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SIMULTANEOUS DETERMINATION OF TOC AND TN_b IN SURFACE AND WASTEWATER BY OPTIMISED HIGH TEMPERATURE CATALYTIC COMBUSTION

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Abstract—Total nutrition parameters as e.g. total organic carbon (TOC) and total bound nitrogen (TN_b) are indispensable to water quality and elemental nutrient balances. The recommended and most often applied wet chemical digestion for TN_b measurement, however, is discouragingly labour intensive. Therefore, high temperature (690°) catalytic (Pt/ Al_2O_3) combustion (HTC) was investigated for simultaneous determination of TOC and TN_b . Using commercially available instruments a fast and simple procedure was established by coupling a TOC-analyzer to a chemiluminescence detector (CLD) for determination of NO_x gases in the combustion exhaust. Dissolved compounds as well as particulate matter were used to test carrier gases, hot zone fillings and injection volumes influencing N-recovery rates. Injecting dissolved wastewater components (e.g. ammonium, urea, antipyrine) direct onto the catalyst yielded low N-recovery rates (40–90%) depending on concentration. Instead of increasing the oven temperature the evaporation of injected sample solution was improved which resulted in quantitative recovery rates for all investigated compounds except hydrazine.

A representative number of TN_b values from river and domestic wastewater obtained by HTC-CLD were compared to wet chemical digestion. No significant differences between the two methods were found. © 2000 Elsevier Science Ltd. All rights reserved

Key words—total bound nitrogen (TN_b), high temperature catalytic combustion, chemiluminescence detection, simultaneous determination of TOC and TN_b , method comparison, surface and wastewater

NOMENCLATURE

M molecular weight
min minutes
ml millilitres
mol moles
Pa pressure in Pascal

INTRODUCTION

Pollution by organic carbon and eutrophication by bioavailable nitrogen and phosphorus compounds (NO_3^- , NH_4^+ , PO_4^{3-}) is the largest threat to all water ecosystems and water resources in densely populated areas of the world. Legislation helps to prevent pollution from point sources, however, diffuse pollution by wash out of fertilised agriculture and of atmosphere is difficult to control.

Observation of total nutrient levels in sewage processing, surface and ground waters is of decisive importance to recognise trends and efficiency of measures against pollution. In addition values of total parameters are indispensable to calculate element balances and fluxes. Total nutrient element contents give a more realistic picture of water quality because all relevant compounds of an element are included ranking them priority parameters in water quality surveillance. If water residence time is long enough for mineralization to be in an equilibrium, the ratios of e.g. TN_b to the single species components (NO_3^- , NH_4^+ , NO_2^-) remain constant during longer time periods. So actual ratios have only to be re-established during special events by additional measurements of single species. Otherwise they can be estimated fairly accurately from known total elemental contents in a given ecosystem during periods of minimal changes. With respect to all these advantages and because TN_b includes total organic nitrogen (TON) for which no direct measurement method exists Rinne and Seckert-Knopp (1997) proposed TN_b instead of the sum of single inorganic N-species as a test parameter for compliance with legislation.

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Unfortunately the recommended and most often applied method to measure TN_b is based on wet chemical digestion using $\text{K}_2\text{S}_2\text{O}_8$ and subsequent photometric determination of nitrate (Nydahl, 1978). This is laborious and so slow that it cannot provide on line information for process steering. Automated liquid handling cannot speed up chemical digestion and in line digestion using flow injection analysis led to no improvement because particles were not digested and hence TN_b cannot be determined by this technique.

TOC and DOC can be measured directly after stripping off inorganic carbon, whereas TON and DON can only be calculated from TN_b minus bound inorganic nitrogen.

The goal is to liberate the determination of total-N parameter from labour intensive restrictions by a simple one step method that provides fast and highly sensitive reliable response and quantitative recovery for all compounds and particles in almost all matrices. The technique that has the potential to integrate all these demands is high temperature combustion. It is well established (Hedges and Lee, 1993) and widely used in carbon analysers where CO_2 is usually detected by IR as well as in nitrogen analysers combined with chemiluminescence (CL) detection. However, the combined determination of both TOC as well as TN_b (DOC and TDN, respectively) by one injection into one combustion instrument (e.g. a carbon analyser) has been barely investigated and so far has been reported (Alvarez-Salgado and Miller, 1998) for only low concentrations in sea water. Working with higher concentrations as e.g. wastewater led Bettler (1998) and Stratz (1998) to reject the method because they obtained reduced recovery rates.

