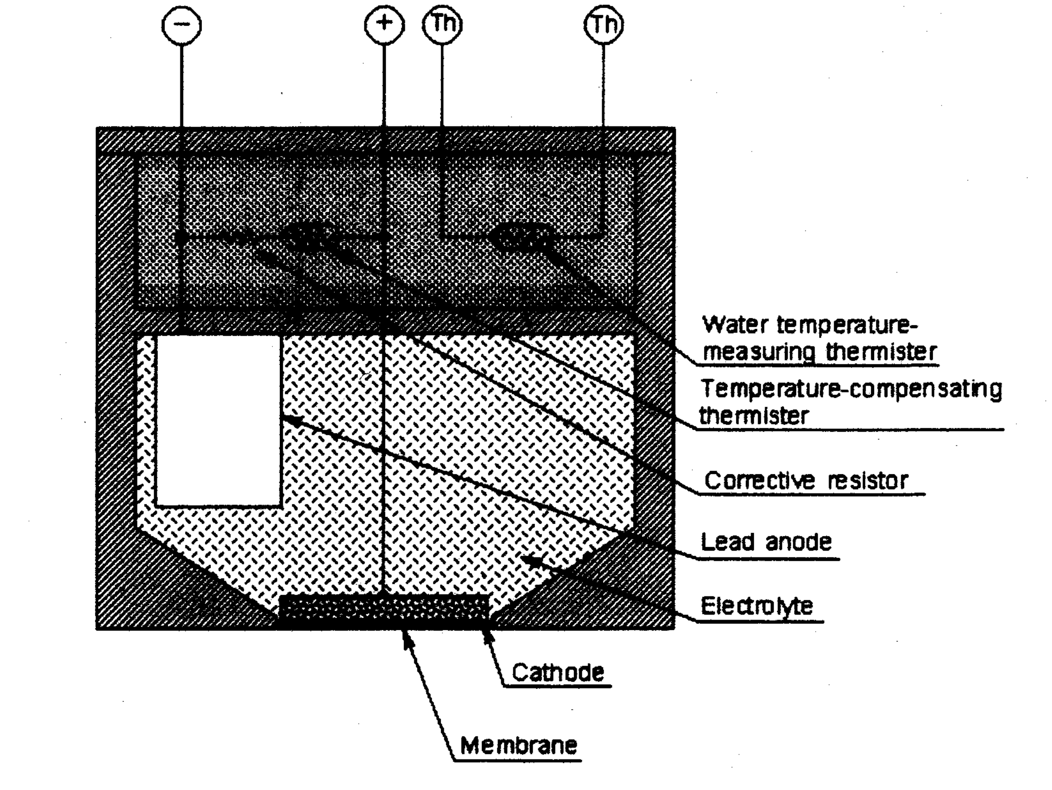
GS dissolved oxygen sensor KDS-25 is a new model one developed by applying the technology of a galvanic cell type oxygen sensor which has been favorably commented upon the market.

GS dissolved oxygen sensor has special features that it is not affected by acidic gas such as carbon dioxide and the expecting service life is extremely longer than those of conventional ones, because a newly patented special acidic electrolytic solution is used. The content of dissolved oxygen in water can be stably determined for a long time by using GS dissolved oxygen sensor.

2. Principle of GS dissolved oxygen sensor

GS dissolved oxygen sensor is composed of a kind of oxygen-lead battery using an acidic electrolytic solution and the oxygen pole comprising the gold electrode as the cathode (positive pole) and lead as the anode (negative pole) as illustrated in the following figure:

Schematic Drawing of Structure of The GS Dissolvrd Oxygen Sensor



The cathode is the gold electrode which is deposited on the non-porous fluoroplastic membrane through which oxygen molecule is diffused slightly and electrochemically reduced on the gold electrode.

A temperature-compensating thermister and a corrective resistor connect between the cathode and anode for converting the current generated by reducing oxygen to voltage.

The current sent to the thermister and corrective resistor is proportional to the dissolved oxygen concentration of the solution (strictly speaking, partial pressure of oxygen) kept in contact with the membrane. The oxygen concentration is, therefore, able to be determined by measuring the terminal voltage of the thermister as the output of the sensor.

In this case, however, the amount of oxygen permeating the membrane is not theoretically proportioned to the content of dissolved oxygen in a solution but to the oxygen concentration in the vapor equilibrated with the solution. The equilibrated value of the vapor with the solution depends upon the temperature and salt concentration. Corresponding with the temperature and the salt concentration, the output of the sensor must be externally corrected for determining the accurate content of dissolved oxygen. For example, the contents of dissolved oxygen in fresh water equilibrated with the gas containing 21% of oxygen (the atmosphere) are approximately 11 and 8 ppm at 10 and 25℃, respectively, of the water temperature. At any temperature, however, the output value of the dissolved oxygen sensor shows the same value as each other.

The KDS-25 sensor has a water temperature-measuring thermister built-in for correcting the variation of the content of dissolved oxygen according to the temperature. Combining DOM series of dissolved oxygen monitor manufactured by Japan Storage Battery Co., Ltd. with the sensor, therefore, the content of dissolved oxygen can be easily determined by automatically correcting the temperature. Since DOM series of dissolved oxygen monitor has a correcting function of the salt content in the seawater built-in, the function can be set at the operation of the sensor.

The electrochemical reactions of the sensor are as follows:

Cathode - positive pole reaction: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ ----------------(1)

Anode - negative pole reaction: $2Pb + 4OH^- \rightarrow 2PbO + 2H_2O + 4e^-$----- (2)

Total reaction: $O_2 + 2Pb \rightarrow 2PbO$ ---------------------------- (3)

Although the potential of the anode is changed by staying of lead oxide (PbO) produced on the anode pole according to the reaction described in Formula (2), thereby remarkably deteriorating the output of the sensor, PbO is actually dissolved in the acidic electrolyte, so the surface of anode is continuously renewed. Accordingly, the output of the sensor caused by the decrease of the potential of the anode is not actually changed at once.

