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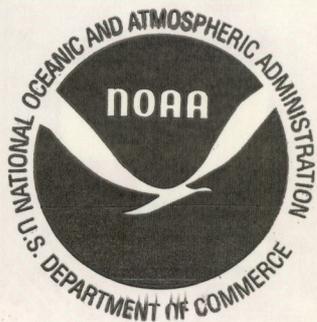
PERFORMANCE EVALUATION OF THE HORIBA INSTRUMENTS,
INC. MODEL U-7 WATER QUALITY CHECKER

Washington, D.C.
June 1979

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PERFORMANCE EVALUATION OF THE HORIBA INSTRUMENTS,
INC. MODEL U-7 WATER QUALITY CHECKER

Jerald M. Peterson, Charles C. White,
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PERFORMANCE EVALUATION OF THE
HORIBA INSTRUMENTS, INC. MODEL U-7 WATER QUALITY CHECKER

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ABSTRACT: Test and evaluation results are reported for a general purpose, handheld water quality checker designed to measure temperature, conductivity, pH, dissolved oxygen, and turbidity. A system description, manufacturer's specifications, and performance results with associated figures and tables giving accuracy, precision, stability, and environmental effects are provided for all parameters with the exception of turbidity.

INTRODUCTION

The Horiba Model U-7 Water Quality Checker is a handheld instrument housed in a moisture-proof case with a luminous three-digit readout and all-solid-state circuitry. The detector package may be immersed in seawater, freshwater, or industrial effluent and has a built-in sample cup for laboratory measurements. The depth of in situ measurements is limited to the sensor cable length (2 m). This five-parameter system measures temperature, conductivity, pH, dissolved oxygen, and turbidity. The turbidity section was not tested for lack of suitable standards and test facilities.

The system was evaluated to determine overall accuracy, precision, long-term stability, response time, and environmental effects on the following measurands: temperature, conductivity, pH, and dissolved oxygen.

SYSTEM DESCRIPTION

The Horiba Model U-7 Water Quality Checker is shown in figure 1. The detector package contains all five sensing elements in a single miniaturized assembly measuring 7 cm (2-3/4 inches) in diameter. Temperature is measured using the thermistor technique. Conductivity is measured by a four-electrode sensor to minimize polarization effects. The pH sensor is the glass electrode type. For dissolved oxygen, a membrane-type galvanic cell is used. For turbidity measurements a ratio turbidimeter is used. The sensing electrodes can be removed, cleaned, and replaced in the field. The multi-core cable is supplied in a standard length of 2 m. Cable connections are hermetically sealed to assure long life when the unit is submerged for extended periods of time. The sensor shell acts as a protective cover for the sensing elements when submerged or as a sample holder when the instrument is used in the laboratory. The sample chamber has a false bottom which houses a stirring motor for obtaining stable dissolved-oxygen readings. A separate battery, switch, and viewing port are contained in the base which allows the operator to monitor the action of the stirrer. The stirrer battery is capable of continuously driving the stirrer for 20 hours. The weight of the detector package is approximately 900 g (29 oz).

The handheld main body is moisture-proof (not waterproof) and houses the signal conditioning circuitry, digital readout, selector and calibration

controls, and the rechargable battery. This battery is capable of 2 hours of continuous operation and can be fully recharged in less than 4 hours. The weight of the main body is approximately 700 g (22 oz).

Accessories supplied with the system include a carrying case, recharger, calibration solutions, electrolytes, and replacements supplies.

The manufacturer's performance specifications are listed in appendix A.

TEST PROCEDURES AND RESULTS*

Temperature

The temperature accuracy and precision determinations were conducted in a non-metallic, constant-temperature water bath. The temperature range for this investigation was from 2°C to 40°C. The bath temperature was measured with either a platinum resistance thermometer in conjunction with a Mueller bridge having a combined accuracy of $\pm 0.002^\circ\text{C}$ or a calibrated quartz thermometer with an accuracy of $\pm 0.02^\circ\text{C}$.

The system temperature accuracy and worst-case precision limit as a function of temperature are shown in figure 2. From this figure it can be seen that the worst-case inaccuracy was 0.77°C and the worst-case imprecision was $\pm 0.19^\circ\text{C}$.

Conductivity

Conductivity measurements were performed in a nonmetallic, constant-temperature water bath. The artificial seawater was prepared from American

*A performance summary is given in appendix B.

Society for Testing and Materials (ASTM) Formula A sea salt at a temperature of 40°C. After the salinity was adjusted to 35±0.1 ppt at 40°C, the bath was allowed to "cook" for 24 hours at this temperature to ensure the dissolution of all salts and to reduce the dissolved gas content.

