



A direct instrument comparison for measurement of total dissolved nitrogen in seawater

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Abstract

A direct comparison has been made for the measurement of total dissolved nitrogen (TDN) in seawater using high temperature combustion (HTC) instruments. A side-by-side comparison in one laboratory (Lewes exercise) was made with two hybrid total organic carbon (TOC) instruments linked to chemiluminescence detectors (CLD), a combined TOC total nitrogen (TN) instrument, and two stand-alone TN instruments. Later, a series of field samples was run in home laboratories of the participants (Homelab exercise) using four hybrid TOC–CLD systems, the combined TOC/TN instrument, and three stand-alone TN instruments. In the Lewes and Homelab exercises, samples were also run by the more established persulfate oxidation method. There was fairly good agreement (group precision) among all the HTC methods; average %CV of $\pm 12.0\%$ for five nitrogen compounds and average %CV of $\pm 7.7\%$ for five natural samples in the Lewes exercise and %CV of $\pm 10.7\%$ for 14 field samples in the Homelab exercise. In both cases, the persulfate method values were similar to those of the HTC instruments.

On a finer scale of evaluation, the stand-alone TN instruments, operating at higher combustion temperatures, gave considerably more scatter and more divergent values than the set of HTC instruments that used a singular combustion environment with a lower temperature. The five hybrid systems, with Shimadzu TOC instruments combined with five different CLD systems and employing individual integration programs, gave a group precision of $\pm 5.8\%$ for the field samples. These systems also provided simultaneous dissolved organic carbon (DOC) concentrations, and the DOC group precision for the 14 samples was $\pm 5.9\%$. Our conclusion is that the five Shimadzu instrument systems provide more accurate TDN measurements than the stand-alone instruments. However, when subtracting inorganic nitrogen (DIN) to calculate dissolved organic nitrogen (DON), there is not good agreement, especially for deep ocean samples. The persulfate method gave slightly higher TDN concentrations for the field samples than the Shimadzu HTC averages, indicating a possibility of incomplete conversion of some nitrogen compounds by the HTC instruments and/or peak integration problems. The inequity with persulfate oxidation and the scatter with the HTC methods require further investigation. A new broad community DON comparison is currently underway

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which includes TDN and DIN analyses. In addition, several of us are informally collaborating to improve and evaluate routine analysis with HTC instrumentation.

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1. Introduction

It was suggested almost 2 decades ago (Suzuki et al., 1985) that high temperature combustion (HTC) analysis gave greater yields for dissolved organic nitrogen (DON) than the, then established, wet chemical oxidation (WCO) methods. Later, Suzuki (1993) retracted his suggestion and several other publications have shown little difference in complete recovery of DON by HTC compared to WCO (Walsh, 1989; Bronk et al., 2000; Sharp et al., 2002a). However, in those comparisons, the variability from multiple analyses of single samples was too large for precise determination of DON. Until recently, the majority of laboratories performing routine total dissolved nitrogen (TDN) analyses have used WCO methods. In the most recent comparison with a large number of analyses (Sharp et al., 2002a), the group of HTC methods showed a tighter fit than the group using persulfate oxidation or UV oxidation. That apparently more consistent result, plus the easier overall analysis, and potential for simultaneous DOC and TDN analysis, made further exploration of HTC method desirable.

Several laboratories have used homemade combustion systems (Hansell, 1993) or Shimadzu TOC analyzers linked to chemiluminescence detectors (CLD) for seawater analysis of TDN (e.g., Lopez-Vernoni and Cifuentes, 1995; Alvarez-Salgado and Miller, 1998; Ogawa et al., 1999; Cauwet, 1999). Also, several laboratories have used stand-alone HTC TDN analyzers (e.g., Walsh, 1989; Seitzinger and Sanders, 1997; Burdige and Zheng, 1998; Nausch et al., 2002). These successes represent progress over the situation in the early 1990s (Hopkinson et al., 1993) when few laboratories had established HTC systems.

This paper describes an effort to explore HTC methodology for routine TDN analysis with the hope that it can provide guidance in the near future. Several instruments were set up in our laboratory at the University of Delaware (Lewes, DE, USA) during September 2001 for comparison of instruments and

consultation among analysts who had previously used them (Lewes exercise). We were able to make side-by-side comparisons of several combustion systems, CLDs, and plumbing connecting the combustion systems to CLDs. Some of the systems for the Lewes exercise were from published works, but it was not possible to include all those used previously by the participants. Three new instruments or models that had not been well tested with seawater were also included. In November 2001, multiple aliquots of samples were collected and sent to the laboratories of the participants after they had established their instruments in good operating order in their home laboratories; this Homelab exercise included a larger number of instruments. The results of both exercises are reported here.

2. Instruments and methods

All the instruments used in both the Lewes and Homelab exercises are listed in Table 1. For the Lewes exercise, there were two hybrid systems that linked Shimadzu TOC-5000 instruments to chemiluminescence detectors from other manufacturers. Both of these hybrid systems had been used successfully elsewhere for seawater analysis and had been described in the literature (cited above). The Shimadzu TOC-5000 has become the most popular instrument internationally for seawater DOC analysis (Sharp et al., 2002b); a number of laboratories have used or are trying to use hybrid systems with this combustion system. The new Shimadzu TOC-V instrument, not previously used for seawater analysis, was also employed in this exercise. Since the combustion system is very similar to that of the earlier TOC-5000 model, similar instrument performance was expected. The new Antek 9000N was used in the Lewes exercise by participants who had used the Antek 7000B instrument previously. It should be noted that this instrument had significant design changes from the previous model and had not been previously used for seawater

Table 1
Instruments used in the two comparison exercises (Lewes, Homelab)