Meanwhile, since the solubility of PbO in the electrolyte is limited, the expecting service life of the sensor expires by the deposition of PbO at the time when PbO is saturated in the electrolyte. In other words, the higher the solubility of PbO in the electrolytic solution, the longer the expecting service life of the sensor is.

The patented acidic electrolyte used in GS dissolved oxygen sensor has the solubility of PbO in the electrolytic solution approximately 20 times as high as that of it in an aqueous solution of potassium hydroxide used for conventional sensor so far. The expecting service life of GS dissolved oxygen sensor is, therefore, extremely longer than them.

When carbon dioxide is contained in the ambience of a sensor using an alkaline electrolytic solution, carbon dioxide permeating the membrane participates in the anode reaction, thereby producing insoluble lead carbonate ($PbCO_3$) or basic lead carbonate ($Pb_2CO_3(OH)_2$) instead of PbO in Formula (2). Accordingly, the service life of the sensor is shortened. On the contrary, when an acidic electrolytic solution is used, such a reaction as that does not proceed. Even though carbon dioxide is contained in the ambience of GS oxygen sensor, the content of oxygen in water can be determined because the anode reaction is not interfered.

When an acidic electrolyte is used, hydrogen is generated at the cathode in low content of oxygen depending upon pH of the electrolyte, whereupon the output of the sensor sometimes errs. Meanwhile, GS dissolved oxygen sensor can stably determine the content of oxygen within the total concentration range of oxygen by using newly deviced cathode material and composition of electrolyte solution.

Since the permeation rate of the membrane to oxygen is generally increased with the increase of the temperature, the electrode reaction of the sensor is so much promoted that consumption of the service life is accelerated. Accordingly, the higher the operating temperature of the sensor, the shorter the service life of it is. Although this applies to GS dissolved oxygen sensor, it is unnecessary to care about so much the operating temperature of GS sensor as conventional ones because the expecting service life of GS sensor is originally long.

3. Special features of GS dissolved oxygen sensor

The special features of GS dissolved oxygen sensor are as follows:

(1) The expecting service life is very long.

(2) The measuring range is as wide as 0.2 to 80 ppm.

(3) The pressure resistance is so high as 1 kg/cm^2G that the sensor can be used at a depth of 10 m of water.

(4) The selectivity for gas is so high that the sensor is hardly affected by almost all types of gas except oxygen.

4. Characteristics of GS dissolved oxygen sensor

1) Relationship between the dissolved oxygen concentration and output (see Fig. 1),

2) Temperature characteristics (see Fig. 2),

3) Relationship between the flow rate of sample water and output (see Fig. 3),

4) Response characteristics to concentration (see Fig. 4),

5) Response characteristics to temperature (see Fig. 5),

6) Drift with time (see Fig. 6),

7) External dimensions of sensor (see a drawing of Drawing No. 90DO-09B),

8) Exchanging time of sensor.

The sensor operated at 20℃ in the atmosphere is desirable to be exchanged at intervals of approximately 2 to 3 years.

The interval is a standard value for the sensor used at 20℃ in water containing approximately 8 ppm of dissolved oxygen (equilibrated value of concentration in fresh water with the air) but it actually largely depends upon the environmental conditions. The expecting service life is shortened with the increase of the temperature and content of dissolved oxygen. The operating period of time of the sensor is shortened owing to the lowering of output and of response time caused by the formation of fur on the surface of membrane.

5. Notice for using dissolved oxygen sensor

1) Calibration

The output of the dissolved oxygen sensor is drifted toward lowering with the passage of time. It is, therefore, necessary to periodically calibrate it for the accurate determination. The calibration is generally made using the oxygen content (21%) in the air as the standard value, though it cannot be accurately made in the following cases:

- The oxygen content in the air at the calibration is not 21%, e.g. in an oxygen-deficient room and near an oxygen generator.
- The atmospheric pressure is extremely different from 1013 hpa, e.g. a low or high atmospheric pressure and a high altitude.
- Sharply changing time of the atmospheric temperature, e.g. just after moving from the outdoor to the indoor or from an air-cooled car to the outdoor.
- The surface of membrane is fouled.

It is, therefore, necessary to calibrate the sensor except those cases.

2) Flow rate at the determination

The dissolved oxygen sensor theoretically consumes part of the dissolved oxygen for determining it. It is, therefore, necessary to supply the sample water to the membrane part of the sensor at a flow rate as fast as 10 cm/sec or higher.

When the sensor is submerged, the content of dissolved oxygen can be determined also by slowly putting the code up and down with the hand.

3) Mechanical strength against shock and vibration

The sensor collects the oxygen-detecting current with a delicate contact structure. The electrolytic solution in the reaction part is kept as a thin layer under pressure in the contact structure put in a plastic holder. The composition and state of contact of the electrolytic solution are, therefore, so much changed by applying vibration or shock to the sensor that the output is also changed.

If the vibration or shock applied to the sensor is slight, the output of it is recovered. Applying large vibration or shock or repeatedly, though slight ones, to the sensor, however, the output of it is not sometimes recovered.

Since the membrane is thin and fragile, it is apprehended that it is broken by striking or pressing it against a hard article. The membrane part should be left alone with care taken not to directly contact with the hands.

4) Drift

In addition to the drifting with the passage of time described in 5.1, attention should be paid to the lowering of the output caused by the temporary drift by a sudden change of temperature and the storage in an oxygen-deficient (oxygen content: 0.1% or less) place for a long time.

- The drift by a sudden change of temperature is a temporary phenomenon by the delayed response of the temperature-compensating thermister in the sensor. It disappears, therefore, when the temperature of the whole sensor is equalized to that of the sample water within 10 to 20 minutes. When the temperature is slowly changed, such a drift as that is not caused.
- The zero point is lowered by leaving the sensor in an oxygen-free place including a sodium sulfite solution for a long time. In such a case, therefore, it is necessary to leave it to stand in the air for a whole day and night for aging.