The conductivity data were collected as the bath temperature was cycled to effect a corresponding conductivity cycle. Care was taken to ensure that there were no trapped bubbles on the conductivity electrodes and that the sensor was suspended at least 15 cm from the walls of the bath to avoid wall effects. The instrument was calibrated to the C_{35,15} point (conductivity of 35-ppt salinity seawater at 15°C) at the beginning of each cycle. At each datum point the bath temperature was measured using the platinum resistance thermometer and the salinity was measured on a laboratory salinometer (Guildline 8400 Autosal) which possesses an accuracy of ±1.0 ppm equivalent salinity. This procedure was repeated for three complete cycles.

Figure 3 shows the error in conductivity as a function of conductivity. The range for the conductivity testing was from 29- to 48- mmho/cm.⁺ The worst-case precision limits are given in the graph. The worst-case inaccuracy was 1.6 mmho/cm. The worst-case imprecision was ±0.95 mmho/cm.

pH

The accuracy and precision data for the pH mode of operation were obtained from three temperature cycles (0°C to 40°C) with the test bath preset at pH of 7 using certified pH buffer solutions. Prior to running

⁺1 mmho/cm = 10⁻³ ohm⁻¹ cm.⁻¹

A graph depicting the error in pH as a function of temperature is shown in figure 4. The pH for these tests ranged from 4 to 9. The average overall precision was ± 0.02 pH units with the worst-case of ± 0.05 pH. The worst-case inaccuracy was $+0.13$ pH units.

DISSOLVED OXYGEN

The dissolved oxygen accuracy and precision data were obtained from instrument readings in a constant temperature water bath in which the concentration of dissolved oxygen was established as follows. The water bath was saturated with a gas mixture of O_2 and N_2 at temperatures of $20^\circ C$, $10^\circ C$, $0^\circ C$, $20^\circ C$, $30^\circ C$, $40^\circ C$, and $20^\circ C$. This saturation process and temperature cycling was repeated two or more times in water of 0 ppt and 35-ppt salinity. The 35-ppt salinity data were obtained using synthetic seawater (Formula A). Three different gas mixtures (4, 8, and 21 percent O_2 in N_2)* were used to saturate the test bath which was temperature cycled to obtain a complete range of dissolved oxygen concentrations. Literature values for the concentration of dissolved oxygen in saturated seawater as a function of temperature and salinity were obtained from Gilbert, et al. (1967)[†]. Water samples were also taken at each test point to be analyzed by the modified Winkler method and gas chromatographic techniques.

*Actual gas mixture oxygen concentrations were obtained to within ± 0.08 mole percent from analyses performed by the National Bureau of Standards.

[†]Gilbert, Pawley, and Park, 1967: Carpenter's oxygen solubility table and nomograph for seawater as a function of temperature and salinity. Oceanographic Society of Japan, 23 (5), p. 252-255.

Dissolved oxygen accuracy as a function of temperature and percent oxygen is shown for freshwater in figure 5 and for 35-ppt seawater in figure 6. The average precision was ± 0.11 ppm and ± 0.14 ppm for freshwater and 35-ppt seawater, respectively. The dissolved oxygen concentration for these tests ranged from 1 ppm (4 percent O_2 at $40^\circ C$) to 14 ppm (21 percent O_2 at $0^\circ C$). The worst-case inaccuracy was 1.03 ppm for freshwater (4 percent O_2 at $2^\circ C$) and 1.2 ppm for 35-ppt seawater (4 percent O_2 at $0^\circ C$).

Response Times

The response times were obtained by subjecting each sensor to a step change in measurand and monitoring the system analog output on a recorder. Care was taken to ensure that the response time of the recorder was less than 10 percent of the response time being measured. The results of the 95 percent response times are summarized in table 1.

Table 1.--Measure response times (seconds)*

Measurand	Response times (s)		
	At $0^\circ C$	At $20^\circ C$	At $40^\circ C$
Temperature	6.6	17.7	191
Conductivity	0.18	0.24	1.2
pH	(334) ⁺	112.0	74.9
Dissolved oxygen	(45) ⁺	15.4	4.4

*Response time is defined here as the time required for the system output to attain 95 percent of the asymptotic value when subjected to a step input. This 95 percent response time is three times the time constant $[(1 - e^{-1}) \text{ value}]$ for a pure exponential response.

⁺Values in parentheses were obtained at $2^\circ C$.

Environmental Effects

To examine the effects of temperature variation on the electronics portion of the system, the sensor inputs were simulated and the electronics package was placed in an environmental chamber where the temperature was cycled from 0°C to 60°C while maintaining the relative humidity at 25 percent. The sensor-simulation circuitry was isolated from these temperature variations. The worst-case temperature error during the environmental evaluation was 0.38°C at 0°C. The worst-case dissolved oxygen error was 0.04 ppm at 10°C.

