An Automated Method for the Determination of Total Inorganic Carbon in Fresh Water

L.R. GRAVELÈT-BLONDIN, H.R. VAN VLIET and B.W.H. SCHOONES
Hydrological Research Institute, Department of Water Affairs, Private Bag X313, Pretoria 0001

Abstract

A simple automated method for the measurement of total inorganic carbon (TIC) in fresh water was developed. The sample stream, segmented with CO_2 free air was acidified and heated to release CO_2 from the dissolved inorganic carbon. A gas permeable silicon membrane was utilised to introduce the released CO_2 into a weakly buffered thymol blue indicator solution. The colour change, measured at 590 nm was proportional to the inorganic carbon content of the water. The accuracy, reproducibility and recovery of the method were measured. TIC could be reliably measured in the range 50 – 500 mg/ℓ HCO_3^- (approximately 10 – 100 mg/ℓ C).

Introduction

All surface waters contain inorganic and organic carbon, the ratio depending on the type of water. The relationship between the two is defined as

Total Carbon (TC) = Total Inorganic Carbon (TIC) + Total Organic Carbon (TOC)

In almost all fresh waters the concentration of inorganic carbon far exceeds that of organic carbon. Depending on the information required, one, two or all three forms of carbon may be measured. TIC in water consists of the anions HCO_3^- and $CO_3^=$ together with dissolved CO_2. These fractions are a potential nutrient source (Goulden and Brooksbank, 1975) and also add to the buffering capacity of the water.

Methods for measuring TIC normally rely on the use of acid and heat to release the CO_2 from the TIC which is quantitatively measured using a number of methods, e.g. infrared analyses (Goulden, 1976; Rider, 1976; Goulden and Brooksbank, 1975), titration (Merz, 1977) and colorimetric determination (Technicon, 1976).

The laboratory of the Hydrological Research Institute is included in a water quality surveillance programme which necessitates the analyses of a large number of samples. Automation is the keynote. Although the methods outlined above have been fully or partially automated, the majority require new expensive apparatus. Since Technicon AutoAnalyzer apparatus is used in our laboratory for water analysis, it was easily adapted to obtain a simple automated TIC method.

The prime reason for developing this method was to secure optimal conditions for the release of the CO_2 from the inorganic carbon, transfer of the CO_2 between two liquid phazes and the subsequent measurement thereof.

Experimental

Apparatus

Technicon AutoAnalyzer comprising sampler IV, proportioning pump AA II, manifold with a 150 mm dialyser (60 μm pore size membrane), heating bath (37°C) colorimeter equipped with 500 nm filters and 15 mm industrial flow cells and a recorder.

Reagents

All reagents were prepared from AR grade chemicals and deionised water.

(a) Sulphuric acid: 0,05 mol/ℓ wetted with 1 mℓ Brij-35 working solution per ℓ H_2SO_4 (Solution A).

(b) Buffer solution: pH 9,6. Add 500 mℓ of boric acid solution (6,2 g/ℓ H_3BO_3 in water) to 370 mℓ of a sodium hydroxide solution (4,0 g/ℓ NaOH in water). If necessary adjust the pH to 9,6 with NaOH or HCl (Solution B).

(c) Thymol Blue Indicator: Dissolve 1 g of thymol blue in 43 mℓ of 0,05 mol/ℓ NaOH and dilute to 1 ℓ with water. Stir mixture for 30 min and filter if necessary (Solution C).

(d) Dilute Brij-35 solution: Dilute 30 mℓ commercial concentrate with 1 ℓ deionised water (Solution D).

(e) Working buffered acid base indicator: Add together the following and make up to 100 mℓ with water; 5 mℓ solution B, plus 2 mℓ solution C and 2 mℓ solution D (Solution F).

(f) Stock standard solution: Dissolve 1,376 8 g $NaHCO_3$ (dried for 1 h at 105°C) in deionised water and make up to 1 ℓ with deionised water. This gives a solution containing 1 000 mg/ℓ HCO_3^- (c. 197 mg/ℓ C). Dilute as necessary for standards.

Both the wash water and acid base indicator are kept in bottles equipped with CO_2 traps.

Method

The sample was segmented, acidified and heated to 37°C, then passed under the dialysis membrane to ensure that a constant fraction of the CO_2 diffused through the membrane into the

