Acta Oceanol. Sin., 2023, Vol. 42, No. 4, P. 41–49
https://doi.org/10.1007/s13131-022-2035-z
http://www.aosocean.com
E-mail: ocean2@hyxb.org.cn

A comparison between high temperature catalytic and persulfate oxidation for the determination of total dissolved nitrogen in natural waters

Tiantian Ge[1, 2†], Xue Yang[1, 2†], Shan Jiang[1, 2], Liju Tan[1, 2*]

[1] College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao 266100, China

[2] Key Laboratory of Marine Chemistry Theory and Technology of Ministry of Education, Ocean University of China, Qingdao 266100, China

Received 23 September 2021; accepted 23 December 2021

Abstract

Total dissolved nitrogen (TDN) is an important parameter for assessing the nutrient cycling and status of natural waters. The accurate determination of TDN in natural waters is essential for assessing its contents and distinguishing different forms of nitrogen in the water. The TDN in various systems has been largely documented, and the concentrations of TDN are usually obtained using high-temperature catalytic (HTC) or persulfate oxidation (PO). However, the accuracy of these methods and their suitability for all types of natural waters are still unclear. To explore both methods in-depth, assorted samples were tested, including eight solutions composed of nitrogen-containing compounds (3 dissolved inorganic nitrogen fractions: NO_3^-, NO_2^- and NH_4^+; 5 organic compounds: EDTA-2Na, vitamin B1, vitamin B12, amino acids, and urea) and 105 natural waters which were collected from an open ocean (Northwest Pacific Ocean, 28), a marginal sea (Yellow Sea, 34), an estuary (Huanghe River mouth, 31), rivers (Huanghe River, 4; Licun River, 4), and precipitations (4 samples). The results showed that heterocycles and molecular dimensions had certain effects on the oxidation efficiency of the PO method but had little effect on HTC. There was no significant difference between the two methods for natural waters, but HTC was more suitable for deep-sea samples with low TDN concentrations (less than 10 μmol/L) and low organic activity. Overall, HTC has a relatively simple measurement process, a high degree of automation, and low error. Therefore, HTC can be recommended to determine the TDN of samples in freshwater and seawater.

Key words: total dissolved nitrogen, high-temperature catalytic, persulfate oxidation, natural waters

Citation: Ge Tiantian, Yang Xue, Jiang Shan, Tan Liju. 2023. A comparison between high temperature catalytic and persulfate oxidation for the determination of total dissolved nitrogen in natural waters. Acta Oceanologica Sinica, 42(4): 41–49, doi: 10.1007/s13131-022-2035-z

1 Introduction

Nitrogen (N) is an essential nutrient for sustaining productivity and an important factor in maintaining life activities in marine environments (McCarthy, 1972; Jackson and Williams, 1985; Agedah et al., 2009). It is also one of the main factors causing the eutrophication of waters (Vitousek et al., 2002). Total dissolved nitrogen (TDN) is a parameter of chief importance to assess nutrient cycling and the status of water systems (Jackson and Williams, 1985; Vitousek et al., 2002). TDN is the sum of the different nitrogen compounds, including dissolved inorganic nitrogen (DIN) and dissolved organic nitrogen (DON), which both play an important role in aquatic ecosystems (Vilmin et al., 2018). DIN is mainly composed of three fractions: nitrate, nitrite, and ammonium. DON is derived from the degradation products of biogenic compounds and anthropogenic organic matters (Minella et al., 2016) and is mainly composed of proteins, nucleic acids, urea, dissolved free amino acids, dissolved combined amino acids, as well as humic and fulvic acids (Sipler and Bronk, 2015). Unlike the inorganic forms of nitrogen, DON cannot be measured directly and needs to be calculated through the difference between TDN and DIN. The concentrations and compositions of nitrogen for different waters are rather complex. Therefore, the precision for the difference of TDN and DIN is an especially problematic factor.

The accurate determination of the TDN in natural waters is crucial to distinguishing nitrogen in its different forms and is important for environmental monitoring and nitrogen cycling assessment (Rogora et al., 2006). Although new methods have been established in recent years to determine the TDN in natural waters (Lin et al., 2018; Pagliano et al., 2018; Yasui-Tamura et al., 2020; Lin et al., 2021), two methods are still widely employed, namely persulfate oxidation (PO) (Solórzano and Sharp, 1980; Scudlark et al., 1998; Yasui-Tamura et al., 2020) and high-temperature catalytic oxidation (HTC) (Suzuki et al., 1985; Miller et

Foundation item: The National Key Research and Development Project of China under contract No. 2019YFC1407802; the Fund of State Environmental Protection Key Laboratory of Coastal Ecosystem under contract No. 202112; the Open Fund of Key Laboratory of Marine Ecological Environment Science and Engineering, Ministry of Natural Resources under contract No. MESE-2019-06; the National Natural Science Foundation of China under contract No. 41876078; the Shandong Provincial Natural Science Foundation of China under contract No. ZR2018MD016.

*Corresponding author, E-mail: lijutan@ouc.edu.cn

†These authors contributed equally to this work.

al., 1993; Sipler and Bronk, 2015; Lu et al., 2016). In these two methods, the crucial process is converting organic nitrogen completely into a single measurable product, nitric oxide (HTC) or nitrate (PO) (Minella et al., 2016; Pagliano et al., 2018). The chemical composition of natural water is rather complex and may include several nitrogen species not easily convertible into a single compound (Rogora et al., 2006). As a frequently used wet chemical oxidation method, PO can convert TDN into nitrate (NO_3^-) through thermal oxidation in the presence of potassium persulfate, and the following quantified method of NO_3^- is spectrophotometry at 220 nm (PO UV 220) or determination of its reduction product (NO_2^-) by spectrophotometry at 540 nm after coloration (Koroleff, 1976). Through several modifications of the reaction conditions, this method has been successfully used for the determination of TDN in natural waters (Solórzano and Sharp, 1980; Walsh, 1989; Scudlark et al., 1998). HTC converts TDN to nitric oxide (NO) and then detects NO through a kind of chemiluminescence detector (Suzuki et al., 1985). The advantages of the easy and convenient analysis and simultaneous determination of DOC and TDN suggested the further development potential of HTC (Sharp et al., 2002). Extensive studies have been conducted to compare these two methods (Walsh, 1989; Rogora et al., 2006; Yan and Wang, 2012; Minella et al., 2016). Bronk (2002) compared PO and HTC by measuring TDN concentrations in aquatic samples and nitrogen-containing standard compounds. TDN analysis performed on five sea samples (from the estuary, coastal, and open ocean environments) with varying TDN concentrations showed the consistent results of both methods (Sharp et al., 2002). Rogora et al. (2006) compared the differences between HTC and PO in the determination of TDN while focusing on freshwaters (lakes, rivers, and atmospheric deposition). It was confirmed that HTC was a reliable method for TDN determination in freshwater samples, as the calculated limit of detection of HTC was lower than PO. There also have been several studies on the relationship between nitrogen conversion and nitrogen-containing molecules (Nydahl, 1978; Jones and Daughton, 1985; Yan and Wang, 2012). Minella et al. (2016) summarized previous reports and studied the relationship between the conversion and the chemical structure of the tested compounds, concluding that HTC was more effective than PO in nitrogen recovery for compounds with s-triazine rings, two or more contiguous N atoms, and purine. Both methods demonstrated full nitrogen recovery for several compounds such as imidazole, indole, and pyrimidine rings containing amido or amino groups or nitrogen atoms.