Power Supply Variation Effects

No detectable errors were observed in the instrument outputs while the power supply input voltage was changed linearly by +20 percent of the specified voltage.

Long-Term Stability

The long-term stability test was conducted for 30 days to determine the instrument reliability for monitoring applications. For this test the sensors were once again placed into the nonmetallic bath containing fresh-water saturated with a mixture of 21 percent oxygen in nitrogen. The bath was resaturated, and readings recorded each day. Figure 7 depicts the dissolved oxygen error as a function of time in days.

PARTS REPLACED OR REPAIRED DURING EVALUATION

- February 1976 - Dissolved oxygen sensor failed and was replaced under warranty.
- February 1976 - Broken sensor was replaced. (See general comment 1.)

- September 1976 - Battery pack replaced when it would not hold charge. One cell was leaking.
- October 1976 - pH sensor flooded and was subsequently returned to manufacturer for warranty repair.
- February 1977 - AC/DC converter failed. The electronics unit was returned for repair at a cost of \$137.50.
- March 1977 - Digital panel meter failed. (See general comment 2.)

GENERAL COMMENTS

1. The retaining cap on the end of the underwater connector is extremely difficult to remove. Without removal it will not fit through the sensor mounting plate. In the process of removing the retaining cap from the dissolved oxygen sensor, the electrical connection was broken.
2. During the environmental testing, the digital panel meter failed at 60°C but became operational again when cooled to room temperature. The same behavior was exhibited at -5°C. The operation of the meter was erratic throughout the remainder of the testing, even at room temperature. The manufacturer later replaced the entire digital panel meter under warranty.
3. The manual is quite complete including circuit descriptions and schematics. There are, however, a few typographical errors (300 meters should read 30 meters) and some errors (i.e., wiring mistake in power supply schematic and missing component designations or values).

ACKNOWLEDGMENT

The authors wish to acknowledge the dedicated efforts of Paul Eichelberger without whose expertise, perserverance, and attention to testing detail, the data in this report could not have been gathered.

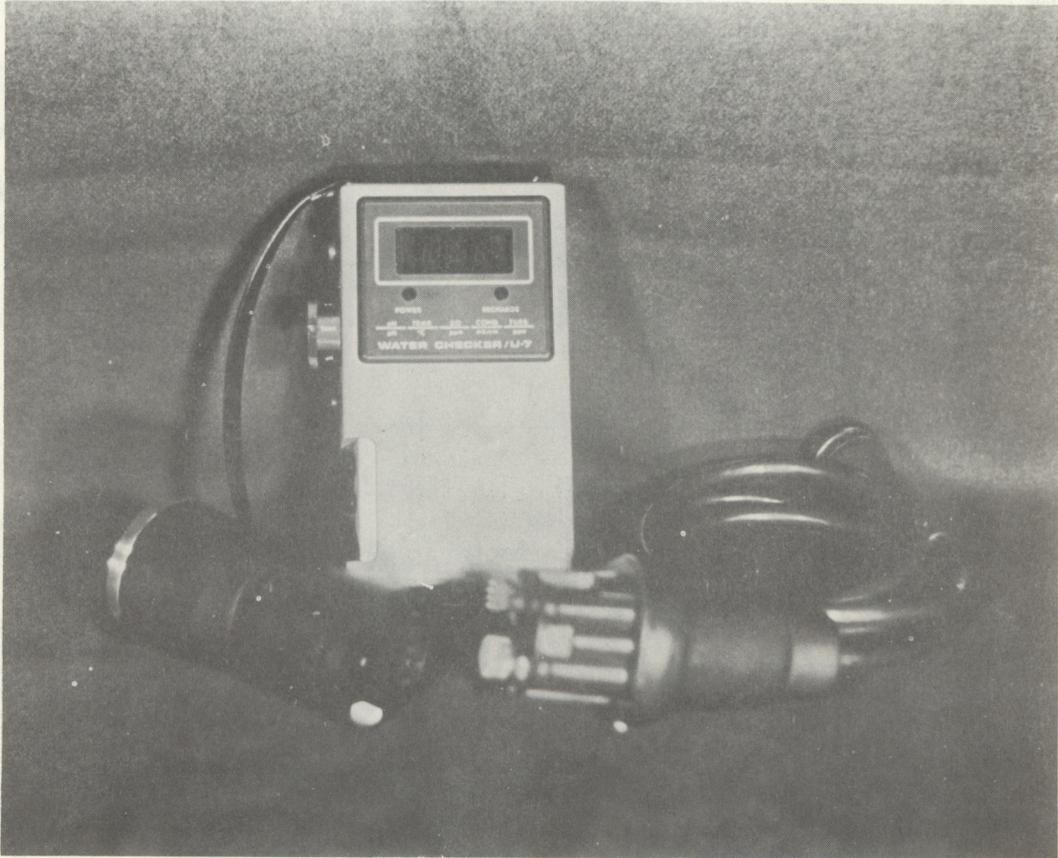


Figure 1.--Horiba Model U-7 Water Quality Checker.

