Measurement of Dissolved Organic Carbon in Seawater: A Comparison between the High-Temperature Catalytic Oxidation Method and the Persulfate Oxidation Method

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ABSTRACT

A high-temperature catalytic oxidation method (HTCO) has been developed to measure dissolved organic carbon (DOC) in natural seawater. The method employs Pt/Al_2O_3 as a catalyst to oxidize DOC at 680°C into CO_2 which is detected by a non-dispersive IR detector. The detection limit of the method was estimated to be 29.5 μMC on the basis of a sample volume of 66 μl. The precision was generally better than 7% with respect to selected organics added to natural seawater. The detection limit and precision are expected to be lower and greater, respectively, if the injection volume is increased. The HTCO method is faster, more reliable, but higher in analytical cost than the persulfate oxidation method for the analysis of DOC in seawater samples. To obtain reliable values of DOC in a land laboratory, the seawater sample should be filtered, acidified and stored at 4°C immediately after sampling. The HTCO method measured the higher values of DOC than did the persulfate method in shelf waters off northeastern and southwestern Taiwan, indicating the incomplete oxidation of the persulfate method. The persulfate method, however, is still recommended for use along with the HTCO method because each method for analyzing DOC provides different geochemical information. The DOC value increases as salinity decreases in surface water off northeastern Taiwan reflecting the influence of terrestrial sources on the distribution of DOC. A vertical decrease of DOC with depth was also found at a station off southwestern Taiwan, indicating that there may be a relationship between DOC distribution and biological turn over of organic carbon. The priorities extended from this study will focus on the spatial and temporal distributions of DOC and their geochemical significance reflected from the use of both methods for marginal seawater under the influence of the Kuroshio.

1. INTRODUCTION

Measurement of dissolved organic carbon in seawater has been made for over a half century, but no reliable method with direct and/or shipboard performance has been fully recognized yet (Toggweiler, 1990; Sharp, 1991). Previous results obtained from different

methods revealed that the high-temperature combustion method has higher oxidation efficiency and gives higher DOC values than do the chemical (eg. persulfate) and UV oxidation methods (Menzel and Vaccaro, 1964; Armstrong *et al.*, 1966; Gordon and Sutcliffe, 1973; Sharp, 1973; Gershey *et al.*, 1979; Kumar *et al.*, 1990; Romankevich and Ljutsarev, 1990). However, the high-temperature combustion method has not been widely applied in seawater analysis largely due to problems with contamination and poor reproducibility (MacKinnon, 1978; Sharp, 1991).

Recently, Sugimura and Suzuki (1988) used the high-temperature catalytic oxidation method (HTCO) to measure total concentration of DOC in seawater by means of a Sumigraph N-200 instrument. The method employs Pt/Al_2O_3 as catalyst to oxidize dissolved organic matter at $680°C$ into CO_2 which was subsequently detected by a nondispersive IR. They reported much higher values in both surface and deep water than those previously measured. The results also indicated that the DOC concentration decreases strongly with depth and correlates inversely with apparent oxygen utilization and nitrate concentrations. These striking features suggest that DOC is actively involved in the biogeochemical cycles of carbon (Togweiller, 1989; Bacastow and Maier-Reimer, 1991). The method, however, has not been fully confirmed because no identical results have been reproduced (Toggweiler, 1989; Sharp, 1991). Nevertheless, the HTCO is still the most attractive and potential method to date in measuring DOC in seawater because of its high efficiency in extraction of DOC from seawater.

On the other hand, the persulfate oxidation, which was commonly used to measure DOC previously, has been reported to be far less efficient in recovering DOC from seawater (Sharp, 1973; Sugimura and Suzuki, 1988). Sugimura and Suzuki (1988) also ascribed the persulfate-resistant fraction of DOC to the newly produced, high molecular-weight organic compounds in the upper layer of the ocean. The findings may suggest that the simultaneous measurements of DOC with HTCO and persulfate methods are required in order to distinguish the phases of DOC. Nevertheless, the boundary of new and old phases of DOC may not be clear-cut if optimal conditions of persulfate oxidation, which were rarely mentioned before, are not rigorously set for seawater. Therefore, the analytical precision of both methods should be evaluated prior to application on the study of DOC distribution in the oceans.

Although a new set of commercialized HTCO instruments (Sumigraph model TOC-90) has been available recently and some DOC results have been revised (Suzuki *et al.*, 1991), we were not inclined to employ this instrument for DOC analysis because of its inacceptably high international price and unknown reliability. Thus we employed the Shimadzu TOC analyzer with a HTCO device for DOC measurements in seawater. The principles of this instrument are basically similar to those of the Sumigraph analyzer, but the price is reasonable enough for us to afford it. The methodology and analytical procedures of the method are addressed as well as the results obtained from the HTCO and persulfate/$100°C$ methods are compared and discussed.