Natural water samples have a chemical composition that is more complex than that of a single-compound solution, which may contain several kinds of nitrogen that are not easily convertible into a single compound and a wide concentration range. However, most previous studies on the comparison of methods for the determination of TDN were concerned with either seawater or freshwater (Sharp et al., 2002; Yan and Wang, 2012; Minella et al., 2016), and most were not systematic or comprehensive.

Based on the above discussion, we conducted a systematic and comprehensive analysis of various natural waters, systematically exploring the effects of the two different methods (HTC and PO) on the measurement of different components and different natural waters. They were 8 kinds of nitrogen-containing compounds and 105 natural waters collected from an open ocean (surface and deep-sea water), a marginal sea, an estuary, rivers, and rainwater. These eight selected N-molecules can be grouped as follows: nitrogen heterocycles of biological origin, amino acids, urea, amides, and inorganic nitrogen compounds. Our specific objectives in this study are to investigate (1) the effects of molecular structure on the determination results; (2) the difference between the two selected methods in determining natural samples; and (3) the applicability of these methods in the marine survey. Through these systematic analyses, we can fully understand the differences and reasons of TDN analysis methods in natural waters, so this work can provide a reference for future investigations of TDN in fresh and marine systems.

2 Materials and methods

2.1 *Methods and principles*

2.1.1 *Persulfate oxidation (PO)*

Firstly, 50 mL of each sample and 5 mL of potassium persulfate buffer solution (25 g of potassium persulfate and 15 g of boric acid dissolved in 500 mL of 3.75 mol/L sodium hydroxide) were pipetted using a Levo Plus Pipette Filler (DragonLab, China) into Teflon tubes. The TDN in each sample was converted to nitrate by the potassium persulfate with borate buffer in an alkaline environment under high-temperature (110–120℃) conditions for 30 min. At above 60℃ in an aqueous solution, potassium persulfate decomposes to produce potassium hydrogen sulfate, and atomic oxygen can react with nitrogen compounds to form nitrate at temperatures of 110–120℃. Nitrate was reduced to nitrite (via cadmium–copper column reduction) and then diazotized with p-aminobenzene sulfonamide. Finally, the product was detected by a spectrophotometer. The results were calculated using 6-point calibration curves derived from the prepared TIN standard (KNO_3) solution. Reagent blank subtraction was carried out using Milli-Q water by performing the same process. Blanks associated with TDN measurement were (3.3± 0.7) μmol/L (n=10) and the detection limit was 0.21 μmol/L. The standard deviation of the triplicate injections was 1.97%–9.74%.

2.1.2 *High-temperature catalytic (HTC)*

HTC was performed using a Shimadzu TOC-L analyzer equipped with a TNM-L nitrogen chemiluminescence detector and an ASI-L auto-sampler (Sharp et al., 2002; Pan et al., 2005). The samples (50 μL) were injected into the combustion column (heated to 720℃ and filled with Pt catalyst), where nitrogen-containing compounds were quantitatively transformed into NO gas. The cooled and dried gas was carried by the carrier gas (high purity oxygen, 99.999% by mass concentration) to a chemiluminescence detector and detected. The instrument was calibrated using 6-point calibration curves derived from prepared TIN standard (KNO_3) solution. Blank subtraction was carried out using Milli-Q water, which was analyzed before each sample was run. Total blanks associated with TDN measurement were (2.4±0.7) μmol/L (n=10) and the detection limit was 2.1 μmol/L. The standard deviation of the triplicate injections was 1.39%–4.17%.

2.2 *Preparation and processing of water samples*

2.2.1 *Solutions of nitrogen-containing compounds*

Several nitrogen-containing inorganic compounds were elected, including 3 DIN fractions (NO_3^-, NO_2^- and NH_4^+) and 5 nitrogen-containing organic compounds (EDTA Disodium Salt (EDTA-2Na), urea, amino acids (a mixture solution of 15 kinds of amino acids), Vitamin B1 (VB1), and Vitamin B12 (VB12)). All agents were prepared using Milli-Q water as a series of solutions with different concentrations between 8 μmol/L and 150 μmol/L. The selected N-molecules were grouped as follows: nitrogen heterocycles of biological origin (VB1 and VB12), amino acids (AAS),

urea, amides, and inorganic nitrogen compounds. Notably, VB1 and VB12 have larger molecular weights and more complex chemical structures than the other compounds.

2.2.2 *Natural waters*

A large number of natural water samples were collected from the sea, river, and rain, as shown in Table 1. All samples were collected and filtered by vacuum filtration with GF/F filters (0.7 μm, Whatman, heated at 450℃ for 4 h). Seawater samples were collected from open ocean areas (Northwest Pacific Ocean, 13°–40°N, 150°E, 28 samples) including surface seawater (SSW), deep seawater (DSW), a marginal sea (Yellow Sea, 34 samples), and an estuary (Huanghe River mouth, 31 samples, salinity range of 4–31) (Fig. 1). Samples from the Northwest Pacific Ocean, the Yellow Sea, and the Huanghe River mouth were collected in November 2019, March 2019, and October 2019, respectively. River water samples were collected from the Huanghe River (4 samples, the second-longest river in China) and the Licun River (4 samples, flowing through Qingdao and heavily influenced by industrial production and human activity) in November 2019.

Table 1. Natural water samples and their collection information

Sample type	Site	Location	Sampling date	Number
Open ocean	Northwest Pacific Ocean	13°–40°N, 150°E	November 2019	28
Marginal sea	Yellow Sea	35.94°–36.13°N, 120.27°–126.27°E	March 2019	34
Estuary	Huanghe River mouth	37.83°–38.32°N, 118.08°–119.26°E	October 2019	31
River water	Huanghe River	37.61°N, 118.54°E	November 2019	4
	Licun River	36.16°N, 120.47°E	November 2019	4
Precipitations	Qingdao, China	36.16°N, 120.50°E	July 2019 and January 2020	4