Instrument	Used	ID	HTC system	CLD system	Temperature/Catalyst
5000-Sievers	Lewes, Homelab	A	Shimadzu TOC-5000	Sievers NOB 170	680/Pt coated alumina
5000-Antek	Lewes, Homelab	B	Shimadzu TOC-5000	Antek 7050	680/Pt coated alumina
TOC-V	Lewes, Homelab	C	Shimadzu TOC-V	Shimadzu TNM	680/Pt coated alumina
5000-Yanaco	Homelab	D	Shimadzu TOC-5000	Yanaco TN7	680/Pt coated alumina
5000-Skalar	Homelab	E	Shimadzu TOC-5000	Skalar ND-10	680/Pt coated alumina
Skalar (old)	Homelab	F	TOC/TN _b with ND-10	Integral	850/CoCr
Skalar (new)	Lewes	G	TOC/TN _b with ND-10	Integral	850/CoCr
Antek (old)	Homelab	H	Antek 7000B	Integral	1000/ceramic insert
Antek (new)	Lewes	I	Antek 9000N	Integral	1000/ceramic insert
Dohrmann	Homelab	J	Dohrmann DN1900	Integral	850/Co
Persulfate	Lewes, Homelab	K	–	–	–

The instrument for the combustion step is indicated as “HTC system” and the chemiluminescence detection is shown as “CLD system”. Temperature indicates the combustion temperature (°C) and Catalyst indicates catalyst used in the combustion. The ID is for the identification of the system (or method) used. Four of the instruments (A, B, D, E) were essentially hybrids of TOC analyzers with separate CLDs; instrument C is sold as two components. The model number of the stand-alone total nitrogen instruments (F, G, H, I, J) is indicated in the HTC system; these had their own CLD detectors (“integral”).

analysis. A new version of the Skalar Formacs^{HT} TOC/TN_b Analyzer was used in the Lewes exercise, operated by participants who had experience with an earlier version of the instrument.

For the Homelab exercise, the Shimadzu–Sievers and Shimadzu–Yanaco were used in the laboratories that originally established these hybrid systems. The Shimadzu–Antek and Shimadzu TOC-V systems were relatively new to the operator using them and the hybrid Shimadzu–Skalar system was a new approach for its operator. The stand-alone Antek, Skalar, and Dohrmann instruments were used by operators who had previous experience with them. In both exercises, the emphasis on Shimadzu instruments is the result of more analysts in the international marine community using them than any other instrument for both DOC analysis and for combustion systems for TDN analysis. Although the goal of this exercise was to compare HTC instruments, the persulfate analysis (Solorzano and Sharp, 1980; Pujo-Pay and Raimbault, 1994; Pujo-Pay et al., 1997) was also used as a check with an established method.

3. Samples and design of comparison

3.1. Lewes laboratory comparison

All instruments were set up in the Lewes laboratory (University of Delaware) in September 2001 for

direct comparison of operation details and for measurement comparison of known samples. In this exercise, instruments were transported and set up just prior to use with analysts working under slightly different conditions than usual. In addition, most of the instrument models or hybrid instruments were new for the operators.

For this comparison, standards were prepared daily using Millipore Milli-Q TOC⁺ water; the same water was used for the blank. Standards were made with a combination of KHP for carbon and KNO₃ for nitrogen. The same set of standards and blanks were used by all analysts to avoid variability in standardization. To evaluate whether there was complete conversion to the final analyte, five nitrogen compounds were used as pure substances. The compounds were EDTA, ammonium sulfate, urea, potassium nitrate, and acetanilide. Each solution was made to contain 10 μM N. These were run on 2 days made in Milli-Q TOC⁺ water and on a third day in low DOC/TDN seawater. Sealed ampoules of the TDN intercalibration samples used in the broad community method comparison (Sharp et al., 2002a) were also analyzed.

3.2. Homelab comparison with samples from the field

Field samples were collected in November 2001 and sent frozen to participants in their home laboratories for comparison after instrument performance was optimized. The samples were collected along a

gradient of estuarine, surface coastal, and deep continental slope environments. Four of the samples (stations 20–26) came from lower Delaware Bay in a salinity gradient from 15 to 30 (on psu scale). A transect from Delaware Bay along the continental shelf to slope waters included four surface samples (stations 51, 53, 54, 55). At the last station, a seven-depth profile to 1900 m was taken. Table 2 gives information about the 14 samples that were collected. Analytical methods used are routine for our sampling of these waters (Sharp et al., 1982; Fogel et al., 1992). As can be seen in Table 2, although there is a slight gradient, the four surface offshore stations all have very low nutrient, particulate carbon, and chlorophyll values.

Water samples, collected in Niskin bottles, were filtered through GF/F filters. Aliquots of the filtrate were transferred by volumetric pipette to 50-ml glass ampoules for persulfate TDN analysis and to HDPE bottles for nutrient analysis. A portion of the filtrate was transferred to an aspirator bottle and acidified at 1/1000 with concentrated “trace metal grade” HCl for the HTC TDN samples. Samples of 5 or 30 ml were collected from the aspirator bottle in glass ampoules (10- and 50-ml size, respectively). Ampoules were

immediately sealed with a propane torch (procedure for filling ampoules and sealing as in Sharp et al., 2002b). All nutrient and TDN samples were quick frozen on dry ice and stored frozen. Frozen samples were later shipped to the participants and were stored frozen until analysis.

3.3. Statistical analyses

To determine consistency among groups of methods (or instruments), we used the concept of “group precision”. This is the pooled replicate precision for a set of samples analyzed by a group of methods. For the calculation, the mean value from a single method (e.g., method A) for an individual sample (e.g., sample 1) is averaged with all other methods (e.g., B...E) for that sample. From the mean and standard deviation for the n different methods, a %CV is calculated for that individual sample. Finally, a mean %CV is calculated for the set of samples analyzed by that group of methods in the comparison. The value of the group precision is to compare different groups of methods, e.g., comparing wet chemical oxidation methods to high temperature combustion methods employed for a set of samples.