2. MATERIALS AND METHODS

a. Instruments

Analysis of DOC in seawater was established on a commercially available instrument with HTCO oxidation system (Shimadzu TOC 5000), and the results were compared with those from the persulfate/100°C oxidation system (O. I. Corporation, model 700). The HTCO system primarily consists of a combustion unit, a gas purification system, a non-dispersive IR (NDIR) detector and a recording system. The water sample was injected into an oxidation column of quartz material containing either normal catalyst (Pt-alumina) or high sensitivity catalyst (Pt-quartz wool), depending on the type of measurement. The column is housed in an electric furnace which is continuously heated at 680°C under the atmosphere of purified air. The generated CO_2 was carried by purified air to the NDIR detector, and the signal was digitally converted into carbon concentration according to the calibration of DOC standards. In case of the model 700 O. I. analyzer, the instrument is widely known in the oceanographic community and detailed description is not necessary. Usually the seawater is directly injected into the system, and dissolved CO_2 is expelled from the acidified seawater by purging with nitrogen. The remaining DOC is then oxidized by persulfate at 100°C and the released CO_2 is measured by a NDIR detector. Standard calibration should be made and recorded in the analyzer prior to analysis of seawater samples.

b. Calibration

A standard stock solution (1000 ppm C) was prepared for both methods by dissolving analytical-grade potassium hydrogen phthalate (Merck) in 0.4% HCl solution ($vHCl:vQ-H_2O$), stored at 4°C in the dark. Working standard solutions were prepared by dilution of stock solution in 0.4% HCl solution. Standard stock and working standard solutions should be prepared weekly and daily, respectively. The injection volume of each sample for the HTCO method can be selected (100 μl max. for using normal catalyst) and operated by an automatic injector, thus the standard solution and seawater were injected with 66 μl throughout this experiment. Peak areas (integrated counts) of standards were least-square fitted and the concentration of seawater sample was calculated from this calibration.

The calibration of persulfate method was made from a single standard. The working standard (10 ppm) was run repeatly by introducing 0.5 ml into the model 700 analyzer to react with 3 ml of persulfate for 13 min. until the detector response was constant; the blank-corrected scaling factor ($\mu gC/mV$) was used to calculate the DOC concentration in seawater.

c. Verification

The recovery of organic compounds spiked in natural seawater was examined to

realize the precision of the HTCO method. The same experiment was also conducted for the persulfate/100°C oxidation method.

d.   Analysis of DOC in seawater

Seawater samples were collected on board the R/V Ocean Researcher 1 with Niskin bottles (2.5 l) mounted on a Rosette sampler from a station (st. A) off southwestern Taiwan and stations (sts. 1-11) of a transect off northeastern Taiwan (Figure 1) during the periods of 20–26 August and 4–7 October, 1991, respectively. One liter of each sample was filtered through the pre-combusted (450°C, 4 h) glass-fiber filter (Whatman GF/F) which was mounted on a Swin-Lock filtration holder (Nucleopore). After discarding the first 800 ml of filtrate, a subsequent 100 ml of filtrate was transferred to the seawater pre-
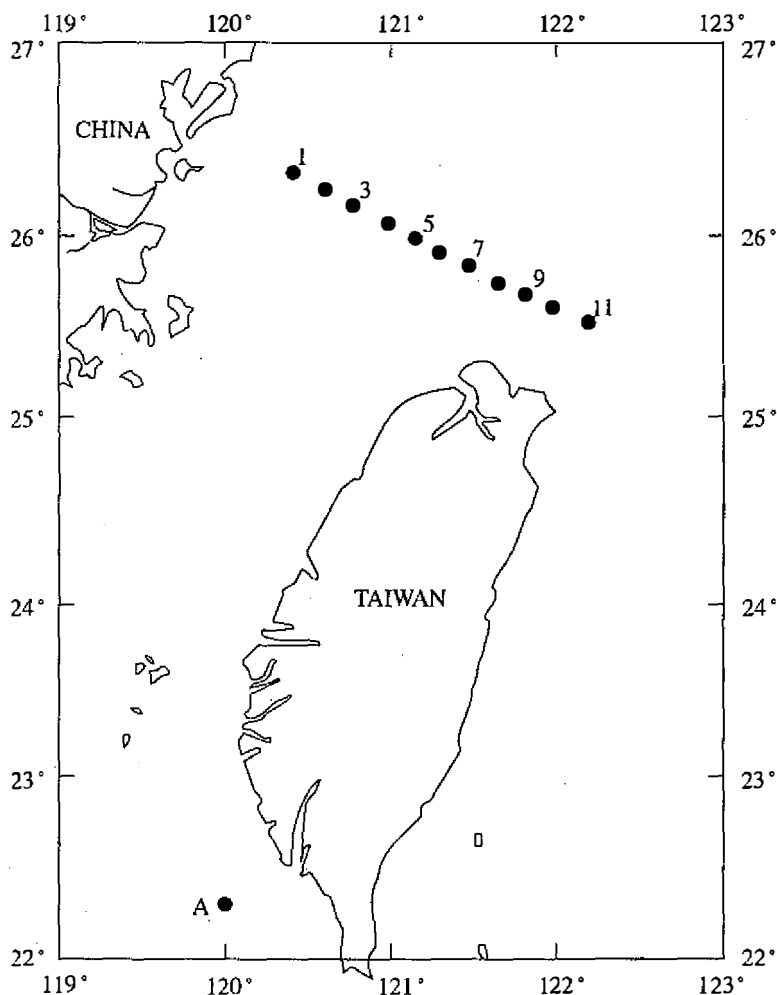

Fig. 1. The map of sampling locations.

rinsed Pyrex glass bottle. The filtrate was immediately acidified with 0.4 *ml* of subboiled HCl and then stored at 4 °C until analyses at a land-based laboratory. The determination of DOC in seawater by the HTCO method was carried out by purging 20 *ml* of filtered and acidified seawater in a Pyrex test tube with purified air for 5 *min.* to remove dissolved CO_2. The 66 μl of decarbonated seawater was injected into the oxidation column by means of an automatic syringe. Each sample was run for at least 5 repeated measurements, and abnormal signals were deleted to ensure that the standard deviation of repeats was less than 2%. The averaged running time for a sample was estimated to be 12 *min.*

If DOC was determined by the persulfate method, a volume of 0.5 *ml* acidified and purged seawater was allowed to react with 3 *ml* of 10% (w/w) potassium persulfate for 13 *min.* At least three repeats, which usually last longer than 45 *min.*, were performed for a sample ensuring that the standard deviation of repeats was less than 5%.

