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A Simple Assembly for Carbon Determination in Water

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The classical assembly for carbon and hydrogen analysis in organic compounds was modified for the determination of carbon in water samples. Numerous analyses of known solutions and of waste and surface waters containing 5 mg—10 g carbon/l were performed. The accuracy and reproducibility of results were satisfactory. The range of applicability is limited by the sensitivity of the gravimetric determination on one side and on the other by the sample volume accessible.

INTRODUCTION

A parameter widely used to indicate the presence of organic impurities in water is the oxygen demand for oxidation of organic compounds by microorganisms *i. e.* the Biological Oxygen Demand (BOD). A 70—90% oxidation takes place after incubation during five days as compared with a period of twenty days, owing to the differences in the oxidation rates at which various classes of compounds are oxidized by microorganisms.

The oxidation time with chemical oxidizing agents varies from one procedure for Chemical Oxygen Demand (COD) to another, but it still takes 2—3 hours on the average. Further shortcomings are the fact that the results obtained can be compared only if all working conditions are strictly identical¹, and the circumstance that a number of classes of compounds remain completely or partially unaffected^{2,3}. Montgomery and Thom⁴ are not the only authors underlining that a complete oxidation of organic compounds dissolved and suspended in water can be achieved only by combustion and oxidation in vapour phase. All relevant methods for the measurement of organic carbon in water published so far involve the combustion of organics to carbon dioxide which is swept through an infrared cell for measurement⁵ or reduced catalytically to methane and measured using flame ionisation detector⁶⁻⁹.

If for one reason or another the needed instrumentation is not available, a simple apparatus can be easily constructed to serve the purpose. The classical assembly used for carbon and hydrogen microdetermination was modified to satisfy the following essentially different propositions:

- continuous addition of the organics present in diluted aqueous solution;
- elimination of water prior to the measurement of carbon dioxide.

EXPERIMENTAL

Apparatus

The complete assembly shown in Fig. 1. includes: a system for oxygen purification (1), a burette for sample introduction (4), a combustion tube (5), a water condensation trap (6), an U-shaped tube with anhydrous (7), a tube with manganese dioxide for the absorption of nitrogen oxides (9) and the carbon dioxide absorption tube containing ascarite (10). For oxygen purification serves a tube with cupric oxide kept at 800°C. The combustion tube is placed in vertical position and heated to 700°C for complete oxidation of the sample on a copper oxide filling. Silver wool plugs are inserted for the retention of halogenides and sulphur oxides. A burette for sample introduction is attached to the sample inlet opening of the combustion tube with a capillary ending 10 cm above the copper oxide filling. The exit beak of the