Table 2
Samples for Homelab TDN comparison

Sample (m)	Temp	Sal	DO	% Sat	DIC	NO ₂ ⁻	NO ₃ ⁻	NH ₄ ⁺	PO ₄ ⁻³	Si	Chlor	Part C	Part N
20 (1)	16.73	15.22	515	93	1450	0.62	61.3	2.9	2.29	38.4	3.01	36.95	4.5
22 (1)	16.71	21.24	533	100	1625	0.97	39.1	3.03	1.62	21.0	2.20	36.6	5.34
24 (1)	16.92	26.66	567	110	1767	1.14	16.1	2.02	0.54	3.3	4.20	58.55	8.98
26 (1)	17.27	29.56	546	108	1876	1.06	6.71	3.12	0.49	3.5	3.56	53.62	7.78
51 (9)	17.82	32.60	520	106	1950	0.01	0.04	0.13	0.20	1.3	0.92	13.76	2.08
53 (9)	17.98	33.59	514	107	1965	0.01	0.01	0.71	0.10	0.9	0.16	7.12	0.97
54 (8)	20.20	34.95	493	107	–	0.01	0.01	0.18	0.02	1.1	0.11	4.98	0.62
55 (8)	21.61	35.71	478	101	2005	0.00	0.06	0.2	0.00	1.9	0.08	4.07	0.51
55 (43)	20.95	35.70	460	73	2015	0.05	0.70	0.18	0.04	4.5	0.62	4.06	0.5
55 (101)	14.88	35.85	371	55	2112	0.02	12.9	0.17	0.66	10.1	0.01	1.4	0.18
55 (247)	10.50	35.32	305	73	2148	0.01	24.0	0.21	1.27	16.1	–	0.8	0.1
55 (498)	6.06	35.02	450	85	–	0.01	21.5	0.07	1.30	15.8	–	1.12	0.11
55 (800)	4.37	34.95	551	84	2130	0.01	18.9	0	1.11	14.9	–	0.6	0.06
55 (1900)	3.67	34.92	555	106	2125	0.01	18.0	0.07	1.10	17.9	–	1.51	0.13

Sample stations are listed with depth of individual samples. Stations 22–26 are routinely sampled locations in the lower Delaware Bay; Stations 51, 53, and 54 are from a transect across the North Atlantic Ocean continental shelf from near the mouth of the Delaware Bay to the shelf break, Station 55 is in 2500 m slope waters. Temperature (Temp, in °C) and salinity (Sal, on Practical Salinity Units scale) are from CTD, all other parameters from analyses of samples collected in Niskin bottles. Dissolved oxygen (DO) is in µg at O/L units and also the computed saturation is given (% Sat). Dissolved inorganic carbon (DIC) is listed as µM C. The nutrients nitrite, nitrate, ammonium, phosphate, and silicate are all listed in µM units for the individual element. Chlorophyll a (Chlor) is given in units of µg/l. Particulate carbon and nitrogen (Part C, Part N) are given as µM C and µM N, respectively.

To test whether means of groups of analyses were significantly different from each other, simple *t*-tests were used based on homoscedastic distributions. One-sample *t*-tests were used to test groups of analysis against known or fixed values; two-sample *t*-tests were used to test groups against each other.

4. Results

4.1. Lab comparison with TDN intercalibration samples and known compounds

This exercise was carried out during September 2001. Two days were allowed to get all the instruments stabilized and running. With the Antek 9000 instrument, standard curves based on DI water were linear and consistent, but there were serious problems with seawater samples; results from this instrument were not used. Most of the results from other instruments for the 3 days of operation were used. Results from the Shimadzu–Antek combination were marred by integration problems and only those results from 1 day were used in the comparison. Otherwise, all data from all four instruments and the persulfate method were used with only three extreme outlier values excluded (in each case, the value was considerably lower than the measured value from the other 2 days by the same method and there was reason to suspect sample loss).

Results for the five known nitrogen compounds indicate that the methods gave comparable results. For the five compounds, the group precision for the four HTC instruments was $\pm 12.0\%$. Using one-sample *t*-test, all five compounds were completely recovered within 95% confidence interval (expected value of 10 $\mu\text{M N}$). However, a relatively large degree of scatter was produced when averaging the four methods. Looking at the individual data, recovery for NH_4 and urea was below expected values on most days by three of the HTC instruments (values of 6.1–8.8 μM) while the other three compounds showed values close to 10 μM by all instruments on all runs (range for all individual values of 7.5–11.9 μM). The Shimadzu TOC-V instrument appeared to give good recovery for NH_4 and urea (averages of 9.6 and 9.3 μM , respectively) as well as the other compounds (averages of 9.7–11.1 μM). The persulfate method

showed complete recovery for all five compounds on each day (averages of 9.8–10.7 μM for the five compounds).

The TDN intercalibration samples were also run on two of the days by each of the five methods. None of the five methods appears to give results divergent from the others. Mean values and %CV for the TDN samples measured by the four HTC methods are given in Table 3; also, results from the persulfate analysis are shown. To compare to previous analyses of these samples, the HTC and persulfate data from Sharp et al. (2002a) are also shown in Table 3. Using two-sample *t*-tests (95% confidence interval), the HTC results from this study (based on replicate runs on 2 days by the four instruments) are not significantly different from those of the previous study (based on means and standard deviations from nine separate instruments). Similarly, the persulfate data from this study (means of two runs) are not significantly different from those of the previous study (from means of 13 separate methods). In a third *t*-test, the HTC and persulfate data of this study showed no significant difference. The mean percent precision for the four HTC instruments is 7.7% compared to 6.9% for nine HTC methods in previous analyses. It should be noted that the %CV values for individual samples were relatively large so that statistical analyses are not as rigorous as it might be where the variability for individual samples was smaller.