3. RESULTS AND DISCUSSION

a. Calibration

Calibration of the HTCO method was based on four-point (2, 4, 6 and 8 ppm C) standards. Output signals (integrated counts) of the four standards were perfactly linear with respect to carbon concentrations as shown in Figure 2. The intercept of regression line on the y-axis indicates the blank signal derived from the instrument (system) itself and the matrix of standard solution (acidified $Q\text{-}H_2O$). The matrix blank was not evaluated
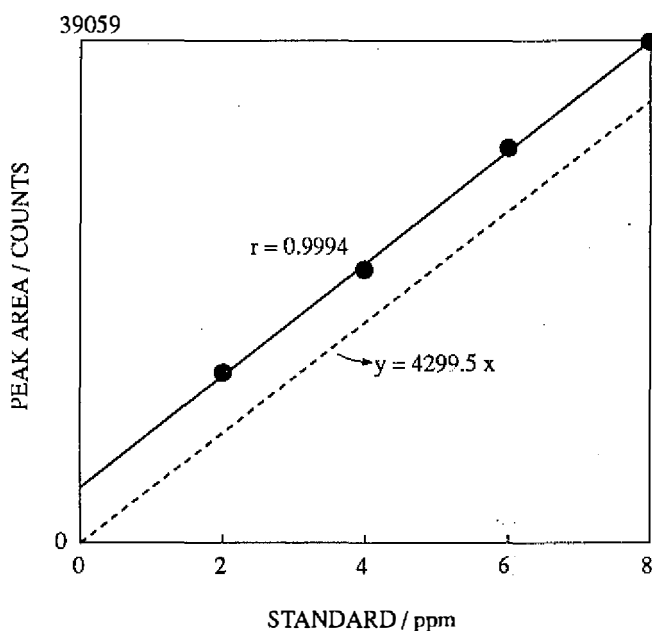

Fig. 2. The calibration curve of DOC standard (—) and shift of the curve to pass the origin (----).

directly because organic-carbon free Q-H_2O was not available. The effect of different matrices on the DOC measurement was not thought significant, because a comparable method has been proved to be effective in the oxidation of DOC in natural seawater (Sugimura and Suzuki, 1988). The non-target gases such as Cl_2 and SO_2 produced from the combustion of seawater, which may affect the DOC detection, have been removed by a halogen scrubber before CO_2 entered the NDIR detector. The system blank, which may come from the carrier gas, catalysts (Pt-alumina) and carry-over (memory) residue during consecutive injections, however, must be known because it is included in the measuring signals of the following natural seawater samples. In practical analysis, the signal of a seawater sample (including system blank) was converted to carbon concentration according to the calibration of net response by shifting the y-intercepted calibration line to pass the origin. The concentration of DOC in seawater sample, therefore, contains a part of carbon derived from the blank. Furthermore, the memory blank, which may be a part of system blank, can stem from the incomplete combustion of organic carbon in the oxidation column and/or adsorption of carbon on the surface of catalyst. This carry-over blank may not be consistently same throughout the measurements and this may result in the variability of the system blank during the experiment. To evaluate this memory blank of HTCO analyzer, samples of seawater and Q-H_2O were alternatively measured with five injections for each determination. From Table 1, we found that the signal of the first injection is usually but not always higher than those of the other injections for the Q-H_2O sample. It should be mentioned that standard deviations of repeated measurements are generally greater than 2% because the data were presented as original counts, and no abnormal count has been deleted. The results indicate that the memory blank may not be neglected when the measurement is switched from the sample of relatively high carbon to the sample of relatively low carbon. In order to avoid the daily variability of system blank, we thus did not consider the value of first injection between samples to eliminate the possibil-

Table 1. Alternative measurements of DOC between seawater (SW) and Q-H_2O by the Shimadzu TOC 5000 analyzer

inj. \ sample counts	SW	Q-H_2O	SW	Q-H_2O	SW	Q-H_2O	SW	Q-H_2O
1	7704	3191	8189	2717	8313	2923	8437	3805
2	7938	2629	7897	2802	8473	2727	8322	2799
3	8064	2712	8021	2706	8081	2888	8283	2916
4	8080	2596	8084	2562	8084	3117	8212	2876
5	8380	2621	7990	2606	8533	2764	7964	2960
mean	8033	2749	8036	2678	8296	2883	8240	2927
(sd.)	(245)	(250)	(108)	(95)	(211)	(154)	(183)	(106)

