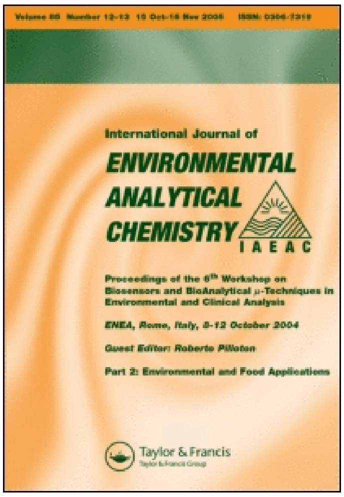

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Conversion efficiency of the high-temperature combustion technique for dissolved organic carbon and total dissolved nitrogen analysis

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Conversion efficiency of the high-temperature combustion technique for dissolved organic carbon and total dissolved nitrogen analysis

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The measurements of dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) in seawater are key in global change and coastal eutrophication studies. Nowadays, the high-temperature combustion (HTC) technique is a widely used method for DOC and TDN analysis. However, uncertainties exist about the operation of the catalyst in the conversion process of DOC and TDN in the HTC method. In this study, five different 'catalyst' materials were tested for their blanks, calibration slopes, and conversion efficiency of DOC and TDN using the Shimadzu TOC 5000A total organic carbon analyser coupled to a Sievers NCD 255 nitrogen chemiluminescence detector. The materials included four metallic catalysts (Shimadzu and Johnson 0.5% Pt–alumina, 13% Cu(II)O–alumina, 0.5% Pd–alumina) and quartz beads. The results indicated that DOC blank signals for the HTC approach using metallic catalysts with an alumina support are higher compared with quartz beads, as a result of the amphoteric nature of the alumina. However, the slopes of the standard calibration graphs were lowest for DOC and TDN determinations on the quartz beads. The DOC recoveries for the metallic catalysts were close to 100% for all compounds tested, with the exception of ammonium pyrrolidine dithiocarbamate. Using quartz beads, poor recoveries were obtained for a range of organic compounds, including the commonly used calibration compounds potassium hydrogen phthalate and glycine. The TDN recoveries for all compounds were typically >90%, with the exception of $NaNO_2$. Furthermore, analysis using the CuO–alumina and Pd–alumina catalysts and quartz beads showed low recoveries for NH_4Cl. This study showed that catalyst performance should be verified on a regular basis using model compounds and blank checks made during every run, and that the Shimadzu 0.5% Pt–alumina material was an efficient catalyst for DOC and TDN analyses using the coupled total organic carbon–nitrogen chemiluminescence detector (TOC-NCD) analyser.

Keywords: Dissolved organic carbon; Dissolved organic nitrogen; Total dissolved nitrogen; High-temperature combustion; Catalyst

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1. Introduction

Investigations of the marine carbon and nitrogen cycles are key to our understanding of global change and coastal eutrophication. Dissolved organic carbon (DOC) forms the vast majority of the organic matter in seawater [1], and on a global scale its contribution to the carbon pool is of the same order of magnitude as that of atmospheric CO_2. Dissolved organic nitrogen (DON) forms on average 60–69% of the total dissolved nitrogen (TDN) pool in marine waters, with highest contributions in the surface waters (90–100%) and lowest in deep oceanic waters (ca $10 \pm 3\%$) [2]. DOC and TDN studies require high-quality analytical measurements. DOC measurements typically involve a direct analysis, whereas the concentration of DON is determined as the difference between TDN and dissolved inorganic nitrogen (DIN), composed of nitrate, nitrite, and ammonium. The DIN species are independently analysed using colorimetric procedures [3]. For the determination of DOC and TDN, one of two approaches is commonly used. The first relies on wet chemical oxidation (WCO) to convert the DOC to CO_2 and TDN to NO_3^-, which are then measured using infrared gas analyses and colorimetry, respectively. WCO methods include alkaline persulfate digestion and UV photo-oxidation [4–6]. The second approach is based on direct aqueous injection of the sample onto a combustion column, and relies on the conversion of the DOC to CO_2 and TDN to NO [7, 8]. The CO_2 is subsequently measured by infrared gas detection, and NO by chemiluminescence following conversion of NO to radical NO_2^* species using ozonation [9–11]. The aqueous injection techniques make use of high-temperature (680–1100°C) combustion (HTC) of carbon and nitrogen compounds, and this process is typically aided by a metallic catalyst or quartz beads [11–14]. The HTC technique is commonly used and allows the simultaneous determination of DOC and TDN in the same sample in a single injection through coupling of commercial instruments (total organic carbon (TOC) analyser and nitrogen chemiluminescence detector (NCD)). The coupled HTC method minimizes the risk of carbon and nitrogen contamination due to minimal sample handling, and exhibits an excellent linearity, a good precision and reported detection limits of ca 8 µM C and 0.6 µM N [14]. The Shimadzu TOC 5000A analyser coupled to either a Sievers or Antek NCD is the most commonly reported configuration. In a recent instrument comparison exercise for TDN analysis in seawater, these instrument configurations showed a tight agreement over a wide TDN concentration range, an excellent performance in terms of reproducibility and 'user-friendliness', and consequently potentially providing an edge over stand-alone HTC NCD and WCO persulfate methods [15].