Table 3
Results of the TDN intercalibration samples in the Lewes exercise (this study)

Sample	HTC instruments				Persulfate methods			
	Previous		This study		Previous		This study	
	Mean	%CV	Mean	%CV	Mean	%CV	Mean	
CSW	6.4	5.1	5.9	14.2	6.8	23.6	6.8	
SBW	14.7	5.4	14.1	4.7	15.7	10.6	16.3	
DSS	22.6	6.8	22.1	3.5	23.9	8.5	21.4	
CPN	17.7	6.1	16.7	8.2	18.8	11.8	17.9	
FHW	22.6	11.0	21.5	7.8	22.6	9.0	21.1	
Average		6.9		7.7		12.7		
		%CV						

The five TDN reference samples prepared for the previous TDN comparison (Sharp et al., 2002a) were used for this exercise. The results are given for the four HTC systems (with %CV) and the persulfate oxidation method of this study. The means and %CVs for the HTC and the persulfate methods in the previous comparison are given for reference.

4.2. Comparison of analyses of field samples

Eight sets of TDN analyses from HTC instruments and results from the persulfate oxidation method are given in Table 4. Because of difficulties with the Dohrmann instrument (J), only half of the samples were run successfully on this instrument. The HTC methods can be viewed in two sets, the five that used the Shimadzu combustion (sample sets A–E) and the three that were stand-alone TDN instruments with individual combustion conditions (sample sets F, H, and J). The Shimadzu systems were all operated with the same combustion temperature and catalyst. The stand-alone systems were all operated at higher combustion temperatures and did not use Pt as the catalyst (see Table 1 for details). The Skalar and Dohrmann instruments were also designed for TOC analysis but with a different catalyst than those used here for TDN analysis.

The agreement for TDN analysis among the HTC instruments appeared to be good. In comparing just the Shimadzu systems, the Skalar CLD hybrid appeared to have a few sample values that were outliers compared to all others. By averaging the TDN values of the other

four instruments, three of the Shimadzu–Skalar sample values were 20% or more higher than those mean values. These were removed from further analyses (shown as bold in Table 4). With all eight HTC methods, the group precision was $\pm 10.7\%$. If only the five Shimadzu systems are considered, this group precision becomes $\pm 5.8\%$, indicating more similarity among the five HTC systems that shared a single set of combustion conditions. Thus, it appears that there was no appreciable difference caused by using the five different CLD detectors of these hybrid systems. It should be noted that, regardless of the total TDN concentration, the %CVs for individual samples were relatively uniform for the five Shimadzu systems (Table 4).

Compared to the five Shimadzu combustion systems, the Skalar TN instrument gave higher values for all samples; the Antek TN instrument gave higher values for samples with high TDN, comparable values for those in the mid-region, and lower values for samples with low TDN; the Dohrmann TN instrument gave slightly lower values for about half the samples run (but only samples in the mid- and lower TDN range were analyzed). In the past, we have shown that the

Table 4
TDN results for Homelab comparison

Sample (m)	Instrument or method									For five Shimadzu systems			
	A	B	C	D	E	F	H	J	K	Mean	SD	%CV	Average %CV
20 (1)	78.0	75.9	84.2	85.4	85.8	94.1	94.3		84.9	81.9	4.59	5.60	5.18
22 (1)	52.5	51.0	56.3	58.2	57.2	62.3	61.3		59.9	55.0	3.12	5.66	
24 (1)	28.9	29.2	32.1	31.1	29.5	31.7	31.3		31.3	30.2	1.38	4.58	
26 (1)	20.3	21.4	23.2	21.3	21.2	23.7	19.9		23.1	21.5	1.04	4.86	
51 (9)	7.2	7.1	7.6	6.9	8.7	8.0	4.6		9.3	7.2	0.30	4.11	6.18
53 (9)	6.7	6.4	6.8	5.9	6.8	8.0	5.2		7.9	6.5	0.38	5.82	
54 (8)	5.8	5.3	5.7	5.0	6.3	6.8	3.0		6.5	5.6	0.47	8.44	
55 (8)	5.2	5.1	5.2	4.6	6.6	6.1	3.0	5.2	6.6	5.0	0.28	5.66	
55 (43)	6.2	5.8	6.2	5.2	6.0	6.4	3.3	4.5	6.9	5.9	0.41	6.88	
55 (101)	15.1	14.1	14.8	15.4	16.8	16.3	15.6	12.9	17.9	15.2	1.00	6.53	5.80
55 (247)	25.3	25.7	24.8	26.8	30.5	27.6	25.1	25.2	27.3	25.7	0.84	3.29	
55 (498)	22.4	22.5	22.2	23.8	25.7	24.7	25.2	21.2	25.1	23.3	1.48	6.33	
55 (800)	19.5	20.1	19.2	21.1	23.1	21.3	20.9	18.6	22.8	20.6	1.57	7.60	
55 (1900)	18.2	19.5	18.7	20.5	20.4	20.9	20.2	19.6		19.5	1.02	5.24	

Sample indicates the station with depth in m in parentheses. The Shimadzu instruments are: A—with Sievers detector, B—with Antek detector, C—Shimadzu TOC-V, D—with Yanaco detector, and E—with Skalar detector. The stand-alone instruments are: F—Skalar, H—Antek, and J—Dohrmann. The persulfate method is K. More detail about the instruments is given in Table 1. Difficulties with the Dohrmann instrument allowed running only half of the samples. Samples were run by persulfate from the same ampoules used for one of HTC instruments, and the last ampoule did not have sufficient sample remaining. Three of the analyses by the Shimadzu–Skalar system were outliers (see text) and are shown in bold.

persulfate oxidation method, performed carefully, can give values comparable to those of HTC instruments (Sharp et al., 2002a). The persulfate data shown in Table 4 are similar to those of the HTC methods, but all have slightly higher TDN concentrations than the average of the HTC instrument. A one-sample *t*-test of the means and standard deviations of the five Shimadzu HTC systems compared to the single sample persulfate data show 10 of the 13 samples to be significantly higher by the persulfate method; samples 20, 24, and 55(498) were not significantly higher (Table 4).