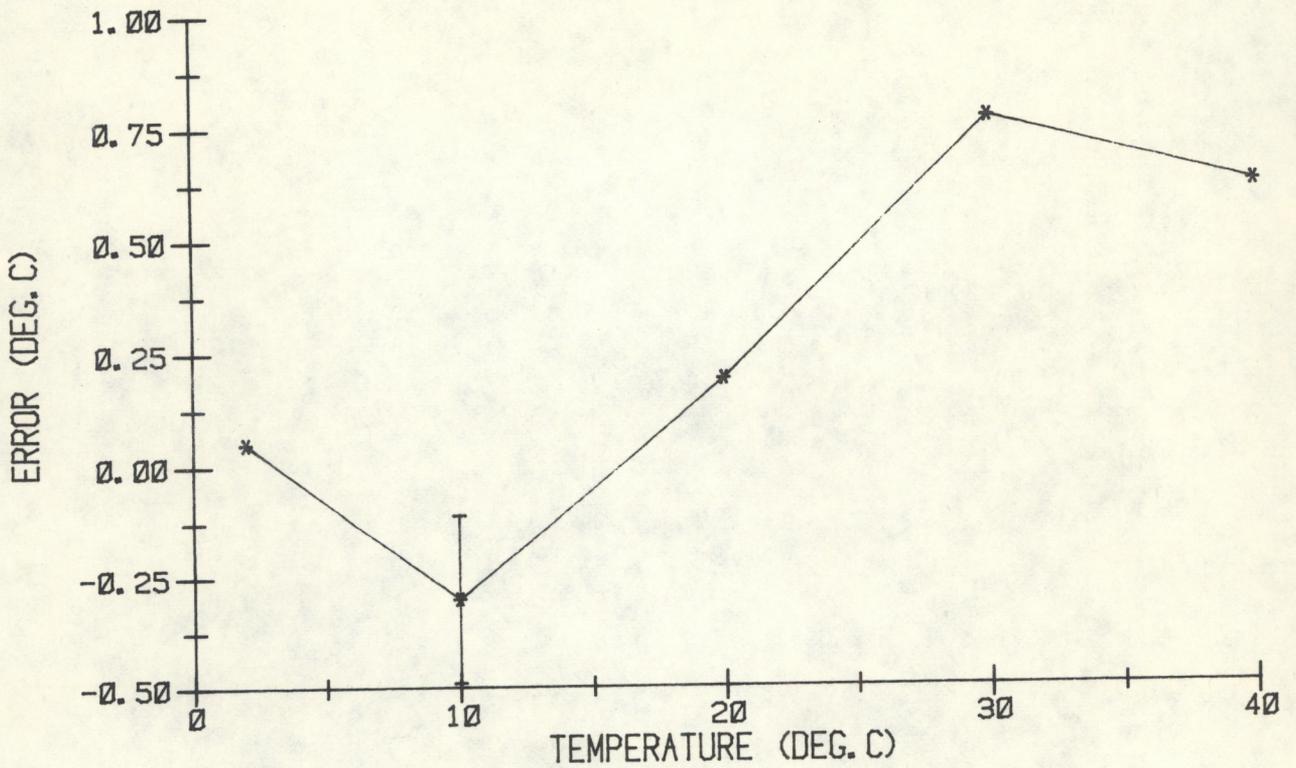


Figure 2.--Temperature accuracy and worst-case precision limit (vertical bar).

