
Simultaneous determination of dissolved organic carbon and total dissolved nitrogen in seawater by high temperature catalytic oxidation: conditions for precise shipboard measurements

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Abstract

Appropriate conditions have been achieved for the accurate, rapid, and highly precise shipboard simultaneous determination of dissolved organic carbon and total dissolved nitrogen in seawater by high temperature catalytic oxidation. A nitrogen-specific Antek 705D chemiluminescence detector and a CO₂-specific LiCor Li6252 IRGA have been coupled in-series with a Shimadzu TOC-5000 organic carbon analyser. Precision of both simultaneous measurements is $\leq 1.5\%$, *i.e.*, $\pm 1 \mu\text{mol C l}^{-1}$ and $\pm 0.3 \mu\text{mol N l}^{-1}$, respectively. Quality of analysis is not compromised by vibrations associated with ocean going research vessels.

Key words: HTCO, DOC, DON, simultaneous measurement

1. Introduction

Despite a retraction of the original papers (Suzuki, 1993), the works by Suzuki et al. (1985) and Sugimura and Suzuki (1988) initiated a debate which has clearly contributed to improve the determination of DOC and DON by high temperature catalytic oxidation (HTCO). During the 1991 Seattle DOC/DON Workshop (Hedges and Lee, 1993), HTCO was recognised as the most precise and efficient technique for the oxidation of dissolved organics in seawater (Hedges, 1993). Subsequently, marine chemists have been largely concerned with the determination of DOC by HTCO (Sharp et al., 1993; Cauwet, 1994; Sharp et al., 1995, etc.), but little attention has been paid to the determination of DON (Hansell et al., 1993; Cifuentes et al.,

1994). The aim of this work was to determine and optimise conditions for the rapid and precise shipboard simultaneous determination of DOC and DON by HTCO.

HTCO techniques typically involve the direct injection of filtered, acidified and decarbonated seawater onto a Pt-coated catalyst at high temperature (≥ 600 °C) in an atmosphere of high purity air or oxygen (Williams, 1992; Perdue et al., 1993; Cauwet, 1994). Quantitative production of CO₂ and NO_x gases occurs under these conditions. DOC concentration is directly related to the amount of CO₂ produced, which is determined by infrared gas analysis. Total dissolved nitrogen is determined by a nitrogen-specific chemiluminescence reaction: DON can be obtained by subtracting the independently measured dissolved inorganic nitrogen to the HTCO-TDN. A problem with the precision of DON measurements remains in deep waters, where the DON contribution to the TDN signal is small, <10% (Hansell, 1993).

2. Methods

HTCO measurements were performed using a commercial Shimadzu TOC-5000 analyser (Shimadzu, Kyoto, Japan) coupled to an Antek 705D nitrogen-specific chemiluminescence detector (Antek Instruments Inc., Texas, USA). Incorporation of a LiCor Li6252, solid-state infrared gas analyser (IRGA; LiCor, Nebraska, USA), in conjunction with a PC-based integration software package (Ati Unicam 4880; Cambridge, UK) allows high precision measurements to be made against a background signal distortion caused by the vibrations usually found on a research ship (Peltzer and Brewer, 1993; Sharp et al., 1993). The Shimadzu-IRGA, with a membrane-based pressure differential detection mechanism, is prone to interference from both low (ship's roll) and high frequency vibrations. The LiCor Li6252 incorporates a lead selenide solid state photometric detection device that is insensitive to such movements (Peltzer and Brewer, 1993).

The pre-treated sample is injected (200 μ l) into the Shimadzu TOC-5000 furnace, filled with a pre-conditioned Shimadzu catalyst (Al₂O₃ impregnated with 0.5% platinum), at 680 °C (Fig. 1a). The combustion products (CO₂, NO_x, H₂O, etc.) are carried by high purity oxygen (99.999%; Linde Gas UK Ltd., Manchester, UK) through a 25% H₃PO₄ solution (IC reaction

vessel) to prevent dissolution of CO₂ into water vapour. Then, the stream passes through an in-built Peltier cooler at ~1°C (electronic dehumidifier) for removal of water vapour, and finally through a Shimadzu halogen scrubber. After passing through a Shimadzu particle filter (20mm Ø, sub-micron membrane), the dried gas mixture enters the measuring cell of the LiCor Li6252, and then, in series, enters the measuring cell of the Shimadzu IRGA (which is necessary to control the automatic injection system of the Shimadzu TOC-5000).