The most challenging and controversial step in DOC and DON determination is the complete decomposition of dissolved organic matter (DOM) [11]. There is no consensus in the HTC community concerning the role the catalyst plays in facilitating DOM oxidation during HTC analysis [16]. The reactions involving the DOM and the heterogeneous catalysts employed in HTC analysis are complex, and the rates, kinetics, and mechanisms are difficult to measure. The relevant equations for complete DOC and DON combustion are:

$$\text{Organic C} + O_2 \rightarrow H_2O + CO_2 \tag{1}$$

$$CO + 0.5O_2 \rightarrow CO_2 \tag{2}$$

$$\text{Organic N} + H_2O \rightarrow NO + H_2. \tag{3}$$

Equations (1) and (3) refer to the combustion of the organic carbon and nitrogen fractions, respectively, of DOM. The oxidation of organic nitrogen appears to occur to NO via HCN and NH_x intermediates [17]. Equation (2) refers to the complete combustion of CO, which may be formed during incomplete combustion processes.

While oxygen is understood to be an important oxidant in DOC combustion, recent work has shown that catalytic DOC breakdown can be performed with N_2 as the carrier gas (instead of O_2), inferring that water forms an important source of oxidizing species [18, 19]. The TDN analysis using HTC methods furthermore involves the conversion of ammonium, nitrite, and nitrate to NO. Reduced nitrogen compounds (organic matter and ammonium) must therefore be oxidized from an oxidation state of -3 to $+2$, whereas nitrite and nitrate must be reduced from $+3$ and $+5$, respectively.

D-electron metals are capable of undertaking catalytic functions; these metals include Ag, Au, Co, Cu, Fe, Ir, Ni, Pd, Pt, Re, Rh, Ru, and Os [20]. Pd and Pt are catalysts used in a wide number of applications for the conversion of hydrocarbons and CO to CO_2, and their high catalytic activity is attributed to the activation of O–O, O–H, and C–H bonds [17]. In addition, these noble metals also readily convert organically bound N and inorganic N to NO [17]. Pt coated on alumina is the catalyst used in the Shimadzu TOC analysers, but a range of different metallic catalysts (including CoO, CoCr, CuO, and MnO_2) are used in other HTC instruments [11]. In addition, the successful application of quartz beads has been reported in TOC instruments as an alternative for metallic catalysts and operate by facilitating DOM breakdown through their action as an inert heat exchanger [12, 21].

Overviews of recovery efficiencies for a range of N and organic C compounds using various catalysts in different HTC instruments have been reported by [13, 14, 22, 23]. Furthermore, comparative DOC measurements of seawaters and deionized water blanks have been reported using platinized alumina catalysts with different Pt concentrations and performed on a single HTC instrument [24, 25]. However, no systematic DOC and TDN recovery experiments for different types of catalysts and catalyst-type materials in a single HTC TOC-TDN instrument are available in the literature. The aim of this study therefore is to investigate the efficiencies of various metallic catalysts and quartz for DOC and TDN conversion in a single coupled TOC-NCD (Shimadzu TOC 5000A-Sievers NCD 255) system.

2. Experimental

All glassware was soaked in 2% Decon (VWR Ltd, Lutterworth, UK) for 24 h, rinsed with UV-irradiated, High Wycombe, UK ultra-high-purity (UV-UHP) water ($>18.2\,M\Omega\,cm^{-1}$, Elga Ltd, High Wycombe, UK), soaked in 10% HCl (Aristar grade, VWR Ltd) for 24 h, and subsequently rinsed five times with UV-UHP water. The glassware was then combusted at ~450°C for 4–6 h to remove any remaining organic residues [13, 14]. DOC and TDN analyses were undertaken using a Shimadzu TOC 5000A, (Milton Keynes, UK) coupled with a Sievers NCD 255 (GE Instruments, Boulder, USA). The Shimadzu TOC furnace temperature was operated at 680°C, with a carrier-gas (high-purity (99.999%) oxygen, BOC Ltd, Guilford, UK) flow rate of $150\,mL\,min^{-1}$. The gas flow rate for the NCD 255 was $100\,mL\,min^{-1}$. Prior to analysis, all injected solutions were sparged for a period of 8 min (at $75\,mL\,min^{-1}$ using high-purity oxygen) in order to remove the majority of the carbon dioxide. As the solutions were not acidified, a minor background carbon signal was detected in the DOC analyses as a consequence of remaining traces of carbon dioxide in the solutions. Replicate injections (three to five in total) of 100 μL were undertaken for each solution. DOC data acquisition and peak area quantification was undertaken using the Shimadzu TOC 5000A software. TDN data acquisition was undertaken using an A/D card (Talisman Electronics Ltd) slotted into a Pentium PC, and the peak area was quantified using LabView software (National Instruments Inc., Newbury, UK). Full details of the TOC-NCD system operations and their coupling can be found in Badr *et al.* [14].