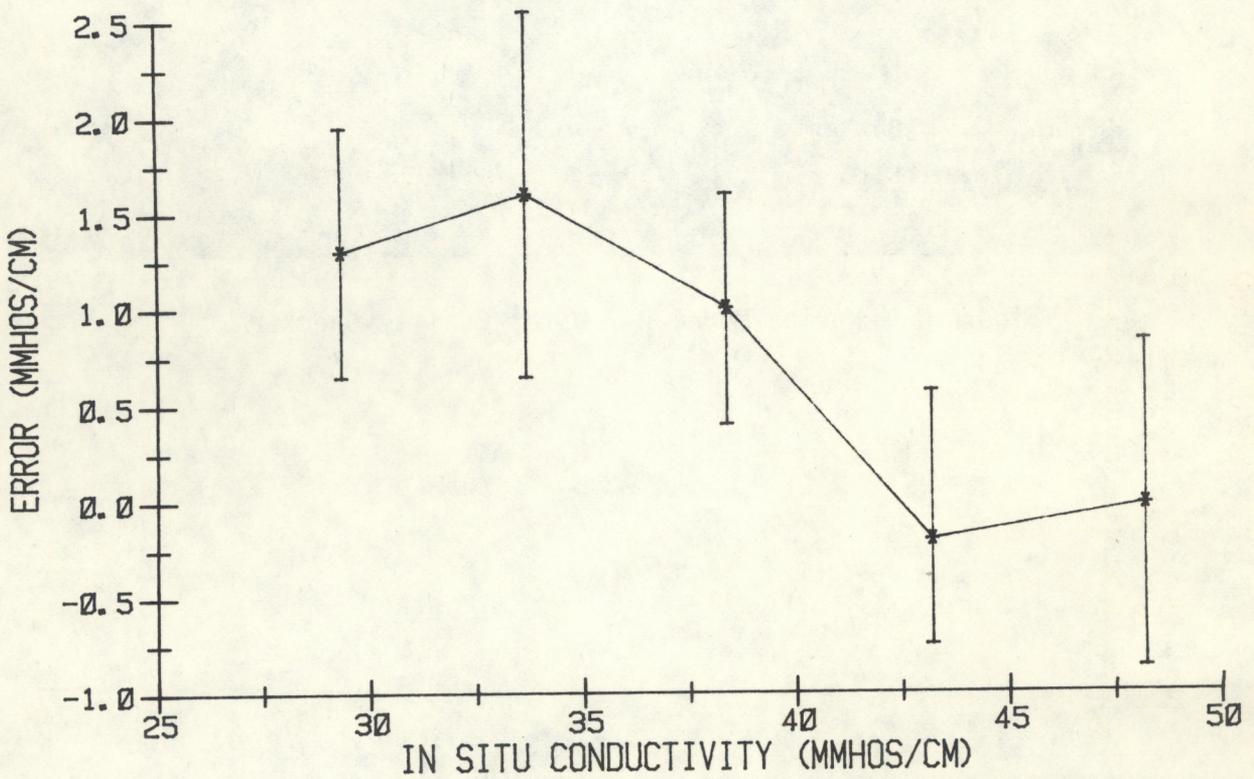


Figure 3.--Conductivity accuracy showing precision limits (vertical bars).

