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Sea-trials of three different methods for measuring non-volatile dissolved organic carbon in seawater during the JGOFS North Atlantic pilot study

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ABSTRACT

De Baar, H.J.W., Brussaard, C., Hegeman, J., Schijf, J. and Stoll, M.H.C., 1993. Sea-trials of three different methods for measuring non-volatile dissolved organic carbon in seawater during the JGOFS North Atlantic pilot study. *Mar. Chem.*, 41: 145–152.

In 1989 the shipboard comparison of three different methods for measuring concentrations of dissolved organic carbon (DOC) resulted in reasonable agreement, with differences likely as a result of a combination of calibration offsets and general instability of the instruments at sea. Typical concentrations were about 80–140 μmol in the upper 1000 m of the water column, with a tendency towards higher values (100–150 μmol) in the surface waters. These elevated surface water levels are below the 200–300 μmol values recently reported for the Atlantic and the Pacific Oceans. In 1990 the small dataset obtained with a further modified High Temperature Combustion instrument showed similar trends. Within the analytical error there is no significant offset between two HTCO methods and one wet oxidation technique.

INTRODUCTION

The accurate determination of dissolved organic carbon (DOC) in seawater is not a trivial task. Duursma (1961) used a wet chemical oxidation and led the evolving gas stream over a hot platinum catalyst to oxidize any residual carbon monoxide to carbon dioxide. The novel high temperature combustion (HTCO) method relies solely on a platinum catalyst for complete conversion of DOC to carbon dioxide. Its recent application has initially led to much higher DOC values than previously obtained with either dry combustion, wet chemical oxidation or UV-irradiation (Sugimura and Suzuki, 1988; Druffel et al., 1989). However, when starting this project in early 1989 no other laboratories had been able

to reproduce either the high absolute concentrations or the accuracy and reproducibility reported by Sugimura and Suzuki (1988). Partly these problems may be attributed to a large part of the DOC pool being biochemically labile hence highly variable (Duursma, 1961; Kirchman et al., 1991). On the other hand, it appeared that success of the HTCO method of Sugimura and Suzuki (1988) still depended very strongly on the skills of the operator in running the specific HTCO instrument. For wide application within such programmes as the Joint Global Ocean Flux Study (JGOFS, De Baar et al., 1989) the reliability of the method would need to be improved such that all trained operators would obtain accurate results. Given the often adverse analytical conditions on shipboard we decided to conduct realistic sea-trials of several methods.

During Leg 1 of the 1989 JGOFS Upper Ocean Study aboard R/V “Tyro” (Rommets et al., 1991a) we compared two high temperature Pt-

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catalytic combustion methods with a batchmode wet chemical oxidation method. Another (fourth) method, continuous wet oxidation, was also intended; initially this instrument functioned properly but when the other two instruments (HTCO) finally were operational unfortunately it failed. Upon many trials and tribulations only a small part of the two HTCO datasets was found to be of acceptable reproducibility. During the 1990 JGOFS Upper Ocean Leg 3 aboard R/V "Tyro" (Rommets et al., 1991b) one of us (C.B.) further developed one HTCO instrument and obtained a small set of promising values. Results of this work have been presented previously (JGOFS, 1990a,b).

METHODS

1989 JGOFS Leg 1 R/V "Tyro"

Adverse weather conditions, in between various hurricane tracks as well as instrumental problems, allowed only a few samples to be collected and analyzed while working in the northern part of the JGOFS section (33–60°N along 20°W). Nevertheless, at some stations (5, 18, 21, 22) in the northern region (approximately 60°N, 20°W) samples were collected and processed for the wet oxidation batch method. Seawater was collected in ultraclean GoFlo samplers and drawn into precleaned glass bottles. The seawater was not filtered so as to avoid contamination and data are total non-volatile (TOC) rather than dissolved non-volatile organic carbon (DOC). Otherwise the difference (Particulate Organic Carbon (POC) = TOC-DOC) would be in the order of 10% of the TOC and is deemed trivial at the current state of the art. Subsamples of 100 ml each were acidified with 5 ml 10% phosphoric acid and sparged for 10 min with nitrogen gas to drive off all inorganic carbon, also removing an unknown volatile organic fraction. These samples were further processed as described below for the wet oxidation technique.

Only upon arrival at the southernmost

stations at or near 33°N, 20°W were we able to execute the intercalibration between the three methods. At two such stations (35 and 62) water samples were collected and acidified as described above and split for analyses with three different methods.

