



A Comparison Study of Method for Determination of Total Dissolved Nitrogen

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ABSTRACT

This paper describes the experiments carried out to analyse total dissolved N involving UV oxidation and high temperature catalytic oxidation (HTCO) methods. Standards of known N concentrations (i.e. ammonium and EDTA) irradiated with UV oxidation for 6 h were found to show good oxidation efficiency (72-107%). However, poor recovery was recorded for urea (2-20%). The addition of reaction initiator (H_2O_2) did not show any significantly difference to the oxidation efficiency of all three compounds. Based on the analysis of seawater samples, UV oxidation method was less efficient (> 90%) of converting organic N to inorganic N relative to HTCO.

Keywords: UV oxidation, High temperature catalytic oxidation, Total dissolved nitrogen.

INTRODUCTION

Presently, method for dissolved organic nitrogen (DON) determination in aquatic system is based on the measurements of total dissolved nitrogen (TDN) and dissolved inorganic nitrogen (DIN). TDN determinations are made using a digestion procedure to oxidise the organic N fraction into inorganic form with all N in the inorganic forms subsequently being measured. The DON concentration is the difference between TDN and the sum of the DIN concentrations prior to sample digestion. There are three types of commonly used oxidation method i.e. UV oxidation, chemical oxidation and high temperature combustion (HTC).

In UV and chemical oxidations methods, which are also known as wet chemical oxidation (WCO), the final analyte of oxidised N ion is ultimately measured as NO_2^- after final reduction from NO_3^- . In the HTC method, all of the TDN is converted to nitric oxide (NO) by pyrolysis and the DON concentration is then defined as the difference between TDN and the sum of the DIN concentrations.

However, there is no general agreement as to which method is best for the TDN measurements. Some studies have indicated that the HTC method gave higher TDN results compared to WCO^{1,2}. Other study has shown that there is little difference between these two methods³. Due to this

reason, a comparison study was carried out to evaluate the performance of UV oxidation and HTC methods of measuring TDN. The UV oxidation method was chosen for its simplicity, minimal sample handling and manipulation, and rapid sample throughput. HTC that is also known as high temperature catalytic oxidations (HTCO) as this technique often includes metals (e.g. Pt) as catalysts is the widely used to analyse TDN because it measures more efficiently, faster, easier and is more readily automated and required much smaller sample volumes (~100 μL)^{4,5}.

MATERIAL AND METHODS

All glassware used in this study were soaked overnight in 10% hydrochloric acid (HCl) and rinsed with copious amounts of deionised water. Then, the glassware was covered with aluminium foil and baked for > 4 h at 550 °C. Analysis of TDN in the standard and seawater samples by UV oxidation method was performed in duplicate. The irradiation unit used in this study contained a 1000 W UV lamp (Hanovia) protected by a quartz jacket. Temperature during the oxidation was ~40 °C. A glass tube holder (8 tubes in total) was fitted around the lamp and held the samples 5 cm from the lamp. A fan placed at the bottom of the unit circulating air across the samples for cooling. The entire unit was placed in a fume hood that was covered with aluminium foil while in use to minimise hazards.

Previous studies have shown that appropriate condition of UV oxidation has to be chosen in order to get a complete oxidation to nitrate which depends on the intensity of the source, irradiation time, pH of sample, total N content of the sample and the presence or absence of an added chemical oxidant (as initiator)^{3,6}. However, in this study, only variations of time of exposure and the effect of the initiator (i.e. hydrogen peroxide, H_2O_2) were tested. To achieve this, different organic N standards i.e. urea, ammonium and EDTA (ethylene diamine tetraacetic acid) were prepared in artificial seawater⁷. A series of oxidation batches were made using the same concentrations (25 μM) of each standard with different oxidation time (1, 2, 3, 4, 6, 12 and 24 h) and with or without addition of reaction initiator (100 μL of 30% H_2O_2 in 10mL standard). Based on this experiment, the optimum

condition of oxidation were no addition of H_2O_2 and irradiation for 6 h (see results and discussion). This same condition was used to analyse the seawater samples collected from the North Sea. Samples were filtered through precombusted (400 °C; 4 h) Whatman GF/F glass fibre filters at <50 mm Hg vacuum and the filtrate was used for TDN measurement.

