An Automated Method for the Determination of Dissolved Organic Carbon in Fresh Water

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Abstract

A simple automated method for the measurement of dissolved organic carbon (DOC) in fresh water was developed. The sample stream, segmented with CO_2 free air, was acidified, heated and sparged with nitrogen to remove the inorganic carbon. The re-sampled stream, again segmented with CO_2 free air was mixed with a solution of potassium persulphate and mercury (II) nitrate and then subjected to ultraviolet radiation. By this process the DOC was oxidised to CO_2 and then introduced into a weakly buffered thymol blue indicator solution at pH 9,6 using a gas permeable silicon membrane. The colour change, measured at 590 nm, was proportional to the amount of DOC in the water sample. The accuracy, reproducibility and recovery of the method were measured. DOC could be reliably measured in the range 0,5 — 20 mg/ℓ C.

Introduction

The value of measuring total organic carbon (TOC) was recognised as early as 1931 (Bortlijz, 1976). Since then numerous reasons for measuring the TOC or dissolved organic carbon (DOC) content of a water sample have been given in the literature and include firstly, that the TOC value can aid in the assessment of pollution and biological degradation in surface waters, effluents and water treatment plants and secondly, the adverse effects of a high concentration of organic compounds, via oxygen depletion, on the aquatic environment (Jirka and Carter, 1976; Bortlijz, 1976; Collins and Williams, 1977; Merz, 1977; Rider, 1975/76; Goulden and Brooksbank, 1975 and Kehoe, 1977). The relationship between TOC and DOC is: TOC = DOC + SOC (suspended organic carbon).

Jirka and Carter (1976) pointed out that DOC provided more information than TOC as it could be measured more precisely and was more indicative of changes in the organic content of water over a long time period.

The traditional methods of obtaining a measure of the organic content of water such as Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD) have numerous drawbacks. BOD determination is time consuming and is neither reproducible nor sensitive enough to detect small changes. COD determination requires expensive and toxic reagents, includes inorganic compounds and does not adequately measure contaminants stable and resistant to biological degradation (Jirka and Carter, 1976; Merz, 1977; Kehoe, 1977; Maier and Swain, 1978). Some of the above problems are overcome by a TOC or DOC measurement.

A number of methods and instruments have been developed to measure TOC and DOC, the majority of which have been listed by Briggs, Schofield and Gorton (1976).

Two methods are used to measure organic carbon:

(a)   Oxidation of the organic material after first removing the inorganic carbon.

(b)   Measurement of both the total carbon (TC) and total inorganic carbon (TIC) and calculation of the organic carbon by subtraction.

The advantages and disadvantages of both methods are widely discussed in the literature.

The organic compounds are oxidised to CO_2 using either high temperature combustion (900°C — 1 000°C) or physical/chemical methods. The CO_2 is subsequently determined using infrared detection, titration, colorimetric measurement or electrical conductivity (Merz, 1976; Collins and Williams, 1977; Goulden and Brooksbank, 1975; Bortlijz, 1977; Dillido, 1976; Jirka and Carter, 1976; and Van Steenderen, 1975). The advantages of wet chemical oxidation over high temperature combustion are listed by Dillido (1976). The wet photochemical oxidation is due to a secondary process of free radical type (Semenov *et al.*, 1977).

Although first stripping off the total inorganic carbon can lead to loss of the volatile organic compounds this is serious only if the following is applicable to the volatiles: (i) relatively high concentrations; (ii) relatively high vapour pressures; and (iii) low solubility in water (Kehoe, 1977). The problems in measuring the volatiles are dealt with by Briggs *et al.* (1976) and Bortlijz (1976).

Pollution of South Africa's water supplies is increasing and a simple automated method capable of analysing a large number of samples was developed to aid in the assessment of pollution. Although some of the methods outlined above have been partially or fully automated, the majority required new expensive instrumentation. Since Technicon AutoAnalyzer apparatus is used in our laboratory for water analysis, this apparatus and the method of Dillido (1976), Jirka and Carter (1976) and Technicon (1976) was chosen as a basis. Modifications were necessary as both the oxidation process and CO_2 detection sensitivity were found to be unsatisfactory. Chloride interference was almost completely eliminated and also the need for a high H_2 flow.

This paper describes a simple automated method to determine organic carbon, which requires little in the way of extra apparatus.