The Ionics 555 analyzer with a pure Pt gauze catalyst and modified configuration (cold trap, Sn for removing HCl evolved, Mg-perchlorate and in-line filter) was operated at 900°C using 3–5 replicate injections of 100 μ l for each sample. Previous calibrations in the shore laboratory had shown the 900°C temperature to be optimal with respect to amplitude and reproducibility of the carbon dioxide signal. At sea the instrument suffered from numerous instabilities, likely resulting to some extent from ship vibration and movement that interfered with the chopper frequency of the infrared CO₂ analyzer.

The Shimadzu TOC 500 analyzer with 0.5% Pt-coated Al₂O₃ catalyst and modified configuration was quite stable. While operating at 680°C and injecting 8–12 replicate 50 μ l samples the standard addition calibration lines gave promising ($r = 0.999$) correlations.

For the two above shipboard combustion methods calibrations were done by addition of potassium phthalate standard solutions to 1000 m depth seawater (Fig. 1). The slope of the line was used as a conversion factor for assessing TOC in real samples.

For the method of batchmode wet oxidation, four 5 ml replicates were transferred into an ampoule, 0.2 g persulfate and 250 μ l phosphoric acid (6%) were added, the ampoule purged with oxygen gas, heatsealed and then heated in a pressure cooker for 4 h at about 120°C. The amount of persulfate oxidizing agent was about twice that recommended by Menzel and Vaccaro (1964). The vials were stored for analyses in the shore laboratory, using an Oceanography International instrument where CO₂ was measured against sodium carbonate standard solutions. For each sample, the mean of the four replicate vials minus the blank is reported. The overall blank was assessed by analyzing a suite of 2, 4, 6,

Fig. 1. Shipboard calibration lines of the response (peak area $\times 10^{-5}$) of the Ionics 555 analyzer for TOC standards (phthalate) added to seawater matrix. The seawater slope was used to calculate seawater values for given Stations 35, 62 and 49 as listed in Table 1 and shown in Figs. 2 and 5. (Upper graph): Station 35 (1989) standard addition to 1000 m water, also shown (open triangles) standard addition to distilled water. (Middle graph) Station 62 (1989) standard addition to 1000 m water, also shown (open triangles) standard addition to distilled water. (Lower graph) Station 49 (1990) standard addition to oxygen minimum water; the more stable baseline allowed higher gain setting, i.e. more counts per peak μmol^{-1} TOC.

8, 10 ml aliquots of the same seawater sample. Regression through the resulting values provided an intercept representing the overall reagent blank, typically about $20 \mu\text{mol}$.

1990 JGOFS Leg 3 RV Tyro

Before the cruise, the configuration of the analytical line of the Ionics 555 was modified to improve the geometry, the cold trap being positioned closely behind the furnace to minimize condensation in the connecting narrow-bore teflon tubing. The trap contained some phosphoric acid. Downline the Sn, Mg-perchlorate and an improved aerosol filter (Baltzer 0.1 micron, E.T. Peltzer, personal communication, 1990) were installed. At sea several electronic instabilities were remedied but the ship's vibrations were always seen in the signal of the IR analyzer, presumably affecting the membrane separating the two compartments of the detector cell. Nevertheless the overall performance was much better during the 1990 cruise as demonstrated by the standard addition calibration line (Fig. 1).

RESULTS AND DISCUSSION

While many values were obtained only those data with acceptable reproducibility between the replicates are reported here (Table 1). From Fig. 2 it is seen that for the Ionics the TOC concentrations at Station 35 are considerably below those at Station 62. There was very good correlation between the Ionics and the Shimadzu results at Station 62 (Fig. 3). On close inspection of Station 62 data the Ionics results are systematically higher than the Shimadzu values by five percent (Table 1). The difference may be related to the rather noisy baseline affecting the performance of the peak integrator. This and other factors may cause the different slopes of the standard addition calibration lines. In addition there are uncertainties about the instrument blank as discussed below. For example, the Ionics calibration lines differ considerably at the two stations (Fig. 1). Also the slopes in seawater

TABLE 1

Total organic carbon (TOC; $\mu\text{mole/kg}$) at various depths at given North Atlantic station

