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Abstract

This paper describes a simple and compact apparatus for the determination of the total dissolved inorganic carbon in sea water. It employs a closed circuit gas flow to remove carbon dioxide from an acidified sample of water. The carbon dioxide is reabsorbed in a sodium hydroxide solution in which the change in conductivity is measured. The apparatus is capable of measuring the dissolved inorganic carbon present in water within the range of 1 to 200 micrograms of carbon. The standard deviation of a measurement in this range is ± 0.5 micrograms. The cyclic rate of analysis is 15 minutes.

INTRODUCTION

In studies of marine primary production using the carbon-14 method it is essential to know the total dissolved inorganic carbon present as carbon dioxide, bicarbonate and carbonate. Errors in this quantity will result in a corresponding error in the estimated production rate. For the purposes of routine primary production measurements, the total dissolved inorganic carbon in the open ocean is usually assumed to have a value of 24.5 gC m^{-3}. Some variation occurs, and Takahashi (1970) has reported an increase from 23.4 in waters above 100 metres to 27.8 gC m^{-3} at 600 metres depth in the eastern Pacific Ocean. In the less saline waters of the Gulf of Thailand, Subba Rao (1964) has reported values between 11.2 and 27.8 gC m^{-3}.

Some previous estimates have been made by measuring pH and alkalinity, but Takahashi (1970) has shown that some of this work was in error due to the use of incorrect dissociation constants. More recent work has been done using gas chromatography as described by Weiss (1973) but this method requires an apparatus which is both complex and costly. The analyser described below uses a modification of the methods of Milburn (1960), Dal Pont (1963) and Subba Rao (1964). Carbon dioxide is removed by the acidification of the sea water sample and reabsorbed in a known volume of sodium hydroxide solution, and the change in conductivity of the latter measured.

The methods and materials for the collection and preservation samples have been reviewed by Takahashi (1970). The methods described by Stainton (1973) could be used to extend the use of this apparatus to the determination of other forms of carbon found in association with sea water.

APPARATUS

Most of the components used in the construction of the apparatus (Fig. 1) are glass, with the exception of the epoxy-resin conductivity cells, the P.T.F.E. plugs in the stopcocks and a short length of 'Tygon' brand polyethlene tubing in the peristaltic pump. 'Tygon' is preferred because of its low permeability to carbon dioxide. Glass ball joints are used where connections are necessary. The internal volume of the apparatus is reduced to a minimum, about 50 cm^3, to ensure quick recycling of the gases. This minimises analysis times.

The absorption column (Fig.1,D) consists of a glass spiral wound around the central glass delivery tube. This column has a diameter of 12 mm and a length of 60 mm. Gas bubbles are released from the bottom of the delivery tube and rise up the spiral column with entrained sodium hydroxide solution, causing circulation of the solution between the absorption column and the conductivity cell (E).

The conductivity cell consists of an epoxy-resin tube in which are embedded the platinised conductivity electrodes and a thermistor for temperature compensation over the range 15 to 30°C. This circuit and cell design is an adaption of a salinity-temperature meter and has been previously described by Dal Pont (1963). The meter (H) is powered by a dry cell battery, and is a null point instrument. The change in conductivity is read from a 'Helipot' graduated from 0 to 1000, where one unit is equal to approximately 0.2 µg of carbon.

The perstaltic pump (K) (Cole Parmer, Mod. No. 7016) is driven by a fractional H.P. electric motor with a reduction gearbox (Langtry, Mod. LG150), giving a flow rate of 1.5 cm^{3}s^{-1}.

METHODS

The apparatus is prepared for use by first filling the 7.5 cm^3 automatic zero pipette (F) with sodium hydroxide solution ($\sim$0.005N) from the reservoir (J) through stopcock V8. Then the aliquot of NaOH solution is introduced to the conductivity cell and absorption column (D,E) through V7 and V6, at the same time opening the apparatus to the atmosphere through V9 and the soda-asbestos guard tube (G). Then V6 is turned to connect the conductivity cell and the absorption column. The volume of NaOH solution is such that when the gas is flowing the solution will just overflow from the column to the cell through the upper connecting tube, giving good solution circulation. Air is used as the carrier gas, from which the carbon dioxide is removed by the procedure set out below, and the soda-asbestos guard tube (G).