5) Fouling of membrane

The output of sensor is lowered by the fouling or sliming of the membrane. The fouled or slimed membrane should be washed down with running clean water such as city water. The membrane of the sensor is exposed to the outside for accurately determining the content of dissolved oxygen. Since it is a tightly spread, very thin plastic film, it is so breakable that a hole is made in it or it is broken by bringing it into contact with a hard article, whereupon the sensor can be operated no more. Accordingly, the membrane should be left alone as careful as possible. If the fouling or sliming cannot be removed only with running water at all, it is desirable to softly - with care taken no to roughly - wipe the surface of membrane with wet floss silk or tissue paper.

Although the membrane is hardly fouled in clean water, the surface of it is relatively easily fouled in muddy water containing much suspended matter.

6) Interference with other gas

Although the sensor neither reacts nor interferes with almost all types of gas except oxygen, it is slightly sensible to some of them. The following table lists the data concerning the interference properties of some types of gas:

Gas Component	Gas Concentration (Note 1)	Interference (Note 2)
CO	0 ~ 100%	Not affected
CO_2	0 ~ 100%	Not affected
NO	0 ~ 1%	Not affected
NO_2	0 ~ 1%	Not affected
SO_2	0 ~ 3%	+3%
H_2S	0 ~ 3%	Not affected
NH_3	0 ~ 3%	+1%
H_2	0 ~ 100%	Not affected
HCl	0 ~ 3%	+1%
C_6H_6	0 ~ 100ppm	+1%
CH_4	0 ~ 100%	Not affected
Toluene (Note 3)	Saturated Vapor Pressure in atmosphere	Deterioration in output Degradation of part or region
H_2O (Water Vapor)	0 ~ 100%	Not affected Condensation not allowed

Note 1: A concentration during a verification test by Japan Storage Battery.

Note 2: Deviation of the sensor output when compared with the output value if an interference gas component does not exist. For example, if a SO_2 gas coexists in the atmosphere (oxygen 20.7%), the sensor output will be about 3% larger and the measured oxygen concentration will be $20.7 \times 1.03 = 21.3\%$

Note 3: If the sensor is exposed in an organic solvent gas, such as toluene, for a certain time, the sensor jackets made of ABS resin degenerate and degrade, resulting in unstable sensor output. Condensation attaching on the oxygen concentration detection part at the tip of the sensor will reduce the output and response speed. In addition to toluene, the following organic solvents have been verified to be harmful to the sensor:

Benzen, Xylene, Acetone, Methyl Ethyl Ketone, Metylene Chloride, Kerosene, Gasoline, Naphtha, and Gas Oil.

7) Abnormality of sensor

Abnormal modes of the sensor are as follows:

- Sudden increase of output caused by a hole made in the membrane or the breaking of it by entraining air bubbles in the electrode parts by vibration, shock or temperature change.
- Sudden decrease of output caused by a hole made in the membrane or the breaking of it by the poor contact in the current-collecting part by vibration, shock or temperature change.

- Continuous decrease of output caused by the expiration of service life or leakage of electrolytic solution.
- Strained linearity caused by the expiration of service life, a hole made in the membrane or breaking of it or leakage of electrolytic solution.
- Delayed response time caused by the expiration of service life, a hole made in the membrane or breaking of it or leakage of electrolytic solution.

8) Variation of output of sensor

The electrodes are supported in the sensor by the tension of a thin membrane. The output of the sensor is temporarily fluctuated by the change of the tension of the membrane caused by changing the position of it or applying shock to it. Although the slight fluctuation is recovered within a few minutes, the sharp fluctuation caused by a high degree of vibration or shock including dropping breaks the electrodes, sometimes never to be recovered again.

9) Service life of sensor

The deterioration of sensor starts proceeding just after manufactured whether it is used or not. The standard service life of the sensor may be defined as the period of time until the output at 20℃ under normal pressure (1013 hpa) goes down to less than 70% of the initial value.

10) Matters to be attended to handling of sensor

(1) Don't expose the sensor to a temperature except the temperature range from -10 to 50℃ so as not to cause the abnormal output and leakage of electrolytic solution by the deterioration or failure of the components.

(2) Operate or preserve the sensor directing the detection part of dissolved oxygen concentration (membrane electrode part at the points end of sensor) horizontally or downward so as not to cause the abnormal output by poor circulation of the inner electrolytic solution.

(3) Don't touch the detection part of dissolved oxygen concentration, or the concentration cannot be accurately determined by the fluctuation of output or delay of the response time because a hole is made in the membrane or it is broken by touching it.

(4) Don't apply a great shock or vibration by a falling body to the sensor so as not to temporarily fluctuate or make the output of the sensor unstable, though this trouble is almost recovered by leaving the sensor to stand in the air of normal temperature for several minutes to several days or the trouble is not sometimes recovered depending upon the degree of the shock and vibration which may damage the inner structure.

(5) Use instruments with input impedance of 1000 kΩ or more for connecting to the sensor, or the temperature compensating-circuit is so much affected that the temperature characteristics of the sensor output are deteriorated.

(6) Use instruments applying no voltage for connecting to the sensor, or the output of the sensor is temporarily made unstable or the response time is delayed, though this trouble of the sensor is almost recovered by leaving it at rest in the air of normal temperature for several days.

Applying the counter voltage or high voltage to the polarity of the sensor (charging), however, the electrode in the sensor is damaged, so it is not recovered. The maximum durability of sensor against inverse voltage is so low that the electrode is damaged by applying the inverse voltage as low as tens millivolts.

(7) Do not disassemble or repair the sensor. Removing a sensor part or remodeling the sensor will damage the sensor or leak the electrolyte and restoration to the original condition may not be possible.

(8) If the electrolyte leaks due to sensor damage, put the sensor in a plastic bag so that the solution will not be smeared on other places and return the sensor to the distributor from which it was purchased.