The combustion gases are routed to the Antek 705D detector, by pulling with a Vacuubrand MZ 2D diaphragm vacuum pump (ABM, Germany) at the exit of an Antek permeation-tube drier (see below) to lower the pressure within the NO_x/O₃ reaction chamber (Fig. 1b). This minimises background luminescence and increases sensitivity (Walsh, 1989). A high precision controller (Orme Scientific Ltd., Manchester, UK) is used to keep a constant vacuum of -25" Hg (-635 mmHg); this is critical to maintain the constant flow through the reaction cell which is necessary to perform precise measurements. To keep the vacuum from drawing water through the Shimadzu TOC-5000, a T-piece has been installed after the Shimadzu IRGA. The flow through the Antek 705D is set to ~75% of the total flow (=150 ml min⁻¹) by means of an extra-fine Nupro (Swagelock) metering valve (Bristol Valve and Fitting Co., Bristol, UK). The remaining ~25% (= 37.5 ml min⁻¹) is vented to the atmosphere. This configuration avoids all backpressure problems derived from running both systems in-line. Moisture not removed by the Shimadzu dehumidifier could exert significant influence on nitrogen recovery and, in addition, it quenches the chemiluminescence reaction, causing peak tailing (Walsh, 1989). This prompted the installation of a 28 ml (140 mm x 8 mm i.d.) Drierite trap (97% CaSO₄, 3% CoCl₃; 10/20 mesh; NBS Biologicals Ltd., Huntingdon, UK) after the T-piece, to visually check the presence of H₂O in the system. Replenishment of wet Drierite is simple and rapid. As a precautionary measure, the Antek membrane drier was installed downstream. The dried NO • is then mixed with O₃, leading to production of the excited chemiluminescent NO₂ species, which emits quantifiable light energy upon decay to its ground state. Oxygen flow through the ozone generator is set to ~50 ml min⁻¹ (1.5 units in the Antek

705D front panel flowmeter), at 0.5 bar pressure. Such low oxygen inflow increases residence time of oxygen in the ozone generator. This enriches the outflow, and enhances the baseline stability. For the TDN levels usually found in seawater (5-50 $\mu\text{mol N l}^{-1}$), the Antek 705D photomultiplier (PMT) voltage must be set to 800 mV, in the range of $\times 10$. An injection cycle takes 5 ½ minutes: as each sample is injected 3-4 times, ~17-22 min are necessary for completion.

3. Results and discussion

3.1. Standardisation and blanks. Consistency of HTCO-DOC and TDN measurements

Peaks obtained with the Li6252 (Fig 2a) correspond to a 5-point calibration curve in the range 0-200 $\mu\text{mol l}^{-1}$ spiked-C, using a mixed standard of potassium hydrogen phthalate (KHP) and glycine in Milli-Q water. Peaks simultaneously obtained with the Antek 705D detector for the same mixed standard (range 0-25 $\mu\text{mol l}^{-1}$ spiked-N) are also shown (Fig. 2b). The CV for the 3-4 replicate analyses of each spiked solution are typically <1.5% for both DOC and TDN measurements, even for the lowest standard: 50 $\mu\text{mol l}^{-1}$ spiked-C and 6.4 $\mu\text{mol l}^{-1}$ spiked-N. So, the system is sufficiently sensitive to accurately detect the lowest DOC and TDN concentrations in natural seawater: ~40 $\mu\text{mol C l}^{-1}$ and 5 $\mu\text{mol N l}^{-1}$. The CV for replicate analyses of Milli-Q water was obviously much larger and the measured concentrations range from 2 to 5 $\mu\text{mol C l}^{-1}$ and 0.3 to 0.7 $\mu\text{mol N l}^{-1}$ from day to day. The system is calibrated on a peak area basis. A collection of five calibration curves, obtained at ~24 hr intervals during routine analysis of natural seawater samples in the laboratory, are shown in Figure 2c. The CVs of the five corresponding slopes were <1% for both DOC and TDN, indicating minimal variation in recovery efficiencies from day to day; even though salt was progressively accumulating within the column. Our results contrast with the >10% increase during a two week period observed by Tanoue (1993).