Station	Date	Lat. Long. (N, W)	Depth (m)	TOC S208	TOC 900°C	TOC 680°C
5	07-08-89	60°02.3 19°54.5	11	130		
			245	112		
			494	122		
			742	77		
18	19-08-89	54°00.4 19°59.5	18	136		
			48	122		
			97	92		
			250	91		
21	24-08-89	46°59.9 19°58.9	10	143		
			27	127		
			50	133		
			71	106		
22	25-08-89	46°58.4 20°03.4	99	86		
			245	83		
			1249	143		
			1998	86		
35	30-08-89	32°57.6 20°00.3	3497	93		
			4443	92		
			11	126	124	156
			21	113	90	150
62	05-09-89	33°00.0 21°11.7	31	101	97	135
			51	116	132	150
			75	100	95	123
			100	87	119	130
20	27-04-90	32°59.3 20°00.9	150	111	100	127
			199	92	111	142
			249	104	82	119
			497	91	69	113
30	07-05-90	32°59.1 19°59.4 32°55.7 20°01.0	744	74	61	105
			992	86	78	116
			9	119	148	141
			20	117	144	137
49	16-05-90	49°00.2 17°02.1	77	99	115	109
			97	101	156	148
			116	99	151	144
			149	98	161	152
30	07-05-90	32°59.1 19°59.4 32°55.7 20°01.0	195	101	195	169
			246	96	163	147
			495	90	107	102
			743	87	122	116
49	16-05-90	49°00.2 17°02.1	990	90	135	128
			750		125	
			1000		116	
			200		125	
49	16-05-90	49°00.2 17°02.1	4350		158	
			50		129	
			100		133	

TABLE 1

Continued

Station	Date	Lat. Long. (N, W)	Depth (m)	TOC S208	TOC 900°C	TOC 680°C
		49°02.3 17°03.3	300		125	
			600		116	
			800		104	
			1000		91	
			2000		91	
			3000		100	

Non-volatile total organic carbon determined with one to three methods. Each value is the mean of several replicates: 4 for the wet oxidation (S208), 3–5 for the Ionics 555 (900°C) and 8–12 for the Shimadzu TOC 500 (680°C). The wet oxidation results have been corrected for the overall reagent blank (approx. $20 \mu\text{mol kg}^{-1}$). For the two HTCO methods the values were calculated from the slopes of the linear regression of standard additions to seawater matrix (e.g. Fig. 1), without subtraction of perceived blank, see text. The thermometers of both HTCO furnaces were not calibrated independently and temperatures are reported as indicated by the instruments.

matrix appear lower than the response slopes for DOC standards in distilled water (Fig. 1). From the inverse relation (DOC as function of peak area) of the latter three calibration points in distilled water we investigated any possible blank taken as the intercept by linear regression (not shown). For example for the Ionics 555 at given stations we found

$$\text{DOC } [\mu\text{mol}] = 10.5 + 0.000372 (\text{Peak Area})$$

$$r = 0.998 \quad n = 3 \quad \text{Station 35}$$

$$\text{DOC } [\mu\text{mol}] = 15.1 + 0.000399 (\text{Peak Area})$$

$$r = 0.997 \quad n = 3 \quad \text{Station 62}$$

Unfortunately it cannot be resolved whether this 'blank' intercept of 10–15 μmol results from the instrument itself (i.e. to be subtracted from the seawater value) or from the distilled water (i.e. not to be subtracted from the seawater value). Also the higher response (slope of the regression) in distilled water versus seawater leaves some ambiguity for blank correction. Therefore no blank correction was applied (Table 1). Otherwise, the blanks of 10.5 and 15.1 μmol are seen as maximum values, i.e. at most our reported seawater values for the two HTCO methods at 1989 Stations 35 and 62 (Table 1) would need to

Fig. 2. Vertical profiles of non-volatile total organic carbon ($\mu\text{mol kg}^{-1}$) determined with three different methods at Stations 35 (1989), 62 (1989). Also shown are three out of four values (filled triangles) of Station 20 (1990) in the same 33°N , 20°W region.

be corrected downward accordingly. For the Shimadzu, the calibrations and blank assessments were very similar and reported values were not blank-corrected either.

At both stations, the Shimadzu profiles tend to be among the higher of our TOC values, while at Station 62 the Shimadzu results virtually coincide with the Ionics results (Fig. 2). Also, Shimadzu results from both Stations 35 and 62 are comparable in magnitude and are not unlike

some datapoints obtained at the same site in 1990 with the then improved Ionics instrument (Fig. 2). The higher levels in surface waters as compared with deep waters (Fig. 2) are not unlike the relative trend suggested by Sugimura and Suzuki (1988). However absolute values (Table 1) are below values obtained by Miller, Peltzer and Suzuki (JGOFS, 1990a) at the more northern 47°N , 20°W station (see Fig. 5) and Pacific Ocean values of Sugimura and Suzuki (1988). When applying the above discussed blank correction of $10\text{--}15\mu\text{mol}$ the difference would become somewhat larger.