inj.: injection number

ity of memory effect for samples of natural seawater. Under these conditions, the system blank is estimated from the y-intercepts of zero volume extrapolated from regression lines between integrated counts and different volumes of injections for various solutions (Figure 3). The greater signals of solution C (2 ppmC in 3% NaCl) over solution B (2 ppmC in Q-H_2O) are ascribed to be largely derived from the organic carbon contamination of NaCl solution rather than from the matrix effect, because the solution of KHP(2 ppm) prepared from pre-combusted NaCl (450°C, 6 hr) gave the less carbon signal than did the same concentration of KHP solution prepared from non-combusted NaCl. The averaged integrated counts of the system blank were estimated at 762, which is equivalent to 11.69 ngC. This value is equal to be 14.75 μMC in the seawater volume of 66 μl, which was considered as the minimum running system blank. It was always subtracted from DOC concentration of seawater samples converted from the origin-passing calibration.
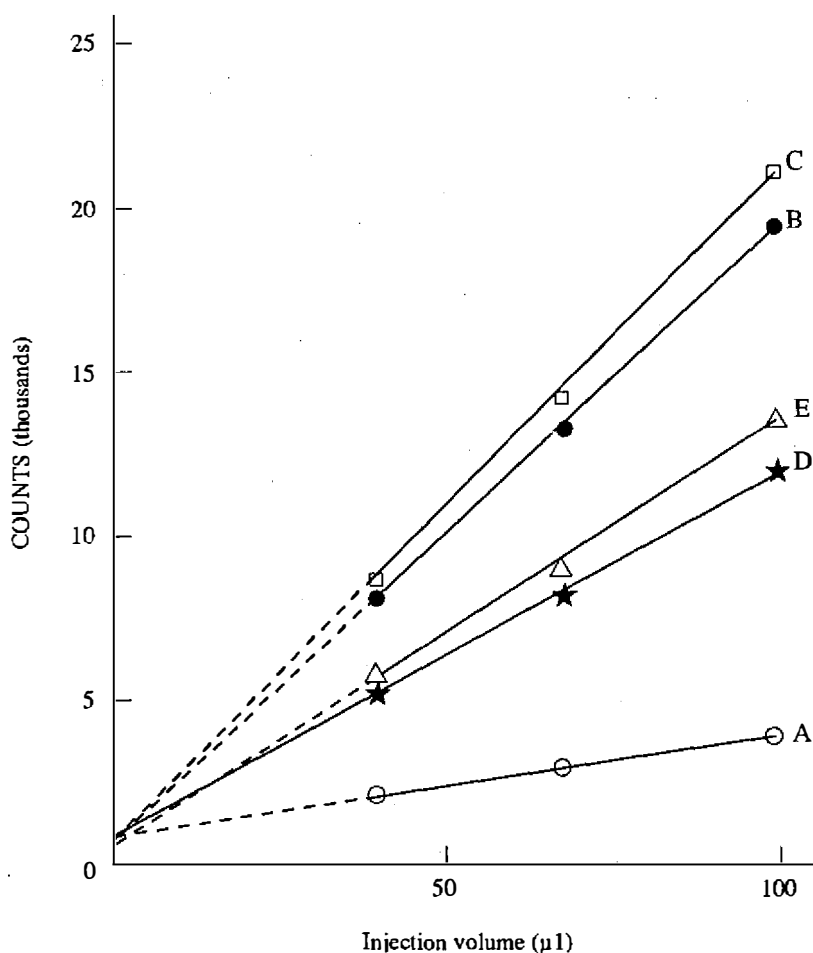

Fig. 3. Relationship between the measuring signals (counts) and injection volumes of various solutions: Q-H_2O (A), KHP (2 ppm) in Q-H_2O (B), KHP (2 ppm) in 3% NaCl (C), and samples of different seawaters (D and E).

The blank of the persulfate method, which comes mainly from reagents, gas, tubing and digestion chamber, is dependent upon the introduced reagent volume. It was generally found to be around 10 mV on the basis of 3 ml of oxidant, which should be subtracted from the signals of standards and samples. The blank was roughly equivalent to 0.45 μgC. This blank is subject to variability and should be checked prior to running standards and samples. The instrument uses $\mu gC/mV$ as scaling factor to convert the measured voltages from samples to DOC concentrations. The linear range of the NDIR detector was reported up to 50 μgC (Operating Manual of O. I. Instrument), which far exceeds the 5 μgC in the standard solution.

b. Verification of DOC measurements in seawater

The reliability of DOC measurements in seawater by means of HTCO and persulfate/100°C methods was examined from the recovery of various amounts of organic compounds (KHP, EDTA, oxalic acid and caffeine) spiked in the offshore seawater of southwestern Taiwan. Recovery of added compounds by the HTCO method was found to be nearly 100% for most measurements, with the exception of EDTA where the uncertainty was up to 7% for a added concentration. The precision is, therefore, believed to be better than 7% with respect to added compounds in natural seawater (Table 3).