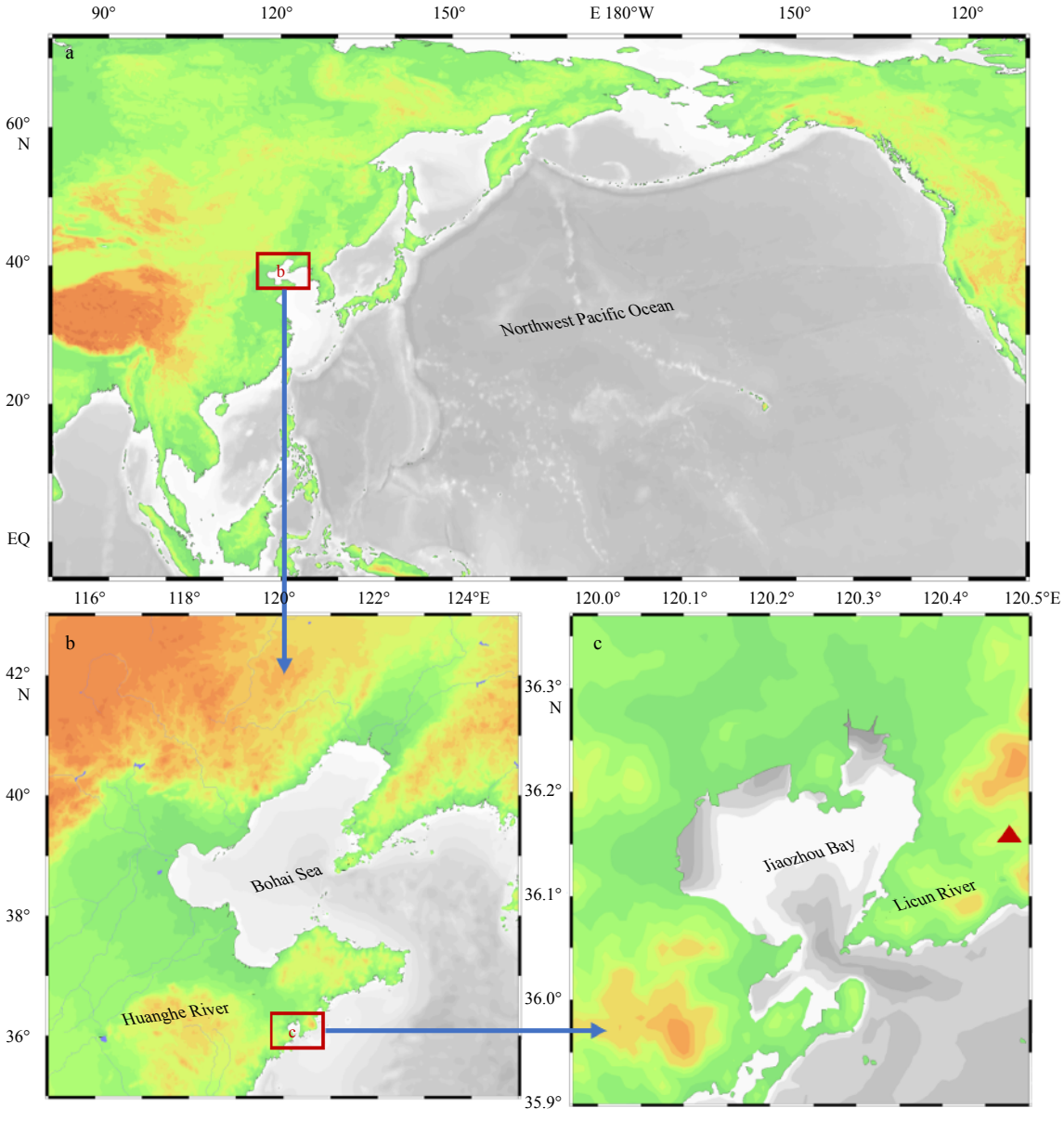

Fig. 1. Locations of natural waters sampling. The triangle is the location of the Ocean University of China.

Precipitations (4 rainwater samples) were collected in four spots in July 2019 and January 2020 at the Ocean University of China, located in Qingdao.

2.3 *Data analysis*

All samples (natural water samples and tested nitrogen-containing compounds) were analyzed for TDN by both methods. The determinations of TDN by PO and HTC were performed simultaneously or in close succession using the same standard (KNO_3) solution. The percentage difference between the results of HTC and PO was calculated as follows: $\text{Difference}=\frac{\text{HTC}_i-\text{PO}_i}{\text{HTC}_i}\times 100\%$ (Rogora et al., 2006). Here, HTC_i and PO_i represent the TDN values measured by the HTC and PO methods.

3 Results

3.1 *Analytical results for nitrogen-containing compounds*

The TDN concentration of nitrogen-containing compounds were measured using HTC and PO methods. Their relative differences were calculated, and the results are shown in Table S1. For VB1, VB12, and EDTA-2Na, 6 different concentrations of solutions were measured using these methods. Six series of VB1 samples were measured by HTC and PO at concentrations ranging from 15.5 μmol/L to 121.1 μmol/L and 16.4 μmol/L to 109.0 μmol/L, respectively, and the difference between the two methods was –1.2% to 17.8%. For VB12, the ranges of the two methods were respectively 9.8–106.4 μmol/L and 10.2–102.7 μmol/L, and the difference of the two methods ranged from –9.2% to 4.7%. The ranges of EDTA-2Na measured by each method were 11.2–131.8 μmol/L and 13.3–126.7 μmol/L, respectively, with the difference ranging from –18.7% to 6.0%.

Two different concentrations of solutions were prepared for NO_3^-, NO_2^-, NH_4^+, AAS, and urea. The differences for AAS and urea measured by HTC and PO ranged from –17.3% to 13.0%. The three fractions of DIN (NO_3^-, NO_2^- and NH_4^+) showed a smaller difference, ranging from 1.9% to 9.6%.

3.2 *Differences between the two methods in determining nitrogen-containing compounds*

The data revealed a strong linear correlation (R^2=0.985 9) between the HTC and PO methods for different tested compounds, and the results indicated that both methods have good stability for the determination of TDN (Fig. 2). The regression lines of the scattering data and the 1:1 line representing the best fit are plotted in Fig. 2. For the results of all solutions and the VB1, VB12, and EDTA-2Na test solutions individually, the regression lines had slopes of 1.051, 1.101, 1.053, and 1.065, respectively, indicating that there were no significant differences between the two methods. However, all slopes were above 1, indicating that the results for HTC were slightly higher. Relative differences between HTC and PO as a function of TDN concentration showed that the difference between the two methods ranged from –18.7% to 17.8% and was positive for the majority of standard samples (Table S1 and Fig. 3). At concentrations lower than 75 μmol/L, the positive and negative values for the difference were not as obvious. However, when the concentrations were higher than 75 μmol/L, the difference was mostly positive (Fig. 3). This indicates that at higher concentrations, HTC may be more suitable for the determination of TDN compared to PO.

3.3 *Results of natural waters using each method*

Analytical results of samples from the open ocean, estuary, marginal sea water, and freshwater from the HTC and PO methods are shown in Table S2. The TDN concentration of the northwest Pacific Ocean measured by HTC ranged from 4.7 μmol/L to 54.7 μmol/L, while the contents measured by PO ranged from 3.1 μmol/L to 48.1 μmol/L (Table S2a). The TDN concentrations of surface seawater samples from the Pacific Ocean using both methods were less than 10 μmol/L, and the vertical profiles of the TDN concentrations for each method reached a maximum value with increasing depth (HTC, 53.9 μmol/L at 1 000 m; PO, 48.1 μmol/L at 1 000 m) and decreased slightly from there onwards.