Low and stable 'systems blanks' are obtained when the catalyst is properly conditioned. Conditioning consists of running the 'blank check' programme of the Shimadzu TOC-5000 several times, to wash the catalyst with a large volume of Milli-Q water (Suzuki et al., 1992;

Benner and Storm, 1993; Cauwet, 1994; Laodong and Santschi, 1997). Injection of pyrolysed water from the pyrowater trap (Fig. 1a) serves to obtain the 'system blank', assuming that this water is carbon-free (Suzuki et al., 1992). High 'system blanks', mainly associated with the amphoteric Al₂O₃ support (Benner and Storm, 1993; Cauwet, 1994), are a major problem with HTCO techniques (Tanoue, 1992; Chen and Wangersky, 1993; Sharp et al., 1993; Sharp et al. 1995). This seems to be the main reason for the large discrepancies among HTCO systems and with wet chemical oxidation techniques (Sugimura and Suzuki, 1988; Martin and Fitzwater, 1992; Suzuki et al., 1992), as recognised in the criticism of the original papers (Suzuki 1993; Sharp et al. 1995). In addition to Al₂O₃-CO₂ sorption-desorption effects, mechanical action can contribute to the HTCO-DOC 'system blank' from a well-conditioned catalyst; the IRGA is affected by changes in flow through the measurement-cell, such as those associated with the expansion (three orders of magnitude increase in volume) of the liquid samples after injection onto the catalyst at 680 °C.

Although 'system blanks' change from catalyst to catalyst (generally from 5 to 12 μmol C l⁻¹ and from <0.3 to 0.6 μmol N l⁻¹ in our records), they typically vary ±2 μmol C l⁻¹ and ±0.2 μmol N l⁻¹ during the lifetime of a properly conditioned catalyst. Our results contrasted with the TDN 'system blanks' obtained by Koike and Tupas (1993) of 2.4± 0.5 μmol N l⁻¹. To keep the background signal low, the carrier gas is passed through CO₂ (hydropurge/mol. sieve 13X; Fisons, Loughborough, UK) and organics (activated Charcoal; Fisons, Loughborough, UK) scrubbers before entering the Shimadzu TOC-5000.

No significant differences have been found between slopes of calibration curves performed in Milli-Q and filtered natural seawater for either DOC nor TDN (not shown). Consequently, calibration in Milli-Q is preferred for routine analysis because of its low organic carbon and nitrogen content and lower risk of biological degradation and contamination (seawater must be previously filtered and decarbonated). No differences have been obtained for DOC when calibrating the system with potassium hydrogen phthalate (KHP) or sodium bicarbonate (NaHCO₃), indicating complete oxidation of the organic standard. In addition, NaHCO₃ injected through the IC port (*ie.* bypassing the TC combustion column; Fig. 1a) yields

the same calibration slope as injection through the TC port. Consequently, no detectable adsorption or losses of combusted products occurs within the column or between the injection sites; in contrast to the large sorption-desorption effects observed by Cauwet (1994). Blanks from injection through the IC port only account for traces of IC in Milli-Q, whilst injection through the TC port produces a combined value from DOC in Milli-Q and the 'system blank' (Laodong and Santschi, 1997).