The stopcocks are set to direct the gas flow through V1, V2, V3 and V9, then the pump is started. Circulation is continued until the change in conductivity has decreased to less than 0.3 units per minute. The conductivity will continue to change slowly due to diffusion of carbon dioxide into the apparatus. The NaOH solution is then discarded through V6 and V7 and a fresh aliquot of NaOH solution added to the cell. When changing the NaOH solution it is important to drain the column and cell to the same extent each time, since any excess solution remaining in the column will decrease the sensitivity.
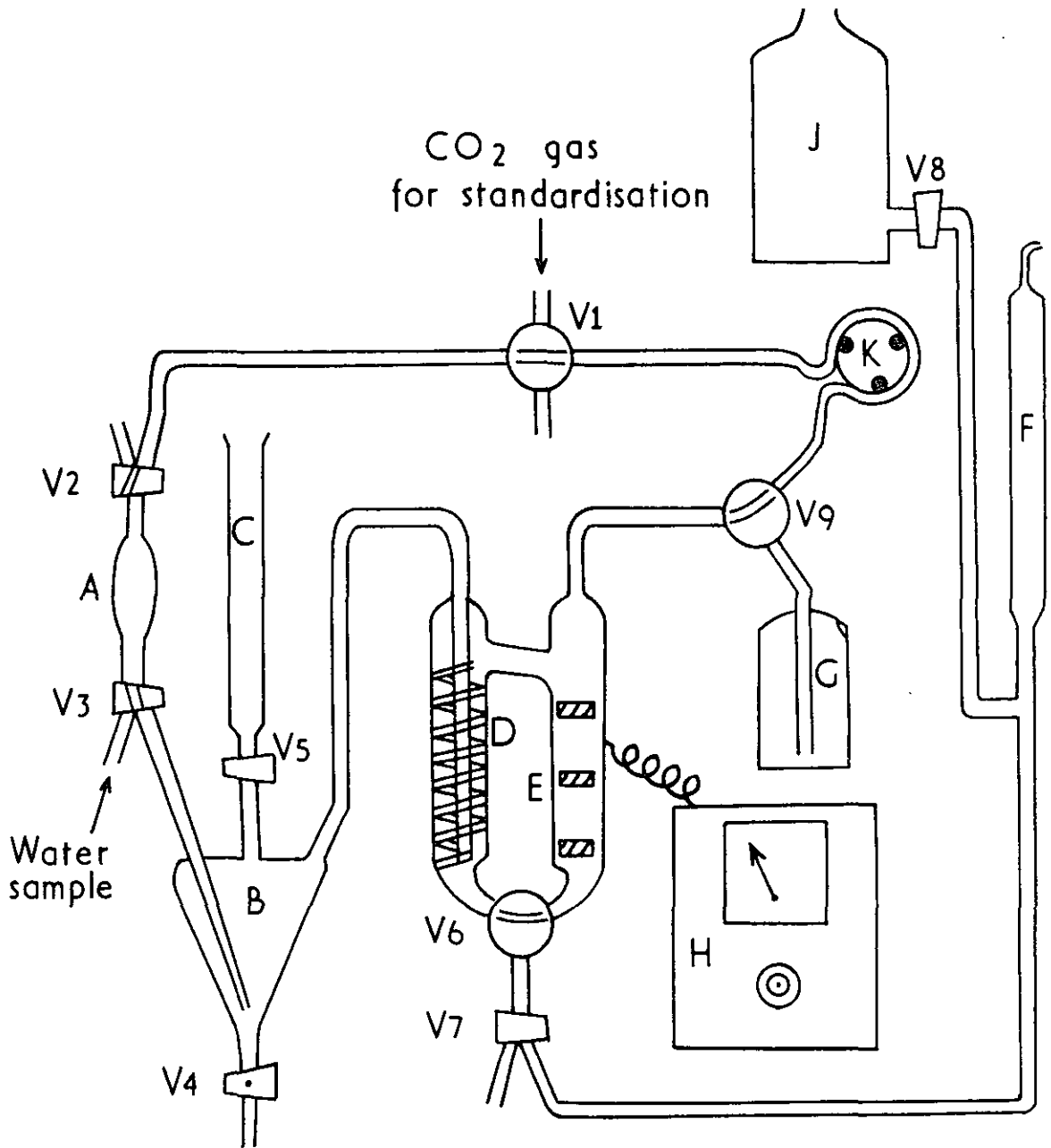
Fig. 1. Schematic diagram of analyser
   A. water sample pipette;   B.   sparging vessel;
   C. acid burette;   D. absorption column;
   E. conductivity cell;   F.   sodium hydroxide pipette;
   G. soda-asbestos guard tube;   H.   conductivity meter;
   J. sodium hydroxide reservoir;
   K. peristaltic pump;   V.   stopcocks (1-9).