Samples from the Yellow Sea range from 5.7 μmol/L to 33.6 μmol/L when measured by HTC and from 5.5 μmol/L to 30.0 μmol/L by PO (Table S2b). The TDN concentration of estuary samples was 20.4–146.3 μmol/L using HTC and 22.0–143.9 μmol/L using PO, showing a strong correlation with salinity. The concentrations of river and rainwater were relatively high in our work, ranging from 67.4 μmol/L to 203.9 μmol/L by HTC and from 66.5 μmol/L to 191.2 μmol/L by PO.

3.4 *Differences between the two methods in determining natural waters*

A scatter plot of the results of the natural waters by HTC and PO is shown in Fig. 4. There is a highly linear relationship existing between the TDN values obtained by the two methods (R^2=0.979 6). Compared with the 1:1 line of best fit, the slope of

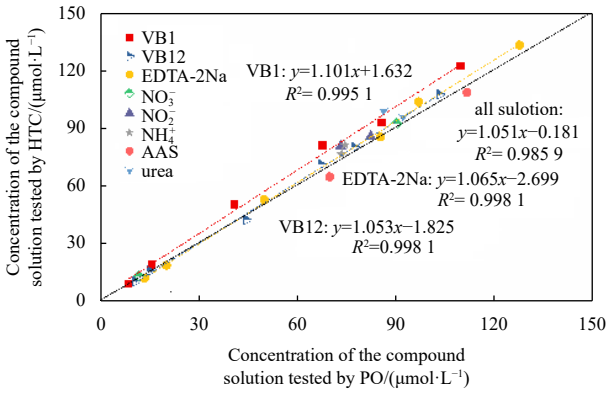

Fig. 2. Scatter plot of the results of the tested compound solution by high-temperature catalytic (HTC) and persulfate oxidation (PO). Dotted lines are the regression lines of vitamin B1 (VB1), VB12, and EDTA-2Na. Black line is the 1:1 line of best fit. AAS: amino acids.

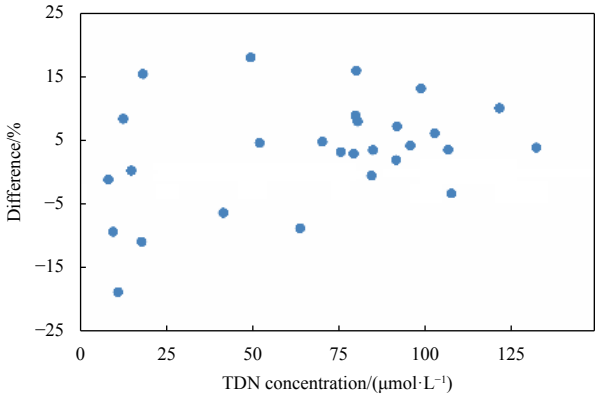

Fig. 3. Relative difference between persulfate oxidation (PO) and high-temperature catalytic (HTC) data as a function of total dissolved nitrogen (TDN) concentration for the tested compound solutions.

the natural water regression line is 0.992. The relative difference between PO and HTC data as a function of the TDN concentration for natural water samples showed that the relative differences between the two methods were positive for most natural water samples, similar to the results of the nitrogen-containing solutions (Fig. 5). According to the relative differences, the data were split into two groups covering the ranges above and below 50 μmol/L (Fig. 5). HTC data tended towards higher values than PO at lower TDN concentrations (<50 μmol/L). At the same time, the absolute values of the relative difference for 13 samples were found to be more than 25% and were characterized by low TDN concentrations (<15 μmol/L).

4 Discussion

4.1 *Influence of different nitrogen-containing compounds*

A highly linear relationship exists between the TDN values obtained by the two methods for different tested compounds (Fig. 2, all solutions: y=1.051x–0.181, R^2=0.985 9), which shows that these methods of TDN measurements have good stability for all nitrogen-containing compounds in laboratory determination. HTC gave a slightly higher value for most solutions (inorganic nitrogen compounds and organic nitrogen compounds) than PO (Fig. 3, Table S1). A possible reason for the lower results from PO is that the reduction efficiency of the Cd column is not 100%. The largest difference between these methods was found in VB1 (Fig. 3, Table S1), where the slope of its regression line was the highest (1.101, Fig. 2) and showed the largest deviation from the 1:1 line compared with other compounds. The nitrogen element of VB1 mainly exists in the nitrogen-containing heterocyclic structure. Some studies noted that HTC was very effective for TDN quantification in the presence of nitrogen-containing heterocycles, while PO yielded low recoveries (Minella et al., 2016).

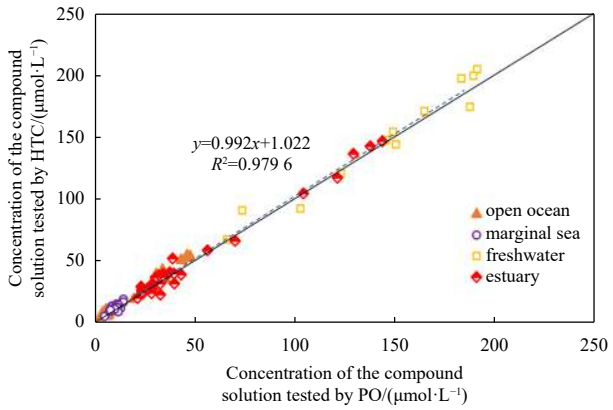

Fig. 4. Scatter plot of the results of the natural waters by high-temperature catalytic (HTC) and persulfate oxidation (PO). Dotted lines are regression lines of all of the natural samples. Black line is the 1:1 line of best fit.

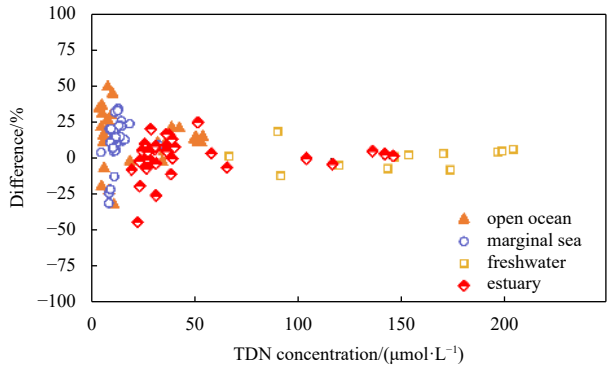

Fig. 5. Relative difference between persulfate oxidation (PO) and high-temperature catalytic (HTC) data as a function of total dissolved nitrogen (TDN) concentration for natural water samples.

