Measuring instrument of carbon dioxide concentration in seawater

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The measuring instrument of carbon dioxide concentration in seawater (pCO_2) is developed. The instrument consists of an equilibrator, a non-dispersive infrared gas analyzer (NDIR), a carrier gas generator and a processing signal generator. The equilibrator has a cross section of 3 cm^2 and is 15 cm tall. The principle of pCO_2 measurement is based on the equilibration of a carrier gas phase with a seawater sample and subsequent determination of the carbon dioxide concentration in the carrier gas. The carrier gas circuit of the NDIR is opened to the atmosphere to maintain the carrier gas line at a barometric pressure. The present instrument can measure pCO_2 within the measuring error of about 2 ppm with sample water of about 180 ml every 20 min.

1. Introduction

Due to the burning of fossil fuel and the human impact on land biota the atmospheric concentration of carbon dioxide is steadily increasing (e.g., Keeling et al., 1995). It is noted that the only about 45% of the total anthropogenic emissions of carbon dioxide remains airborne (Houghton et al., 1990). The ocean has long since been recognized as an important sink for a significant portion of the missing anthropogenic carbon dioxide. Therefore, the carbon dioxide concentration in seawater (pCO_2) has been measured extensively (e.g., Gordon et al., 1971; Wong and Chan, 1991; Inoue and Sugimura, 1992).

The principle of pCO_2 measurement is based on the equilibration of a carrier gas phase with a seawater sample. A great variety of equilibrators has been described in the literature. Essentially three different design principles can be distinguished; 1) the shower type equilibrator (e.g., Keeling et al., 1965; Inoue et al., 1987), 2) the bubble type equilibrator (e.g., Takahashi, 1961; Goyet et al., 1991; Ohtaki et al., 1993), 3) the laminary flow type equilibrator (Poisson

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et al., 1993). In order to avoid the question of comparability of pCO_2 data from different analytical system, there are several efforts to standardize the pCO_2 instruments in recent years. In June 1994, the inter-comparison experiment of pCO_2 was carried out in charge of Prof. Dickson of University of California. Thirteen groups from eight different countries brought pCO_2 instruments to La Jolla, and compared the operation of their instruments. Similar comparison experiment for Japanese scientists was carried out in charge of Prof. Tsunogai of Hokkaido University in 1995. It is noted that highly comparable measurements are possible with different designs of pCO_2 instrument (Dickson, 1995).

We operated our newest version of pCO_2 instrument during these two comparison experiments. The instrument showed advantages: The measuring principle of the instrument is clearer than those of traditional equilibrator instruments, and the instrument can measure the pCO_2 with a small amount of sample seawater of about 180 ml (Ohtaki et al., 1993; Yamashita et al., 1993). In the present paper, we would like to describe the configuration and operation of the instrument. Later papers will present the pCO_2 data measured by the instrument.

2. Description of pCO_2 instrument

A schematic diagram of pCO_2 instrument is shown in Fig. 1. The pCO_2 instrument consists of five parts from UNIT 1 to UNIT 5. At first, we briefly describe characteristics of each UNIT, and then present operations of main parts of the instrument.