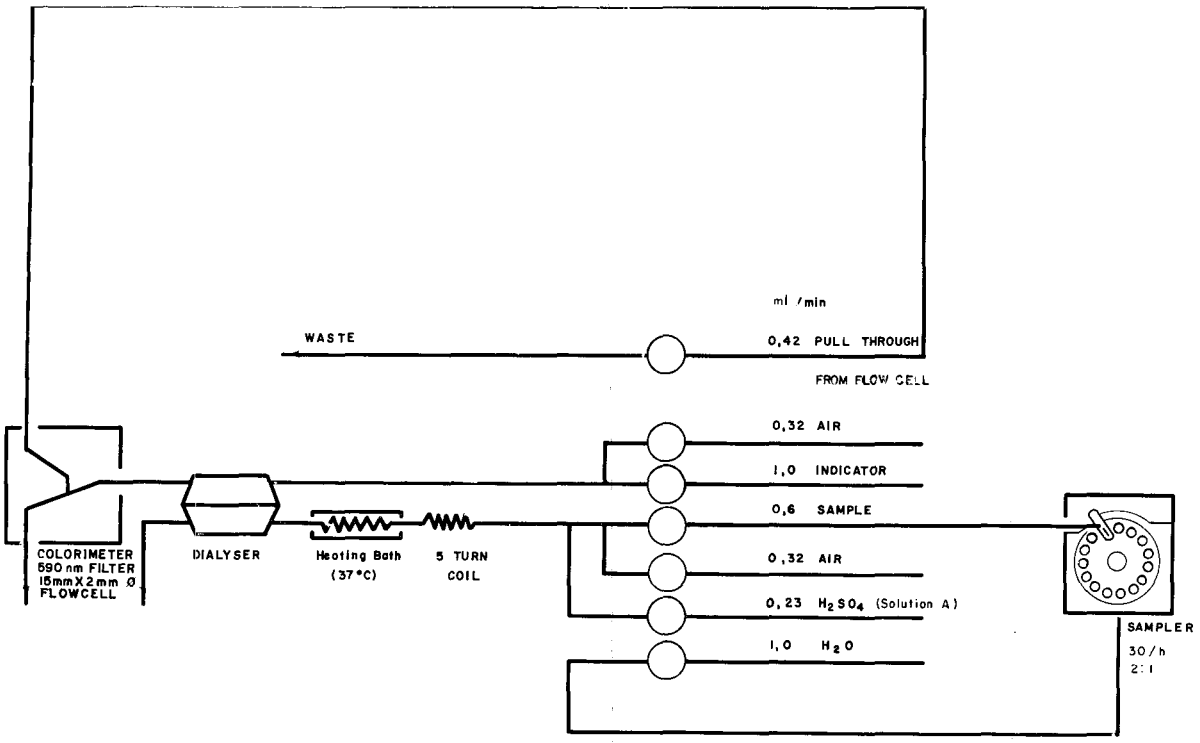

Figure 1
TIC flow diagram

buffered indicator stream (Solution F). The flow diagram is shown in Fig. 1. The air used for segmentation was scrubbed to remove CO_2 and other acidic gasses by passing it through a solution of 1,25 mol/ℓ NaOH.

Results and Discussion

The linearity of the method is satisfactory in the range 50 to 500 mg/ℓ HCO_3^- (Fig. 2). The buffered indicator solution concentrations were selected to obtain optimum linearity and sensitivity. The smaller the volume of buffer used, the higher the sensitivity but then linearity was adversely affected, thus a suitable compromise had to be found.

The reproducibility and recovery of the method were determined. For reproducibility measurements two water samples were used. The results, given in Table 1, show that for each measurement, the coefficient of variation is less than 1,1%.

For recovery measurements, two water samples of 10 mℓ each were each spiked with 0,5; 1,0 and 1,5 mℓ of 1 g/ℓ HCO_3^- solution. The results, given in Table 2 show that the recoveries averaged between 98% and 102%. Standards were prepared in a 10 g/ℓ NaCl solution and run against standards prepared in deionised water to ascertain whether a high salt concentration had any adverse effect on the gas permeability of the membrane. The results showed that a salt concentration of as much as 10 g/ℓ had no effect.

The effect of heat on the conversion of TIC to CO_2 was investigated by using temperatures of 20°C, 30°C, 40°C and 50°C. The results shown in Fig. 3, indicate that the optimum linearity and sensitivity is achieved in the temperature range 40°C to 50°C. The membrane was not subjected to temperatures greater than 50°C, as according to the manufacturers this is the maximum operating temperature.

Technicon (1972) suggested the use of phenolphthalein as indicator but thymol blue was found to give better sensitivity. Triton X-100 as wetting agent was replaced by Brij-35 since the former wetting agent damaged the membrane.

Conclusion

The method can be successfully used in the range 50 – 500 mg/ℓ HCO_3^- for TIC measurement. Successful methodology was developed for the release of CO_2 from inorganic carbon, transfer of the CO_2 between two liquid phases and subsequent measurement thereof.

Acknowledgement

The authors wish to thank Mr P.L. Kempster for his help and advice in preparing the manuscript. This paper is published with the permission of the Department of Water Affairs.