Experimental

Apparatus

Technicon AutoAnalyzer comprising Sampler IV, proportioning pump AA II, manifold and colorimeter with 590 nm filters and 15 mm industrial flow cells. Included in the manifold are:

(a) 56°C heating coil

(b) Modified Technicon A2 fitting for sparging

(c) 26 turn; 23,5 mm diameter quartz coil of 2,4 mm i.d. housed in a fume cupboard

(d) 254 nm ultraviolet light. PCQ9G — 1 Immersion Lamp supplied by ULTRA-VIOLET PRODUCTS, Inc. California.

(e) 150 mm dialyser with a gas permeable silicon membrane (pore size 60 μm).

Reagents

(a) Sulphuric acid: 2,5 mol/ℓ (Solution A).

(b) Buffer solution: pH 9,6. Add 500 mℓ of boric acid (6,2 g/ℓ H_3BO_3 in water) to 370 mℓ of 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 indicator in 43 mℓ of 0,05 mol/ℓ NaOH and dilute to 1 ℓ with deionised water (Solution C).

(d) Brij-35 commercial concentrate diluted to 30 mℓ/ℓ with deionised water (Solution D).

(e) Working buffered acid base indicator: Add together the following and make up to 500 mℓ with deionised water: 6 mℓ solution B, 10 mℓ solution C and 20 mℓ solution D (Solution E).

(f) Oxidant mixture: Add together the following and make up to 100 mℓ with 1 mol/ℓ H_2SO_4:4 g $K_2S_2O_8$ and 5 g $Hg(NO_3)_2$ (Solution F).

(g) Wetting agent. Add 10 mℓ solution C to 10 mℓ 0,5 mol/ℓ H_2SO_4 and make up to 100 mℓ with Solution D.

(h) Standards: Stock solution.

Dissolve 2,125 g of potassium biphthalate ($C_8H_5O_5K$), (dried at 105°C) in deionised water and make up to 1 ℓ. This solution contains 1 000 mg/ℓ C. Dilute as necessary for standards. Both the acid base indicator and wash water are kept in bottles equipped with CO_2 traps.

Method

Erhardt (1969) first used ultraviolet light for photochemical oxidation of organic carbon and the present method is based upon this principle.