UNIT 1: This is the analytical part including a non-dispersive infrared gas analyzer (NDIR). The measuring range and the accuracy of the NDIR are 0-2000 ppm and about 0.1 ppm,
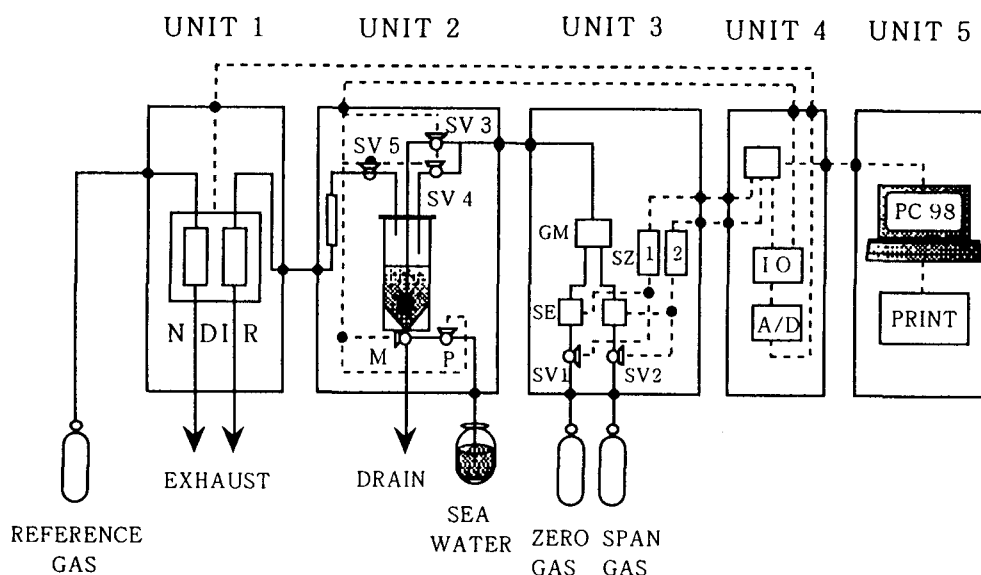

Fig. 1 Schematic diagram of newly developed pCO_2 instrument.

respectively. The carrier gas of known concentration of carbon dioxide, generated by UNIT 3, is flushed into the equilibrator in UNIT 2, and then passed through the measuring cell of the NDIR. If the carbon dioxide concentration of the carrier gas equals that in seawater, the NDIR signal does not show any change, because the dissolved carbon dioxide and various carbonate species are in their equilibrium state during the bubbling procedure. The measuring purpose of the present instrument is to find out such carrier gas concentration. The carrier gas generated, however, has a discrete concentration. Therefore, the output signal of the NDIR comes to have a positive or a negative peak. These peak heights relate to the concentration difference between carrier gas and pCO_2 in seawater. The positive peak means that the carbon dioxide is extracted from sample seawater to the carrier gas, and the negative peak means that the carbon dioxide in carrier gas resolves into the sample seawater. The peak height and peak occurrence time vary with flow rate of the carrier gas. The peak height decreases with increasing flow rate. For example, the peak height is about 130 mV at the rate of 100 ml per min, and it decreases to 100 mV at 250 ml per min (Fig. 2). The peak occurrence time also shortens with increasing flow rate (Fig. 3). In order to have an adequate sensitivity and to measure pCO_2 as quick as possible, the flow rate of 200 ml per min is selected in the present instrument. The outlet of the measuring cell is opened to the atmosphere to maintain the carrier gas line at a barometric pressure.
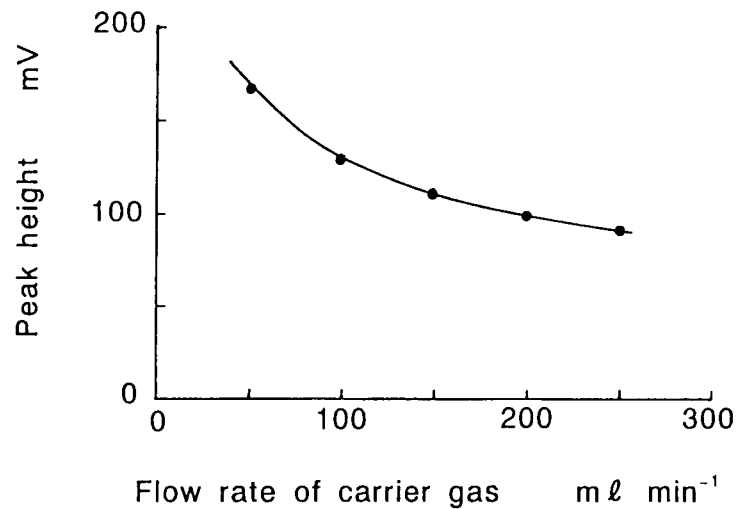
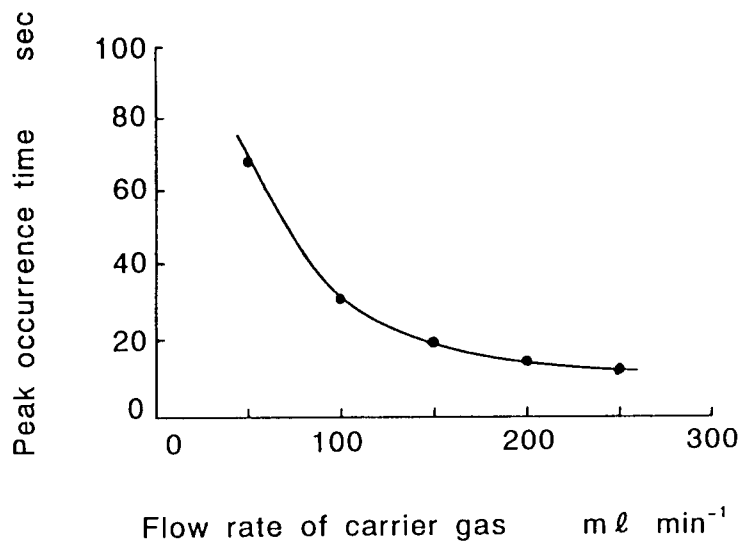Fig. 2 Relationship between peak height and flow rate of carrier gas.