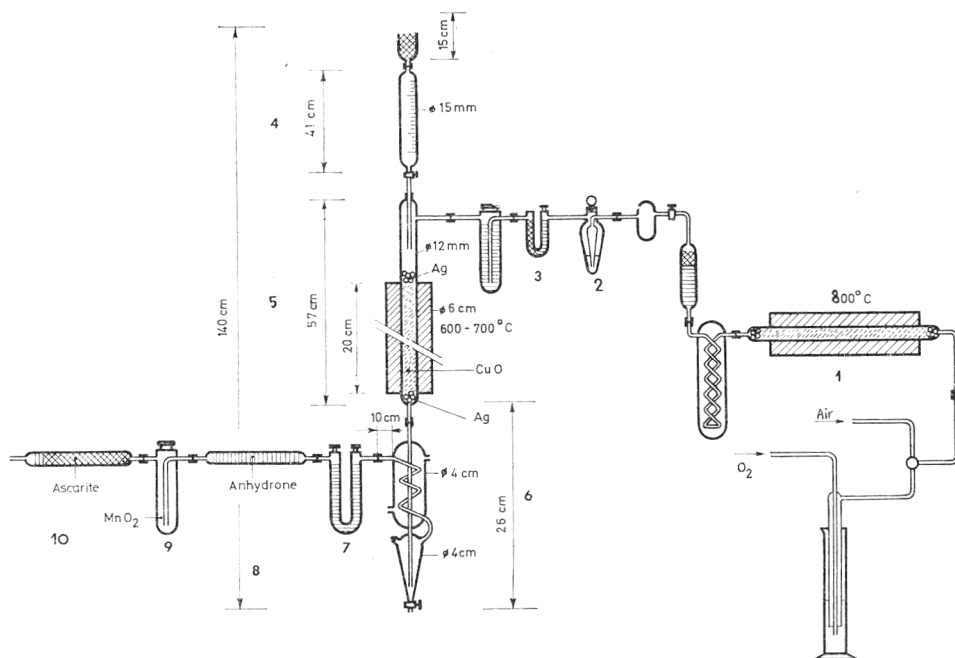


Fig. 1. Apparatus for carbon determination in water samples. 1. oxygen purification tube filled with CuO ; 2. bubbler with sulphuric acid; 3. U-shaped tube filled with ascarite and anhydrous; 4. burette for sample introduction; 5. combustion tube; 6. water condensation trap; 7. U-shaped tube filled with anhydrous; 8. absorption tube filled with manganese dioxide; 9. absorption tube for nitrogen oxides filled with manganese dioxide; 10. absorption tube for carbon dioxide filled with ascarite and anhydrous.

combustion tube is connected with a water condensation trap. The trap is operated at room temperature, with a few drops of sulphuric acid (1 : 1) added to prevent the carbon dioxide binding in condensed water. Two units — U-shaped tube and normal absorption tube — for the elimination of water vapour, precede the manganese dioxide absorption tube for the elimination of nitrogen oxides. The carbon dioxide absorption tube is followed by a Mariotte's bottle, connected through a tube with a desiccant, helping to adjust the flow rate through the system. A bubbler was used with the central part widened so that the sulphuric acid content could be retained without danger of being possibly sucked into the preceding parts of the assembly by the negative pressure.

Procedure

Waste water has to be filtered prior to transfer into burette. Oily layers, if present, are separated from the bulk of water in extraction funnel. From the burette a measured volume is continuously added, the burette being connected by an ascarite filled tube with the surrounding atmosphere. By a small size of the drops and a slow rate of their addition, the risk is avoided that the pressure forces gas out through the stopcock of the burette. The combustion is performed in an oxygen flow 25 ml/min, with pressure higher than usual in elemental analysis. The volume of sample is varied from 1–5 ml according to the degree of contamination. The top of the cupric oxide with the silver wool plug is not heated by the furnace to adequate temperature. This zone is shortly heated with an auxiliary heater at the end of the sample combustion to expell the possibly retained part of carbon.

The products of pyrolysis are swept to the condensation trap by an air stream (6 ml/min), and further through the absorption system for water and nitrogen oxides to the carbon dioxide absorption tube. The pyrolysis of a 3 ml sample was performed during 20–30 minutes and the elution of the combustion products with air during another 20 minutes. The total carbon content (TC), the volatile organic carbon (VOC), the inorganic carbon (IC), as well as the heavy volatile organic carbon (HOC) can be determined. The sample is divided in three aliquots, and by combustion of the first one the total carbon content is determined. Through the second aliquot a nitrogen stream is bubbled. The carbon determination of this aliquot gives the sum of the inorganic and heavy organic carbon. The third aliquot of the sample is acidified to pH 4–5 and ventilated with a nitrogen flow. By the combustion of this aliquot the heavy volatile organic carbon is determined.

RESULTS AND DISCUSSION

Several compounds were added to distilled water to increase its concentration of organic carbon. Test solutions were prepared with compounds on a weight basis by dilution of a concentrated stock solution. The results for the selected compounds are shown in Table I.

TABLE I.
Analyses of Known Solutions for the Total Organic Carbon

Compound	Sample volume	mg T O C/l		S. D.	Number of determinations
	ml	added	found		
Sucrose	3.00	718.8	733.2	11.03	8
Sucrose	3.00	143.8	152.4	2.76	8
Sucrose	5.00	71.9	77.3	5.60	10
Alanine	3.00	360.3	378.0	12.85	12

TABLE II.
Analyses of Known Solutions for the Total Carbon

Compound		Sample volume ml	mg T C/l		S. D.	Number of determinations
Organic	Inorganic		added	found		
Alanine	NaHCO ₃	1.00	2403.0	2250.9	128.4	7
Alanine	NaHCO ₃	3.00	240.0	231.1	11.01	16
Alanine	NaHCO ₃	3.00	360.0	370.7	15.44	10

TABLE III.
Analyses of Known Solutions for Total, Organic and Inorganic Carbon

Compound	Sample volume ml	mg T C/l		S. D.	mg T O C/l		S. D.	mg I C/l		S. D.
		added	found		added	found		added	found	
Alanine NaHCO ₃	1.00	2403.0	2250.9	128.4	1802.0	1872.4	107.2	601.0	402.8	163.9
Alanine NaHCO ₃	3.00	360.0	370.7	15.4	180.0	207.5	9.7	180.0	164.2	12.5

* Number of determinations performed was 6 and 10 in the first and second line respectively.