Five different materials were tested for their conversion efficiency, including four metallic catalysts (1) Shimadzu 0.5% Pt on alumina beads (1.5–3 mm diameter; Shimadzu, Milton Keynes, UK), (2) Johnson 0.5% Pt on alumina pellets (3 mm diameter; Johnson Matthey plc., London, UK), (3) 13% Cu(II)O on alumina pellets ($-14+20$ mesh; Aldrich Chemical Company Inc., Milwaukee, USA), (4) 0.5% Pd on alumina pellets (3.2 mm diameter; Aldrich Chemical Company Inc., Milwaukee, USA), and Quartz beads (3×3 mm; Quartz Scientific Inc., Fairport Harbor, USA). These materials were chosen because they are used in other HTC systems, or offered a potential as a suitable catalyst (e.g. Pd). In order to support the materials, a Pt gauze and quartz wool were placed at the bottom of the quartz combustion column, and quartz wool was placed at the top of the catalyst.

New catalyst materials were directly placed in the combustion tube (i.e. without prior treatment) to assess their immediate blank performance. After placing the new material in the tube, the blank was determined using UV-UHP water until a low and stable DOC signal was obtained. The nitrogen blank values were monitored in a similar manner. This experiment was not conducted for the Johnson 0.5% Pt–alumina catalyst, as this had been used previously (received approximately 3500 injections).

Carbon and nitrogen calibrations were undertaken using a mixture of potassium hydrogen phthalate (KHP) and glycine (VWR Ltd) in UV-UHP water. The C : N atomic ratio of the mixture was 10 : 1. Calibrations were undertaken at two concentration levels, in order to study the influence of C concentration on catalyst performance. A first set of six standards for DOC was prepared in the concentration range of 100–1500 μM C and determined at sensitivity setting 5 for the TOC software; TDN was not determined on these standards as the top concentrations exceeded the range of the NCD. A second set of four standards was prepared with concentrations of 40–300 μM C and 4–30 μM N, and the DOC calibrations on these standards were undertaken at the most sensitive setting of the TOC instrument (setting 1). The chosen TDN calibration standards were in line with those required for calibration of TDN concentrations observed in marine waters (typical TDN concentrations: 5–200 μM). The DOC standards were somewhat higher than required for calibration of samples from marine waters (typical observed DOC concentrations: 40–150 μM); this approach was taken in order to obtain high-precision DOC measurements of the standards for the sensitivity and recovery experiments. In agreement with findings by Alvarez-Salgado and Miller [22], no significant differences were observed between the slopes of standard calibrations performed in UV-UHP water and filtered seawater for both DOC and TDN. Consequently, standard calibrations and recovery experiments (see below) were undertaken in UV-UHP because of its low carbon and nitrogen concentration and low risk of microbiological degradation and contamination.

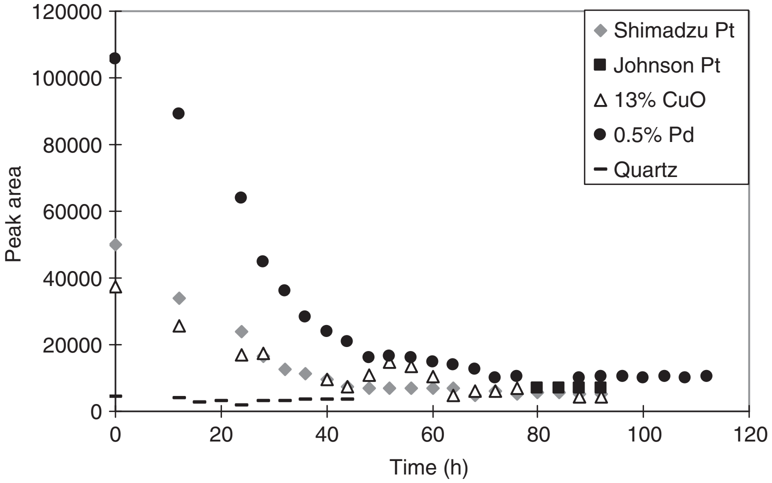

Figure 1. Carbon blank experiments. Peak area *vs.* blank UHP water injection period for the various metallic catalysts and quartz beads.