Fig. 3 Relationship between peak occurrence time and flow rate of carrier gas.

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UNIT 2: This part includes the equilibrator which has a cross section of 3 cm^2 and 12 cm tall. Sample seawater of 18 ml is pumped up into the equilibrator. The diffuser (diameter = 1.2 cm; length = 2 cm) is fixed in the equilibrator. The carrier gas is flushed into this diffuser to make fine bubbles in the sample seawater. Fine bubbles drift about 6 cm in the seawater, and interact with dissolved carbon dioxide. The equilibrator is surrounded by a water jacket to minimize the temperature change of sample seawater during measurements. The temperature of sample seawater is monitored by a Pt-resistance thermometer fixed in the equilibrator. It is noted that the temperature change of sample seawater is suppressed within 0.01 °C during the bubbling procedure. This temperature change may cause a difference of pCO_2 by about 0.2 ppm. A level sensor mounted at 7 cm above the bottom of equilibrator protects the instrument from overflow of sample seawater.

UNIT 3: The carrier gas concentration specified is generated from changing the mixing rate of zero and span standard gases under controlling by a personal computer in UNIT 5. The flow rate of these standard gases is adjusted by two flow controllers, SZ1 and SZ2. The concentration difference of carbon dioxide between generated and specified values is within 2 ppm.

UNIT 4: This UNIT generates processing signals for UNIT 2, and UNIT 3. The electronic power for another UNIT is also generated by this UNIT.

UNIT 5: The personal computer controls following procedures; feed and drainage of sample seawater, purging and bubbling of carrier gas, and determination of pCO_2 value by the least square calculation between peak voltages and carrier gas concentrations. These data are stored on a floppy disk after measurements.

Here, we would like to show the operation of main parts of the instrument. Figure 4 illustrates the operation chart of the equilibrator, carrier gases and sample seawater. The operating procedures are as follows.

(1) First carrier gas is generated, and flushed into the diffuser through the electronic valve SV3 shown in Fig. 1. At the same time, the motor (M) turns off, and sample water in the equilibrator is drained off.

(2) The SV3 is turned off. The carrier gas line is changed to the circuit of electronic valves of SV4 and SV5. This procedure is shown as purging in Fig. 4. The sample seawater of 18 ml is pumped up into the equilibrator. The NDIR signal is measured every two seconds. It is noted that the NDIR signal does not show any appreciable change during the purging procedure. This means that the exchange rate of carbon dioxide between carrier gas and sample seawater is not effective during the purging procedure.