3.2. Recovery experiments

Recovery experiments with nitrogen compounds were performed, covering the whole range of oxidation states of naturally occurring nitrogen (from -3 to +5) and representing a variety of chemical structures. Quantitative recovery (96-103%) relative to glycine (Table 1) has been obtained for all inorganic nitrogen salts tested (NH_4Cl , NaNO_2 , KNO_3) and some reference organic compounds (caffeine, EDTA, nicotinic acid, thiourea, urea), recalcitrant organic compounds (e.g. sulphathiazole), poorly oxidised by Suzuki et al. (1985), and biochemicals (arginine, histidine, tyrimidine). However, antipyrine yielded a relatively low recovery of nitrogen (85%), as observed by Cifuentes et al. (1994). Antipyrine has been shown to yield about 30% by persulphate oxidation, 50% by UV oxidation and 94% by HTO at 1100 °C (Hopkinson et al., 1993). Addition of an on-line chromatography furnace at 1100 °C after the T-piece (Fig. 1b) did not effect the recovery of antipyrine. Low recovery of antipyrine could be due to formation of NO_2 instead of $\text{NO}\bullet$ and subsequent loss as HNO_3 , with condensation on the walls of the analyser tubing. NO_2 arriving to the furnace should be decomposed to $\text{NO}\bullet$ at 1100 °C. Alternatively, production of N_2 instead of $\text{NO}\bullet$ in the combustion tube (at 680 °C) from DON compounds containing -N-N- bonds (e.g. antipyrine), may be a quantitatively significant reaction pathway. Since N_2 is thermodynamically much more stable than $\text{NO}\bullet$, the relative success of the HTO method at 1100 °C (Walsh, 1989) may be due to the predominance of kinetic over thermodynamic control on the oxidation of antipyrine at higher temperatures. Accordingly, -N-N- or -N=N- compounds, would not be recalcitrant (i.e. difficult to oxidise), but would be only semi-quantitatively decomposed to $\text{NO}\bullet$.

3.3. Nature of bonded-N and peak shape

It is important to note that strong dependence of peak shape on the nature of the nitrogen compound has been observed during the recovery experiments, even though peak areas are consistent. A conspicuous example is shown in Figure 3, for the three inorganic nitrogen salts: ammonium (N-oxidation state, -3), nitrite (+3) and nitrate (+5). Note that by contrast with ammonium-N, both nitrite-N and nitrate-N must be 'reduced' to NO^\bullet (N-oxidation state, +2), and that such a 'reduction' must occur under oxidative conditions; i.e. decomposition to NO^\bullet must occur through different reaction mechanisms depending on the nature of the nitrogen compound.

Measuring peak height instead of peak area can obviously lead to significant errors. Using a glycine standard (N-oxidation state, -3), TDN would be underestimated in deep-water samples, where nitrate is dominant. On the contrary, if a nitrate standard was used, DON in nitrate-free surface waters would be clearly overestimated. This was one of the reasons argued by Suzuki (1993) to explain the extremely high DON numbers in surface waters; even though a urea (oxidation state -3) standard had been used in the original paper (Suzuki et al. 1985).

Repeated injections of sea water progressively improves peak shape as sea-salt gradually 'cements' the Shimadzu Al_2O_3 balls, thus reducing pressure surges caused by expansion of the sample upon injection. Peak shape improvement when adding CuO wire at the top of the catalyst (Sharp et al., 1993) may be due to the same mechanical effect, rather than any catalytic effect. Peak area is not affected by progressive improvement in peak shape.

3.4. Shipboard analysis

The analytical system was tested aboard ship, during cruise R.R.S. Challenger 123B, from 29 November to 15 December 1995. In spite of bad weather conditions over the Hebridean Shelf (West of Scotland, UK), shipboard HT CO-DOC and TDN analyses were successfully performed immediately after sample collection. Precision of the measurements was not compromised by the vibrations associated with the ship. The calibration procedure onboard was the same as in the base laboratory (see section 3.1). The CV for the slope of the 8 calibrations

run was 1.5% for HTCO-DOC and 0.9% for HTCO-TDN. The system blanks were $10 \mu\text{mol C l}^{-1}$ and $<0.3 \mu\text{mol C l}^{-1}$, respectively.