10 mL samples were irradiated for 6 h in 15 mL quartz glass tubes with glass stoppers. After irradiation, samples were analysed for nitrate using Scalar San Plus Autoanalyser following colourimetric methods according to Kirkwood⁸. Calibration was achieved using KNO_3 . Testing of the recovery of known standards, such as Certified Reference Material (CRM) of Deep Sea (DS) from Hansell's laboratory (University of Miami), urea, ammonium and EDTA during the oxidation were also carried out in each batch.

The same seawater samples used in UV oxidation was measured by HTCO with a Thermalox TOC/TN analyser (Cambridge, U.K.), which was coupled to a chemiluminescence detector. The detector measured NO_x gases produced by HTCO of all N species. The temperature of the combustion tube was set at 680 ± 10 °C and the catalyst was 0.5% Pt/ Al_2O_3 . Calibration of the instrument was performed with KNO_3 (0-25 μM) in ultrapure water (18.2 M Ω). The system blank was estimated for each individual run by injected ultrapure water with typical values of 1.6-3.7 μM (2.3 ± 0.6 μM , n=10) and blank corrections were applied to the TDN data. DS from the Sargasso Sea obtained from the Hansell's laboratory (University of Miami) was used during the routine analyses of water samples as recommended by Badr et al.⁹. The recovery of the TDN in the DS was between 91-110% ($101 \pm 6\%$, n=10). The oxidation efficiency was also checked on each analytical day by comparing with urea and resulted in values in the range of 96-103% ($100 \pm 2\%$, n=10). The instrument used ≥ 3 injections per analysis until a precision of $\pm 5\%$ or better was achieved.

RESULTS AND DISCUSSION

In order to determine the appropriate time of sample irradiation, preliminary experiments were

carried out using ammonium, urea and EDTA standards which were prepared in artificial seawater. Analyses were performed in duplicate using 25 μM standards which were irradiated with different oxidation times (1, 2, 3, 4, 6, 12 and 24 h). In addition, comparison was also made to address the effects of H_2O_2 during the oxidation. After irradiation, it was confirmed that organic N in the standards was converted to nitrate and nitrite so that subsequent analytical determination of the sum of nitrate and nitrite gave the TDN content of the standards with results presented in Fig. 1. For blanks (with and without addition of H_2O_2), the TDN concentration increased from 1 to 3 h after irradiation and then the concentrations were constant throughout the experiments. There was no significant difference ($P < 0.05$) for both blank concentrations, although the concentrations of the blank with H_2O_2 were slightly higher compared to without addition of H_2O_2 .

The TDN concentrations presented in Fig. 1 for ammonium, urea and EDTA were blank corrected with their respective blank. In contrast to urea, good oxidation efficiency was recorded for ammonium and EDTA standards. If the results were expressed as percentage oxidation, ammonium recorded higher recoveries (100-107%) both with and without H_2O_2 throughout the whole experiments. EDTA showed recoveries in between 72-86% and 82-92% for standards without H_2O_2 and with H_2O_2 respectively. In contrast to ammonium, EDTA recorded increased concentrations until 3 to 4 hours after irradiation, after which the concentrations were constant. Poor recoveries were found for urea (with and without H_2O_2) which was in the range of 2-20%. In addition, the results also showed that the concentrations of standards with and without addition of H_2O_2 were not significantly different ($P > 0.05$).

Table 1: Results for quality control during TDN analysis using UV oxidation

No. of experiment	Concentration and recovery					
	DS		Urea		EDTA	
	21.5 μM	%	25 μM	%	25 μM	%
1	20.4	95	3.8	15	20.7	83
2	19.7	92	2.9	12	22.7	91
3	nd	-	3.6	14	20.8	83
4	20.1	94	3.8	15	21.5	86
5	19.7	92	0.7	3	21.0	84

nd = not determined

Table 2: Comparison results of seawater samples between HTCO and UV oxidation methods

Samples	Concentration (μM)		Oxidation efficiency (%)
	HTCO	UV oxidation	
1	26.2	23.7	91
2	19.2	17.2	90
3	14.2	13.0	92
4	10.5	9.5	91
5	8.5	7.8	92