Recovery experiments were conducted to investigate the combustion efficiency of the various metallic catalysts and quartz beads using a range of organic compounds with different chemical structures: caffeine, thiourea, urea, ethylenediaminetetraacetic acid (EDTA), ammonium pyrrolidine dithiocarbamate (APDC); and inorganic nitrogen salts: ammonium chloride, sodium nitrate, sodium nitrite (all chemicals from VWR Ltd). All solutions were prepared in UV-UHP water.

3. Results and discussion

3.1 *Carbon and nitrogen blank experiments*

Water blank analyses are routine operations on HTC TOC–NCD instruments for conditioning the metallic catalyst, removing salts from the combustion column, reducing memory effects and more generally to obtain an indication of the instrument's operations. The DOC blank value provides an estimate of the combined blank resulting from components of the analytical system (instrument blank) and residual carbon in the UV-UHP water. With the use of low carbon UV-UHP water, the metallic catalyst forms the most important contribution to the DOC water and system blanks [24]. Determination of the DOC system blank using the automated blank checking programme on our Shimadzu TOC 5000A typically resulted in values close to the UV-UHP water blanks (ca 1–3 μM C lower), indicating the low carbon content of our UV-UHP water (which includes a minor contribution from residual carbon dioxide; see section 2). The UV-UHP water blanks hence provided a good indication of the DOC blank caused by the catalyst used in the combustion tube.

Figure 1 shows the results of the DOC blank experiments for the various metallic catalysts and quartz beads investigated using the Shimadzu-Sievers TOC-NCD instrument. The materials showed high initial UV-UHP water DOC blank values, with the exception of the quartz beads. For example, the initial blank values for the first injections of the Shimadzu 0.5% Pt–alumina and 0.5% Pd–alumina catalysts

Table 1. Calibration data, figures of merits, and blank data for DOC measurements of calibration standards in the concentration range 40–300 μM C (instrument sensitivity setting: 1) and 100–1500 μM C (instrument sensitivity setting: 5).

	Slope	*y*-intercept	R^2	LOD[a] (μM)	CV (%)	Blank (μM)
Catalyst/sensitivity setting 1						
Shimadzu 0.5% Pt–alumina	143.9	2643	0.9996	2.4	<1.5	23
13% CuO–alumina	105.8	3383.5	0.9999	1.9	<2.5	30
0.5% Pd–alumina	109.3	8400.1	0.9999	1.7	<2.0	77
Quartz	74.9	1047.7	0.9981	2.7	<3.0	21
Catalyst/sensitivity setting 5						
Shimadzu 0.5% Pt–alumina	22.7	−461	0.9993	50.3	<1.7	<LOD
Johnson 0.5% Pt–alumina	25.6	770	0.9999	13.4	<2.0	38
13% CuO–alumina	20.7	401	0.9998	11	<1.0	5
0.5% Pd–alumina	22	1490	0.9999	5	<0.7	70
Quartz	14.5	−140	0.9998	36.5	<2.0	<LOD

[a] Limit of detection.

were ca 50,000 and 105,000 area units, respectively. A good approach for reduction of the blanks for new catalysts with an alumina support involves combustion (without injections) for at least 24 h in the HTC column at 680°C, or muffle oven (450–550°C), followed by numerous injections of UV-UHP water (>50 h, >750 injections). In case of the Shimadzu 0.5% Pt–alumina catalyst, heating in the TOC instrument for 24 h resulted in a decrease in the blank area from 50,000 to 24,000 area units. Furthermore, following a large number of injections (ca 600) using UV-UHP water for 40 h, the blank value decreased further for this catalyst and reached stable readings (ca 3000 area units, equivalent to ca 29 μM C). Following heat treatment of the 0.5% Pd–alumina catalyst, UV-UHP water injections for >80 h were required to reduce the blank value to 10% of its initial value (10,500 area units).