At both Stations 35 and 62 the wet oxidation TOC results are very similar with values of about $90\mu\text{mol}$ at depth and a maximum near $120\mu\text{mol}$ at the surface, with the surface waters of Station 62 showing the smoother trend (Fig. 2). There might be a slight trend towards higher values for the two high temperature combustion methods as compared with the wet oxidation method, but it should be noted that latter values were blank-corrected. Without blank correction the wet oxidation values would range from 100 to $140\mu\text{mol}$, comparable with the HTCO values.

At more northern stations (approximately 60°N , 20°W) some data were obtained with the same wet oxidation method (Fig. 4). When combining data from these northern stations a fairly consistent vertical distribution appears, with

Fig. 3. Correlations between the two high temperature combustion methods at two stations. Differences between methods are likely as a result of similar differences in the calibration lines (see Fig. 1).

Fig. 4. Vertical profile of non-volatile total organic carbon ($\mu\text{mol kg}^{-1}$) determined by wet oxidation batch method at four stations in the 60°N , 20°W region. Note change in vertical scale at 800–1000 m depth.

blank-corrected TOC in deeper waters at about $80 \mu\text{mol}$ and a surface maximum of about $140 \mu\text{mol}$. This trend at approximately 60°N , 20°W is similar to that found at approximately 33°N , 20°W in 1989 (Fig. 2) as well as at approximately 49°N , 20°W in 1990 using the Ionics instrument (Fig. 5). From our observations, albeit limited, there is no reason to assume that HTCO yields higher DOC values than wet chemical oxidation.

The vertical profile (Fig. 5) of TOC determined with the modified Ionics 555 at 49°N , 17°W on 5 May 1990 shows the expected inverse relation with Apparent Oxygen Utilization (AOU) in the upper 1000 m of the water column. An even stronger decrease with depth of TOC was found by Peltzer and Suzuki when intercalibrating with Miller, at nearby Station 47°N ,

Fig. 5. Vertical profile of non-volatile total organic carbon (filled circles) ($\mu\text{mol kg}^{-1}$) determined with the modified Ionics 555, as well as apparent oxygen utilization (AOU, filled squares) on 5 May 1990 at 49°N , 17°W . Also shown for comparison, the TOC results of E.T. Peltzer (open triangles), Y. Suzuki (open circles) and A. Miller (crosses) and AOI (open squares) at their intercalibration Station 25 (47°N , 20°W) occupied 1 year (18 May 1989) before (JGOFS, 1990a).

20°W on the 18 May of 1989 (Fig. 5), although their absolute TOC values were considerably higher at the latter station. At greater depth our TOC values are fairly constant, judging from the two additional datapoints. The higher TOC values of the three 1989 datasets versus our 1990 results in the general 47°N , 20°W region may be ascribed to either different water masses or analytical discrepancy. Differences in degree of mineralization are less probable as the AOI in 1989 is virtually the same as in 1990 (Fig. 5). Analytical discrepancy may partly be ascribed to differences in calibrations. Responses of various instruments (slopes of standard addition lines) likely vary between instruments, cruises and over time. Finally it is noted that the commonly used standard addition technique would improve upon better understanding of the analytical

blanks and their variability (Hedges, 1993; Tanoue, 1993).

SUMMARY

The two HTCO methods with various modifications look promising. Improvements in sample handling and assessment of response and blanks may lead to better reproducibility, provided that ship-induced interferences with the final CO₂ infrared analyzer will be circumvented. New types of infrared CO₂ analyzers operating at higher frequencies (approximately 500 Hz) are now available and would appear useful.

Absolute TOC values found with both the two HTCO methods as well as the wet chemical oxidation method are 100–150 μmol in surface waters and 80–100 μmol in deeper waters of the northeast Atlantic Ocean. The reasonable agreement of the wet oxidation method is mostly ascribed to the higher amount of persulfate used. Earlier investigations of the Atlantic Ocean were based on methods other than HTCO, with reported TOC values either similar to or lower than our results (Table 1 of Sugimura and Suzuki, 1988). Values in the range of 70–140 μmol , found in the open northwest Atlantic Ocean (Kepkay and Wells, 1993) are similar to ours. Recently reported values for three Pacific stations are also in the same range as ours and fairly uniform with depth, except for a distinct surface maximum of 170 μmol at one station (Tanoue, 1993). During a recent intercalibration in the Mediterranean Sea the TOC values obtained with a Shimadzu TOC 500 instrument rarely exceeded 125 $\mu\text{mol kg}^{-1}$ in surface waters, while lower deep water values of about 50–60 $\mu\text{mol kg}^{-1}$ showed good agreement with results from a traditional UV-persulfate method (Cauwet et al., 1990). On the other hand our highest values of about 150 μmol for surface waters are below the values recently reported by others for the same region (Fig. 5) and for the Pacific Ocean (Sugimura and Suzuki, 1988).

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