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Precise Determination of Dissolved Gases in Sea Water by Shipboard Gas Chromatography

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A gas chromatographic system is applied to shipboard measurement of dissolved argon, oxygen, nitrogen, and total inorganic carbon dioxide in sea water. Gases are stripped from acidified sea water with helium carrier gas, separated by passing through silica-gel and molecular sieve 5A columns, and subsequently analyzed with a thermal conductivity detector and an ultrasonic detector. *Ca.* 15 min is required to analyze a 3 cm^3 sea water sample. Intercalibration by other analytical techniques for oxygen and total carbon dioxide confirmed the accuracy of this method. Vertical profiles of the gases in the Pacific Ocean demonstrate the merit of the method.

Oxygen, nitrogen, argon, and total inorganic carbon dioxide ($\sum CO_2$), which are the major dissolved gases in sea water, afford valuable information on chemical and physical processes in the ocean. O_2 and $\sum CO_2$ are involved in life processes in sea water. Near the ocean surface, photosynthesis causes enrichment of O_2 and depletion of $\sum CO_2$, while in the deep layer O_2 is consumed, changing into $\sum CO_2$ by oxidative decomposition of organic material falling from the surface. N_2 and Ar, on the other hand, are little affected by biochemical reactions because of their inertness, and can thus be used as conservative tracers. Except for O_2, however, little data on the oceanic distributions of these gases are available due to the lack of an adequate analytical method for accurate shipboard measurement.

Since Swinnerton *et al.*[1,2] developed a simple on-line gas stripping technique combined with gas chromatography, it has subsequently been adopted by a number of workers for the determination of dissolved gases in aqueous solutions.[3–7] Weiss and Craig[5] developed a set of gas chromatographs for shipboard measurement of dissolved N_2, O_2, Ar, and $\sum CO_2$. In their systems, it is necessary to inject two aliquots of a sample separately, one for the measurement of N_2, O_2, and Ar, and the other for $\sum CO_2$. It would be desirable to measure all the gases simultaneously using the same aliquot.

In this paper, a report is given on a gas chromatograph as a simpler and more convenient system for routine shipboard operations for simultaneous analysis of the four dissolved gases. Swinnerton's technique was applied to gas extraction from sea water, two detectors being employed in series: a thermal conductivity detector for the analysis of $\sum CO_2$, and an ultrasonic detector for that of Ar, O_2, and N_2. The high sensitivity of the ultrasonic detector caused significant reduction in sample volume. The dual detector system made it possible to analyze the four gases simultaneously with a single aliquot of a sample.

Experimental

Sampling and Gas Extraction. Sea water samples were taken in 60 cm^3 glass bottles with rubber stoppers from Niskin-type samplers immediately after each sampler had been brought aboard. The sample was allowed to overflow more than four times the volume of the bottle in order to avoid air contamination during the course of transfer.[8] Samples were kept in the dark before analysis for less than 10 h in order to prevent biological alteration of the dissolved gases.[9]

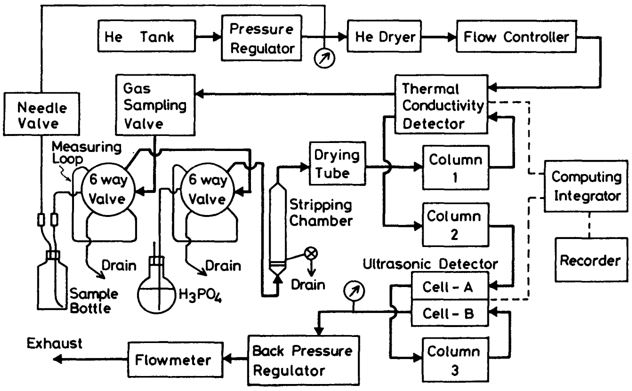

Fig. 1. Schematic diagram of the shipboard gas chromatograph. The thick arrows are the path of the carrier gas in the analysis procedure, and the broken lines are electric connections.