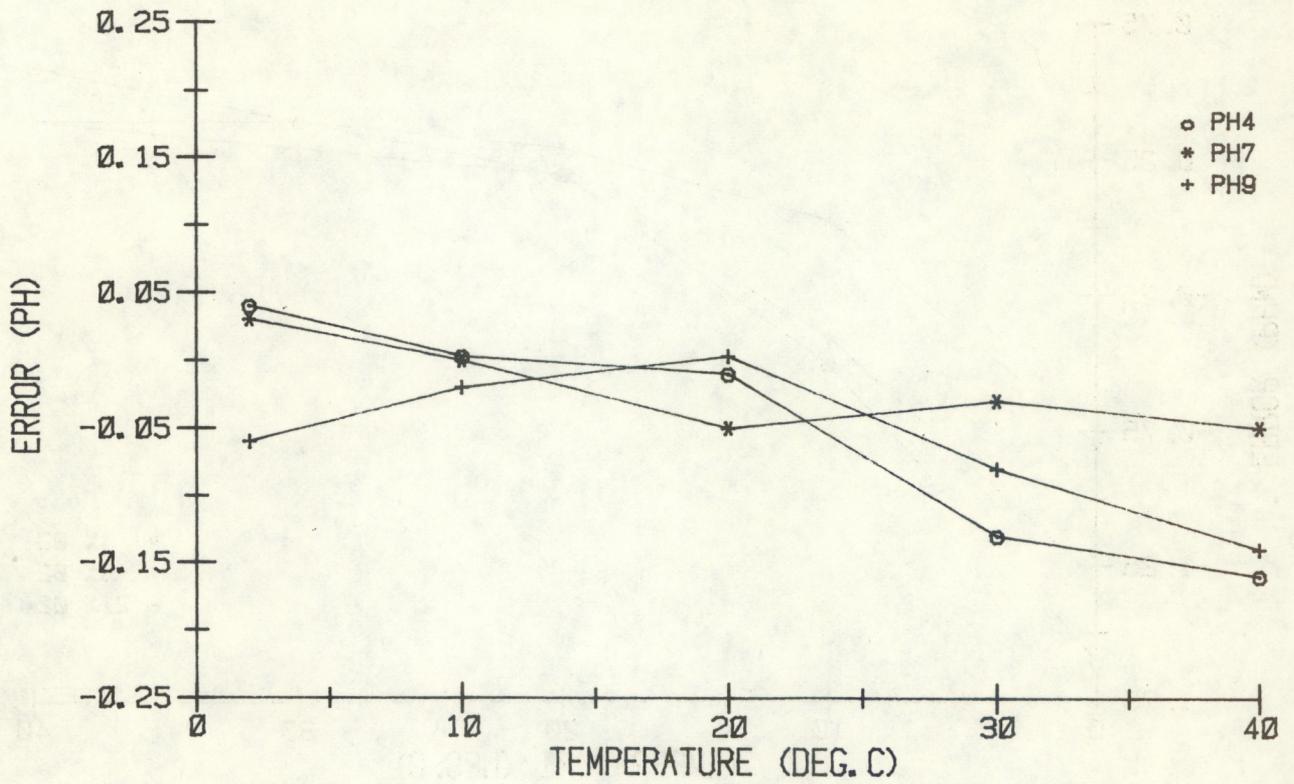


Figure 4.--pH accuracy.

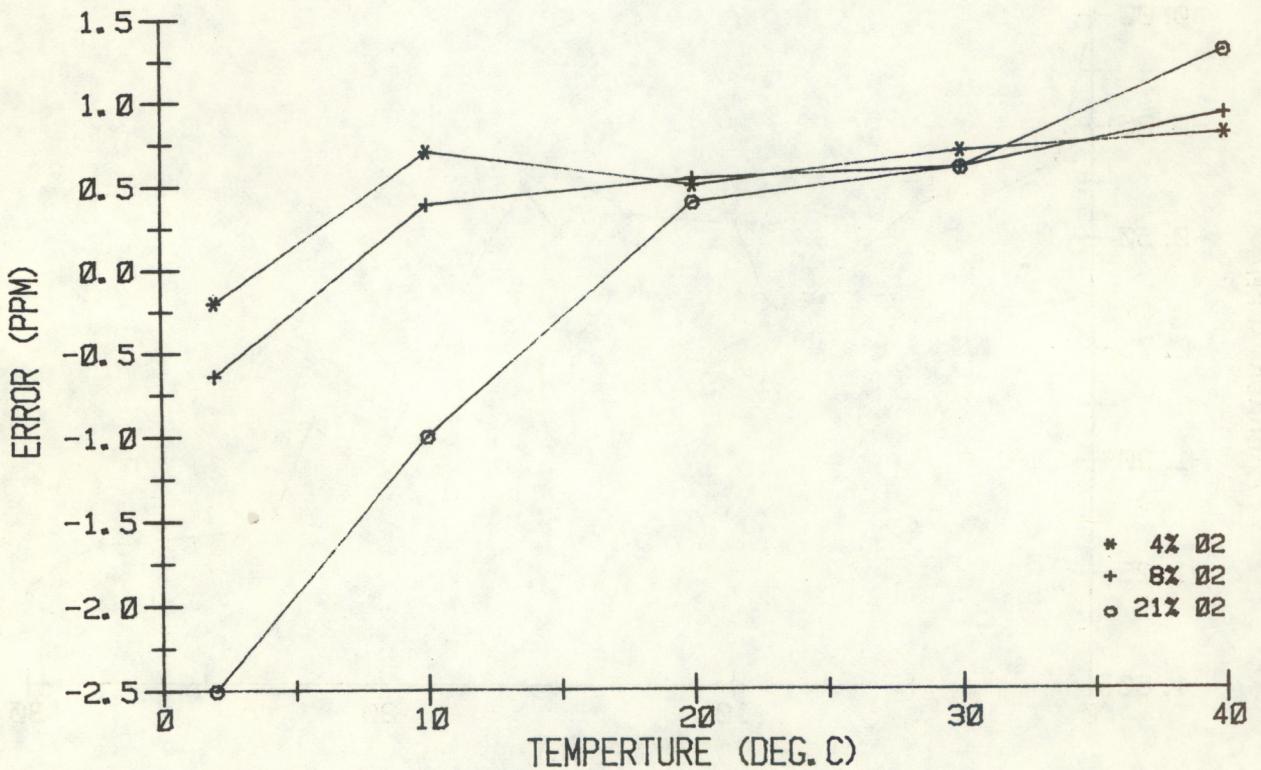


Figure 5.--Dissolved oxygen accuracy in freshwater.