As far as the oxidization efficiency of the persulfate/100°C method is concerned, it is dependent on the chloride content of sample, oxidant amount and reaction time. The analytical conditions, which can completely oxidize KHP in Q-H_2O, did not oxidize KHP efficiently in NaCl solutions of various chlorinity (Figure 4). Experimental results also showed that increases of oxidant amount and reaction time can greatly enhance the recovery of KHP in NaCl (3.5%) solutions, thus an operational condition (seawater: 0.5 ml; persulfate (10%): 3 ml; reaction time: 13 $min.$) was set for measuring DOC in natural seawater. However, the optimal condition found from synthetic solutions may not be also optimal for DOC analyses in natural seawater. The data in Table 3 show that the added organic compounds in natural seawater were not totally recovered, indicating the incomplete oxidation of DOC in natural seawater by the persulfate oxidation.

c. Detection limits of methods

The system blank of the HTCO method was estimated to be 11.69 ngC. The detection limit of the instrument (35.07 ngC) is defined as a three-fold intensity of system blank. This signal is equal to that produced from a seawater sample containing 23.38 ngC because the system blank (11.69 ngC) is always present and added to any determination. The concentration of detection limit in seawater is therefore equivalent to 29.5 μMC on the basis of an injection volume of 66 μl (Table 3). This value is relatively smaller than the lowest concentration of DOC found from the deep open ocean (Sugimura and Suzuki, 1988). Obviously, the method is suitable for the measurement of DOC in the ocean. Because the signal of system blank was assumed to be independent of injection volume,

Table 2. Determination of blank and detection limit for the HTCO and persulfate methods

Method	System blank signal (ngC)	System + reagent (total) blank signal (ngC)	Detection * limit of the instrument (ngC)	Detection limit # in seawater ngc (μMC)
HTCO	11.69	11.69	35.07	23.38 (29.50)
Persulfate	< 45.0	450	135	90.0 (15.0)

* Detection limit of the instrument is defined as three-fold intensity of the system noises.

\# Detection limit in seawater is about one half less than that of the instrument (see explanation in text) and the concentration is calculated on the basis of injection volume, 66 μl and 0.5 ml, respectively, for the HTCO and persulfate methods.

Table 3. Recovery of added synthetic organics in natural seawater

| Organic compound	Added μM	HTCO method		Persulfate / 100 °C method	
		Found μM	Recovery %	Found μM	Recovery %
Potassium hydrogen phthalate	100	95.8	96	90	90
	200	193	96	184	92
	300	302	101	264	88
	400	396	99	368	92
Oxalic acid	100	96.3	96	87	87
	200	196	98	166	83
	300	294	98	267	89
	400	400	100	356	89
EDTA	100	93	93	90	90
	200	188	94	176	88
	300	282	94	264	88
	400	376	94	360	90
Caffeine	100	101	101	94	94
	200	198	99	172	86
	300	309	103	243	81
	400	416	104	304	76
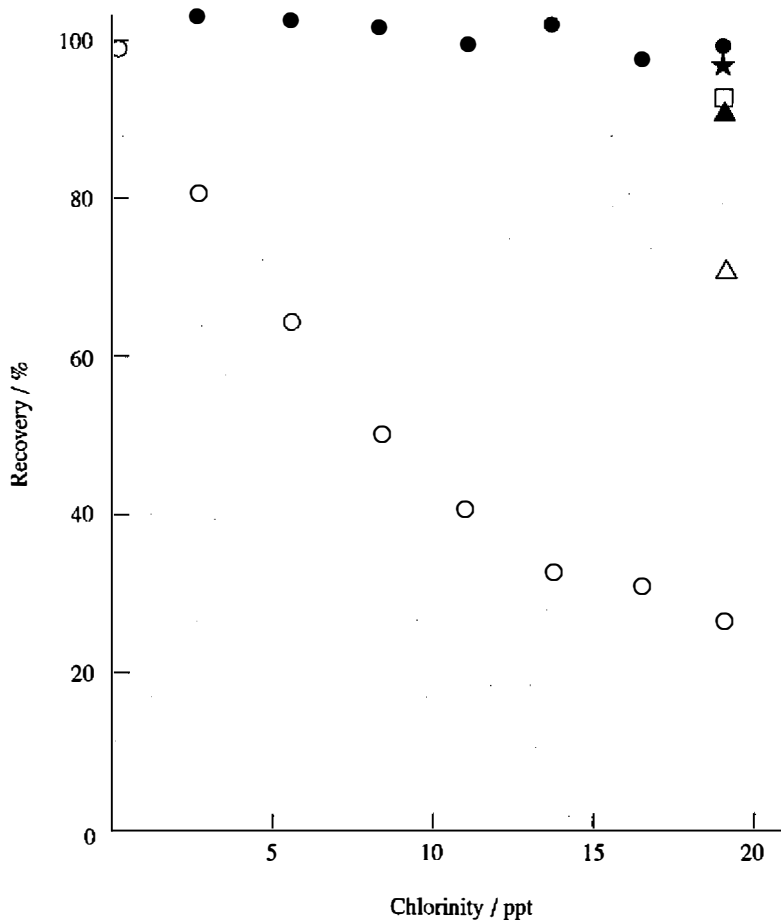
Fig. 4. Effects of chloride content, oxidant volume and reation time on the recovery of 10 ppm KHP by the persulfate method through the Model 700 of O. I. analyzer: (O) is solutions of various clorinity measured by procedures recommended by the O. I. analyzer for non-saline water (sample: 1 *ml*, oxidant: 0.5 *ml*, reaction time: 8 *min.*), (●) is measured from the modified procedures (sample: 0.5 *ml*, oxidant: 3 *ml*, reaction time: 13 *min.*), (△) is a solution of 3.5% NaCl measured by the conditions of (sample: 0.5 *ml*, oxidant: 0.5 *ml*, reaction time: 10 *min.*), (□) is measured by the conditions of (sample: 0.5 *ml*, oxidant: 1.5 *ml*, reaction time: 12 *min.*), (★) is measured by the conditions of (sample: 0.5 *ml*, oxidant: 1.5 *ml*, reaction time: 13 *min.*), (▲) is measured by the conditions of (sample: 0.5 *ml*, oxidant: 3 *ml*, reaction time: 11 *min.*).

the increase in injection volume will decrease the concentration of blank in solution, which will result in a decrease of the detection limit. However, this increase of injection volume will shorten the life of catalysts which should be replaced more frequently.