The gas chromatographic system is shown schematically in Fig. 1. Helium was used as a carrier gas. The head and back pressures were regulated at 3.2 and 1.5 kg cm^{-2}, respectively. A constant flow rate of 75 cm^3 min^{-1} supplied by a flow controller (Matheson, series 8287) was occasionally monitored by a soap bubble flowmeter at the end of the flow system, the average HETP of columns being the smallest at this flow rate. Helium (purity$>$99.995%) was dried and purified by passing through a large trap of molecular sieve 5A (10/20 mesh) at ambient temperature before it entered the flow system.

A sample bottle was connected to a six-way rotary valve. By application of helium pressure, the sample sea water was continuously made to flow out of the bottle through a measuring loop made of nylon tubing (i. d. 2 mm), its volume being calibrated accurately to 2.865 ± 0.002 cm^3. The volume was selected to maximize the Ar output of the ultrasonic detector without permitting ultrasonic phase foldover due to N_2 peak.

By turning the six-way valve, the sample was transferred to the stripping chamber, a glass cylinder (length 70 mm, i. d. 10 mm) with a coarse glass frit at the bottom. The carrier gas immediately began to strip the sample of the dissolved gases, carrying them into subsequent columns.

Carbonate and bicarbonate extractions as CO_2 were facilitated by mixing the sample with *ca.* 0.8 cm^3 of H_3PO_4 solution (1 : 10) which had been introduced into the chamber through another six-way valve (Fig. 1) and degassed similarly by carrier gas bubbling prior to the sample injection.

Separation and Detection. The gases evolved were dried by passing through a glass U-tube packed with 16/32 mesh $Mg(ClO_4)_2$. Three separation columns (stainless steel, i. d. 3 mm) were employed in series for isolating the four gas components. Column 1 (length 35 cm, packed with 40/60 mesh silica gel) separated CO_2 from the gas component (Ar, O_2, and N_2), column 2 (length 105 cm, packed with 30/60 mesh molecular sieve 5A) separated N_2 from Ar and O_2, and column 3 (length 80 cm, packed with 80/100 mesh molecular sieve 5A) separated Ar from O_2. Columns 1 and 2 were used at ambient temperature (24±1 °C), and column 3 was cooled at Dry Ice temperature.[10] It was necessary to raise the temperature of column 3 to ambient temperature for every 10 samples in order to regenerate its activity by releasing trapped N_2 out of it, while the other columns were kept activated after more than 200 analyses.

Analysis of CO_2 was carried out with a thermal conductivity cell (Gasukuro Kogyo Co., Ltd., E-121), and that of Ar, O_2, and N_2 with an ultrasonic detector (Tracor Inc., U-90) because of its high sensitivity.[11] Although the ultrasonic detector has two independent cells A and B, it is impossible to detect signals of both cells at the same time. Thus, the lengths of columns 2 and 3 were adjusted in such a way that Ar enters cell B after N_2 has finished passing through cell A.

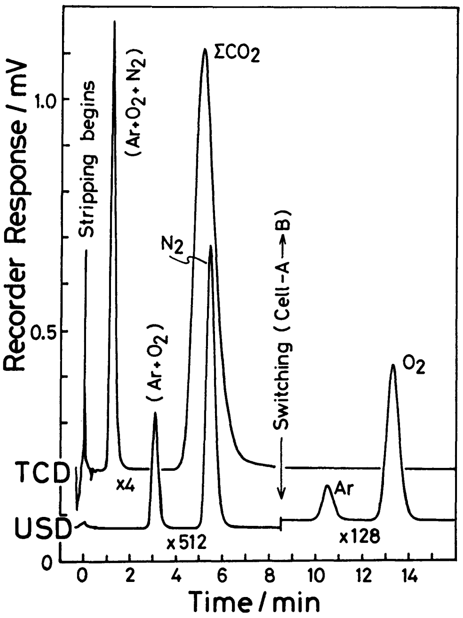

Fig. 2. Typical chromatograms of the thermal conductivity detector (TCD) and the ultrasonic detector (USD).

Typical chromatograms of both detectors are shown in Fig. 2. Retension times were 5.0, 5.4, 10.5, and 13.3 min for CO_2, N_2, Ar, and O_2, respectively. In order to calculate each peak area immediately and automatically, outputs of the detectors were connected to a computing integrator (Spectra-Physics, Autolab System IV). The relative precision of the measured values was estimated from the dispersion of shipboard analyses of a sea water sample. The standard deviations were as follows: ±0.3% for Ar and O_2, ±0.2% for N_2, and ±0.5% for CO_2.