To further explain the problem, the recovery between measured nitrogen data (C_m) and nominal nitrogen concentration (C_0) at different concentration solutions (recovery = $C_m/C_0 \times 100\%$) was calculated (Fig. 6). For the VB1, VB12, and EDTA-2Na solutions with above 20 μmol/L concentration, the measured values were less than the nominal concentration, and nitrogen recovery for these tested compounds with HTC and PO decrease with the concentration increasing. Above 20 μmol/L, the recovery between measured nitrogen data of VB1 by HTC and the nominal concentration (>90%) was significantly larger than using PO (<85%) (Fig. 6a). This indicates that nitrogen recovery for VB1 by HTC is effective for nitrogen-containing heterocycles structure of VB1, consistent with previous research (Minella et al., 2016). For VB12 with a concentration greater than 90 μmol/L, the nitrogen recoveries for HTC and PO were both about 80% (Fig. 6b). Due to the complex molecular structure of VB12, it should not be easy for either method to achieve complete nitrogen recovery. In other words, for some refractory compounds, the poor recovery for these methods suggests that the concentrations of TDN, and subsequently DON, will likely be underestimated with either method to some degree depending on the composition of the TDN pool in the field. In some cases, the absence of nitrogen recovery was related to incomplete mineralization during the oxidation phase, in other cases due to the formation of products other than NO (HTC) or nitrate (PO) depending on the relative kinetics of the various concurrent oxidation pathways of these molecules (Minella et al., 2016). For the other tested compounds in this study (NO_3^-, NO_2^-, NH_4^+, AAS, and urea), there was no obvious difference between measured nitrogen data and the nominal concentration (Fig. 6d). To some extent, the reduction efficiency of the Cd column for the PO method in this study did not reduce the measurement results. Creatinine, urea, and amino acids with structures of molecular weight bioavailable nitrogen could have an almost complete nitrogen recovery by both HTC and PO in previous studies (Yan and Wang, 2002). Different conversion steps and molecular structures can lead to different recoveries. In many cases, TDN measurements provided systematically low results, which can be related to the structures of the nitrogen-containing compounds in the natural waters.

4.2 *Influence of different water samples*

The relationship between the results of open ocean, estuary, marginal sea, and freshwater samples produced by the PO and HTC are plotted in Fig. 7. The strong linear correlation (R^2 = 0.979 6) between HTC and PO for natural water samples (Fig. 4) indicates that both methods show good stability for the detection of TDN in the natural water samples, which is the same as the results of the tested nitrogen-containing solutions.

4.2.1 *Freshwater samples*

The TDN concentration of freshwater samples ranged from 66.5 μmol/L to 203.9 μmol/L for the two methods. The average value of the relative difference between HTC and PO data was the smallest compared to other samples (Fig. 5). The data points of

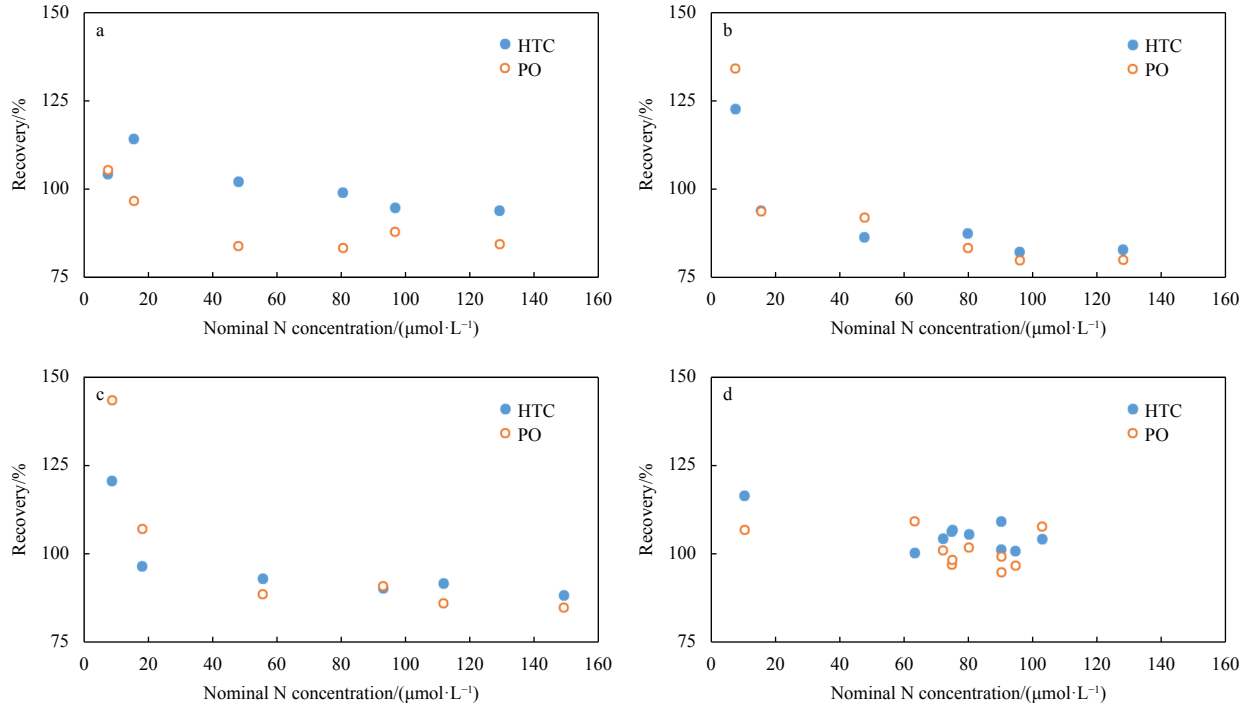

Fig. 6. Recovery between measured nitrogen data and nominal N concentration for different solutions, VB1 (a), VB12 (b), EDTA-2Na (c) and the other tested compounds (d). The solid dots represent high-temperature catalytic (HTC), and the hollow dots represent persulfate oxidation (PO).