On the other hand, we did not triple the total blank of the persulfate method as the detection limit of the method because the blank was quite high (0.45 μgC), the major fraction of which was derived from reagents rather than from system noises. Meanwhile, the total blank was initially recorded in the instrument and signals of standards and

samples were then automatically offset by this value before they were used for calibration or concentration derivation. Therefore, we still use the triple intensity of system noises as the detection limit of the instrument, although the signal has been blanketed by the reagent blank (personal communication with Dr. S. R. Huang, professor of analytical chemistry, National Sun Yat-sen Univ.). It should be kept in mind, however, the concentration of DOC in seawater, which can be reliably measured, may be greater than the detection limit because the effect of a relatively high reagent blank.

d. Analysis of DOC in seawater

Sugimura and Suzuki (1988) suggested carrying out the analysis of DOC on board a ship after seawater was sampled and filtered. However, this was difficult to perform on the R/V Ocean Researcher 1 because of the limitations of ship time and rough shipboard conditions for most seasons of the year while sailing in the surrounding seas of Taiwan. Therefore, the effect of preservation on the DOC concentration should be evaluated prior to the DOC measurement at a land laboratory. For this matter the seawater sample was taken from nearshore southwestern Taiwan, immediately filtered through GF/F filters and acidified with subboiled HCl. The acidified filtrate was equally divided and stored in Pyrex glass bottles at $4\,^\circ C$ and $-20\,^\circ C$, respectively. The DOC in the samples of initial and various storage intervals was measured by the HTCO method. Figure 5 shows that the
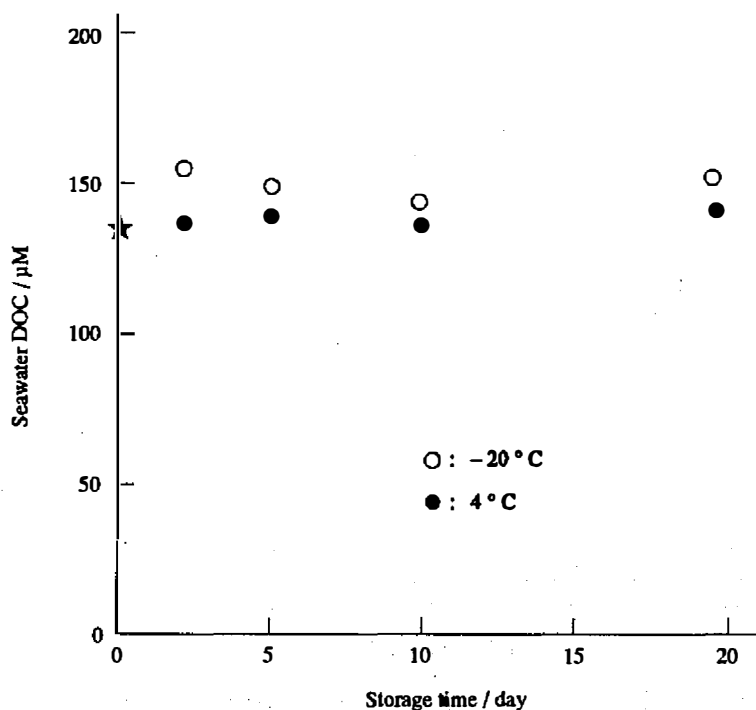

Fig. 5. Effect of sample storing intervals and temperatures ($4\,^\circ C$: ●; $-20\,^\circ C$: ○) on the concentration of DOC.