Calibration. A calibration curve of each gas component was prepared over the proper concentration range prior to a cruise, by using a mixture of tank CO_2 and fresh air. Both gases were dried by passing through a dry ice trap before mixing. When the stripping chamber was filled with degassed sea water, a known amount of the calibration gas was injected through a gas sampling valve, and subsequently analyzed by the same procedure as used for analysis of unknown samples. Since the sensitivity of the ultrasonic detector was found not to be proportional to the amount of gas,[12] Ar, O_2, and N_2 calibrations were performed particularly in detail.

Shipboard calibration was performed every 4-5 h of operation by analyzing dried tank CO_2 or fresh air at one or two representative concentration points for each gas, in order to correct systematic shifting of the original calibration curve because of slight change in experimental conditions.

Results and Discussion

Intercalibrations with other conventional analytical methods were carried out in order to confirm the absolute accuracy of gas chromatography (GC) during routine shipboard operations. Dissolved oxygen values determined by GC were compared with those by the Carpenter-modified Winkler titration,[13] and the $\sum CO_2$ values by GC were compared with those calculated from pH and titration alkalinity.[14]

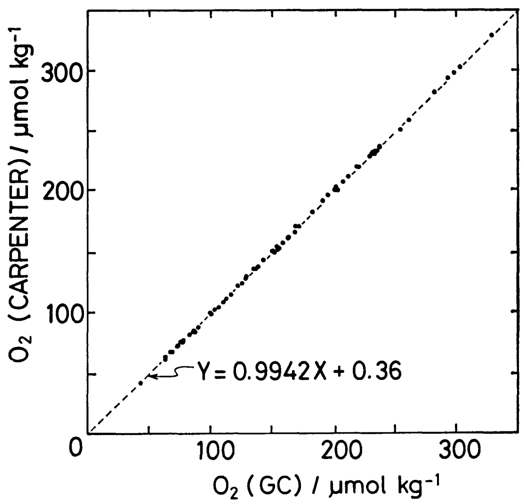

Fig. 3. Intercomparison of dissolved oxygen concentrations by the gas chromatography (GC) and the Carpenter-modified Winkler titration.
The broken line is the best fitted line by the method of least squares.

Figure 3 shows the relationship between the two sets of O_2 data obtained during the Pegasus Expedition in the Japan Sea,[15] and Vega Expedition in the Philippine Sea.[16] The estimated standard deviation of the titration method was ± 1 μmol kg^{-1}. Each set of data by GC and titration was in good agreement within analytical errors of both methods. By using the method of least squares with statistical weighting,[17] a straight line of $Y = AX + B$ was fitted to the data (74 pairs), where X and Y are the GC value and the titration value, respectively. The calculated parameters with standard deviation ($\pm\sigma$) are as follows:

$$A = 0.9942 \pm 0.0017,$$

$$B = 0.36 \pm 0.28 \ (\mu\text{mol kg}^{-1}).$$

T-tests for A and B indicate that B is not significantly different from zero, while A is slightly different from unity, when α (level of significance) is 0.05. The

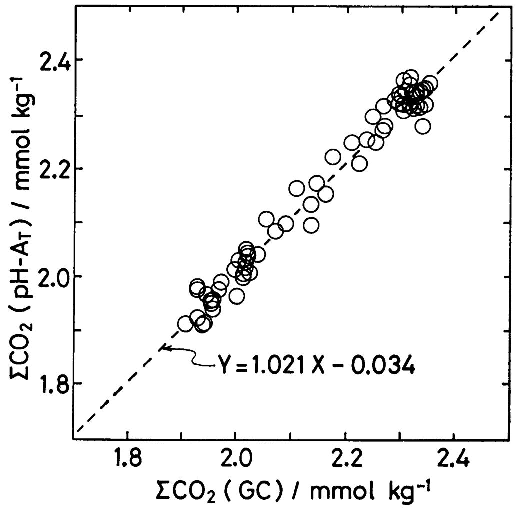

Fig. 4. Intercomparison of $\sum CO_2$ data measured by the gas chromatography (GC) and calculated from pH and titration alkalinity.
The broken line is the best fitted line by the method of least squares.