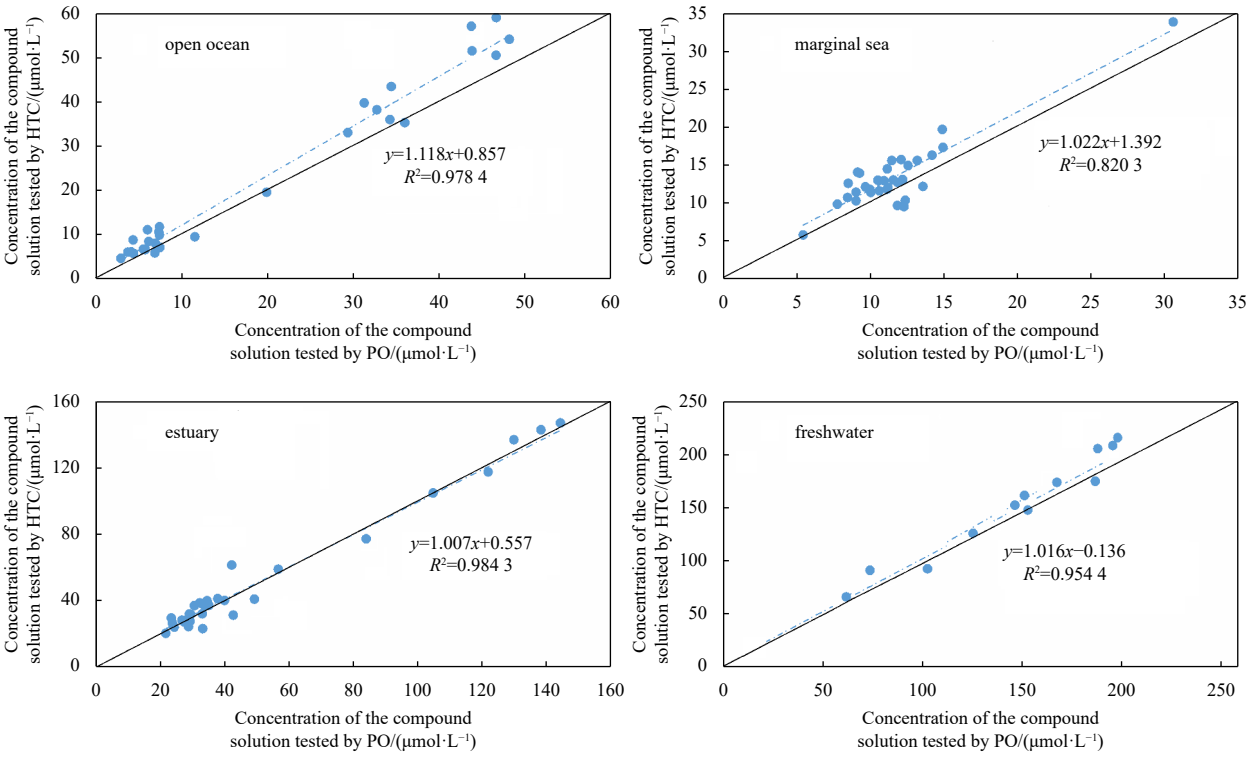

Fig. 7. Scatter plots of results of the open ocean, the marginal sea, an estuary, and freshwater by high-temperature catalytic (HTC) and persulfate oxidation (PO). Dotted lines are regression lines. Black lines are the 1:1 line of best fit.

freshwater results obtained by HTC and PO were very close to the line of best fit (Fig. 7, y=1.016x–0.136, R^2=0.954 4), showing that both methods were effective for TDN quantification in freshwater samples with high TDN concentration. Rivers have been impacted by population growth and nitrogen fertilizer application (Tao et al., 2010; Liu et al., 2012; Vilmin et al., 2018). DIN accounted for more than 80% of TDN in the Huanghe River (Wang et al., 2013). The largest contributor to total nitrogen is inorganic spe-

cies (55%–70%) with smaller contributions of organic nitrogen (30%–45%) in rainwater (Gioda et al., 2011). By measuring the DIN of our rainwater (unpublished data), we found that the contribution of DIN was over 85% in our rainwater samples. Rogora et al. (2006) compared HTC and PO for the determination of TDN in about 800 freshwater samples with concentrations ranging from 7 μmol/L to 500 μmol/L (lakes, rivers, and atmospheric deposition), revealing that both HTC and PO were reliable methods for the determination of TDN in freshwater samples. Studies have also shown that PO was well suited for freshwaters, where DIN and humic compounds that have high oxidation efficiency can be significant fractions of the TDN pool (Bronk, 2002).

4.2.2 *Seawater*

The relationship between these methods for the Northwest Pacific water sample samples indicated that overall, a relatively positive linear correlation exists between the HTC and PO method (R^2 = 0.983 0). The slope of the trend line (1.118) for the Northwest Pacific water was higher than the 1:1 line of best fit (Fig. 7). This indicated that the results of the two methods for open ocean water have relatively large differences and that the results of the HTC method were higher than the PO method, especially for DSW (Table S2a, Fig. 8). In the surface waters of the oligotrophic subtropical gyres, the TDN concentration of SWS were lower than 10 μmol/L (Letscher et al., 2013) and DON contributed more than 90% of the TDN concentration (Torres-Valdés et al., 2009; Sipler and Bronk, 2015), indicating that the accurate determination of low-concentration samples (<10 μmol/L) should not only consider the influence of conversion but also the detection limits and blanks of both methods.

The contents of samples collected from the Yellow Sea ranged from 5.5 μmol/L to 33.6 μmol/L as measured by the two methods. Field investigation in the southern Yellow Sea by Shi et al. (2015) showed that the average concentrations of TDN were 20–36 μmol/L in spring, in which DON accounted for above 90% of TDN. The relationship of TDN concentration of the Yellow Sea samples had a good linear correlation (R^2=0.820 3), and the slope of linear equations is 1.022 (y=1.022x+1.392), which is smaller than the result of open ocean samples. The range of TDN concentration of estuary samples was 20–160 μmol/L, and the slope of linear equations for the results of HTC against PO was 1.007 (y=1.007x+0.557, R^2=0.984 3). The regression line of the two methods for estuary samples was the nearest line of best fit compared to other seawater samples. Most data points were on the best fit line or very close to this line, but the regression lines of the two methods for the Pacific Ocean and the Yellow Sea were above the optimal fitting line.

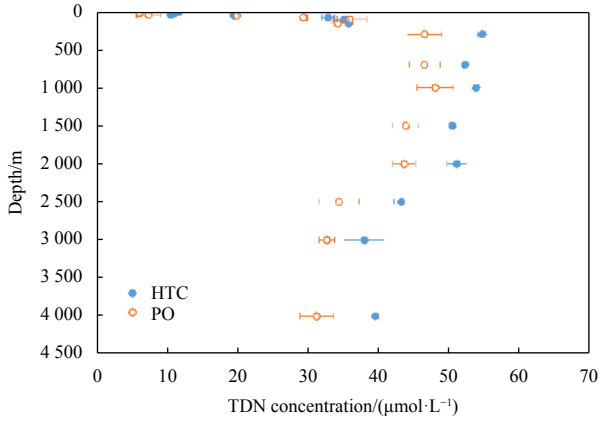

Fig. 8. Depth profile of total dissolved nitrogen (TDN) measurements by the high-temperature catalytic (HTC) and persulfate oxidation (PO) methods in the Northwest Pacific. Error bars represent the standard deviation for each sample after three analyses.

TDN concentrations and the proportions of DIN and DON in TDN were diverse among different water bodies. Studies have shown that DON is the main form of nitrogen in the surface water of the open ocean, accounting for about 90% of TDN, while DIN is the dominant form in estuaries. The results of the tests solutions showed that the HTC and PO methods had similar measurement results for DIN (Fig. 2), indicating that the proportion of DON may account for the differences in results in different water areas. The minor difference for estuary samples measured by these two methods may illustrate their suitability for estuary samples with low DON concentrations.