To follow the protocol of the mentioned analytical demand for total nutrients determination we connected our TOC analysers to a CL-detector for NO_x ($x = 1, 2$) gases. Recoveries of C and N containing model compounds were used to investigate the effects of hot zone fillings and carrier gases. For simultaneous determination of TOC and TN_b an optimised TOC analyzer was used. A representative number of TN_b values obtained from HTC-CLD of surface and domestic sewage water samples were compared for the first time to wet chemical $\text{K}_2\text{S}_2\text{O}_8$ digestion.

MATERIAL AND METHODS

High temperature combustion

Automated Shimadzu TOC-500 and TOC-5000 instruments were operated according to the manufacturer's instructions including amount and type of catalyst filling and all chemicals the instruments required were purchased from Shimadzu. On connecting the CLD the only change made was to flush the outside of the IR-cell windows by a branch of the carrier gas supply. This allowed the use of 100% of the outlet from the infra red detection cell which was connected by a tube (ID 4 mm/OD 6 mm) in tube

(ID 16 mm/OD 18 mm) coupler to a 700AL Ecophysics (CH-Dürnten) chemiluminescence detector (CLD). Connector tubes (ID 4 mm, length 0.8–2 m) made of PVC or HD-PE were indifferent to results. The CLD was equipped with a NO_2 converter (Mo) for measurement of total NO_x ($x = 1, 2$) in three range settings (0.1, 1, 10 and 100 ppm) and a reduced consumption of sample gas flow (110 ml min^{-1}). In general purified air (molecular sieve, PEAK) was used as a carrier gas (150 ml min^{-1}). The analogue signal was recorded on a pen recorder for peak heights and on an integrator (LCI-100, Perkin Elmer) for peak areas.

Standards and response curves

Chemicals of highest purity available from Fluka or Merck were used to prepare C and N containing stock solutions in purified water (double reverse osmosis and mixed bed exchanger (Nanopure, Barnstead)). Potassium hydrogen phthalate (KHP) and sodium nitrate (up to C 100 mg l^{-1} and N 50 mg l^{-1}) have been used exclusively to obtain linear C- and N- response curves. Linearity of the two response curves has been established by freshly prepared 8–10 standard concentrations. Two freshly prepared standard concentrations were measured before and after a sample batch (8–12 samples) in each routine run. This allowed the validation of a previously established response curve and kept track of instrument drift. Background signals obtained from purified water usually corresponded to less than C 0.3 mg l^{-1} and N 0.05 mg l^{-1} , respectively. Each value determined was the arithmetic mean of 3–5 injections. C- and N-recovery rates were calculated on the basis of the compositional purity (manufacturer's certificate) and are compared exclusively to phthalate and nitrate, respectively.

Sample treatment

Samples were prepared according to direct organic carbon analysis, e.g. filtration ($0.45 \mu\text{m}$), acidification (conc. HCl, to final pH 2) and CO_2 degassing for simultaneous determination of non-purgeable DOC and TDN, or high speed homogenising of raw samples, acidification and stripping off CO_2 for non-purgeable TOC and TN_b . Therefore, no separate treatment for simultaneous N-determination is needed. Sufficiently acidified samples are not only essential for direct carbon measurements but to prevent loss of ammonia while purging. In addition non-reproducible results were obtained when non-acidified samples had been injected.

Wet chemical digestion

The procedure by Nydahl (1978) was followed for digesting samples (25 ml river or 10 ml wastewater) with basic $\text{K}_2\text{S}_2\text{O}_8$ (0.075 mol l^{-1}) in sealed glass flasks at 120°C for 2 h at 100 kPa. After adjusting pH to 8 nitrate was quantified photometrically by reducing to nitrite and coupling it to a chromophore.