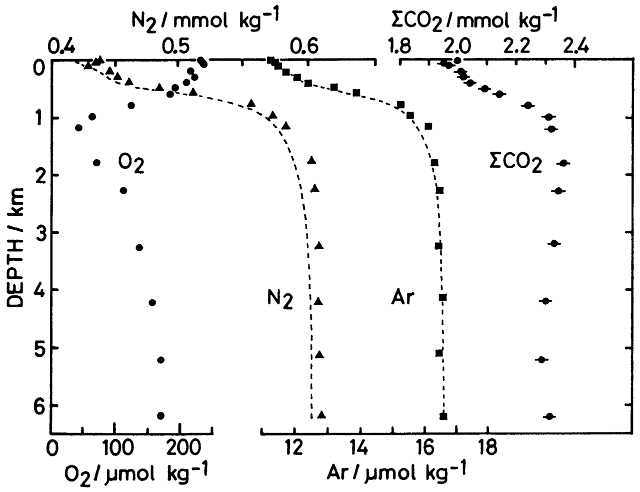

Fig. 5. Vertical profiles of O_2, N_2, Ar, and $\sum CO_2$ at Vega station 11 (29°39′N, 146°15′E).
Broken lines indicate the solubility values calculated from potential temperature and salinity at each depth.

tendency that the titration value is systematically lower than the GC value can be attributed to the loss of iodine by vaporization during the course of titration.

Figure 4 shows a comparison of $\sum CO_2$ data obtained during the Vega Expedition. The abscissa (X-axis) represents the GC value, and the ordinate (Y-axis) the value calculated by Tsubota (unpublished data) from pH and titration alkalinity measurements. The estimated standard deviation of the calculated value is $\pm 0.5\%$. The method of least squares was also applied to the sets of data (80 pairs) to give the following parameters:

$$A = 1.021 \pm 0.016,$$

$$B = -0.034 \pm 0.036 \text{ (mmol kg}^{-1}\text{)}.$$

There is a tendency that the calculated value is somewhat greater than the GC value. T-tests show, however, that A and B do not differ from unity and zero, respectively, at the level of $\alpha = 0.05$. The GC values are in good agreement with the calculated values in view of statistics.

The results of intercalibrations confirmed that the present gas chromatographic system is correctly calibrated, giving accurate and reliable O_2 and $\sum CO_2$ data on board. The accuracy of the determination of Ar and N_2 should not differ a great deal from that for O_2 and $\sum CO_2$, since all the gases were analyzed simultaneously under the same conditions.

As an example of simultaneous shipboard measurement, Fig. 5 shows vertical profiles of Ar, O_2, N_2, and $\sum CO_2$ at Vega station 11 (29°39′N, 146°15′E). The broken lines for Ar and N_2 are the saturation values calculated from the potential temperature and salinity at each depth by using the solubility equation of Weiss.[18] From surface to bottom, N_2 values are supersaturated by an average of 1.8%, Ar values being less supersaturated by an average of 0.7%. This saturation anomaly of both inert gases might reflect the effect of air injection at the ocean surface under turbulent conditions, since the N_2/Ar ratio in air bubbles is approximately twice that in sea water in equilibrium with the atmosphere.[18]

Except for the euphotic zone of the ocean surface, O_2 is only consumed by the decomposition of organic matters to produce CO_2 and nutrients. This is the reason why vertical profiles of O_2 and $\sum CO_2$ are inversely correlated with each other. By applying a vertical diffusion-advection model[19] to the deep layer (depth, 1—3 km) of station 11, the average O_2 consumption and CO_2 production rates were estimated to be 0.45 and 0.34 µmol kg⁻¹ per year, respectively, when upward advection velocity of sea water was assumed to be 5 m per year. Oceanographical considerations of the results are given elsewhere in detail.[20]

The present gas chromatographic system was used for the analysis of volcanic CO_2 gas dissolved in northern Kagoshima Bay in order to calculate the CO_2 flux from bottom fumaroles.[21] With some modifications, the system will also be applicable to analysis of dissolved gases in fresh water or polluted water samples as well as sea water.

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