Samples were collected from 10 l PVC Niskin bottles in 250 ml all-glass flasks. They were immediately filtered through Whatman GF/F filters (ashed 450°C , 4 hours), under positive pressure of high purity oxygen, in an all-glass filtration system, and collected in 10 ml glass ampoules (ashed 450°C , 12 hours). After acidification with H_3PO_4 to $\text{pH} < 2$, ampoules were heat-sealed and preserved in the dark at 4°C , until analysed on board. The CVs for the 4 replicate analyses of each sample were typically $<1.5\%$ for both DOC and TDN measurements. Examples of full water column profiles showing HTCO-DOC and TDN are illustrated in figure 4. A poleward-flowing surface mixed layer (100m deep) has been found, both warmer and fresher than the waters below. HTCO-DOC and DON concentrations are *quasi*-homogeneously distributed through this layer and are clearly higher than in deeper waters.

4. Conclusions

Simultaneous, rapid, and highly precise shipboard measurements of HTCO-DOC and TDN can be routinely performed by coupling commercially available instruments. Comparison of a broad range of standard materials indicates quantitative recovery of oceanic dissolved organic matter (DOM). Most of the initial methodological problems associated with the application of HTCO technology to oceanographic DOC analysis have been resolved. Consequently, the technique is now being applied in studies of the biogeochemical and ecological dynamics of marine DOM. Parallel development of the HTCO-DON methodology, leading to simultaneous determination of the DOM-C/N ratios will contribute significantly to these goals.

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Table 1. Results of the recovery experiments with N-containing materials. Percentages relative to glycine recovery (100%). No of replicates, 3-5; C.V.(%) <2%.

Material	Spiked-N ($\mu\text{M-N}$)	Recovery (%)
ammonium chloride	+25.3	97%
antypirine	+24.6	85%
arginine	+25.4	102%
caffeine	+25.3	97%
EDTA	+24.8	102%
histidine	+26.7	102%
nicotinic acid	+24.5	101%
sodium nitrite	+24.7	101%
potassium nitrate	+24.8	102%
sulphathiazole	+24.3	99%
thiourea	+23.9	96%
thymidine	+25.7	103%
urea	+25.2	101%

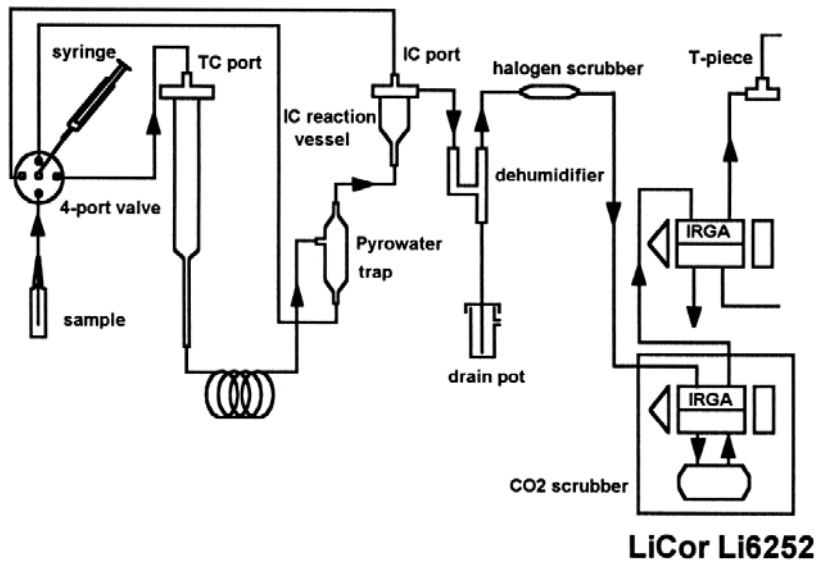
Fig. 1. Analytical system for the simultaneous determination of DOC and TDN by HTCO. (a) Details of the Shimadzu TOC-5000 analyser and the LiCor Li6252 IRGA; (b) and details of the LiCor Li6252 IRGA and Antek 705D Nitrogen Detector.