To remove the inorganic carbon, the sample was segmented, acidified, heated to 56°C and sparged with N_2 (350 mℓ/min). The oxidant mixture was then added to the resampled, segmented stream before it passed through the quartz
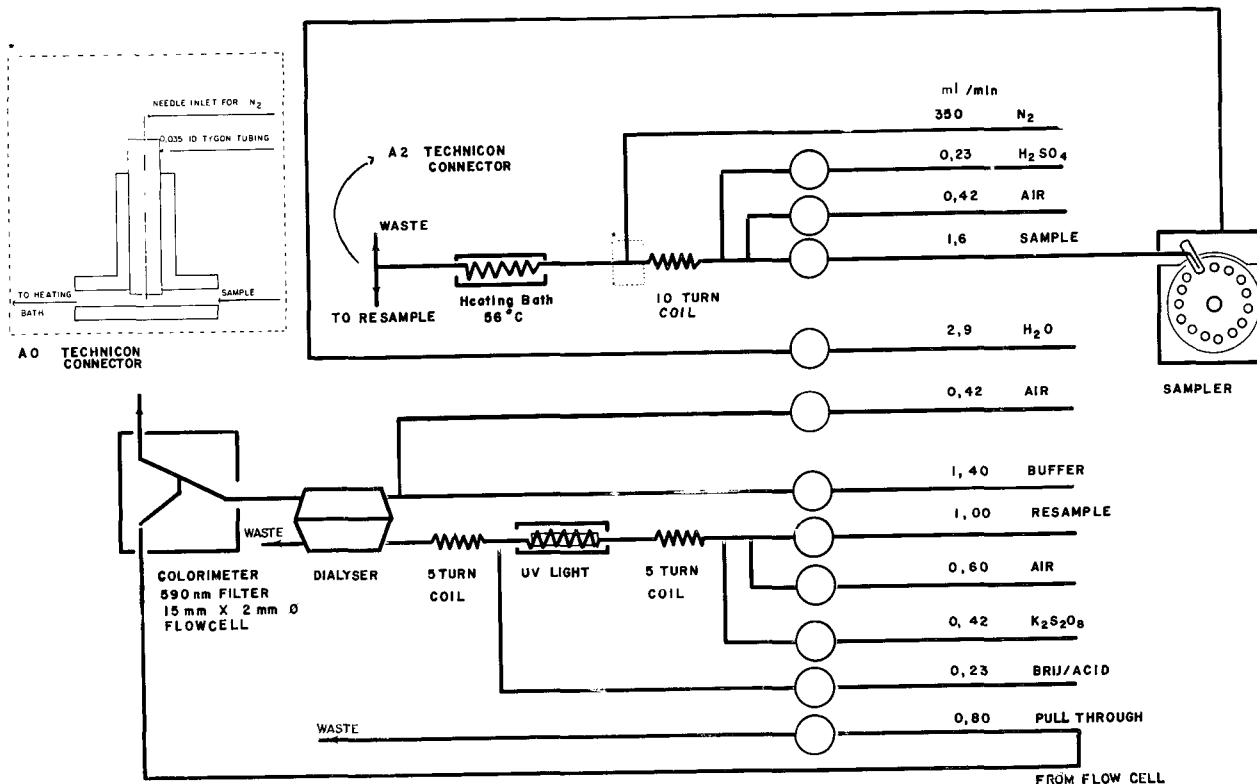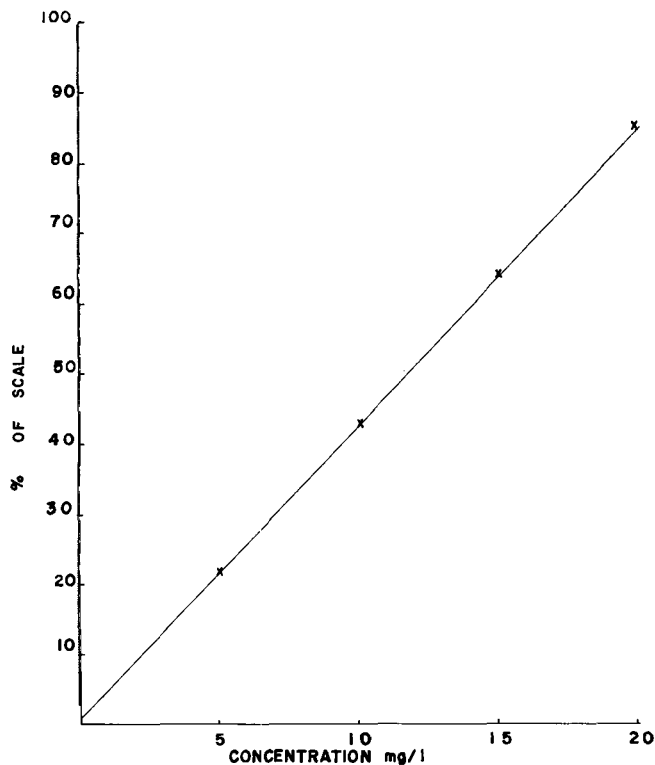

Figure 1
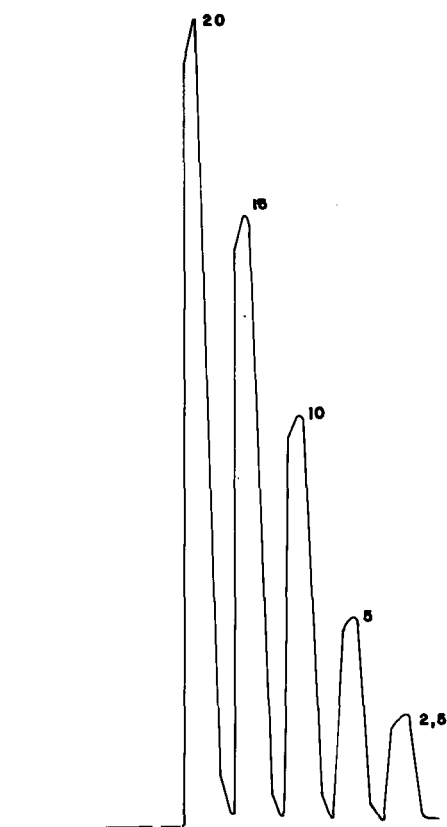*DOC Flow Diagram*

Figure 2
DOC Calibration Graph

Figure 3
Recorder tracing of standards used for DOC calibration

coil and was irradiated by the UV light. After addition of the Brij wetting agent the sample stream passed through the dialyser. A constant fraction of the CO_2 diffused through the membrane into the buffered indicator stream. 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 upper limit of the method was chosen as 20 mg/ℓ C, since according to Kehoe (1977) the analyses of 529 lake water samples in 1934 for TOC gave results between 1,2 and 28,6 mg/ℓ C. Kehoe (1977) actually suggested that the range should be 1 — 5 mg/ℓ C whilst Bortlijz (1976) suggested an upper limit of 10 mg/ℓ C. This was found to be too low for our purpose.