The UV-UHP water blank signal for the Johnson 0.5% Pt–alumina (pre-used) and 13% CuO–alumina catalysts reached a stable value at about 7000 and 4000 area units, respectively. The blank signals for the quartz beads reached low and stable values (ca 3000 units) within 30 h of injections (450 injections), without prior heating. UV-UHP water analyses undertaken with acidified (pH 2) solutions and utilizing quartz and Shimadzu 0.5% Pt–alumina materials, resulted in even lower blank signals (ca 700–1100 area units; results not presented), as a consequence of a full removal of residual carbon dioxide from the UV-UHP water prior to analysis. Table 1 presents UV-UHP water DOC blank values for the materials, determined after ca 5 days use (>1500 injections). For the high sensitivity setting of the Shimadzu instrument (setting 1), the materials (with the exception of the Johnson 0.5% Pt–alumina and 0.5% Pd–alumina catalysts) provided UV-UHP water blank values close to the instrument blanks of 10–30 μM C and 5–15 μM C reported by Benner and Strom [24] and Alvarez-Salgado and Miller [22], respectively. These workers used the TOC 5000A instruments with Shimadzu 0.5% Pt–alumina catalysts.

The enhanced blank signal values of the metal–alumina catalysts are understood to be caused by the alumina support [11]. The alumina used in the catalysts is an amphoteric oxide and absorbs acid as well as alkaline molecules. The acidic properties of CO_2 result in absorption by the alumina. Consequently, the absorbed CO_2 needs to be removed from a new catalyst, and furthermore the absorption process will result

Table 2. Calibration data, figures of merits, and blank data for TDN measurements of calibration standards in the concentration range 4–30 μM N.

Catalyst	Slope	*y*-intercept	R^2	LOD[a] (μM)	CV (%)	Blank (μM)
Shimadzu 0.5% Pt–alumina	31.8	32.8	0.9999	0.35	<2.0	0.1–1.0
Johnson 0.5% Pt–alumina	41.6	16.2	0.9999	0.37	<3.5	0.4
13% CuO–alumina	32.2	178.4	0.9999	0.32	<3.0	5.6
0.5% Pd–alumina	34.2	27.7	0.999	0.83	<4.0	1.4
Quartz	23.5	76.9	0.998	0.81	<2.0	1.7

[a] Limit of detection.

in a memory effect during DOC analyses which may influence the quality of the measurements. The more rapid conditioning of the quartz beads, and associated low UV-UHP water blank, can be explained by the acidic nature of this material [20], resulting in a low capacity to absorb CO_2.

Table 2 presents the TDN blank values for all the investigated materials. Stable UV-UHP water blank values were obtained for the TDN analysis following only 20–30 injections. The UV-UHP water TDN blanks for the Shimadzu 0.5% Pt–alumina, Johnson 0.5% Pt–alumina, 0.5% Pd–alumina catalysts and quartz beads were 25–45 area units (equivalent to ca 0.25–1.7 μM N). These results compare well with TDN system blanks of <0.3–0.6 μM reported by Alvarez-Salgado and Miller [22]. The blank area of the 13% CuO–alumina catalyst levelled off at a stable value of 140 area units (equivalent to ca 5.6 μM N). This result is possibly caused by N impurities in the catalyst material, and consequently this catalyst is less well suited for low-level TDN analyses.

3.2 *Sensitivity of DOC and TDN analysis*

Instrument sensitivity, as ascertained from the slope of the standard calibrations, forms an important characteristic of the HTC analysis of DOC and TDN. A low instrument sensitivity increases the limit of detection of the analysis, and also provides an indication of poor catalyst or detector performance. The details of the DOC and TDN standard calibrations, obtained using a mixture of KHP and glycine, for the five materials is presented in tables 1 and 2. The DOC calibrations undertaken using standards with concentrations of 100–1500 μM C (sensitivity setting 5 for the TOC instrument) resulted in good linear plots with regression coefficients (R^2) >0.999 for all five materials (table 1). The slope of the linear regression for the DOC standard calibration using the quartz beads was lower (14.5) than for the metallic catalysts (20–25), indicating an incomplete breakdown of the KHP–glycine mixture. The quartz beads furthermore showed the lowest R^2 value (0.998) and slope of linear regression (74.9 compared with 105–110 for the metallic catalysts) for DOC calibrations undertaken using standards with low concentrations (40–300 μM C; instrument sensitivity setting 1). The R^2 values for all TDN calibration graphs obtained using the different materials were >0.998. The slope of the TDN calibration graph for quartz beads was lower (23.5) than for the other catalysts (32–42), a similar observation as for the DOC calibration.

The limits of detection (LODs; determined as 3σ of the blank) for DOC and TDN analyses ranged between 1.7 and 2.7 μM C (instrument sensitivity setting 1) and between 0.32 and 0.83 μM N, respectively, for the materials investigated in this study (tables 1 and 2). These LODs indicate that the materials would allow the detection of the lowest DOC and TDN concentrations in marine waters. The coefficient of variance (CV) for five replicate DOC analyses of standards and samples was highest for the quartz beads (<3%), and lowest (<1.5%) for the Shimadzu 0.5% Pt–alumina catalyst. In case of TDN measurements, the CVs for analyses using the quartz beads and Shimadzu 0.5% Pt–alumina catalyst were <2%. In comparison, the precision of TDN analyses undertaken using Johnson 0.5% Pt–alumina, 13% CuO–alumina and 0.5% Pd–alumina catalysts was weaker. The CV results for the Shimadzu 0.5% Pt–alumina catalyst are in agreement with values (<1.5% for DOC and TDN analyses) reported by Alvarez-Salgado and Miller [22].