DOC concentration didn't change while samples were stored at $4\,^{\circ}C$ up to 20 days, but the DOC displayed a little increase after storage at $-20\,^{\circ}C$. No particular reason can be given for the enhancement of DOC by means of $-20\,^{\circ}C$ storage. Nevertheless, the lysis of bacteria and microplankton, which passed through the GF/F filter (nomial pore size: $0.7\,\mu m$), was possible. Thus we stored the pretreated samples at $4\,^{\circ}C$ until they were analyzed at a land laboratory. The concentrations of DOC in shelf waters off northeastern and southwestern Taiwan (Figure 1) are shown in Table 4 and Figures 6 & 7. The concentrations found by the HTCO method are higher than those measured by the persulfate method; the DOC ratio of the persulfate method to the HTCO method ranges from 56% to 76% for northeastern shelf water and ranges from 72% to 95% for a southwestern water column (st. A). The results imply that the HTCO method provides relatively complete oxidation and yields consistently higher values of DOC over the persulfate method. The concentration of DOC measured by the HTCO method decreases as salinity increases for surface water ($4\,m$) from st. 2 to st. 11 , indicating a relatively important contribution of DOC from the terrestrial source. The chemical characteristics of terrestrial DOC are somewhat different from those of marine DOC. The former is generally composed of a significant fraction of high molecular-weight geopolymer which is resistant to the persulfate oxidation. As a result, the DOC ratio of persulfate/HTCO oxidations was generally lower for northeastern shelf water than for southwestern shelf water especially for those stations closing to the mainland China and island Taiwan. Although there is no significant difference in the vertical distribution of DOC in northeastern shelf water, it does show a vertical decrease of DOC with depth at station A. A relatively high concentration of DOC in the surface layer may stem from the relatively high biological productivity which results in greater newly formed DOC and gives lower persulfate/HTCO ratios in the surface layer. The sharp decrease of HTCO-DOC below the depth of $100\,m$ may be due to the microbial degradation of downward fluxed new DOC from surface and be reflected by a relatively high persulfate/HTCO ratio. The relatively lower ratios also appearing in the depth below $500\,m$ are largely derived from the decrease of persulfate-DOC as a result of cyclings of downward fluxed DOC and sinking particles, as well as from the effect of laterally intruded water masses. Accordingly, DOC may play an important role in carbon biogeochemical cycles in the ocean (Williams and Druffel, 1987; Kumar *et al.*, 1990; Sharp, 1991).

4. CONCLUSION

The HTCO method is promising for the analysis of DOC in natural seawater. The method is suitable for shipboard measurement but it also can be carried out in a land laboratory if seawater samples are well preserved. The method measured higher DOC values than did the persulfate method , supporting the previous evidence of incomplete oxidation of DOC by the persulfate method. Both methods, however, provide useful information in the understanding of oceanic DOC biogeochemistry. Preliminary data show

Table 4. The concentration of DOC in shelf waters off northeastern and southwestern Taiwan

| Station - depth	Location N	Location E	Temperature °C	Salinity psu	DOC (μM) HTCO method (A)	DOC (μM) Persulfate method (B)	B/A (%)
1 - 20 m	26° 19'	120° 28'	26.08	30.81	186	127	68
2 - 4 m	26° 15'	120° 39'	26.22	31.63	241	134	56
3 - 4 m	26° 09'	120° 49'	26.23	31.93	182	113	62
4 - 4 m	26° 04'	121° 00'	26.40	31.71	180	113	63
5 - 4 m	25° 59'	121° 09'	26.67	31.96	156	114	73
- 20 m	25° 59'	121° 09'	26.67	31.96	169	118	70
- 75 m	25° 59'	121° 09'	26.69	31.97	154	107	70
6 - 4 m	25° 55'	121° 18'	26.51	31.96	145	104	72
7 - 4 m	25° 50'	121° 29'	26.35	32.11	148	112	76
8 - 4 m	25° 44'	121° 40'	26.24	32.13	155	114	74
9 - 4 m	25° 39'	121° 49'	26.00	32.18	154	100	65
10 - 4 m	25° 37'	121° 57'	25.18	32.28	160	103	64
- 20 m	25° 36'	121° 58'	25.19	32.27	145	105	72
- 100 m	25° 35'	121° 59'	17.38	32.63	172	115	67
11 - 4 m	25° 30'	122° 10'	—	—	155	97	63
A - 2 m	22° 20'	120° 00'	29.64	32.30	182	135	74
- 20 m	22° 20'	120° 00'	29.22	32.09	156	123	79
- 50 m	22° 20'	120° 00'	28.63	32.15	161	125	78
- 100 m	22° 20'	120° 00'	23.28	32.46	131	124	95
- 200 m	22° 20'	120° 00'	16.23	32.69	131	122	93
- 400 m	22° 20'	120° 00'	10.37	32.53	130	115	88
- 500 m	22° 20'	120° 00'	9.02	32.51	134	101	75
- 600 m	22° 20'	120° 00'	7.41	32.52	121	90.7	75
- 830 m	22° 20'	120° 00'	6.14	32.56	128	92.3	72
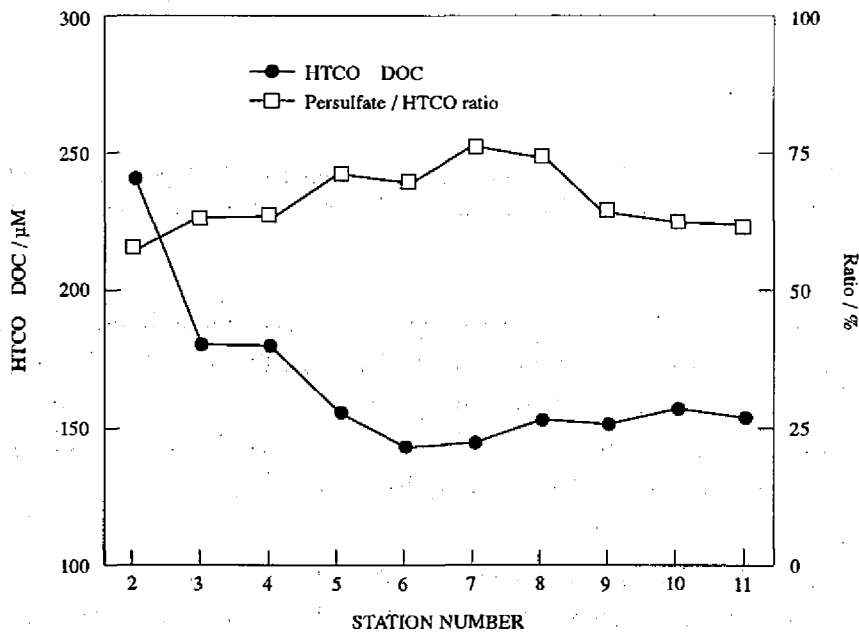
Fig. 6. Distribution of HTCO-DOC (solid circle) and persulfate/HTCO ratio (square) in shelf surface water off northeastern Taiwan.
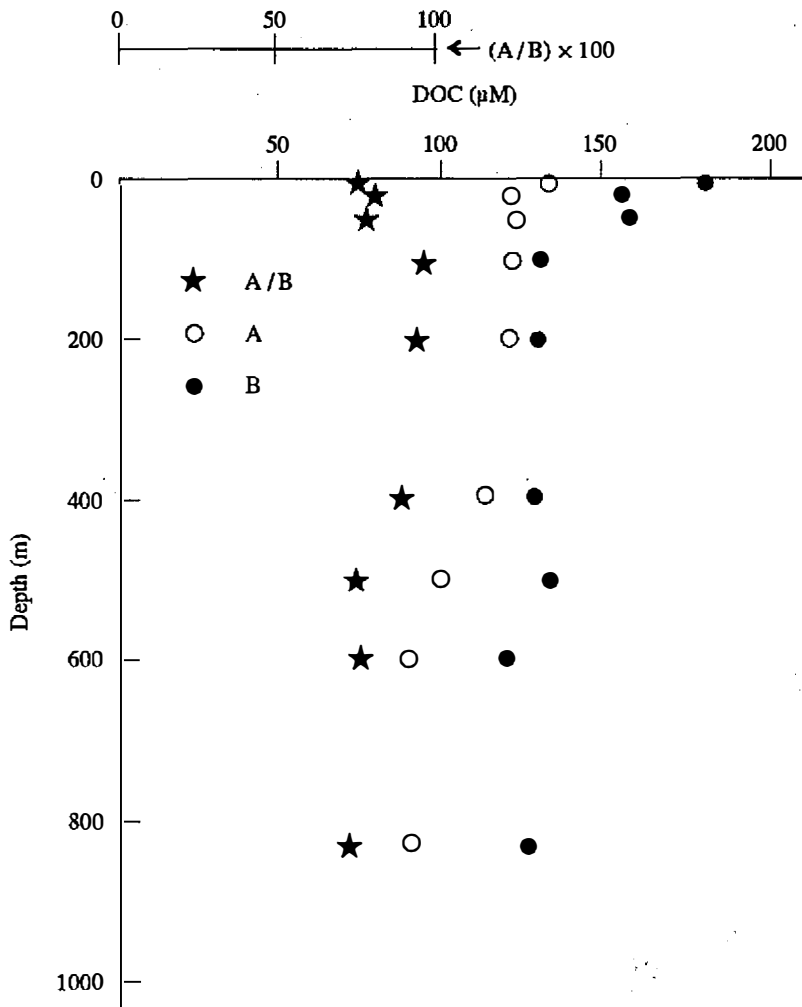
Fig. 7. Vertial profiles of HTCO-DOC (solid circle), persulfate-DOC (open circle) and persulfate/ HTCO ratio (star) in the station (22° 20'*N*, 122° 00'*E*) off southwestern Taiwan.