(3) When four successive readings of NDIR signal show the same value, the carrier gas line is changed to the diffuser circuit (SV3 is turned on, and SV4 is turned off). Small bubbles of carrier gas interact with sample seawater during drifting about 6 cm in the equilibrator. This
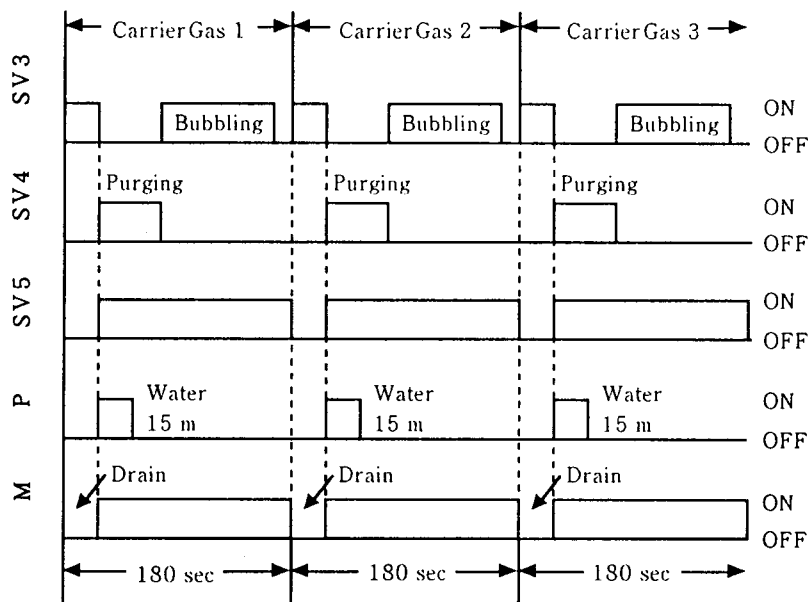
Fig. 4 Operation chart of equilibrator, carrier gas and sample seawater.

procedure is specified as bubbling in Fig. 4. The bubbling procedure is kept for 40 seconds. The present instrument requires about 180 seconds to finish all procedures from step (1) to (3) mentioned above.

(4) In order to determine the pCO_2 value, procedures from step (1) to (3) are repeated with five different concentrations of carrier gas. Results are shown in Fig. 5. The abscissa is the time axis scaled every 15 sec, and the ordinate is the output voltage of the NDIR which automatically expands from 10 to 100 mV per division. The output signal of the NDIR is forced to zero after peak appearance. The carrier gas concentration and the peak voltage are printed at the upper part of each figure. The pCO_2 value is determined by the linear regression calculation from peak height and carrier gas concentration (Fig. 6). The pCO_2 is determined to be 317.8 ppm in the present case. The instrument can measure the pCO_2 every 20 min with a sample seawater of 180 ml.

In order to check the precision of the instrument, the pCO_2 values are measured using the same sample seawater which is kept in temperature controlled water bath (20 ± 0.2 °C). Eight successive values of pCO_2 measured are as follows.

331.0 ppm	330.9 ppm	328.2 ppm	328.7 ppm
329.1 "	332.8 "	326.8 "	330.2 "

The average value is 329.7 ppm with a standard deviation of 1.9 ppm. This result means that the present instrument can be applicable to measure the pCO_2 in seawater. More details of the pCO_2 instrument has been given in previous paper (Ohtaki et al., 1994).