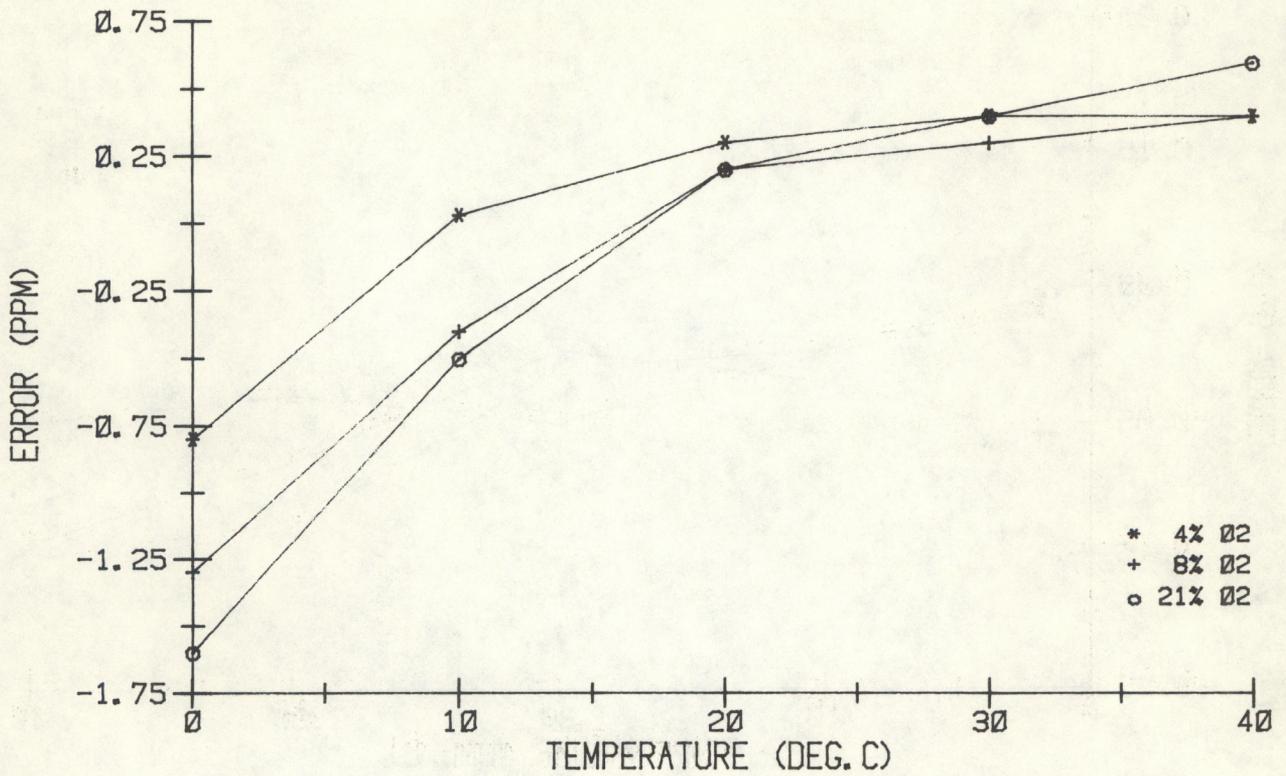


Figure 6.--Dissolved oxygen accuracy in seawater (35 ppt).