The Shimadzu systems have the added advantage of simultaneously measuring DOC as well as TDN. DOC data from the five Shimadzu systems are shown in Table 5. By averaging the %CV values for each sample, the group precision for the 14 samples is $\pm 5.9\%$. Four of the five analysts also reported specific values for the DOC reference material run with the samples, the fifth analyst analyzed the reference and found the value within the range of 44–48 μM normally experienced, but did not report the actual value. Reference use is critical to make sure the instrument is running well when the analysis is being performed. As a sensitivity exercise, the raw

data for the five sets of DOC analyses were adjusted to a perfect fit of the calibrated value of 44.0 μM for the DSW reference, i.e., adding or subtracting to each value an amount equivalent to the difference between the measured value and 44. These adjusted data give a group precision of $\pm 3.7\%$ (Table 5). This adjustment of data was performed only to emphasize the value of the reference materials; it does indicate that it might have been possible to get a concurrence of data even closer than that achieved if an analytical run was delayed until the instrument gave closer to the expected value for the reference.

Dissolved inorganic nitrogen (DIN) concentrations were determined in the lab of the first author; values are shown in Table 2 along with other nutrient data. Nitrate plus nitrite analysis is routinely performed in our laboratory with a replicate precision on the order of $\pm 0.03 \mu\text{M N}$ for sample concentrations less than 10 $\mu\text{M N}$ and about $\pm 0.2 \mu\text{M N}$ for higher concentrations; ammonium analysis is usually performed with a precision of $\pm 0.05 \mu\text{M N}$. None of the other laboratories did exhaustive nutrient analyses and most do not routinely analyze nutrients at surface ocean low-level concentrations. Two of the other labs did analyze for nitrate plus nitrite for the higher concen-

Table 5
DOC data from the five Shimadzu systems in the Homelab exercise; all values are as $\mu\text{M C}$

Sample (m)	Instrument					From raw data			From adjusted data		
	A	B	C	D	E	Mean	SD	%CV	Mean	SD	%CV
20 (1)	227.0	232.7	232.3	229.9	234.6	231.3	2.95	1.27	230.4	3.44	1.59
22 (1)	210.1	206.3	207.1	209.7	205.8	207.8	1.96	0.94	205.2	3.31	1.69
24 (1)	177.9	178.5	179.5	178.9	176.6	178.3	1.11	0.62	176.4	4.08	2.42
26 (1)	152.2	146.4	148.8	147.1	148.9	148.7	2.22	1.50	145.8	2.91	2.09
51 (9)	106.2	91.9	98.3	103.1	102.8	100.5	5.55	5.53	96.9	2.94	3.04
53 (9)	94.0	85.4	84.6	87.5	90.0	88.3	3.83	4.33	84.7	1.08	1.28
54 (8)	88.5	77.0	77.0	81.9	82.9	81.5	4.79	5.88	77.5	0.33	0.43
55 (8)	84.5	74.6	72.9	78.6	79.9	78.1	4.56	5.84	74.3	0.92	1.23
55 (43)	78.7	75.2	70.9	82.3	77.7	77.0	4.24	5.51	74.4	3.35	4.50
55 (101)	58.1	51.1	50.4	65.9	55.4	56.2	6.29	11.19	53.5	5.64	10.54
55 (247)	52.2	47.2	45.4	61.8	58.6	53.0	7.09	13.36	51.1	5.45	10.66
55 (498)	49.7	43.2	42.6	48.0	56.1	47.9	5.49	11.46	45.3	3.51	7.75
55 (800)	49.9	46.4	44.2	50.9	52.5	48.8	3.40	6.96	46.3	1.29	2.78
55 (1900)	53.8	44.8	44.4	48.4	49.9	48.3	3.86	8.01	44.7	0.55	1.23
DSW	42.6/43.3		43.8	48	49.6	Average %CV=5.89			Average %CV=3.66		

The instruments are identified in Table 1. For four of the data sets, the DOC reference samples were recorded as part of the analysis; the value for the reference is given in row DSW; for instrument A, the values were reported as “OK”, indicating between 44 and 48 $\mu\text{M C}$; for instrument B, the run was split over 2 days. The raw data statistics show the values for the four sets of data in which the DSW was run; the adjusted data statistics are based on adjusted values for each set of analyses where the calculated DOC concentration is adjusted to a DSW reference value of 44. Baseline stability problems occurred during analysis by instrument D, especially for samples 55(10), 55(45), 55(100), and 55(250); see text.

tration samples (estuarine and deep Station 55 samples, where $>5 \mu\text{M}$ was found), which agreed well with that of the primary laboratory; the %CV for the three independent analyses of the nine samples was $\pm 2.8\%$.