The electrolyte is a weak acid aqueous solution of 5 to 6 in pH with an irritating odor. It will not ignite spontaneously even if it is left. Nevertheless, lead acetate, which is a component of the solution, is harmful to human bodies and should be handled with care as follows:

- If the electrolyte leaked due to sensor damage is smeared on the skin or clothing, immediately wash the contacted part with soapy water and wash off the solution with a large amount of tap water.

- If the electrolyte leaked due to sensor damage gets into an eye, immediately wash the eye with a large amount of tap water for 15 minutes and consult a doctor promptly.

- If the electrolytic solution or atomized electrolytic solution leaked due to sensor damage is inhaled, immediately wash the nostrils and gargle with tap water and consult a doctor promptly.

- If the electrolyte leaked due to sensor damage is swallowed, immediately wash the mouth with tap water. Swallow a large amount of tap water or 600 cc of milk and vomit it. Consult a doctor promptly.

(9) Discarded sensors may cause environmental pollution. Return a used sensor to Japan Storage Battery or an industrial waste management

contractor when discarding a used sensor.

11) When Designing Equipment Using GS Oxygen Sensor

The sensor has a life and is not absolutely free of troubles during its operation depending on operating conditions and dispersion in its durability and performance. Therefore, the equipment and apparatuses incorporating the sensor must be designed and used providing redundancy, safety and anti-malfunction design to prevent personal accidents or social damage due to the life, characteristics or failures of the sensor. Should any damage or fault occur, the sensor does not assume any responsibility thereof.

Japan Storage Battery requests that diagrams of the electric circuits of the equipment or apparatuses to which the sensor will be connected be shown to it for its confirmation in case this sensor is used in them. Japan Storage Battery is making this request to study whether or not the electric circuits connected with the affect the sensor to cause low performance or performance degradation and in no way guarantees normal operation of the amplifying, filtering, smoothing or other electric circuits

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Fig.1 Relationship between dissolved oxygen concentration and sensor outputat water temperature 25℃