3.3 *Recovery experiments*

DOM in marine waters comprises a spectrum of compounds with different levels of resistance to breakdown by the HTC method. The use of KHP-glycine standards for calibration purposes is therefore not representative of DOC and DON in marine waters. Hence, recovery experiments using organic compounds with different chemical structures and refractivities are undertaken on a regular basis to test the breakdown efficiency of the HTC instrument. In addition, a good recovery for DIN is required in their conversion to NO. Experiments were undertaken in this study to investigate the conversion activities of the different materials. The chosen TDN compound concentrations of 8 μM N and 20 μM N can be considered relevant for marine waters, whereas higher DOC concentrations of 200 and 1000 μM C were chosen to allow small differences in recovery efficiencies to be observed.

Figure 2(a) shows the results of the DOC recovery experiments for the five different materials at compound concentrations of 200 μM C. Using the Shimadzu 0.5% Pt–alumina, Johnson 0.5% Pt–alumina, 13% CuO–alumina and 0.5% Pd–alumina catalysts, the recoveries were approximately 100% for caffeine, thiourea, urea and EDTA. These results are in good agreement with previous findings by Chen and Wangersky [26] and Aiken *et al.* [27]. However, APDC was relatively difficult to oxidize by these catalysts, showing recoveries between 79 and 95%. This observation is thought to result from the adsorption onto the catalyst surface of the heterocyclic structure of APDC, which includes nitrogen and two sulfur groups, causing interference with the catalytic breakdown. Similar observations of a reduced recovery were made for the recalcitrant N,S-containing compound sulfathiazole by Sugimura and Suzuki [7] and Chen and Wangersky [26] (50% and 95%, respectively).

In a number of measurements, recoveries were higher than 100%, which were most likely caused by carbon-rich impurities in the test compounds. For all catalysts, the recovery results for compounds at a higher concentration (1000 μM C; determined using sensitivity setting 5) showed a similar trend (figure 2b) compared with the lower concentration (200 μM C). This indicates that the catalyst efficiency for breakdown of specific organic compounds is determined by the nature of the compounds rather than their concentrations (at 200 and 1000 μM C).

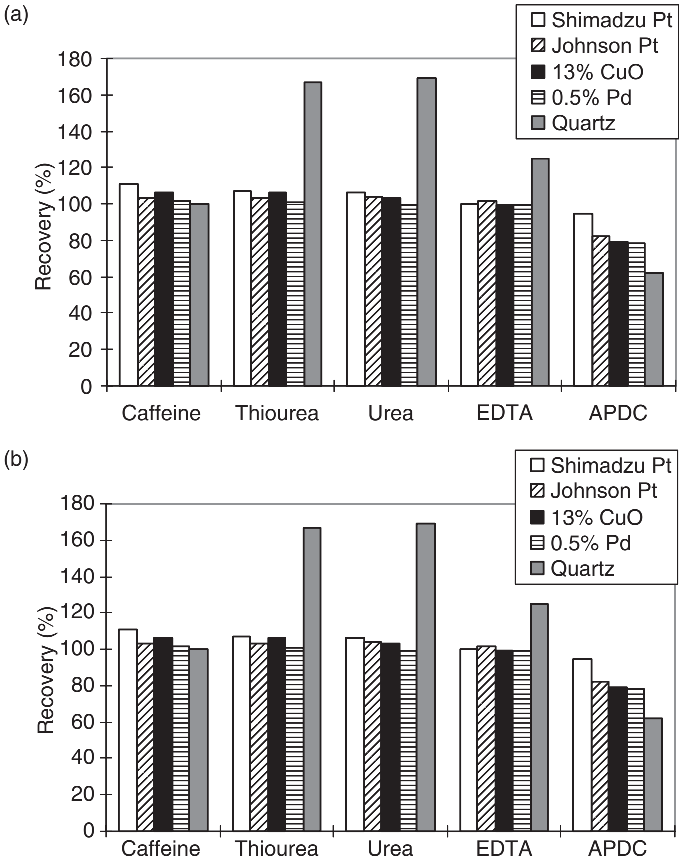

Figure 2. Results of recovery experiments for DOC at 200 μM C (a) and 1000 μM C (b) concentrations of model compounds.