The linearity of the method is excellent in the range 0,1 to 20 mg/ℓ C. According to Dillido (1976) this method should give a linear response to within 1% of the theoretical least squared line fit in the range 10 — 1 000 mg/ℓ C. The present method gives a linear response to within 0,001%. In comparison, the typical combustion:IR detection method exhibits 3% or more non-linearity in the range 10 — 1 000 mg/ℓ C. Figures 2 and 3 show the linear calibration graph and an example of the strip chart tracing used to plot the graph.

The concentration of the working buffered indicator solution was determined as outlined elsewhere (Gravelét-Blondin, van Vliet and Schoones, 1980).

Both the reproducibility and recovery of the method were measured. For the reproducibility measurements two standard solutions and one water sample were used. The results, given in Table 1, show that for the standards, the coefficients of variation are less than 1% while for the water sample it is slightly above 1%.

TABLE 1
REPRODUCIBILITY OF THE PRESENT DOC METHOD USING TWO STANDARD SOLUTIONS AND ONE RAW WATER SAMPLE

	Average	Coefficient of Variation (%)
Standard solution 15 mg/ℓ C	15,08	0,4
Standard solution 10 mg/ℓ C	9,88	0,7
Raw water sample	3,70	1,2

number of analyses = 10

In recovery tests two water samples of 10 mℓ were each spiked with 1 mℓ of a 100 mg/mℓ C solution ($C_8H_5O_5K$) and with 1 mℓ of a 50 mg/ℓ C solution. In addition, two other water samples of 10 mℓ were each spiked with 1 mℓ of a 25 mg/mℓ C solution. The results, given in Table 2 show that the recoveries ranged between 104,8% and 99,9% with an average value of 103,1%.

The following organic compounds were prepared as standard solutions (15 mg/ℓ C): rhamanose (L+) $C_6H_{12}O_5H_2O$; nicotinic acid $C_6H_5NO_2$; hexamethylenetetramine $C_6H_{12}N_4$; disodium ethylene dinitrilotetra-acetate $Na_2C_{10}H_{14}N_2O_8.2H_2O$; urea H_2NCONH_2; vanillin $C_8H_8O_3$ and oxalic acid $C_2H_2O_4.2H_2O$. These were analysed to measure the oxidation efficiency of the present method. The results, listed in Table 3, show the oxidation efficiency to be very good, ranging between 90,9% and 100,8%, with the average value of 97,8%. This is an improvement on both the silver catalysed $K_2Cr_2O_7$ (89% effective), and the high temperature combustion process (95% effective) (Bortlijz, 1976). Table 4 lists the results of similar measurements that have been reported in the literature. These results show that the present method compares favourably with existing methods.

TABLE 3
OXIDATION EFFICIENCY OF THE PRESENT METHOD USING SEVEN ORGANIC COMPOUNDS OF 15 mg/ℓ EACH. AVERAGE OF TWO ANALYSES

Compound	Concentration found (mg/ℓ)	% Oxidation efficiency
1. Rhamanose (L+) $C_6H_{12}O_5.H_2O$	14,9	99,3%
2. Nicotinic acid $C_6H_5NO_2$	14,9	99,5%
3. Hexamethylenetetramine $C_6H_{12}N_4$	13,6	90,9%
4. Disodium ethylene dinitrilo tetra-acetate $Na_2C_{10}H_{14}H_2O_8.2H_2O$	15,1	100,8%
5. Urea H_2NCONH_2	15,0	100,0%
6. Vanillin $C_8H_8O_3$	14,3	95,3%
7. Oxalic acid $C_2H_2O_4.2H_2O$	14,8	99,8%
Average	14,7	97,8%