TABLE IV.
Analyses of Waste Water for the Total Carbon and the Heavy Organic Carbon

Sample volume ml	mg T C/l		mg H O C/l	
	added	found	added	found
3.00	199.8	199.8	131.4	131.4
3.00	195.8	195.8	130.6	130.6
3.00	197.4	197.4	122.1	122.1
3.00	197.0	197.0	125.7	125.7
3.00	198.0	198.0	123.9	123.9
	Mean value:	197.6	126.7	126.7
	S. D.:	1.5	4.1	4.1

The total carbon content 3—5 mg/l — the »carbon blank« — was frequently controlled for the distilled water used. If the sample contains inorganic forms of carbon, the total organic carbon cannot be determined until the sample has been acidified and purged with an inert gas which is free of carbon dioxide and organic impurities. The purging serves to distinguish between heavy volatile organics and carbonates plus volatile organics, if present, in water. With a solution containing alanine and sodium hydrogen carbonate the determination of the total organic carbon was carried out (Table II) as well as of the total carbon, the total organic and the total inorganic carbon (Table III). In the case of high values for total organic carbon reproducibility of results is poor with sample volumes of 1 ml or less. Increasing concentration of sodium giving carbonate which does not decompose at 700—800 °C causes low values for TC (First line, Tables II and III). Consequently, for water samples with high level of alkali metals the relevant systematic error has to be taken into account, or the procedure modified.

In Table IV the results obtained in a series of determinations of a waste water samples are shown. Values for the total carbon are in the first and those for heavy volatile organic carbon in the second column.

The drawbacks of the described procedure are the following:

- one determination takes about 40—50 minutes;
- the results obtained for water samples with a low level organic contamination are not reliable.

The gravimetric final measurement is shown to be sufficiently sensitive only if organic carbon is not below 10 mg/l. The upper limit is not critical and can be extended by dilution or by use of smaller sample volumes but not those of 1 ml or smaller (Tables V and VI).

The procedure has been found suitable especially when analyses are performed sporadically, because no calibration is required.

TABLE V.
Analyses of Waste Waters

Waste water origin	Sample volume ml	mg T C/l	Organic matter as mg O ₂ /l by the consumption of	
			KMnO ₄	K ₂ Cr ₂ O ₇
Sanitary waste water	3.00	210.7	13.7	14.6
		455.2 ^a	22.0	25.0
Oil sewage system	3.00	618.7	838	1204
		384.9 ^a	277	343
		189.9 ^b	88	118
Leveling reservoir	2.00	9185.4	14795	15422
		8144.6 ^a	14631	15667

^{a, b} Samples taken at various times.

For sanitary waste water the values given are mean values of three determinations, while in other cases two simultaneous determinations were carried out; for Total Carbon S. D. = 20.0.

TABLE VI.

Analyses of River Water for the Total Carbon and the Heavy Organic Carbon

River	Sample volume	mg T C/l	mg H O C/l
	ml		
Sava	5.00	67.1	
Sava ^a	5.00	68.3	18
Drava	5.00	69	
	5.00	66	
Kupa	5.00	61.9	
Kupa ^a	5.00	45.8	5
Korana	5.00	54.1	8
Slušnica	5.00	50.9	5

Results are mean values obtained by at least two determinations: S. D. = 1.7.

^a Samples taken at various times.

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SAŽETAK

Jednostavan uređaj za određivanje ugljika u vodi

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Klasična aparatura za određivanje ugljika i vodika u organskim spojevima oblikovana je za određivanje ugljika u uzorcima vode. Izvršene su mnogobrojne analize poznatih otopina kao i uzoraka otpadnih i površinskih voda sa sadržajem ugljika 5 mg—10 g/l. Točnost i ponovljivost rezultata je zadovoljavajuća. Područje primjene ograničeno je s jedne strane osjetljivošću gravimetrijskog određivanja, a s druge prihvatljivim volumenom uzorka.

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