Fig. 2. Peaks simultaneously obtained with: (a) the LiCor Li6252 IRGA and (b) the Antek 705D Nitrogen Detector, in conjunction with the integration software package ATI Unicam 4880. (c) Collection of calibration curves for HTCO-DOC and TDN, obtained with the same combustion column during routine analysis in the laboratory. m , slope; a , intercept; r^2 , correlation coefficient for the composite calibration curve. System blank for the column: $6 \mu\text{mol C l}^{-1}$ and $<0.3 \mu\text{mol N l}^{-1}$.

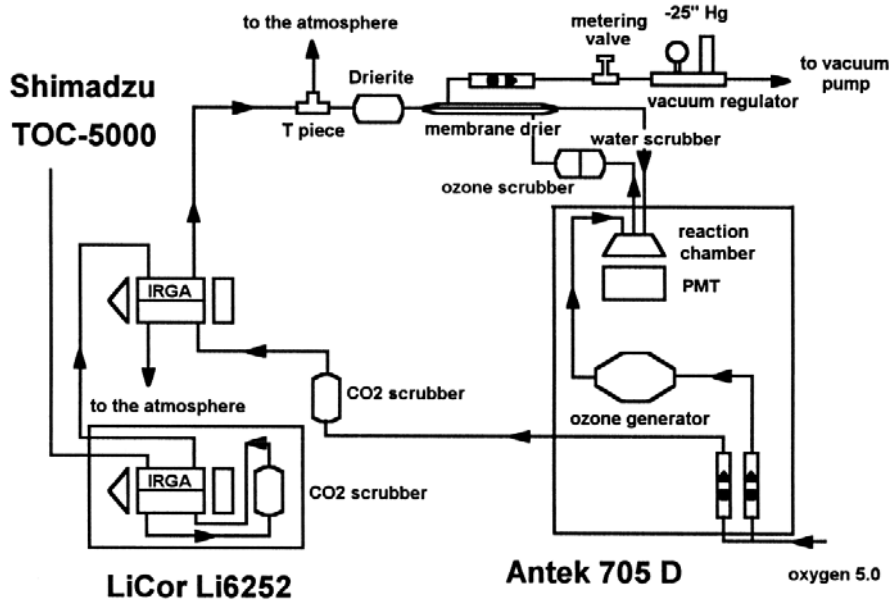
Fig. 3. Comparative peak shape for NH_4Cl , NaNO_2 , and KNO_3 spiked in Milli-Q[®] water. Concentration is $\sim 25 \mu\text{mol N l}^{-1}$ for the three inorganic nitrogen salts.

Fig. 4. Full water column profiles of (a) HTCO-DOC and (b) HTCO-TDN, for station S1500 (1500m deep), in the Hebridean Shelf (West of Scotland, UK). Average CVs 1.2 % ($\pm 0.8 \mu\text{mol C l}^{-1}$) for HTCO-DOC and 0.7% ($\pm 0.1 \mu\text{mol N l}^{-1}$) for HTCO-TDN.