RESULTS AND DISCUSSION

TN_b determination by unaltered carbon combustion instruments

In order not to affect C-recovery we first used our carbon combustion instruments without any further changes. N-recovery was evaluated by injecting directly onto the catalyst. This procedure gave quantitative carbon recovery rates for the model compound used (Table 1). However N-recovery rates ranged from 55 to 100%. In using urea dependency of N-recovery on concentration was

Table 1. Recovery rates of dissolved compounds of known compositional purity injected direct on the catalyst (Pt(Al₂O₃)) and on a quartz wool (1 cm) on top of a catalyst (QW-Pt(Al₂O₃))

Compounds	C mg l ⁻¹	N mg l ⁻¹	Recoveries (%)		
			QW-Pt(Al ₂ O ₃)	Pt(Al ₂ O ₃)	QW-Pt(Al ₂ O ₃)
Urea	0.86	2.0	100	73	100
	3.43	8.0	102	60	103
4-NH ₂ Antipyrine	6.28	2.0	99	72	100
	25.1	8.0	99	57	91
4-OH-Bezonitril	75.0	14.0	103	67	98
Picolinic acid	72.0	14.0		63	98
EDTA	8.57	2.0	102	86	101
	34.3	8.0	97	64	96
Cysteine	5.19	2.0	98	85	106
	20.75	8.0		77	99
Ammonium	—	2.0	—	55	
	—	8.0	—	70	99
Hydrazinesulfate	—	2.0	—	7	24
	—	8.0	—	6	21
Laurylsulfate	3.0	—	103	—	—
	6.0	—	98	—	—

tested with both TOC instruments. N-recovery rates ranged between 50 and 100% for the TOC-500, and between 36 and 100% for the TOC-5000 (Fig. 1) with high reproducibility ($\pm 3\%$). Noteworthy are the identical results of the two instruments that differ considerably in their hot zone volumes. For concentrations up to urea-N 6 mg l⁻¹ recovery rates decreased to 60%. A further decrease to 36% occurred with concentrations up to urea-N 100 mg l⁻¹. A 100% recovery was only obtained from urea solutions containing less than N 1 mg l⁻¹. Similar N-recovery rates were observed by Holtzhauer (1998, personal communication). Bettler (1998) reported linear response up to N 200 mg l⁻¹ and, compared to nitrate, recovery rates of 70–85% for ammonium and 62–67% for urea (10, 20 and N 50 mg l⁻¹) using a Pt catalyst at 850° in a Dohrmann DC190 instrument. Measurements of an urea solution (N 8 mg l⁻¹) on a Pt/Ir catalyst and a Formacs[®] analyzer (Skalar) revealed a 50% recovery at 680° and 63% recovery at 950°.

Experimenting with urea solutions we observed that the lowest recovery was obtained by a new cat-

alyst filling. Surprisingly, afterwards N-recovery rates of urea increased by 20–30% by further injections on the catalyst. After removal of decomposition debris (powder) from the used catalyst the same low N-recovery rates were obtained like those from an unused catalyst.

From these findings and the fact that urea decomposes at a temperature $> 140^\circ$, we concluded that urea gives low recovery rates not because of insufficient harsh conditions (widely accepted opinion) but because of direct contact of sufficiently concentrated urea solution with the catalyst's surface that prevents to some extent the oxidation to NO. Therefore our investigation was conducted by the idea of transferring the sample into the gas phase before it came into contact with the catalyst. To benefit from all the advantages of working around 700° (lifetime of expensive parts) compared to 800–1100° we decided to completely vaporise the sample by a pellet of quartz wool instead of increasing the oven temperature.

Optimising the C-analyser for simultaneous total C- and N-determination

Carrier gases. The effects of different carrier gas flows on C- and N-response was investigated. In order to accommodate the CLD consumption of combustion-gas carrier gas flow rates of 120, 150, 200 and 300 ml min⁻¹ of air were tested. The C-response was inverse proportional to the carrier flow. The higher the flow the lower the signal (less sensitive). The recovery rates however remained constant ($\pm 5\%$). For flows below 150 ml min⁻¹ a gain in C-signal occurred that was due to an increase in background signal. Higher carrier flows resulted in poorer sensitivities. Therefore the recommended TOC carrier gas flow was not changed and consequently the sample gas consumption of the CLD had to be adjusted by the manufacturer.