With the pump stopped, one cm^3 of 70% Phosphoric acid is added to the sparging vessel (B) from the acid burette (C) through V5, then the pump restarted for one minute to measure the conductivity of the NaOH solution and to ensure that there is no large change in conductivity due to leaks. With the pump stopped the water sample is introduced through V3 and V2 to the water sampling pipette (A). The capacity of this pipette is 5 cm^3.

The pump is then restarted and the time and initial conductivity noted. The gas flow displaces the water sample from the water sampling pipette into the sparging vessel where it is acidified, the released carbon dioxide being carried to the absorption column. Since the absorption column is small, it is necessary to recirculate the gas in the apparatus for about twelve minutes until the rate of change of conductivity returns to that determined in blank measurements described below. The final conductivity reading is noted together with the time elapsed. The acidified sample in the sparging vessel is discarded through V4 in preparation for the next sample cycle.

The blank is determined by recording the change in conductivity for the same period of time as a sample, immediately after a sample has been measured, without removing the sample. It is not necessary to measure the blank value for every sample, since the blank will remain constant unless a leak has developed in the system allowing atmospheric CO_2 to enter, e.g. failure of the pump tubing. This can be checked occasionally by noting the rate of change of conductivity in the last minutes of a sample cycle.

The total dissolved inorganic carbon content of the water is calculated by subtracting the blank from the sample reading, then multiplying by the calibration factor, which is determined as described below.

CALIBRATION

The sensitivity of the instrument is determined by preparing the instrument as described before, but instead of introducing a water sample, a small (0.4 cm^3) volume of carbon dioxide gas is introduced using the calibration valve, V1. The volume of the bore of this stopcock plug is measured before assembling the instrument by weighing the amount of mercury needed to fill it.

With the gas flow stopped the stopcock V1 is turned across the normal direction of flow and flushed with pure carbon dioxide gas. The stopcock is now returned to its normal position to release the carbon dioxide contained in the bore of the stopcock to the gas stream. The measurement then proceeds as before, with the change in conductivity being noted and the blank subtracted from this. The atmospheric pressure and temperature are measured so that the mass of carbon dioxide introduced can be calculated.

Carbon dioxide is used in preference to carbonate solutions because of the greater certainty of its purity and the difficulty of preparing standard carbonate solutions for use in the field. In the laboratory, carbonate solutions could be used as standards in this apparatus if desired, in the same manner as a water sample, provided that the purity of the water and the carbonate has been determined.

The sensitivity of this instrument alters slowly. A decrease of 3% in the first seven months was found, but less than 1% change occurred in the following eight months, indicating that frequent calibrations are not necessary.

The 7.5 cm^3 sodium hydroxide pipette is not calibrated, nor is the normality of the sodium hydroxide solution checked, since it is the reproduceability that is important. The volume of the 5 cm^3 water sampling pipette is measured by weighing the quantity of water delivered from the pipette.

SENSITIVITY AND ACCURACY

Using the methods above, ten blanks were measured for 16 minutes and the mean conductivity change found to be 3.3 conductivity units with a standard deviation of ± 0.35 units.

Ten replicates of an estuarine water sample, collected at Cronulla were measured and the mean change found to be 501.9 units with a standard deviation of ± 1.2 units.

Twelve carbon dioxide standards were measured. When the 0.4 cm^3 volume was corrected for temperature and pressure the mean mass was equivalent to 192.6 μg of carbon. These yielded a mean conductivity change after subtracting the blank, of 847.4 units, with a standard deviation of 1.0 unit. The instrument thus has a sensitivity of 4.40 units per microgram of carbon.

Using the methods of Moroney (1958) the standard deviation for a single water sample measurement was calculated to be 0.5 μgC. Since most of this error is due to the measurement of the change in conductivity of the sample and the blank, this error will not alter for other values within the 200 μgC range of the instrument. The error which the calibration factor contributes to the sample standard deviation does not include the systematic errors due to the calibration of the water sample pipette, or the volume of carbon dioxide used for calibration. These errors are estimated to be less than 0.2% since they are based on weighing techniques.

If the detection limit is defined as the concentration which can be detected with a 95% certainty, then this is equal to 1.96 times the standard deviation of a measurement near the zero level. The limit of detection for this instrument is 1.0 μgC.

Since the volume of the water sampling pipette is 4.99 cm^3, the calibration factor for this instrument is 0.0455 gC m^{-3}unit^{-1}.

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