Dissolved organic matter (DOM) in aqueous is composed of myriad of compounds, which can be divided into labile DOM (LDOC) and refractory DOM (RDOC) (Bauer et al., 1992; Druffel et al., 1992; Carlson and Hansell, 2015). The LDOC pool (including urea and amino acids) as bioavailable substances has simple structures that can easily be converted into measurable products. From coastal to oceanic systems, the proportions of LDOM in the total DOM vary spatially with an apparent gradient of decreasing concentrations of LDOM (del Giorgio and Davis, 2003), which may be another reason for the difference between the two methods for samples from different sources. The average value of the relative difference of these two methods was highest in the Northwest Pacific samples, followed by Yellow Sea and estuary samples. Besides, HTC might be more applicable to samples of different properties, as the conversion rate of HTC is higher than PO for most samples.

4.3 *Practical application in the Pacific Ocean using two methods*

The depth profiles of TDN measurements in the Northwest Pacific waters by the HTC and PO methods were plotted (Fig. 8). The concentration of TDN increased rapidly with depth until above 1 000 m, where it then began to decrease with slight fluctuation. Similar profiles have been shown in many previous deep-sea studies (Maita and Yanada, 1993; Sharp et al., 2004; Torres-Valdés et al., 2009). From the surface to the seafloor, the ratios and concentrations of DIN and DON varied with depth. The concentrations of DON contribute above 90% of the TDN in surface waters of the oligotrophic ocean and decrease with depth, coinciding with an increase in NO_3^- content (Karl et al., 2001; Torres-Valdés et al., 2009).

The high DIN concentrations in the deep-sea result in only ~34% of the TDN pool being composed of DON in these environments (Sipler and Bronk, 2015). The results of HTC were higher than those of PO at depths below 300 m. The difference between the two methods can range from 7.3% to 21% for DSW in the open ocean (Table S2b), which likely reveals that the PO method may significantly underestimate the presence of DON in the deep sea. Letscher et al. (2013) demonstrated that DON is primarily removed through vertical mixing and subsequent remineralization by microbes below the mixed layer. The organic matter of DSW may be more stable than that of SSW (Carlson and Hansell, 2015). Organic matter from SSW is carried to the deep sea by biological pumps, and micro-biological ecological processes can convert active DOC into RDOC, which can be stored for long periods in the ocean. The stability of RDOC becomes evident in the vertical DOC gradients observed in deeper portions of the

mesopelagic zones (>500–1 000 m) of ocean regions. The difference between the two methods in DSW of the open ocean illustrates that HTC might be better applied to measure the refractory DON of DSW. The standard deviations of HTC are significantly lower than for PO (Table S2b, Fig. 8). Under these conditions, TDN (and subsequent DON) estimated by PO are inherently plagued by high uncertainties for DSW. The standard deviations of the PO method were higher than the HTC method for samples collected from the Northwest Pacific in the three analyses, prompting the PO method to be used cautiously in low-TDN open ocean waters due to the potential for high blanks.

5 Conclusions

The molecular structure has a certain effect on the determination of TDN. Molecules containing heterocycles, such as VB1, and organic macromolecules, such as VB12, have higher oxidation efficiencies for HTC than PO. However, low molecular compounds (organic and inorganic) do not differ significantly in the results of the two methods, and their oxidation efficiencies were high enough to meet the measurement requirements. For natural water, the concentrations obtained by HTC were higher than those from PO for most samples, but for freshwater and Huanghe River Estuary samples, the two methods were closer in value. For seawater, the differences between the two methods were obvious, possibly due to the different activities of organic matter in different waters. From coastal to ocean systems, the proportion of LDOM varies spatially with an apparent decreasing gradient, therefore, the differences between the two methods gradually increased. In general, for nearshore waters containing high amounts of biologically active organic nitrogen, the two methods are not much different. However, for samples with lower TDN concentrations (less than 10 μmol/L) and deep-sea lower organic activity, HTC might be more suitable. In short, HTC has a relatively simple measurement process, a higher degree of automation, and a smaller standard deviation. Therefore, HTC is more ideal to determine the TDN of samples in seawater.

References

Agedah E C, Binalaiyifa H E, Ball A S, et al. 2009. Sources, turnover and bioavailability of dissolved organic nitrogen (DON) in the Colne Estuary, UK. Marine Ecology Progress Series, 382: 23–33, doi: 10.3354/meps07938

Bauer J E, Williams P M, Druffel E R M. 1992. ^{14}C activity of dissolved organic carbon fractions in the north-central Pacific and Sargasso Sea. Nature, 357(6380): 667–670, doi: 10.1038/357667a0

Bronk D A. 2002. Dynamics of DON. In: Hansell D A, Carlson C A, eds. Biogeochemistry of Marine Dissolved Organic Matter. San Diego: Academic Press, 153–247

Carlson C A, Hansell D A. 2015. DOM sources, sinks, reactivity, and budgets. In: Hansell D A, Carlson C A, eds. Biogeochemistry of Marine Dissolved Organic Matter. 2nd ed. San Diego: Academic Press, 65–126

del Giorgio P A, Davis J. 2003. Patterns in dissolved organic matter lability and consumption across aquatic ecosystems. In: Findlay S E G, Sinsabaugh R L, eds. Aquatic Ecosystems: Interactivity of Dissolved Organic Matter. San Diego: Academic Press, 399–424

Druffel E R M, Williams P M, Bauer J E, et al. 1992. Cycling of dissolved and particulate organic matter in the open ocean. Journal of Geophysical Research, 97(C10): 15639–15659, doi: 10.1029/92JC01511

Gioda A, Reyes-Rodríguez G J, Santos-Figueroa G, et al. 2011. Speciation of water-soluble inorganic, organic, and total nitrogen in a background marine environment: Cloud water, rainwater, and aerosol particles. Journal of Geophysical Research: Atmospheres, 116(D5): D05203

Jackson G A, Williams P M. 1985. Importance of dissolved organic nitrogen and phosphorus to biological nutrient cycling. Deep-Sea Research Part A: Oceanographic Research Papers, 32(2): 223–235, doi: 10.1016/0198-0149(85)90030-5

Jones B M, Daughton C G. 1985. Chemiluminescence vs. Kjeldahl determination of nitrogen in oil shale retort waters and organonitrogen compounds. Analytical Chemistry, 57(12): 2320–2325, doi: 10.1021/ac00289a034

Koroleff F. 1976. Determination of nutrients. In: Grasshof E, Kremling E, eds. Methods of the Seawater Analysis. Weinhein and New York: Verlag Chemie

Letscher R T, Hansell D A, Carlson C A, et al. 2013. Dissolved organic nitrogen in the global surface ocean: Distribution and fate. Global Biogeochemical Cycles, 27(1): 141–153, doi: 10.1029/2012GB004449