The reactivity of nitrate and KHP was evalu-

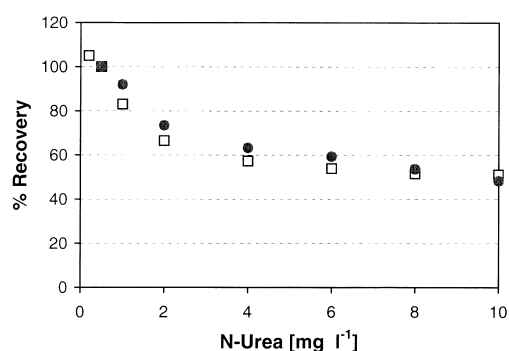


Fig. 1. Decrease of N-recovery with increasing urea concentrations injected into TOC-500 (●, 40 μ l) and TOC-5000 (□, 50 μ l) direct on to the same catalyst (0.5% Pt/Al₂O₃) at 690° C.

ated in the carrier gases N₂, O₂ and purified air. Carbon sensitivity was found to be the same in purified air and in oxygen whereas it was only 7% lower in N₂ as carrier gas. This confirmed the findings of Skoog *et al.* (1997) who reported identical carbon response in O₂ and N₂.

The response from nitrate was more impacted by the carrier gas applied. The highest sensitivity was reached by the inert gas N₂ (100%), in air it was lower (85%) and in O₂ it dropped to 75%. Working with pure O₂ had another serious drawback: the quartz wool was degraded during 1–2 batch runs. Because purified air, the most economical carrier, turned out to be an optimal compromise it was used for all simultaneous determination of total C- and N-contents.

Pyrolytic zone filling. Investigations on total dissolved nitrogen (TDN) determination by high temperature conversion and CL-detection have been performed on specialised N-analysers (Suzuki *et al.*, 1985; Walsh 1989; Braun *et al.*, 1991; Koike and Tupas, 1993) that were operated at 680, 1100, 800 and 900°, respectively. The same method was applied on C-analysers (Hansell 1993; Williams *et al.*, 1993; Lopez-Veneroni and Cifuentes, 1994; Merriam *et al.*, 1996; Alvarez-Salgado and Miller, 1998) operated all around 700°. All the work conducted on C-analysers utilised seawater samples containing TDN concentrations below N 0.5 mg l⁻¹ which resulted in quantitative recoveries. Only Merriam *et al.* (1996) injected filtered and diluted soil leachate (TDN 10 < mg l⁻¹) on CuO-wire separated by quartz wool from the usual Pt/Al₂O₃ hot zone filling. For urea-N solutions (1–10 mg l⁻¹) they found 80–90% recoveries compared to ammonium.

Williams *et al.* (1993) and we observed that C-recovery was not affected by non-metal coated pyrolytic zone fillings and Hansell (1993) demonstrated the role of the catalyst for NO-losses. This supported our idea of preventing a direct contact of the sample solution with the catalyst and that such a procedure should not affect C-recovery. In our investigation on the simultaneous determination of TOC and TN_b a quartz wool pellet (1 cm thick) on

top of the Pt/Al₂O₃ catalyst was used for complete evaporation of the injected sample solution.