TABLE 4
OXIDATION EFFICIENCY IN PER CENT OF PRESENT METHOD COMPARED TO PUBLISHED RESULTS

DIFFERENT METHODS

Compound	A	B	C	D	E	F	G
1. Rhamanose $C_6H_{12}O_5.H_2O$	99,3						90
2. Nicotinic acid $C_6H_5NO_2$	99,5				106		102
3. Hexamethylene tetramine $C_6H_{12}N_4$	90,9		92				
4. Disodium ethylene dinitrilotetra-acetate $Na_2C_{10}H_{14}N_2.O_8 2H_2O$	100,9	108			108	98	100
5. Urea N_2NCONH_2	99,9	98,6		99,8		101	100
6. Vanillin $C_8H_8O_3$	95,3						93
7. Oxalic acid $C_2H_2O_4.2H_2O$	98,8		97,5		104	101	

A. Present method.
B. Bortlijz, (1976)
   High temperature (900°) combustion.
C. Bortlijz, (1976)
   Silver catalysed $K_2Cr_2O_7$ oxidation (165°C).
D. Kehoe, (1977)
   High temperature combustion.
E. Jirka and Carter, (1976)
   uv + $K_2S_2O_8$ oxidation.
F. Collins and Williams, (1976)
   uv + $K_2S_2O_8$ oxidation.
G. Kabot and Dillido, (1976)
   uv + $K_2S_2O_8$ oxidation.

Contrary to the findings of Dillido (1976), chlorine formed by the oxidation of chloride under ultraviolet radiation was found to interfere. Figure 4 shows the interference caused by increasing chloride concentration. This problem was solved by complexing the Cl⁻ with Hg^{2+} before the sample stream entered the ultraviolet light/quartz coil. Figure 5 shows the suppressive effect of 0,15 mol/ℓ $Hg(NO_3)_2$ on chloride interference. Mercury (II) has the added advantage in that it has a photocatalytic effect (Semenov et al., 1977).

Table 5 gives the results of the effect of the presence of inorganic carbon using the present method and shows that a value of 1 000 mg/ℓ HCO_3^- (i.e. 197 mg/ℓ C) produce a value of only 0,46 mg/ℓ organic carbon; a stripping efficiency of 99,8%.