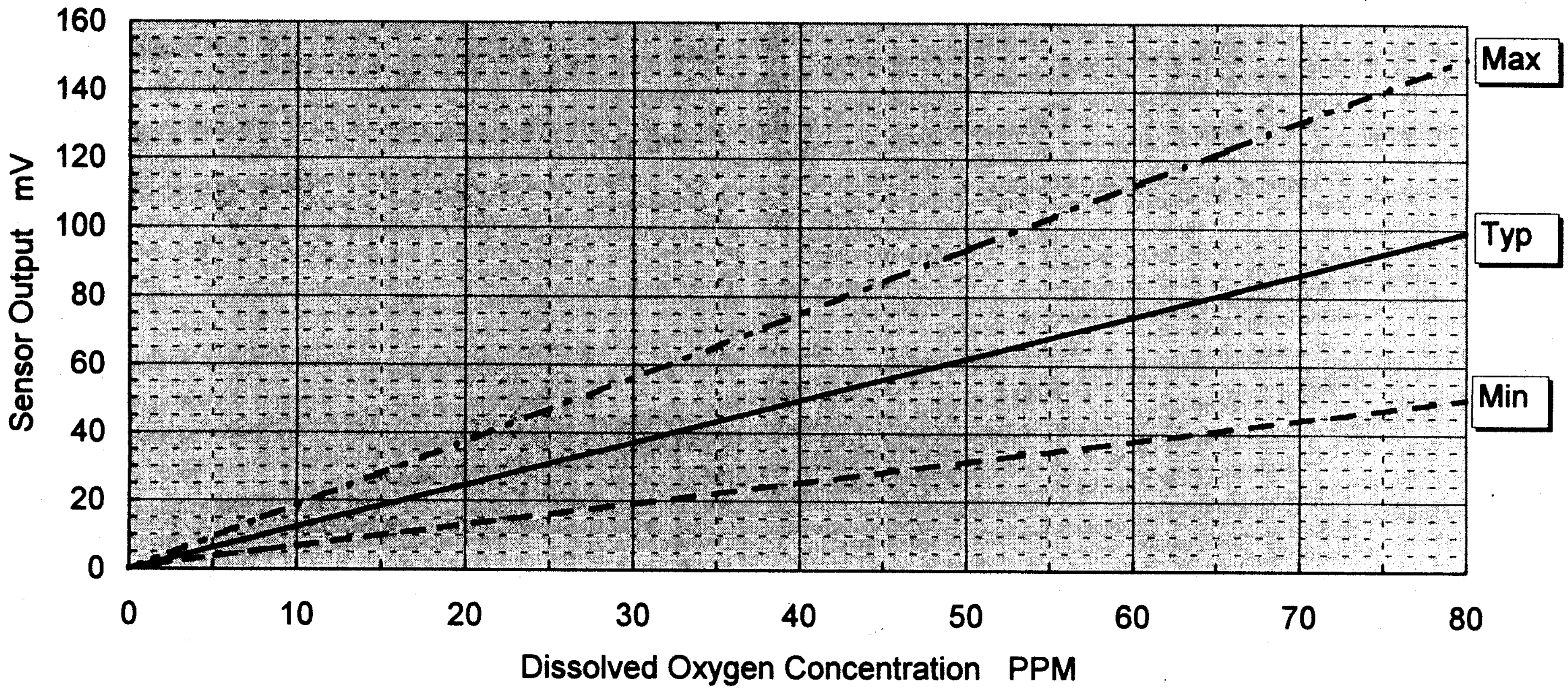


Fig.2 Temperature characteristics - Typical value -

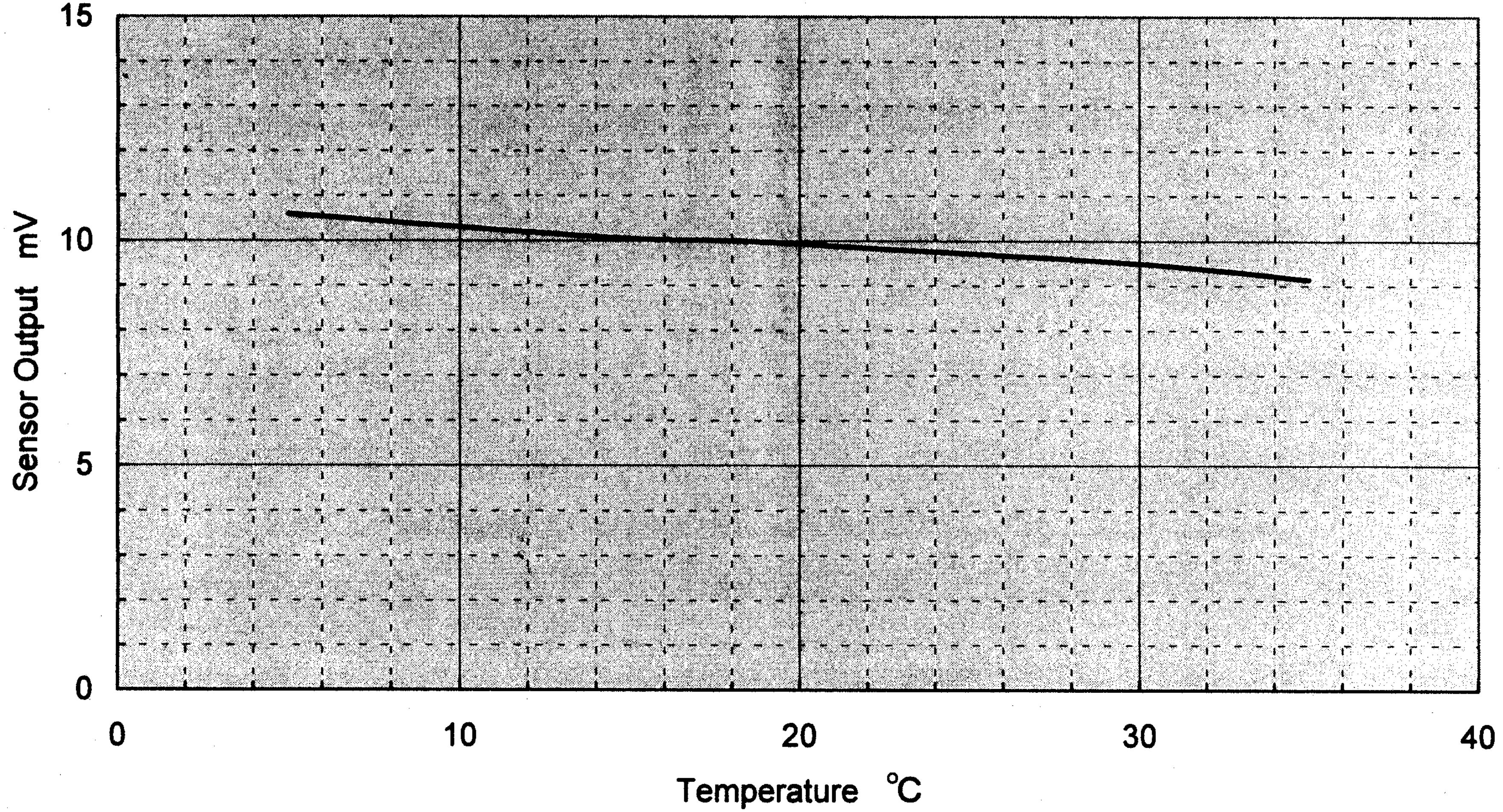


Fig.3 Relationship between flow rate of sample water and sensor output at water temperature 22℃