Shimadzu TOC-5000

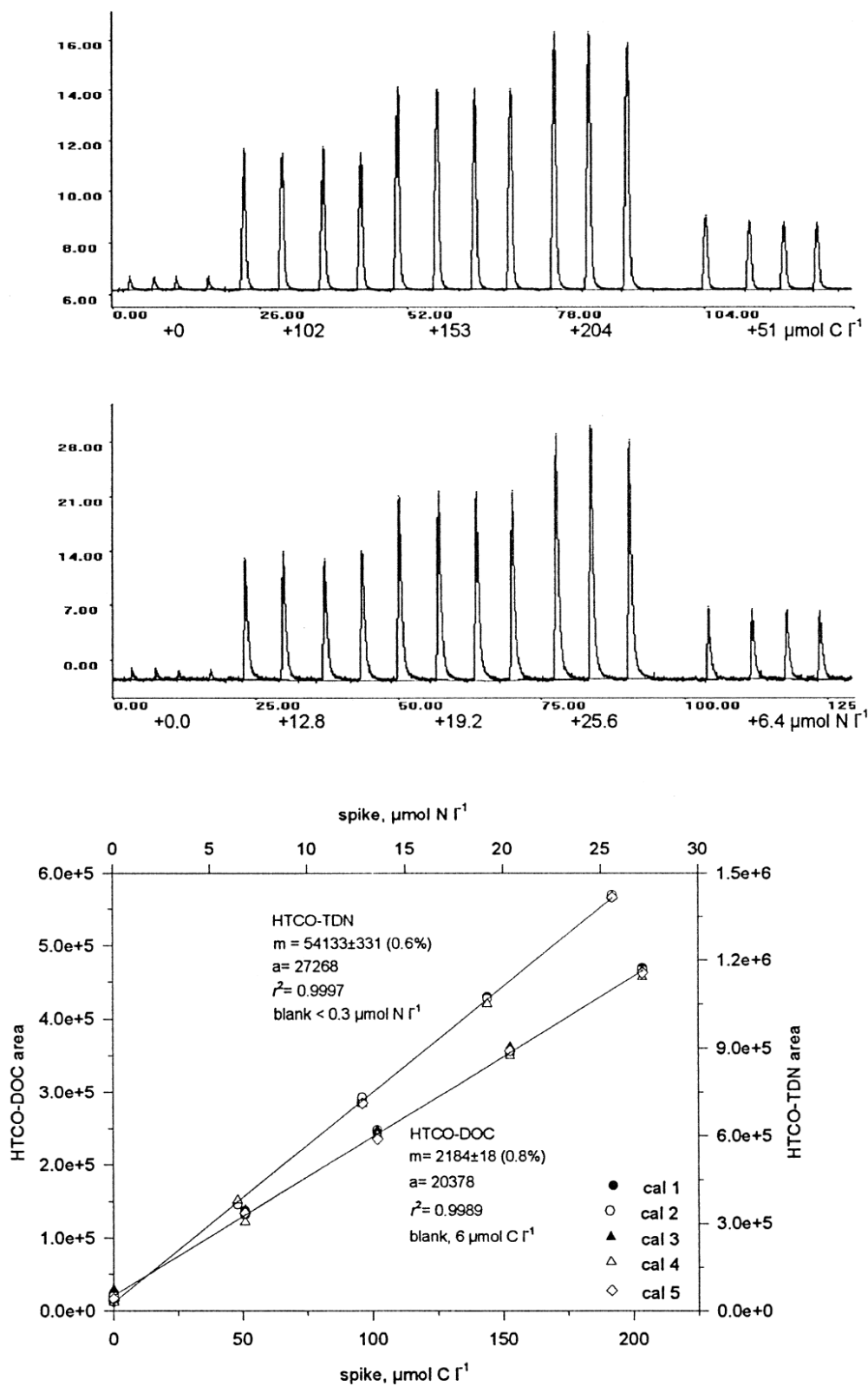


(a)



(b)

Figure 1



(c)