The experiments involving quartz beads showed recoveries of >100% for thiourea, urea and EDTA (at 200 and 1000 μM C). These observations were the result of the incomplete oxidation of the calibration compounds (KHP and glycine) with a consequent overestimation of compound recoveries (see figure 2a and b). The relatively low slope of the calibration graph obtained using the quartz beads (see table 1) underpins this explanation. Further recovery experiments were undertaken using the quartz beads and with thiourea as calibration compound, as this compound showed a high yield in the original recovery experiment. This resulted in recoveries of EDTA (58 and 62%), APDC (44 and 33%), KHP (49 and 39%) and glycine (56 and 59%) at concentrations of 200 and 1000 μM C, respectively. These results indicate that a poor recovery occurred during the HTC combustion of a range of organic compounds using the quartz beads, including the commonly used calibration standards KHP and glycine. Our findings are not in agreement with those by Qian and Mopper [12, 28] who reported ca 100% DOC recoveries for a range of compounds including caffeine, EDTA, thiourea, methanol, antipyrine and sulfathiazole by use of a column with quartz beads (same type as tested in this study) in a MQ Scientific DOC instrument. Additional sulfix and CuO was added to the quartz beads by Qian and Mopper [12] to enhance oxidation efficiency and remove sulfur and halogens from the gas stream, but the use of sulfix and CuO was not reported by Qian and Mopper [28]. Possible reasons for the observed differences between our results and Qian and Mopper's work involve the operation of their HTC column at higher temperatures of 700–800°C [12, 28] and the addition of sulfix and CuO to the combustion column [12]. The former explanation is supported by the low recoveries these workers observed for EDTA (65%) and phthalate (85%) when operating the combustion column at lower temperatures (600–640°C) [12]. Our findings suggest that the quartz beads may require higher temperatures and/or that the relatively small amounts of sulfix and CuO are required in addition to the quartz beads for optimal DOC recoveries.

Figure 3(a) and (b) show the results of the recovery experiments for TDN at 8 and 20 μM, respectively, using the metallic catalysts and quartz beads. In addition to the new Shimadzu 0.5% Pt–alumina catalyst, a pre-used Shimadzu catalyst (>4000 injections) was used in these experiments (no other pre-used catalysts materials were available). Similar trends in recovery efficiencies for the different nitrogen containing compounds using the metallic catalysts and quartz beads were observed using concentrations of 8 μM N and 20 μM N. The recoveries for all compounds were typically >90%, and the new (less than 500 injections) Shimadzu 0.5% Pt–alumina catalyst yielded the best results, corresponding with findings by Alvarez-Salgado and Miller [22]. $NaNO_2$ and ammonia showed low recoveries in a number of experiments. The recoveries for $NaNO_2$ were <92% for all materials investigated. Furthermore, using the 13% CuO–alumina, 0.5% Pd–alumina catalysts, and quartz beads, the recoveries for NH_4Cl were also low.

The conversion of NO_2^- (oxidation state +3) and NO_3^- (+5) on metallic catalysts to N_2 (0), N_2O (+1) and NO_2 (+4) has been reported by Morrison [29]. These compounds will not be detected by the NCD following the ozonation step. Indeed, the conversion of NO_2^- to NO_2 constitutes an oxidation process, and this process may occur in the combustion column instead of reduction to NO. The observed low recovery of nitrite may therefore be inherent to the HTC method for particular metallic catalysts. The Shimadzu 0.5% Pt–alumina catalyst showed the best recovery for nitrite (92% at 8 μM N and 88% at 20 μM N), which is in reasonable agreement with findings (101% for 25 μM N) by Alvarez-Salgado and Miller [22].

The low recovery for NH_4Cl (77% at 8 μM N and 76% at 20 μM N) using the CuO catalyst can be explained by the oxidation of ammonia to N_2O as well as NO on the surface of the CuO catalyst [30]. In contrast, ammonia is chiefly oxidized to NO at high temperatures on the surface of Pt catalysts [30]. A possible explanation for the low recovery of NH_4Cl using quartz beads (24% at 8 μM N and 28% at 20 μM N) is the production of N_2 and/or N_2O rather than NO during the oxidation of NH_4Cl [30], and the same mechanism may explain the lower NH_4Cl recoveries using the Pd catalyst.

The experiments using the pre-used (>4000 injections) Shimadzu 0.5% Pt–alumina catalyst indicated lower recoveries of NO_2^- and NO_3^- compared with the new Shimadzu catalyst (see figure 3a and b). This indicates that the long-term use of the Shimadzu catalyst did not appear to affect the oxidation efficiency of ammonia and organic nitrogen compounds to NO, but that catalyst de-activation occurred with respect to the reduction efficiency of NO_2^- and NO_3^- to NO. Therefore, it is important to undertake regular DOC and TDN recovery experiments before commencing seawater analysis and to replace the catalyst when recovery efficiencies decrease.