Lin Kunning, Pei Junxian, Li Peicong, et al. 2018. Simultaneous determination of total dissolved nitrogen and total dissolved phosphorus in natural waters with an on-line UV and thermal digestion. Talanta, 185: 419–426, doi: 10.1016/j.talanta.2018.03.085

Lin Kunning, Xu Jin, Guo Huige, et al. 2021. Flow injection analysis method for determination of total dissolved nitrogen in natural waters using on-line ultraviolet digestion and vanadium chloride reduction. Microchemical Journal, 164: 105993, doi: 10.1016/j.microc.2021.105993

Liu Sumei, Li Lingwei, Zhang Guiling, et al. 2012. Impacts of human activities on nutrient transports in the Huanghe (Yellow River) Estuary. Journal of Hydrology, 430–431: 103–110

Lu Dongliang, Yang Nannan, Liang Shengkang, et al. 2016. Comparison of land-based sources with ambient estuarine concentrations of total dissolved nitrogen in Jiaozhou Bay (China). Estuarine, Coastal and Shelf Science, 180: 82–90

Maita Y, Yanada M. 1993. Distribution of dissolved organic nitrogen in the North Pacific Ocean. Elsevier Oceanography Series, 59: 185–197

McCarthy J J. 1972. The uptake of urea by natural populations of marine phytoplankton. Limnology and Oceanography, 17(5): 738–748, doi: 10.4319/lo.1972.17.5.0738

Miller A E J, Mantoura R F C, Preston M R. 1993. Shipboard investigation of DOC in the NE Atlantic using platinum-based catalysts in a Shimadzu TOC-500 HTCO analyser. Marine Chemistry, 41(1–3): 215–221

Minella M, Tartari G A, Rogora M, et al. 2016. Influence of nitrogen speciation on the TDN measurement in fresh waters by high temperature catalytic oxidation and persulfate digestion. International Journal of Environmental Analytical Chemistry, 96(5): 474–489, doi: 10.1080/03067319.2016.1150467

Nydahl F. 1978. On the peroxodisulphate oxidation of total nitrogen in waters to nitrate. Water Research, 12(12): 1123–1130, doi: 10.1016/0043-1354(78)90060-X

Pagliano E, Campanella B, Shi Lisa, et al. 2018. Determination of total dissolved nitrogen in seawater by isotope dilution gas chromatography mass spectrometry following digestion with persulfate and derivatization with aqueous triethyloxonium. Journal of Chromatography A, 1569: 193–199, doi: 10.1016/j.chroma.2018.07.055

Pan Xi, Sanders R, Tappin A D, et al. 2005. Simultaneous determination of dissolved organic carbon and total dissolved nitrogen on a coupled high-temperature combustion total organic carbon-nitrogen chemiluminescence detection (HTC TOC-NCD) system. Journal of Analytical Methods in Chemistry, 2005: 103057

Rogora M, Minella M, Orrù A, et al. 2006. A comparison between high-temperature catalytic oxidation and persulphate oxidation for the determination of total nitrogen in freshwater. International Journal of Environmental Analytical Chemistry, 86(14): 1065–1078, doi: 10.1080/03067310600739632

Scudlark J R, Russell K M, Galloway J N, et al. 1998. Organic nitrogen in precipitation at the mid-Atlantic U. S. coast—methods evaluation and preliminary. Atmospheric Environment, 32(10): 1719–1728, doi: 10.1016/S1352-2310(97)00458-5

Sharp J H, Beauregard A Y, Burdige D, et al. 2004. A direct instrument

comparison for measurement of total dissolved nitrogen in seawater. Marine Chemistry, 84(3–4): 181–193
Sharp J H, Rinker K R, Savidge K B, et al. 2002. A preliminary methods comparison for measurement of dissolved organic nitrogen in seawater. Marine Chemistry, 78(4): 171–184, doi: 10.1016/S0304-4203(02)00020-8
Shi Xiaoyong, Qi Mingyan, Tang Hongjie, et al. 2015. Spatial and temporal nutrient variations in the Yellow Sea and their effects on *Ulva prolifera* blooms. Estuarine, Coastal and Shelf Science, 163: 36–43
Sipler R E, Bronk D A. 2015. Dynamics of dissolved organic nitrogen. In: Hansell D A, Carlson C A, eds. Biogeochemistry of Marine Dissolved Organic Matter. 2nd ed. San Diego: Academic Press, 127–232
Solórzano L, Sharp J H. 1980. Determination of total dissolved nitrogen in natural waters. Limnology and Oceanography, 25(4): 751–754, doi: 10.4319/lo.1980.25.4.0751
Suzuki Y, Sugimura Y, Itoh T. 1985. A catalytic oxidation method for the determination of total nitrogen dissolved in seawater. Marine Chemistry, 16(1): 83–97, doi: 10.1016/0304-4203(85)90029-5
Tao Yu, Wei Meng, Ongley E, et al. 2010. Long-term variations and causal factors in nitrogen and phosphorus transport in the Yellow River, China. Estuarine, Coastal and Shelf Science, 86(3): 345–351
Torres-Valdés S, Roussenov V M, Sanders R, et al. 2009. Distribution of dissolved organic nutrients and their effect on export production over the Atlantic Ocean. Global Biogeochemical Cycles, 23(4): GB4019
Vilmin L, Mogollón J M, Beusen A H W, et al. 2018. Forms and subannual variability of nitrogen and phosphorus loading to global river networks over the 20th century. Global and Planetary Change, 163: 67–85, doi: 10.1016/j.gloplacha.2018.02.007
Vitousek P M, Hättenschwiler S, Olander L, et al. 2002. Nitrogen and nature. Ambio, 31(2): 97–101, doi: 10.1579/0044-7447-31.2.97
Walsh T W. 1989. Total dissolved nitrogen in seawater: a new-high-temperature combustion method and a comparison with photo-oxidation. Marine Chemistry, 26(4): 295–311, doi: 10.1016/0304-4203(89)90036-4
Wang Zhimin, Song Xianfang, Li Guomin, et al. 2013. Variations of nitrogen transport in the mainstream of the Yellow River, China. International Journal of Environment and Pollution, 52(1–2): 82–103
Yan Xuejiao, Wang Jiangtao. 2012. Method comparison for measurement of dissolved organic nitrogen in seawater using high temperature combustion and persulfate oxidation. Marine Sciences (in Chinese), 36(5): 103–108
Yasui-Tamura S, Hashihama F, Ogawa H, et al. 2020. Automated simultaneous determination of total dissolved nitrogen and phosphorus in seawater by persulfate oxidation method. Talanta Open, 2: 100016, doi: 10.1016/j.talo.2020.100016

Supplementary information:

Table S1. The total dissolved nitrogen results of nitrogen-containing compounds by using high-temperature catalytic and persulfate oxidation methods.

Table S2. The total dissolved nitrogen results of two methods for samples from the open ocean, marginal sea, estuary and freshwater.

The supplementary information is available online at https://doi.org/10.1007/s13131-022-2035-z and http://www.aosocean.com/. The supplementary information is published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.