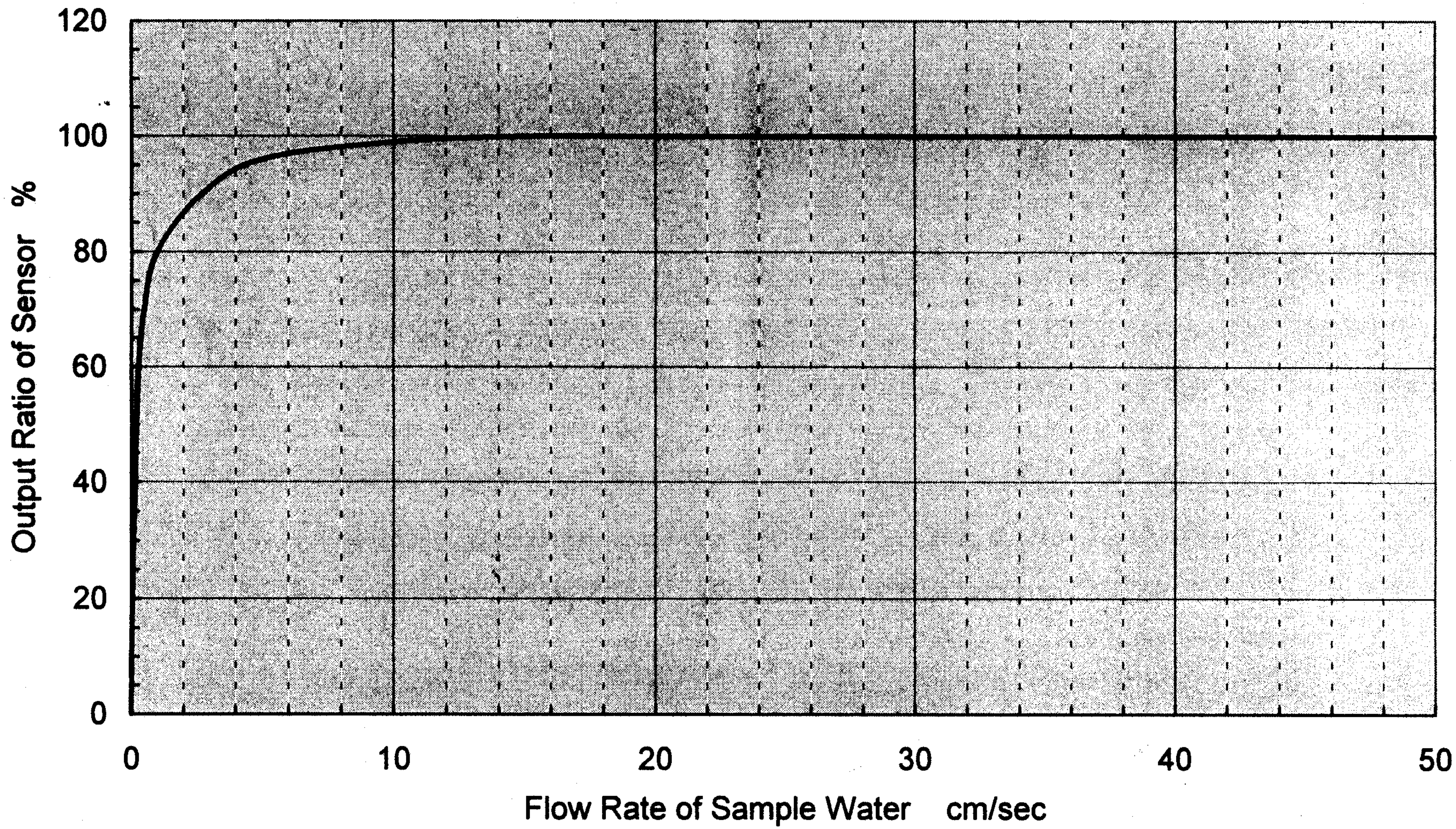


Fig.4 Response characteristics
- Relationship between time and sensor output -

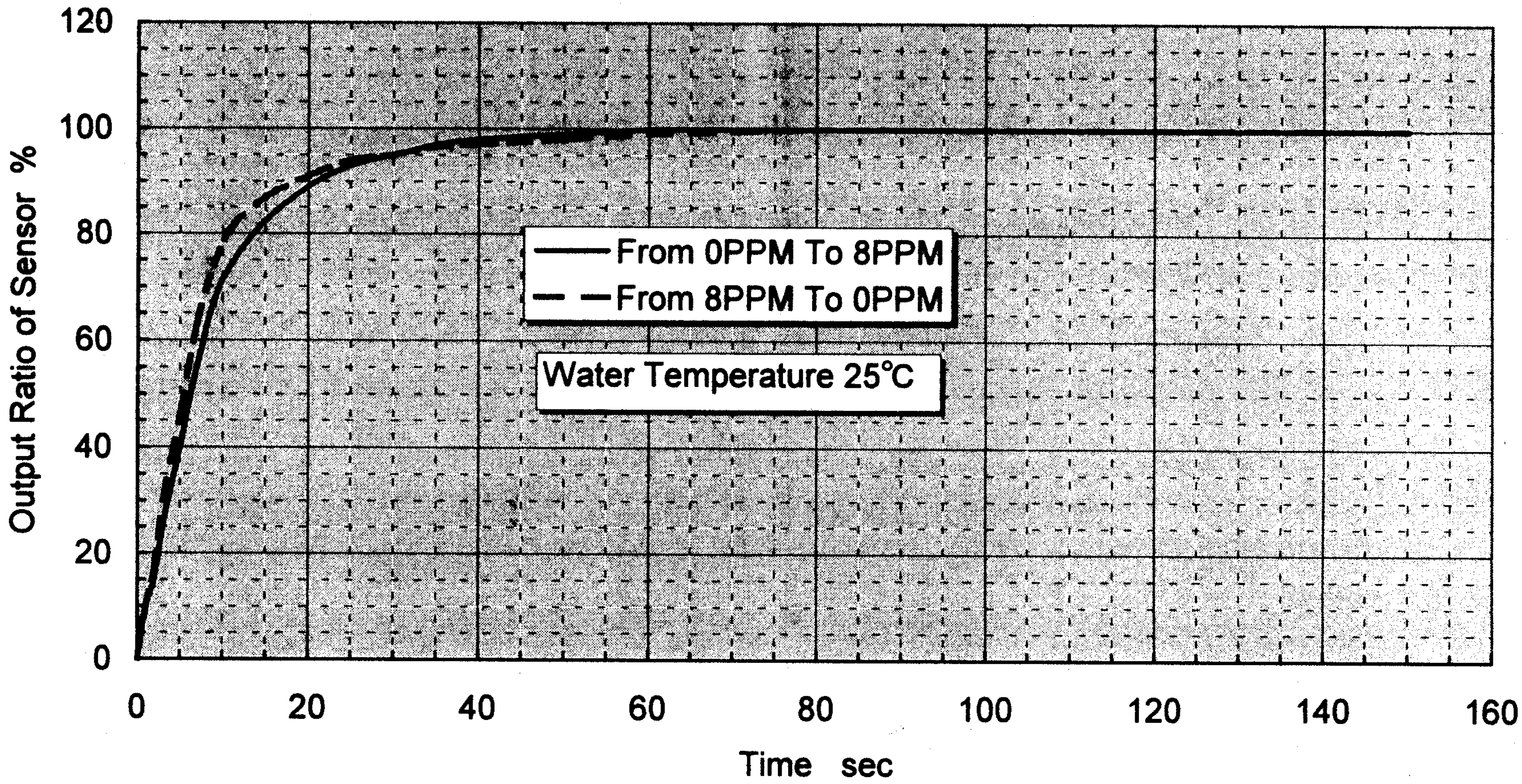


Fig.5 Relationship between sensor output and temperature response characteristics illustrated by relationship between time and output deviation