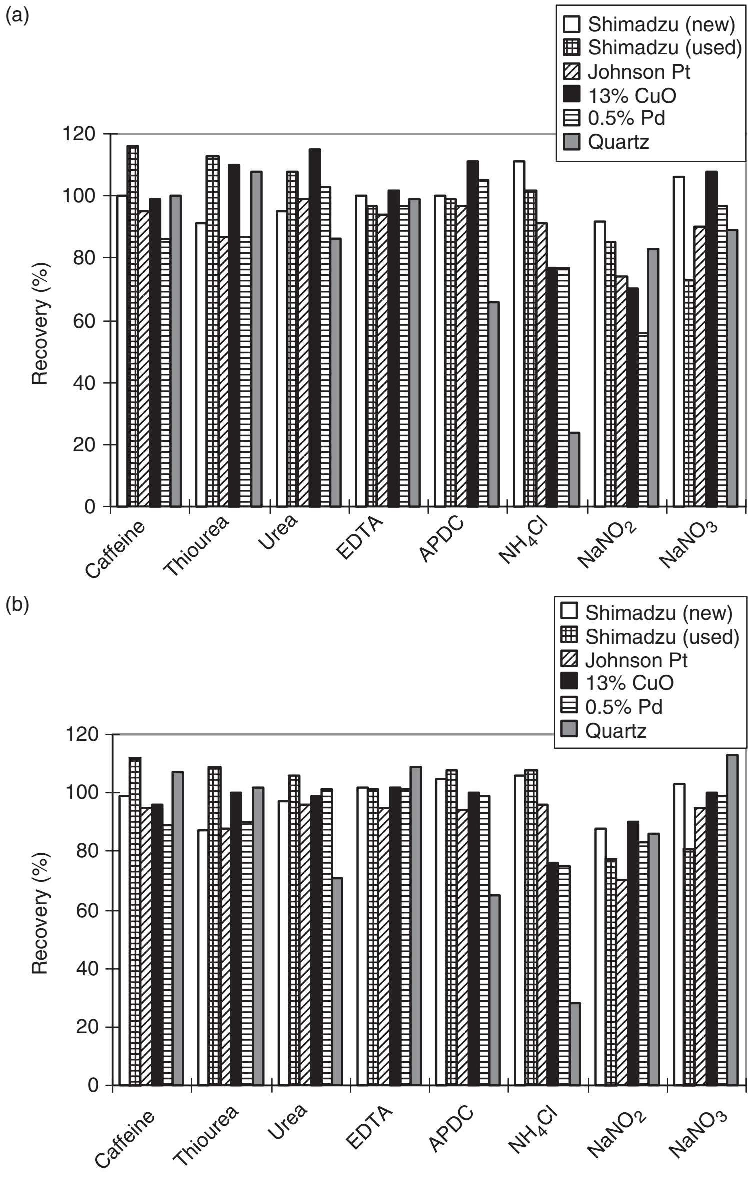

Figure 3. Results of recovery experiments for TDN at 8 µM N (a) and 20 µM N (b) concentrations of model compounds.

4. Conclusions

The HTC technique using a coupled TOC-NCD instrument package is now a widely used approach for DOC and TDN analysis. The coupled TOC-NCD technique allows the simultaneous determination of DOC and TDN in the same sample in a single injection. This approach enhances sample throughput and minimizes the risk of carbon and nitrogen contamination. A range of different materials, including metallic catalysts and quartz beads, are used in the HTC technique to enhance the conversion efficiency of DOC and TDN to CO_2 and NO, respectively. A systematic investigation into the efficiencies of a range of noble and transition metal catalysts, and quartz beads showed that the 0.5% Pt–alumina beads supplied by Shimadzu constitute the best catalyst for simultaneous DOC-TDN analyses using the Shimadzu TOC 5000A analyser coupled to the Sievers NCD 255. Sub-optimal conversion of NO_2^- to NO by metallic catalysts in general, and NH_4Cl to NO by 13% CuO–alumina and 0.5% Pd–alumina catalysts in particular, can be attributed to alternative reaction pathways on the catalysts surface. Consequently, CuO and Pd are not the most efficient catalysts for DOC-TDN analyses in the Shimadzu-Sievers instrument. The weak performance of the quartz beads in terms of DOC conversion can most likely be attributed to the lower operation temperatures (680°C) of the combustion column in the Shimadzu TOC 5000A, compared with the MQ Scientific instrument. In addition, the quartz beads showed a poor conversion of NH_4Cl which was attributed to the production of N_2 and/or N_2O rather than NO.

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