DON concentrations were calculated by subtracting the single set of DIN concentrations from the TDN values (Table 6). After subtraction of the DIN, the same standard deviation for a group of analyses gives a larger %CV since the resultant DON is smaller than the TDN value. The average %CV for DON of the 14 samples on the five Shimadzu instruments is $\pm 33\%$ as contrasted by the %CV for the TDN of $\pm 5.8\%$; Table 6 shows average %CVs for groups of the samples. The deep ocean samples (101–1900 m) have standard deviations on the order of $1\text{--}1.5 \mu\text{M N}$, but since derived DON values are of similar magnitude, this gives an average %CV of $\pm 70\%$. This group of samples had DIN concentrations of $13.1\text{--}24.2 \mu\text{M}$ with average calculated DON values of $1.4\text{--}2.2 \mu\text{M}$. The estuarine samples, with DIN concentrations of $11\text{--}65 \mu\text{M}$ and average calculated DON concentrations of $10.6\text{--}17 \mu\text{M}$, showed an average %CV of $\pm 18.9\%$ for the five instruments. The shallow oceanic samples showed an average %CV of $\pm 6.7\%$ for the five instruments. These samples had DIN concentrations ranging from 0.18 to $0.93 \mu\text{M}$ with average

calculated DON concentrations of $4.8\text{--}7 \mu\text{M}$. In contrast, the three groups of samples show fairly uniform %CVs for TDN in the $\pm 5.2\text{--}6.2\%$ range (Table 4). Clearly, derived DON group precisions are not as good when the DON values are low and the subtracted DIN values are high, but are comparable to TDN precisions when DIN concentrations are very low (surface ocean samples).

5. Discussion and conclusions

In the Lewes exercise, the four HTC instruments were not operating as well as would be desired and thus results gave relatively high variability. However, within that variability, the results did show complete recovery of all known compounds within statistical limits. Also, all showed reasonable results for the TDN intercalibration samples of Sharp et al. (2002a). In the Homelab phase of this instrument comparison, better tuning and more established conditions in the home laboratory improved chances for complete conversion of all nitrogen.

For the 14 field samples, group precision in measuring TDN for the eight HTC systems was $\pm 10.7\%$. The three stand-alone TN instruments, with higher combustion temperatures and a different combustion

Table 6
DON data (as $\mu\text{M N}$) for the eight HTC instruments and the persulfate method (K) in the Homelab exercise

Sample (m)	DIN	DON for instrument or method									For five Shimadzu systems			
		A	B	C	D	E	F	H	J	K	Mean	SD	%CV	Average %CV
20 (1)	64.80	13.2	11.1	19.4	20.6	21.0	29.3	29.5		20.1	17.1	4.59	26.89	18.9
22 (1)	43.14	9.4	7.9	13.2	15.1	14.1	19.2	18.2		16.8	11.9	3.12	26.18	
24 (1)	19.24	9.6	10.0	12.9	11.9	10.3	12.5	12.1		12.0	10.9	1.38	12.66	
26 (1)	10.89	9.5	10.5	12.3	10.4	10.3	12.8	9.0		12.2	10.6	1.04	9.85	
51 (9)	0.18	7.0	6.9	7.4	6.7	8.5	7.8	4.4		9.2	7.0	0.30	4.22	
53 (9)	0.73	5.9	5.7	6.0	5.2	6.1	7.3	4.5		7.1	5.8	0.38	6.56	
54 (8)	0.20	5.6	5.1	5.5	4.8	6.1	6.6	2.8		6.3	5.4	0.47	8.75	
55 (8)	0.26	5.0	4.8	4.9	4.3	6.3	5.8	2.7	4.9	6.3	4.8	0.28	5.97	
55 (43)	0.93	5.2	4.9	5.3	4.3	5.1	5.5	2.4	3.5	6.0	5.0	0.41	8.17	
55 (101)	13.09	2.0	1.0	1.7	2.3	3.7	3.2	2.5	-0.2	4.8	2.2	1.00	46.24	70.4
55 (247)	24.18	1.2	1.5	0.6	2.6	6.3	3.4	0.9	1.0	3.1	1.5	0.84	57.05	
55 (498)	21.57	0.8	0.9	0.6	2.2	4.1	3.1	3.6	-0.4	3.5	1.7	1.48	84.56	
55 (800)	18.87	0.7	1.2	0.3	2.2	4.2	2.4	2.0	-0.3	3.9	1.7	1.57	90.09	
55 (1900)	18.08	0.1	1.4	0.6	2.4	2.3	2.8	2.1	1.5		1.4	1.02	74.02	

The instruments are identified in Table 4. The three data from analysis set E that were removed in Table 4 are shown in bold. Statistics for the five Shimadzu systems (A–E) are shown with average %CV values for the estuarine samples, the shallow oceanic samples, and the deep oceanic samples. DIN data are also shown (second column) for perspective.

environment than the Shimadzu systems, gave greater variability than the five Shimadzu systems. For those five systems sharing essentially identical combustion chemistry and temperature, the group precision was $\pm 5.8\%$. Possibly, the well-established and robust combustion system with salt removal at the front of the combustion environment gave more consistent chemistry. A seven-sample depth profile of the data from these five analyses is shown in Fig. 1 with error bars for the means by multiple analyses. This agreement is a slight improvement over the $\pm 6.9\%$ shown previously for HTC methods in the larger community comparison (Sharp et al., 2002a) but is a large improvement over the group precisions of persulfate and UV methods in that comparison. Thus, it is confirmed that relatively new HTC methods as a family have potential for better group precision than the more established older persulfate and UV methods. This is partly due to the more efficient and reproducible nature of the combustion environment and the fact that less manipulation is needed; essen-

tially, more “user-friendly” methods. With both the hybrid Antek and Skalar methods, new and unfamiliar peak integration programs were employed; more experience and better peak integration programs could further improve analysis with these instruments. This was the first use of the Shimadzu TOC-V, and tuning of that instrument probably will give more reliable results. Two of our laboratories now have that instrument and we are coordinating with several other marine laboratories that also have Shimadzu TOC-V instruments to improve operating protocols for more reliable performance in seawater measurements. Agreement on DOC concentrations by these Shimadzu instrument systems further emphasizes that there is probably complete degradation of all the organic matter in the combustion stage.