that the distribution of DOC was influenced by the terrestrial input, biological productivity and bacterial decomposition. The application of two methods on the detailing study of DOC in the KEEP (Kuroshio Edge Exchange Processes) related areas will be extended from this study. The spatial and temporal distributions of DOC can hopefully provide the signatures of biological productivity resulting from upwelling.

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海水中溶解性有機碳之測定:高溫催化氧化法與過硫酸氧化法之比較

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摘　　要

　　本研究旨在確定高溫催化氧化法之分析條件以測定海水中溶解性有機碳。此方法乃利用鉑／氧化鋁為催化劑在 680°C 下分解溶解性有機碳為二氧化碳,然後以非散性紅外光譜法測定二氧化碳之濃度。此方法之海水偵測下限在體積 66 μl 時約為 29.5 μMC,而其不準確度由數種有機物之海水添加試驗顯示約為 7%。此方法之偵測下限及精確度將因體積之增加而分別降低及增加。對於海水中溶解性有機碳之測定,高溫催化氧化法比過硫酸氧化法快速且可靠,但分析成本較高。若以高溫催化氧化法於陸上實驗室進行海水分析時,海水樣本需經現場過濾,酸化及儲存於不透光之 4°C 中方能測得可信濃度。高溫催化氧化法測得台灣東北及西南海域海水溶解性有機碳濃度均比利用過硫酸氧化法測得之濃度高,顯示過硫酸氧化法無法完全分解海水中有機碳。高溫催化氧化法測得台灣東北海域表水之溶解性有機碳隨鹽度之降低而增加,此表示可能陸源溶解性有機碳輸入之影響所致。另一方面台灣西南海域之一測站溶解性有機碳之分佈有隨深度漸減之趨勢,暗示溶解性有機碳分佈與生物對有機物轉換之間的相關性。利用此兩種方法分析台灣東北海域水團交換影響下之溶解性有機碳分佈將有助於溶解性有機碳特性之瞭解。