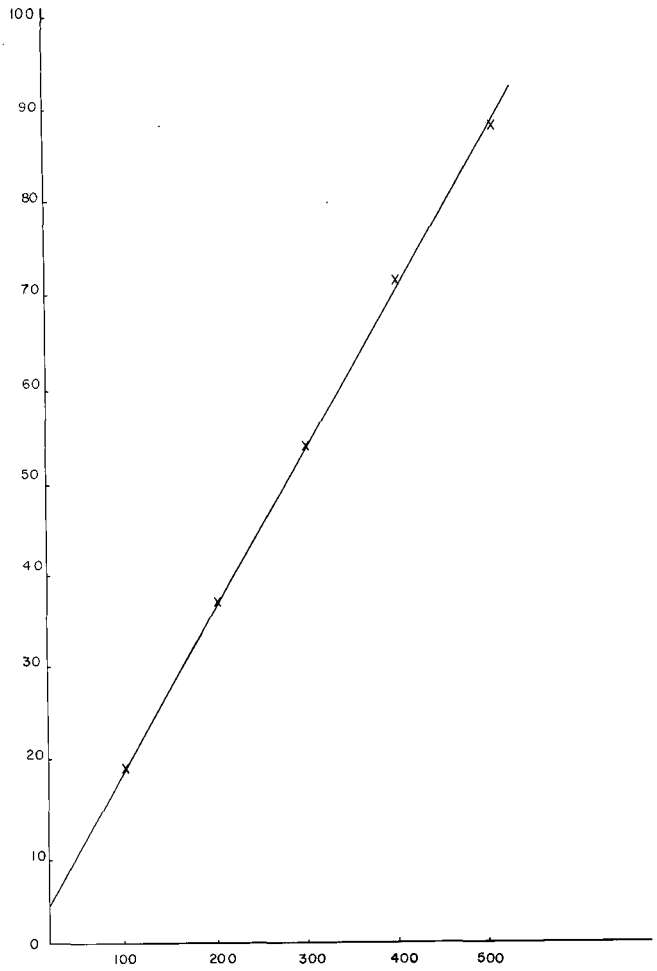

Figure 2
TIC calibration curve

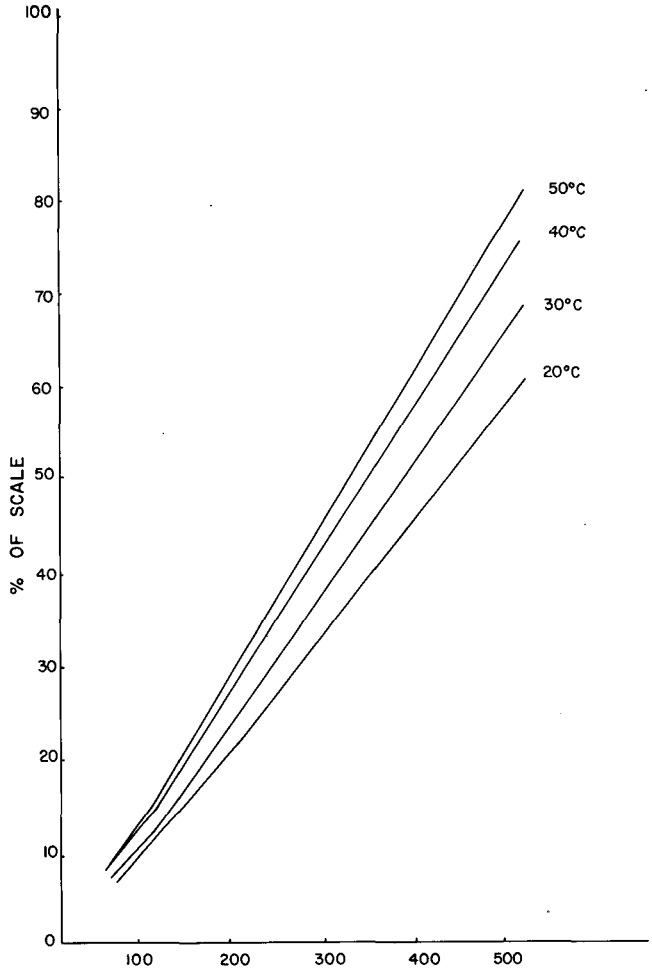

Figure 3
The effect of temperature on the release of CO_2 from total inorganic carbon

TABLE 1
REPRODUCIBILITY OF THE TOTAL INORGANIC CARBON METHOD; AVERAGE OF TEN ANALYSES

Average value (mg/ℓ)	Coefficient of variation (%)
98,4	1,09
312,7	0,59

TABLE 2
RECOVERY OF TOTAL INORGANIC CARBON USING TWO WATER SAMPLES; AVERAGE OF TWO ANALYSES

Concentration (mg HCO_3^-/ℓ)				
Original	Added	Found		Recovery (%)
102	43	143		98,6
102	81	180		98,4
102	117	215		98,2
			Average	98,4
310	33	343		100,3
310	61	370		99,5
310	90	417		104,3
			Average	101,3

References

GOULDEN, P.D. (1976) Automated determination of carbon in natural water. *Wat. Res.* **10** 487–490.

GOULDEN, P.D. and BROOKSBANK, P. (1975) Automated determinations of dissolved organic carbon in lake water. *Analyt. Chem.* **47** (12) 1943–1947.

MERZ, W. (1977) Determination of total organic carbon in potable water, sewage, industrial effluents and boiler feed water. *Internat. Lab. Jan/Feb 1977*, ppf 49–55.

RIDER, M.D. (1976) Monitoring organic pollutants continuously by total carbon analyser (TCA). *Industr. Wat. Eng.* (Minneapolis) **12** (6) 10–13.

TECHNICON INDUSTRIAL METHOD NO. 439–76 WM, (1976) Total dissolved carbon in plant effluents.