In evaluating the resulting DON data, samples with subtraction of low DIN concentrations give more consistent DON values than those with high DIN. The three groupings of samples (Table 6) may give some information on errors in the analysis. The deep ocean samples have high DIN (as nitrate) and very low DON, while the estuarine samples have moderately high DON and high DIN (nitrate plus some ammonium). With higher overall TDN, the estuarine samples give better agreement than the deep ocean samples. Station 26 with a similar TDN to the deep station 55 samples (101–1900 m) shows much better DON agreement among the five instruments than the deep samples. Also, the deep ocean concentration of DON derived for instruments A, B, and C is lower than expected from the literature (Table 6). Explanations include incomplete recovery of nitrate in these instruments, standardization problems, and peak integration problems. It is possible that standardization with a pure compound gives slightly different standard peak shapes than those of samples. Instrument system D was the most established in this comparison while instrument systems B, C, and E were new to the laboratories using them. More familiarity with HTC instrument systems allows continual small changes that give improved reliability. Iterative improvement was seen over a period of several years with the international community adoption of the Shimadzu TOC-5000 instrument as the norm for oceanic DOC analysis (Sharp et al., 2002b).

Further evaluation of the DON data was achieved by comparing %CV values to the TDN concentration

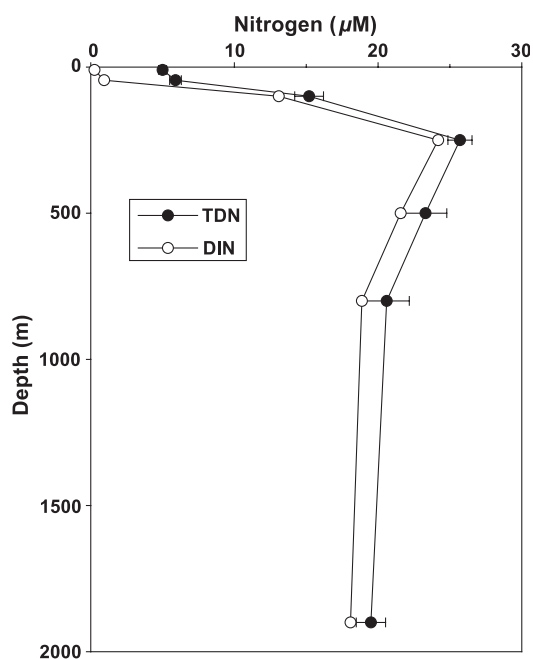


Fig. 1. A depth profile of TDN measurements in Atlantic Ocean continental shelf waters. The TDN values are means of the five Shimadzu HTC systems; error bars represent the average %CV for one standard deviation for each sample by the five analyses. Dissolved inorganic nitrogen (DIN) values are also shown.

(arranging the 14 samples by increasing TDN concentration) for groups of analyses (Fig. 2). The Shimadzu system instruments appear to have similar %CV values independent of TDN concentration. When all eight HTC systems plus the persulfate method are compared, the variability at low TDN concentrations is larger than that for higher TDN. This is largely caused by the high variability of the stand-alone HTC instruments, variability that is very high (%CVs of >30%) for the surface offshore samples with very low DIN and low DON. In contrast, the stand-alone instruments show very good comparability (%CVs of 1% or less) at high TDN concentrations (>30 μM), where DIN is high and DON is moderately high. It should be noted that these instruments have been used primarily for high TDN concentration samples in the past (Burdige and Zheng, 1998; Seitzinger and Sanders, 1997; Nausch et al., 2002).

With the simultaneous measurement of DOC and TDN using the Shimadzu instruments, it was possible to compare DOC data in this exercise. The group precision for the 14 samples by the five methods was $\pm 5.9\%$ (Table 5). This is almost identical to the $\pm 6\%$ shown for the “ten best Shimadzu” instruments in the previous DOC comparison (Sharp et al., 2002b). By a posteriori adjustment of the data to fit a uniform value

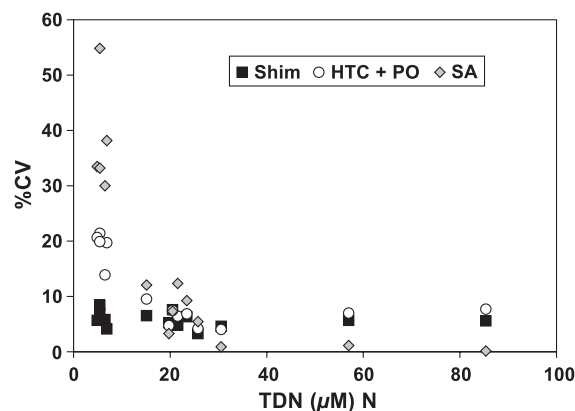


Fig. 2. Comparison of coefficients of variation for sets of analyses. The %CV for the multiple methods for each individual sample is plotted against the mean TDN concentration (from all eight HTC instruments) for that sample. Comparison of values for the five Shimadzu instruments (Shim), for the eight HTC instruments plus persulfate oxidation (HTC+PO), and for the three stand-alone instruments (SA). Samples with TDN <10 μM N are from surface offshore locations; those with TDN >30 μM N are from estuarine samples.

for the DOC deep ocean reference, this group precision became $\pm 3.7\%$ (Table 5). While it is not suggested that one should adjust data to fit performance of reference materials, it does show the value of reference materials in evaluating analytical runs; the recommended procedure is to delay analysis of samples and improve instrument conditions when one cannot obtain the appropriate value for the reference. Individual laboratories may vary the way DOC reference materials are used to determine how closely the daily measured value comes to the expected value. An estimate of the range of day-to-day replicability of individual laboratory analyses was seen in the DOC comparison (Sharp et al., 2002b). The analysis sets in that study where n was greater than 20 showed that the replicate precision for the DOC references ranged from $\pm 1.8\%$ to 12.9% (average of 5%); the calibration of the reference materials was $\pm 3.4\%$. In all cases, the analyses were apparently accurate but the precisions maintained by the individual laboratories varied, i.e., the correct value for the reference was within the precision of each laboratory. The results shown here plus those from the previous DOC comparison emphasize that day-to-day reproducibility within an individual laboratory or among laboratories for DOC analysis can be quite good (on the order of $\pm 5\%$ or better).