The pCO_2 values given above are presented by ppm unit instead of μatm unit. The
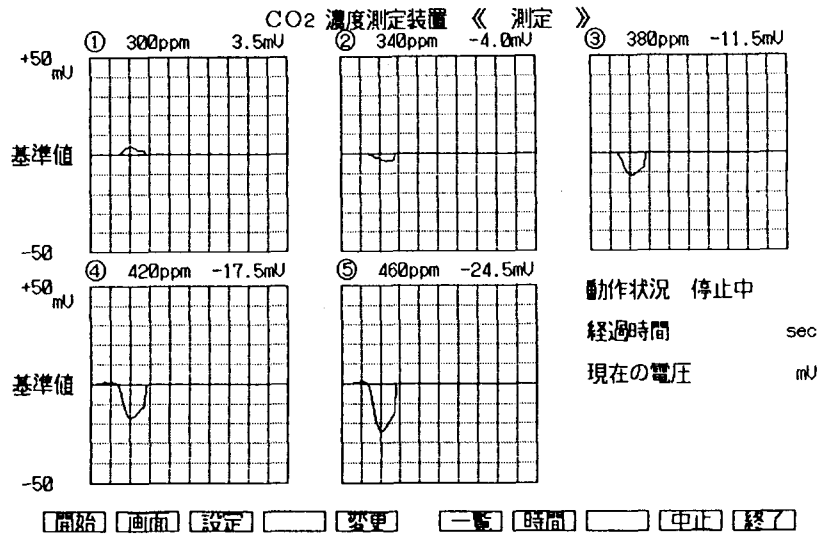
Fig. 5　Output signal of infrared gas analyzer during bubbling procedure for five carrier gases of 300, 340, 380, 420 and 460 ppm.
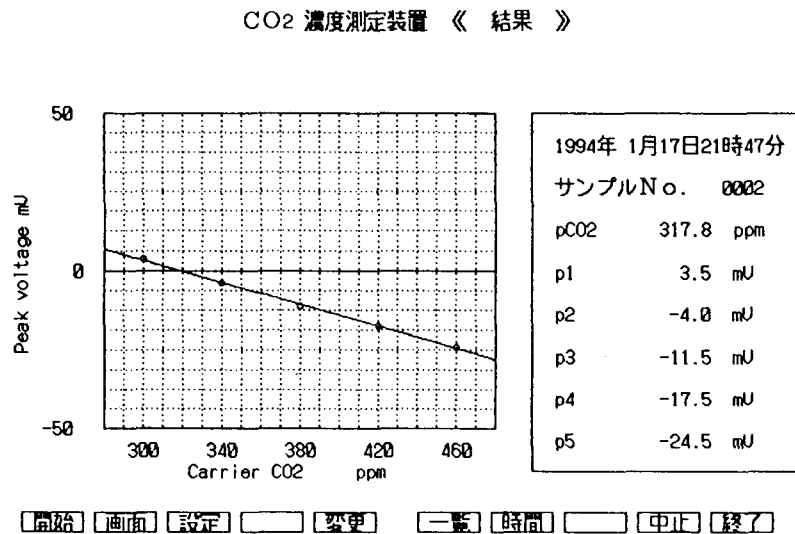

Fig. 6　Relationship between peak height and carrier gas concentration. pCO₂ in seawater is assumed to be carrier gas concentration where the peak height is zero.

conversion from pCO_2 in ppm unit to pCO_2 in μatm unit can be done according to the relationship.

$$pCO_2 \text{ (μatm)} = pCO_2 \text{ (ppm)} [P - X],$$

where P is the atmospheric total pressure, and X is the water vapor pressure at seawater temperature. In general, X is at most 1 to 3% of P in the natural environmental conditions.

3. Conclusions

A newly developed pCO_2 instrument is described. The instrument is designed to measure the carbon dioxide concentration of carrier gas which equilibrates with the sample seawater. The gas outlet of the infrared gas analyzer is opened to the atmosphere to maintain the carrier gas line at a barometric pressure. The instrument can automatically measure pCO_2 every 20 min with sample seawater of 180 ml. The measuring error is about 2 ppm. This denotes that the present instrument is adequate to measure pCO_2 under field conditions

Acknowledgments

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