It was found that the base line was far more stable if the oxidant solution was made up 12 h before running the channel. The system must be carefully checked for leaks as any unwanted CO_2 causes serious problems. The method is run at 20 samples per h at a 1:1 wash ratio (but has since been changed to run at 30 samples per h with a small increase in carry over effects).
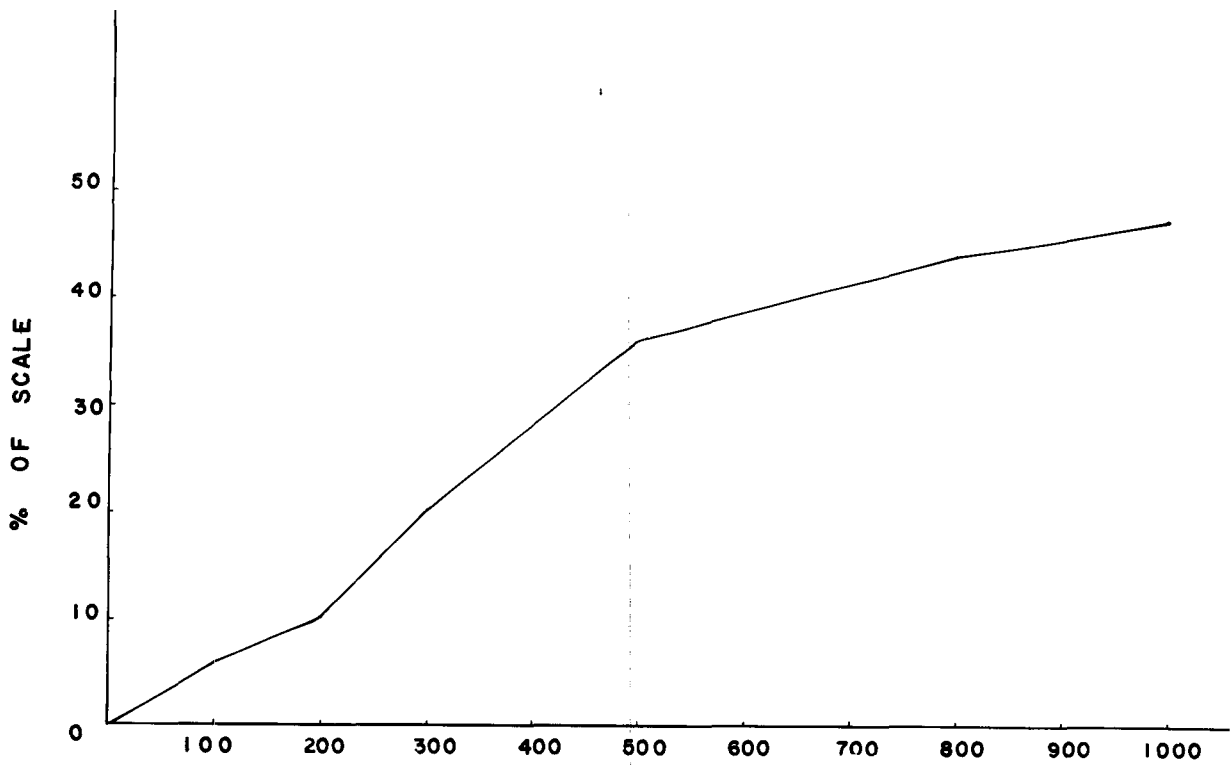
Figure 4
*The interference caused by increasing chloride concentrations on the
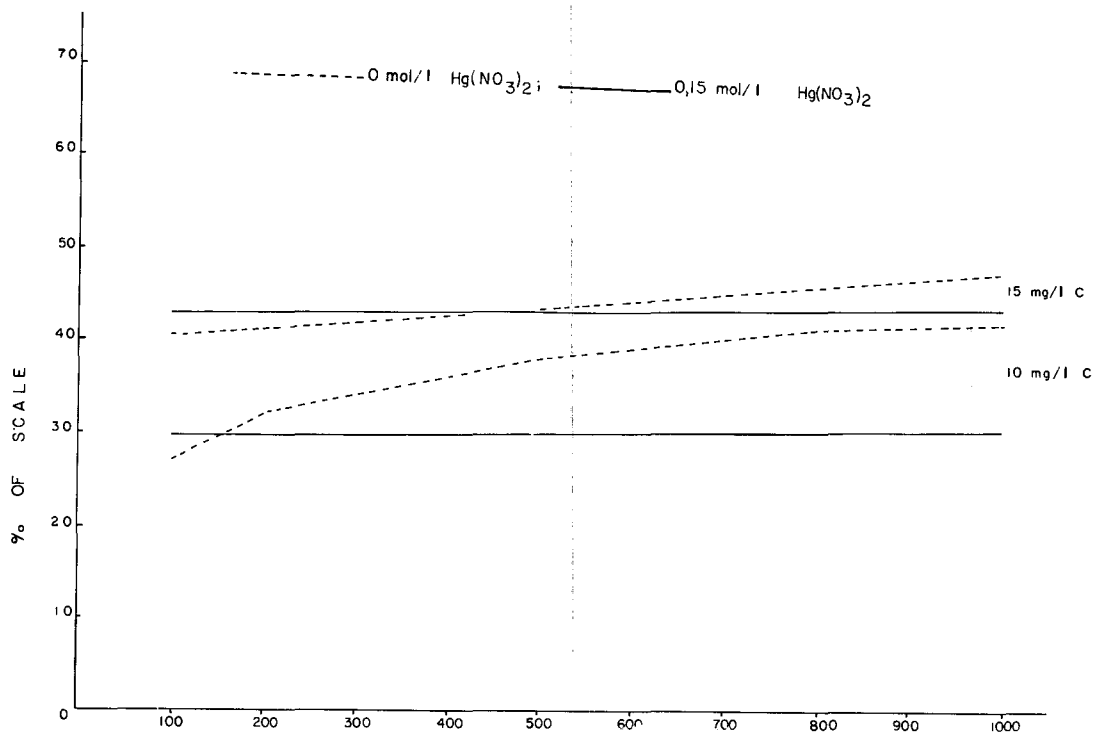measurement of DOC*

Figure 5
*The suppression of the chloride interference using Hg(NO₃)₂ on DOC
measurement*

TABLE 5
THE INTERFERENCE CAUSED BY INCREASING CONCENTRATIONS OF INORGANIC CARBON (AS HCO₃⁻) ON DISSOLVED ORGANIC CARBON (DOC). RESULTS IN mg/ℓ

HCO₃⁻	DOC
150	0,19
200	0,26
400	0,32
600	0,41
800	0,43
1000	0,46

Conclusion

This method is ideally suited for the measurement of DOC in fresh water. It is accurate, fast, easy to operate and the reagents are inexpensive. In contrast to the high temperature combination/IR method which requires special instrumentation, the present method can be easily built up on an existing AutoAnalyzer system.

Acknowledgements

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