Figure 2

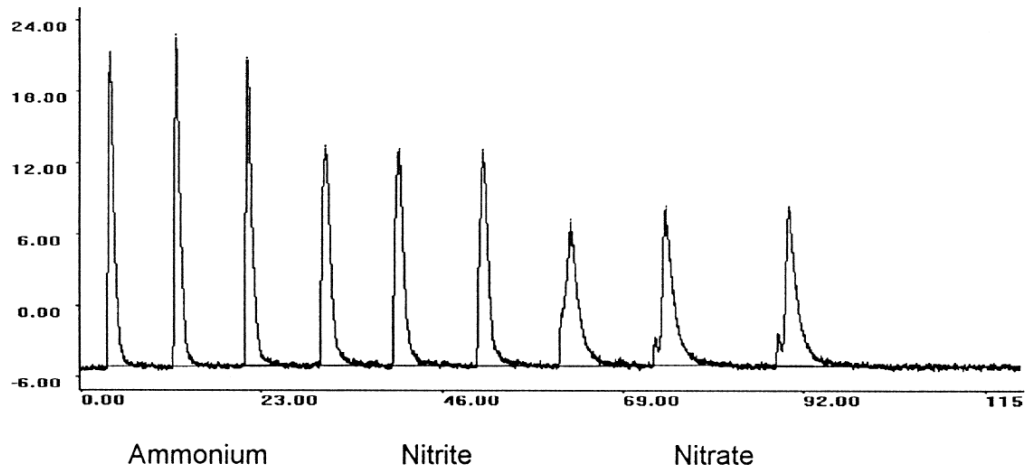


Figure 3

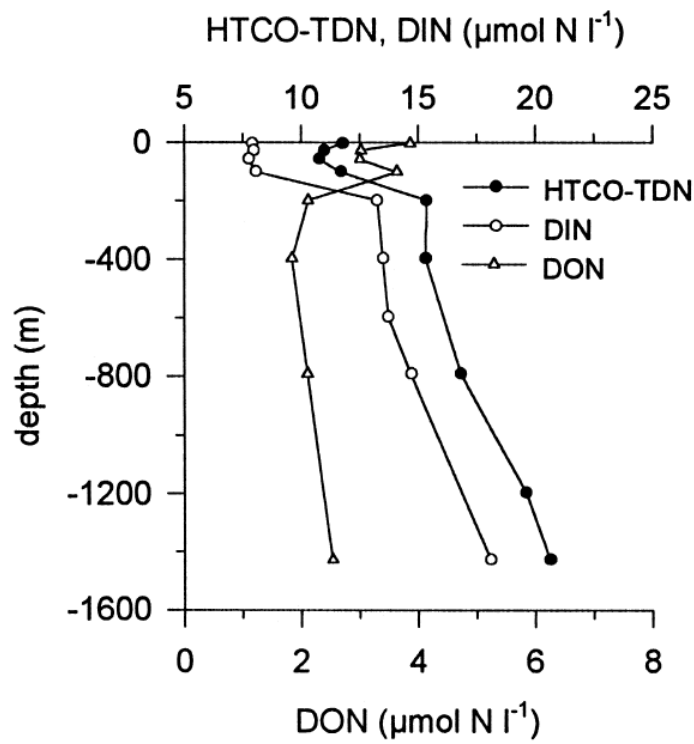
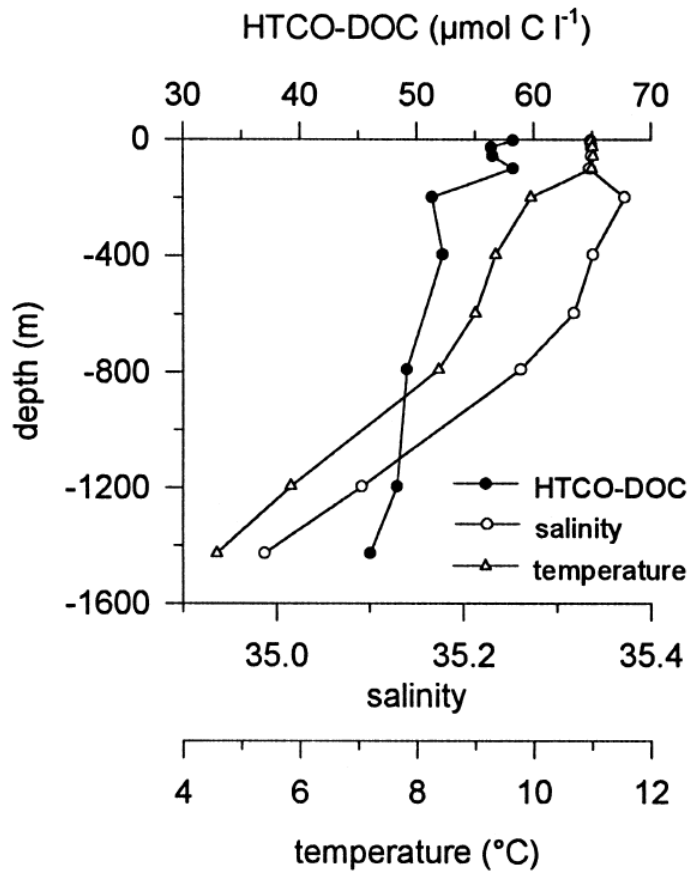


Figure 4