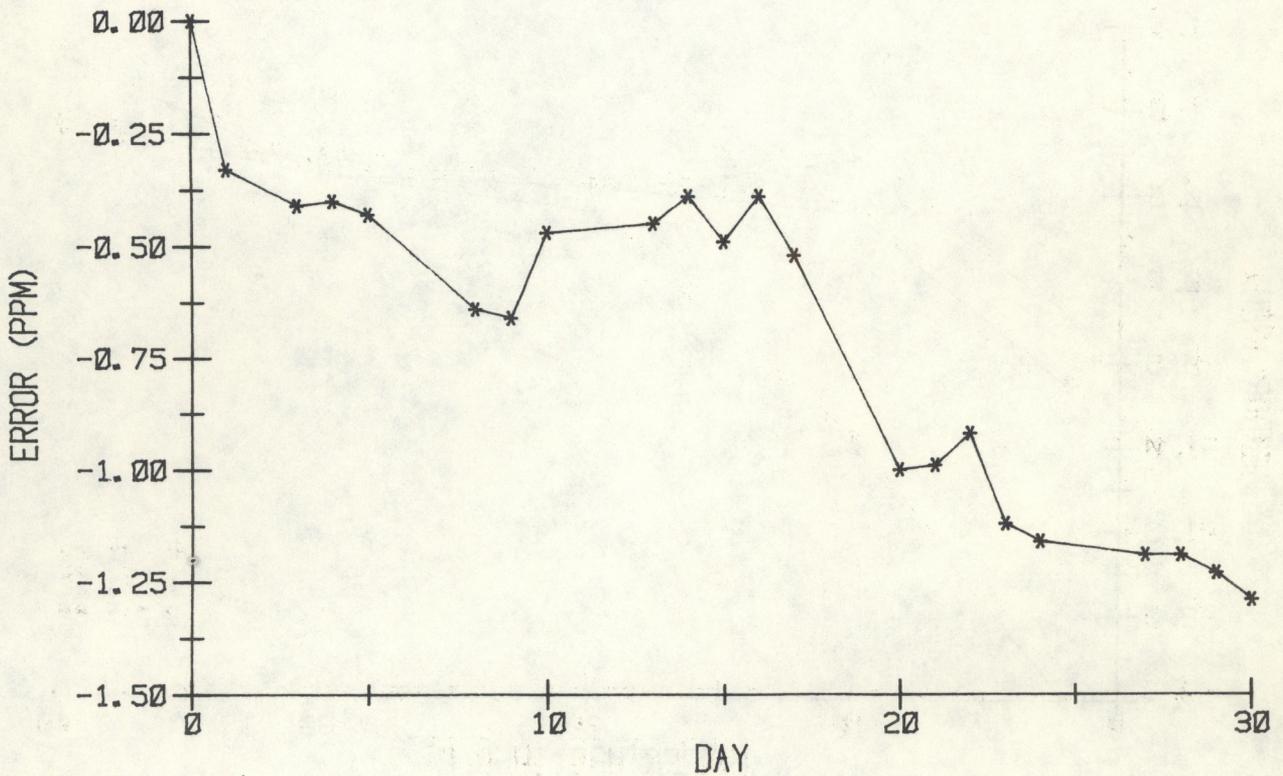


Figure 7.--Dissolved oxygen error vs. time (days).

APPENDIX A -- MANUFACTURER'S PERFORMANCE SPECIFICATIONS

Temperature

Range 0°C to 40°C

Accuracy $\pm 0.5^\circ\text{C}$

Conductivity

Range* 0 to 50 mmho/cm

Accuracy ± 2.5 mmho/cm

pH

Range 0.0 to 14.0 pH

Accuracy ± 0.1 pH units

Dissolved oxygen

Range 0 to 20.0 ppm

Accuracy ± 1.0 ppm

Turbidity

Range 0 to 400 ppm suspended solids

Accuracy ± 20 ppm

*0 to 1 mmho/cm sensor also available

APPENDIX B -- PERFORMANCE SUMMARY**

Temperature

Range tested	2°C to 40°C
Accuracy	0.77°C
Precision	<u>+0.19°C</u>

Conductivity

Range tested	29 to 48 mmho/cm**
Accuracy	1.60 mmho/cm
Precision	<u>+0.95 mmho/cm</u>

pH

Range tested	4 to 9 pH
Accuracy	-0.16 to pH units
Precision	<u>+0.12 pH units</u>

Dissolved oxygen

Range tested	1 to 14 ppm (mg/l)
Accuracy, freshwater	-2.5 ppm
Accuracy, seawater	-1.6 ppm
Precision, freshwater	<u>+0.35 ppm</u>
Precision, seawater	<u>+0.30 ppm</u>

*Abbreviated from the Test Procedures and Results and associated graphs.

†All test results are worst-case values averaged from three or more cycles unless otherwise specified.

**1 mmho/cm = 10^{-3} ohm⁻¹ cm⁻¹

APPENDIX C - GLOSSARY

Measurand - A physical quantity, property, or condition which is measured.

Error - The algebraic difference between the indicated value and the true value of the measurand, usually expressed in percent of the full-scale output, sometimes expressed in percent of the output reading of the instrument.

Accuracy - The ratio of the error to the full-scale output (usually expressed as "within \pm ---- percent of full-scale output") or the ratio of the error to the output, expressed in percent. Accuracy may also be expressed in terms of units of measurand.

Precision (repeatability) - The ability of an instrument to reproduce output readings when the same measurand value is applied to it repeatedly, under the same conditions, and in the same direction. Precision is expressed as the maximum difference between output readings or as "within ---- percent of full-scale output." Three calibration cycles are used to determine precision unless otherwise specified.

Throughout this report, the values for errors, accuracies, and precisions are reported in terms of units of measurand. Accuracies are the average errors from the true value determined from two or more calibration cycles and are reported as + or - biases. Precisions are averages of the worst-case high and low values obtained with the same measurand input value under the same conditions over two or more calibration cycles unless otherwise noted. These precision averages are reported in measurand units as \pm (highest value - lowest value)/2.

(Continued from inside front cover)

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- NOS 21 National Ocean Survey Abstracts - 1976. October 1977, 20 pp. (PB-275293)
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