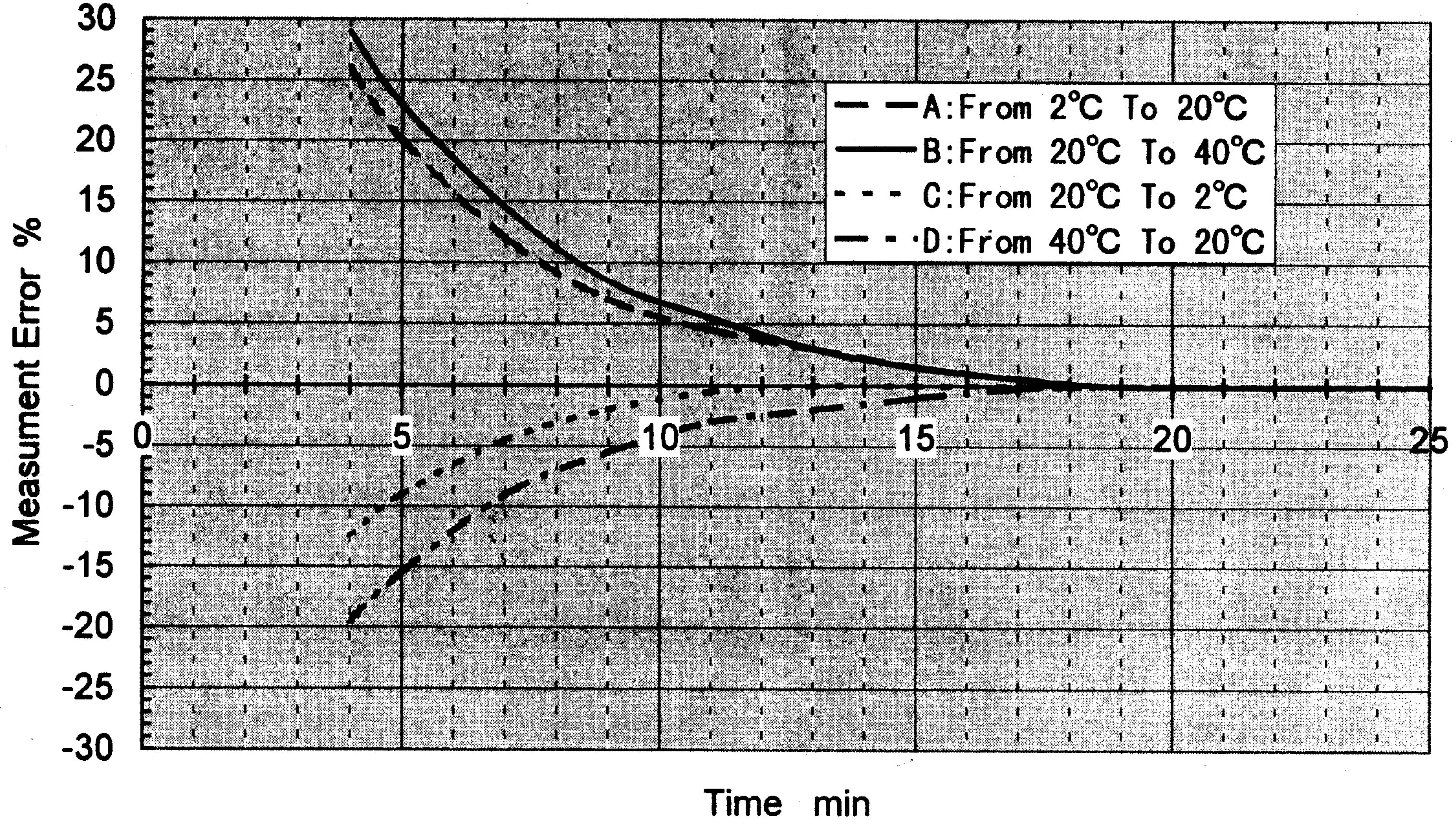
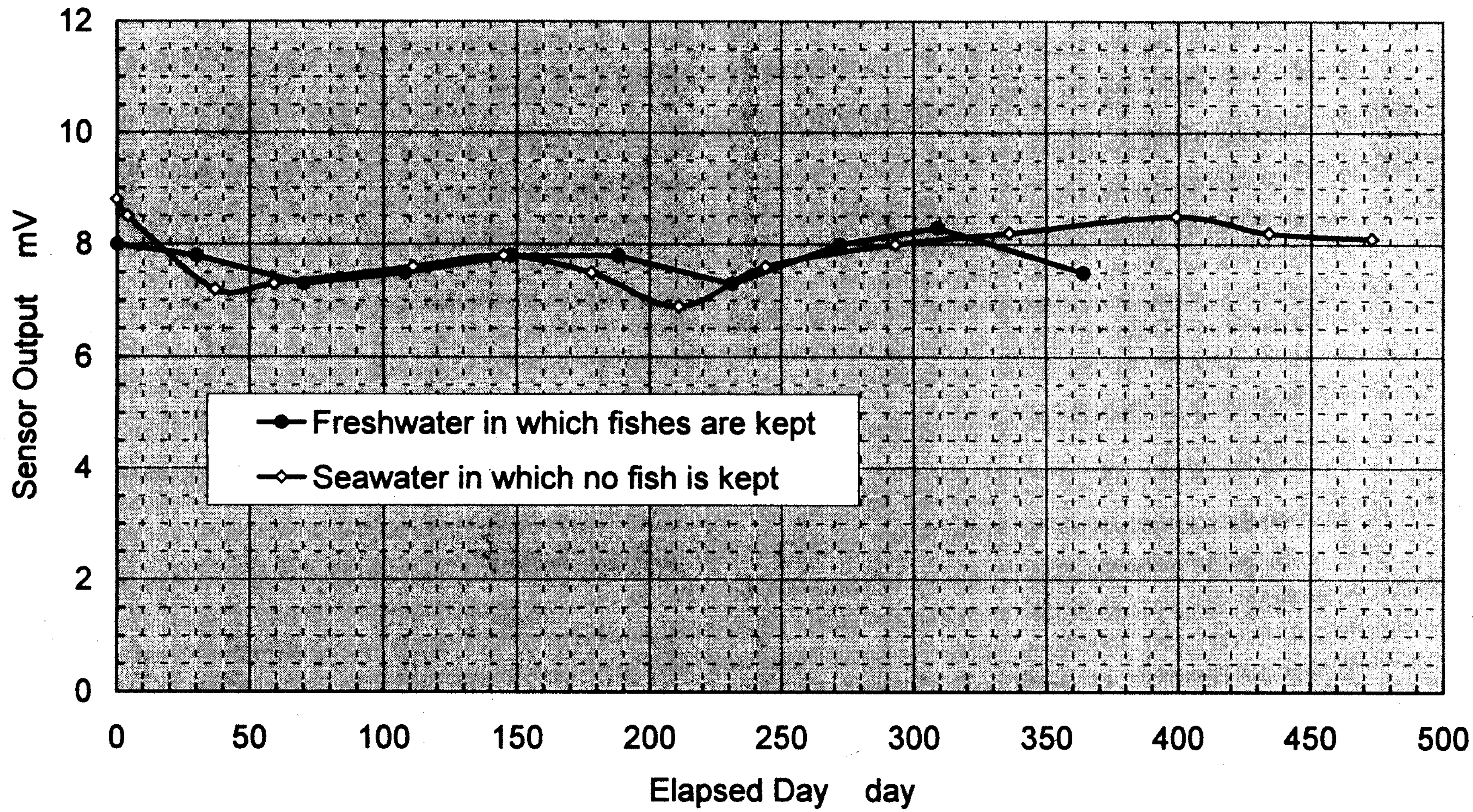
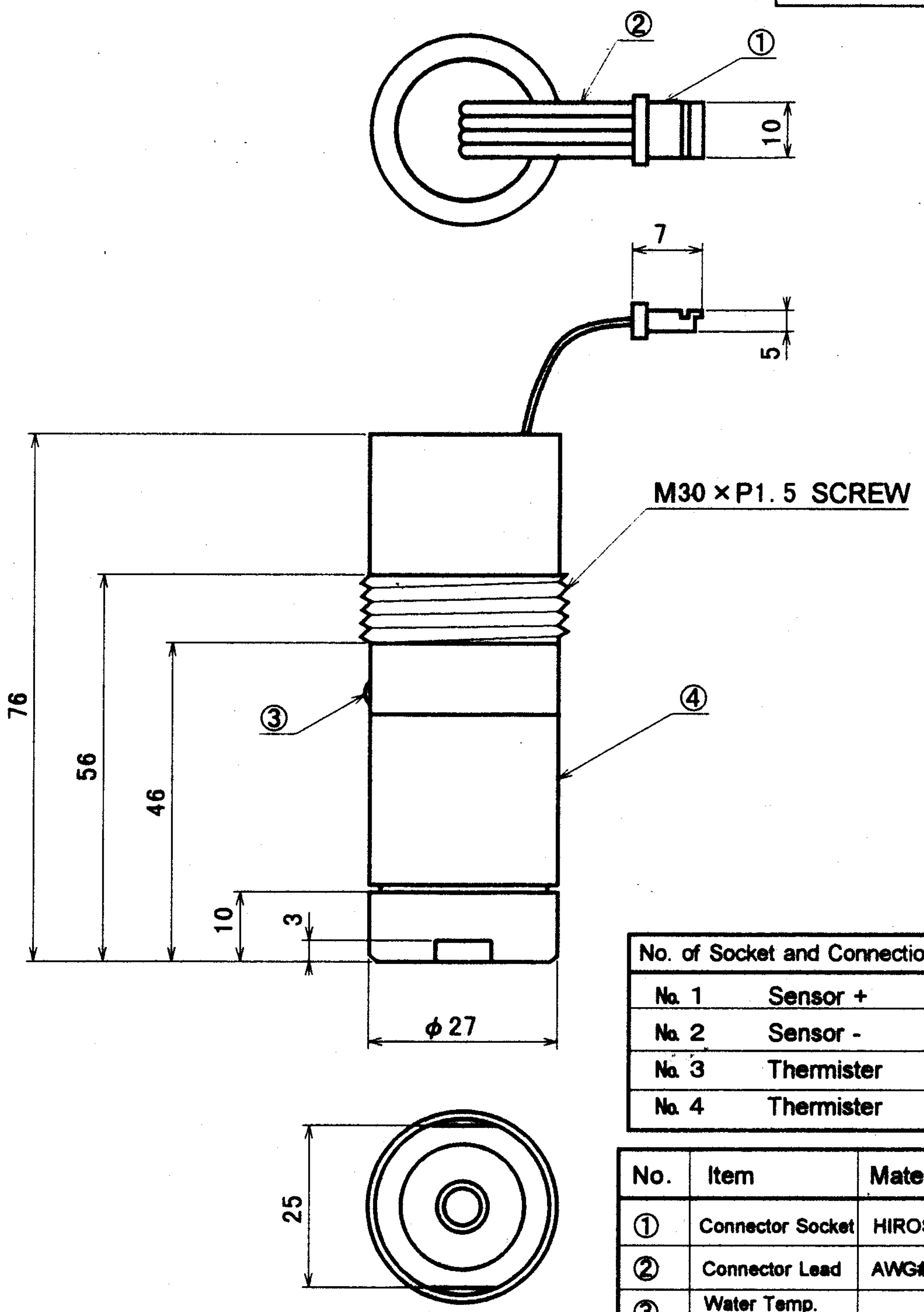


Fig.6 The result of life test - The water temperature and DO value are equilibrated with the room temperature and atmosphere. -





No. of Socket and Connection Apparatus	
No. 1	Sensor +
No. 2	Sensor -
No. 3	Thermister
No. 4	Thermister

No.	Item	Material, etc.
①	Connector Socket	HIROSE DF3-4S-2C
②	Connector Lead	AWG#24
③	Water Temp. Sensor	
④	Main Body	ABS resin, etc.

Appl.	Check.	Dsgn.	Draw.		title
N. Kitamura	N. Kitamura	T. Sato	N. Kitamura		Dissolved Oxygen Sensor KDS-25B for Exchanging
				Scale;1/1	External Dimensions
Japan Strage Battery Co.,Ltd.				Date;1995/09/30	Drawing No. 90DO-09B

Specialty Division Tech. Sec.