The simultaneous measurement of DOC and TDN also allows calculation of C/N ratios for dissolved organic matter (Table 7). Looking at that table, HTC method D shows values that are similar to what would be expected from the literature (e.g., Hansell and Carlson, 2001). For the deep ocean samples, the other HTC methods have many values that seem too high, indicating probable low DON estimates; they also show inconsistency in deep ocean samples. The persulfate method has C/N ratios that appear to be slightly low for the deep ocean samples and inconsistent with expected trends; expected to increase with depth and distance from land.

It is interesting to note that the persulfate method appears to produce slightly higher TDN values than the HTC methods (Tables 4 and 6). When averaged over the 14 samples, the persulfate method gave significantly higher values in most cases compared to the five Shimadzu systems. In the earlier multi-method comparison, the average persulfate methods gave higher values than the average HTC methods for all

Table 7
C/N ratios for samples from measured DOC and calculated DON

Sample (m)	A	B	C	D	E	K
20 (1)	17.2	21.0	12.0	11.2	11.2	9.1
22 (1)	22.4	26.2	15.7	13.9	14.6	10.2
24 (1)	18.5	17.9	14.0	15.1	17.2	11.9
26 (1)	16.1	13.9	12.1	14.1	14.4	10.3
51 (9)	15.2	13.3	13.2	15.3	12.1	10.0
53 (9)	15.8	15.0	14.1	17.0	14.8	12.0
54 (8)	15.9	15.0	14.1	16.9	13.6	12.1
55 (8)	17.0	15.4	14.9	18.1	12.6	12.9
55 (43)	15.0	15.4	13.4	19.1	15.3	12.3
55 (101)	28.6	50.6	29.5	28.5	14.9	11.0
55 (247)	44.9	31.1	73.2	23.6	9.3	10.0
55 (498)	61.6	46.5	67.6	21.5	13.6	10.4
55 (800)	73.7	37.7	133.9	22.8	12.4	10.3
55 (1900)	493.3	31.5	71.6	20.0	21.5	9.8

For instruments A–E, the DOC values measured by each instrument are used for the ratios; for method K (persulfate oxidation), the average of the five DOC analyses is used for DOC.

five samples, but differences were not statistically significant (Sharp et al., 2002a). Because of greater scatter and varying problems with blank corrections, it is possible for the persulfate method to give values that are too high. At this time, we assume that the persulfate method, as used here, is accurate and that the discrepancy primarily indicates problems with the HTC method. An additional feature of the persulfate method is that it can be performed as a simultaneous TDN and TDP method to get DON and DOP on the same samples (Pujo-Pay and Raimbault, 1994). The major disadvantage is that the method is time-consuming, prone to contamination problems, and can produce good results only with considerable experience.

Several of the HTC instruments, but not all, gave a low recovery of ammonium and urea in the Lewes exercise. The initial combustion product in the HTC method is NO_x (probably a combination of NO and NO_2), which is later converted to NO_2 in the chemiluminescence detector. Reduced nitrogen compounds like ammonium and organic matter must be oxidized from an oxidation state of -2 to at least $+2$. At the same time, nitrate must be reduced from an oxidation state of $+5$. If nitrate alone is used as the standard, it is difficult to determine if there was incomplete reduction of nitrate. A mixture of nitrate and ammonium is now used as a standard in some of our laboratories. To better assess instrument performance, it is a good idea to analyze reference materials

throughout a run rather than just once in a run; this is the protocol in some laboratories (Carlson et al., 2000, personal communication). While the results reported here indicate good performance by the HTC instruments, we are further evaluating if the HTC methods are not achieving complete conversion of all TDN to the final analyte.

It is our interim conclusion that the HTC instruments, especially those using the Shimadzu combustion conditions, appear to have potential to give reliable and accurate TDN values for calculating DON. However, more effort is needed before reliable DON measurements can be made for all samples. The comparability of the derived DON concentrations in the current comparison for the shallow ocean samples is pretty good ($\pm 6.7\%$ for the five Shimadzu instruments), while that for the deep ocean samples is poor ($\pm 70\%$). Reasons that we feel the HTC instruments show great promise are that the comparison of a group of HTC methods appears to give fairly tight agreement across a broad range of concentrations, the methods do not have major blank problems, and a broad range of concentrations can be measured without external sample dilution. The persulfate methods appear to be more variable from one laboratory to another, to have variable and very large blank problems, and to need dilution when high and low concentrations are analyzed together. We acknowledge that the persulfate method performed by a very experienced analyst could probably give accurate results and future improvements of HTC methodology will use comparison to persulfate as the indication of accuracy.

The ultimate goal is to improve the capability of measuring DON. In this exercise, uniform DIN values were used to calculate DON from the reported TDN measurements. A more accurate estimate of group analytical ability would involve all analysts measuring DIN as well as TDN. There is recognition that nutrient analyses are often not performed consistently. Some observations are based on indirect comparisons (e.g., Aminot and Kerouel, 1995; Zhang et al., 2000). Recently, we have shown poor agreement in a direct comparison of DIN analyses (e.g., Sharp et al., 2002a). The very small comparison here of three laboratories for eight samples with relatively high concentrations did show good agreement for nitrate plus nitrate analysis of $\pm 2.8\%$. This is an issue in need of further attention. Another large community

comparison is currently underway to extend involvement to the larger international community and to further evaluate improved community ability to measure DON. In that comparison, analysts were asked to measure both TDN and DIN if possible, so a more direct DON method comparison will result. In order to get good comparability among laboratories for DON measurement, it will be necessary to obtain group %CV values for both TDN and DON lower than $\pm 5\%$. This is a major challenge.

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