The results of higher recovery for both ammonium and EDTA but lower for urea by UV oxidation have also been observed in other studies^{3,5,10}. For example, Walsh⁵ recorded recoveries of 99.5%, 95.7% and 72.5% for ammonium, EDTA and urea in seawater respectively. However, Walsh⁵ irradiated the standards for 18-22 h with addition of H₂O₂. Higher recoveries were also found for ammonium and EDTA in freshwater samples (100% and 83% respectively) after the standards were irradiated for 4 h with the addition of H₂O₂¹⁰. By adding H₂O₂ and irradiating for 24 h, Bronk *et al.*³ recorded recoveries of 96-103% (EDTA), 50-100% (ammonium) and 64-83% (urea) in seawater. However, it is unclear why urea was poorly oxidised (2-20%) in this present study in comparison with others^{3,5}. Most studies have reported the use of H₂O₂ to enhance the oxidation^{3,5,10}. However, this was not observed in this study as the concentrations of TDN between

samples with H₂O₂ and without H₂O₂ was similar. Furthermore, some studies have found that the addition of reaction initiators (e.g. H₂O₂) did not increase the yield or oxidation rate but only caused higher blanks^{6,11,12}. Thus, based on the experiments using the standards, seawater samples were oxidised without adding the H₂O₂ and 6 h was selected as oxidation time.

During sample oxidation, the oxidation efficiency (recovery) in each batch was checked by using the DS standard reference material, as for HTCO, and standard addition method with 25 µM urea and EDTA. Samples were analysed using the UV oxidation method were reanalysed using the HTCO. The results show that the oxidation efficiency of DS ranged from 92-95% (93 ± 2%, n=4) (Table 1). It should be noted that much of the TDN in the DS sample was present as nitrate, so the DON oxidation efficiency may be less than implied by the

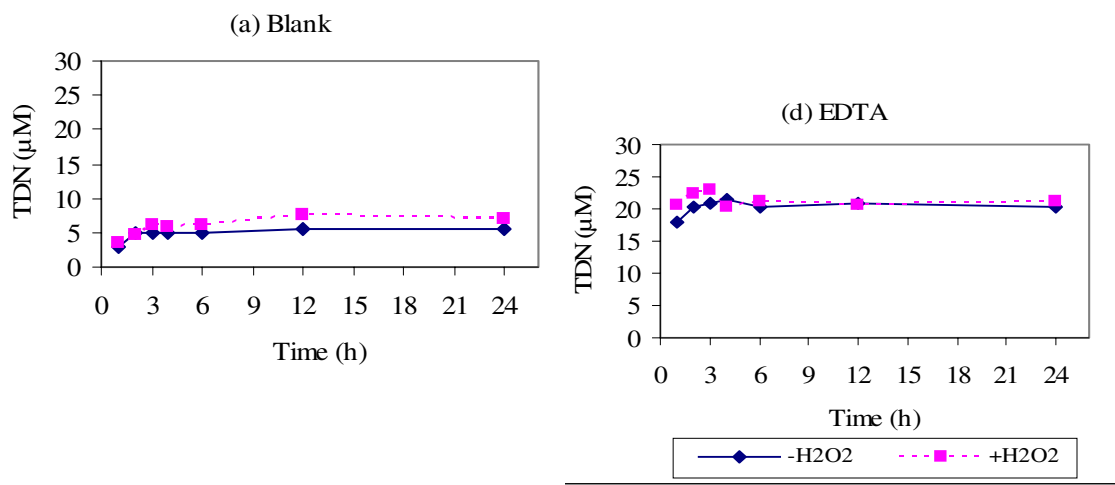


Fig. 1: Effect of irradiation time on the oxidation of different N standard compounds with (+) and without (-) addition of H₂O₂

total N oxidation efficiency. In addition, the oxidation efficiency of urea and EDTA varied from 3-15% ($12 \pm 5\%$, $n=5$) and 83-91% ($85 \pm 3\%$, $n=5$), respectively (Table 1). In addition, good oxidation efficiency of samples was obtained using the UV oxidation method relative to HTCO which ranged from 90-92% ($91 \pm 1\%$, $n=5$) (Table 2).

In conclusions, oxidation efficiency using the UV oxidation method was generally high but consistently less than 100% and particularly low for urea. The results reported using the UV oxidation method here likely underestimate TDN and thus the DON concentration. However, the UV oxidation

method can still provide the opportunity to evaluate changes in DON.

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