Effects of different pellet sizes on C- and N-recovery rates were investigated. Urea and 4-aminoantipyrine known as difficult to transform (Alvarez-Salgado and Miller, 1998) were used as sensitive wastewater constituents. Solutions containing N 3, 6, 25 and 50 mg l⁻¹ were injected on quartz wool pellets of 1, 2 and 5 cm height on top of reduced (–2 cm) catalyst filling. No influence was observed on quantitative C-recovery (Table 2), whereas a slightly reduced N-recovery rate was obtained from 4-aminoantipyrine with 2 cm (96 ± 3%) and 5 cm (93 ± 3%) of quartz wool. These results demonstrated that 1 cm of quartz wool was sufficient to yield simultaneously quantitative recoveries for N and C as well. The findings were scrutinised by a number of other dissolved critical compounds (compare Table 1) containing different types of N-bonds. C-recoveries of none of the dissolved aromatic and aliphatic compounds were affected by quartz wool. Irrespective of bond strength and oxidation level all the N-recovery rates were significantly reduced when injected directly on the Pt-coated catalyst. Like urea (see above) N-recovery was inversely correlated with concentration, in fact the higher the concentration the lower the recovery (identical effects have been observed by Holtzhauer 1998, personal communication). Only ammonia followed a reversed trend where N-recovery was higher at higher concentration. However, injecting the same solutions on a quartz wool covered catalyst, nitrogen was recovered quantitatively within experimental error compared to nitrate-N. In comparison to the multiple bound nitrogen (–C≡N) in hydroxibenzonitrile and –C=N in picolinic acid) and the single N–N bond of 4-aminoantipyrine the doubly bound nitrogens (–N=N–) in the carbon free hydrazine revealed low recovery. But also for hydrazine that easily forms N₂ a three times higher N-recovery was found from injections on a quartz pellet than compared to direct injection on the catalyst. The Pt-coating was identified to be responsible for reduced N-recovery by injecting urea and 4-aminoantipyrine solutions (N 0.5, 1.0, 2.0, 3.0 and 6.

Table 2. C- and N-recoveries from urea and aminoantipyrine for different concentrations and quartz wool fillings

Component	Quartz wool		C-recoveries (%)			N-recoveries (%)		
	C mg l ⁻¹	N mg l ⁻¹	1 cm	2 cm	5 cm	1 cm	2 cm	5 cm
Urea	1.29	3.0	102	100	108	103	105	106
	2.57	6.0	103	90	100	100	102	99
	10.71	25.0	101	104	104	102	100	98
	21.43	50.0	97	100	102	102	101	98
Aminoantipyrine	9.43	3.0	100	106	99	87	87	87
	18.86	6.0	98	107	98	87	88	81
	78.57	25.0	103	100	102	97	96	84
	157.1	50.0	101	101	101	101	96	93

mg l⁻¹) twice on the same amount of quartz wool once Pt-coated and non-coated in the other run. A similar picture was observed: C-recoveries were the same in both cases but N-recoveries were reduced by 10–20% for injections directly onto the Pt-coated quartz wool.

In addition to dissolved compounds the effect of quartz wool pellet on recovery rates was investigated by C- and N-containing particulate matter. Non-filtered domestic wastewater was used to test for dependency on injection volumes. If incomplete oxidation of particulate matter would occur on quartz wool TOC or TN_b should depend on the sample volume injected. No such trend was observed when ten different and homogenised domestic wastewaters were diluted to finally contain C 3–12 mg l⁻¹ TOC and injected (10, 20 and 40 µl) by the auto-sampler of TOC-500. The version of auto-sampler we received for TOC-5000 was not suitable for samples of high concentration of particles. Reproducibility was best (±3%) for 20 and 40 µl injection volumes and little worse (±5%) for 10 µl. The mean N-recovery of 40 µl injections was 5% lower. On TOC-500 therefore 20 µl was the optimal injection volume for wastewater.

Further, the particulate matter ethylene imine polymer (rel. M 6–10 · 10⁻⁵), humic acid (< 63 µm) and river water suspended solids were used to compare TOC and TN_b values obtained from the two hot zone fillings. Results of this comparison are summarised in Table 3 for different injection volumes (10, 20 and 40 µl) of each sample. Injections of lower concentrated samples on quartz wool revealed no systematically and significantly reduced TOC-values. At concentrations higher than C 200 mg l⁻¹ in particulate matter C-recovery appeared to be reduced by a few percent probably due to C-overload. On the other hand TN_b values of the same samples and injection procedure were 10–25% higher, a trend already observed from dissolved compounds. With respect to TOC it can be concluded that in high temperature combustion a catalyst protected by a quartz wool pellet will not yield lower values for all environmental and domestic wastewater because concentrations in these waters are below C 200 mg l⁻¹. In addition routine

measurements revealed indispensable advantages: a 4 times increased lifetime of the catalyst, a better stabilised sensitivity over a longer period and a much simpler maintenance (change of quartz wool only) of good performance.

COMPARISON OF TN_b METHODS FOR RIVER AND DOMESTIC WASTEWATER

Results obtained so far encouraged a comparison of high temperature combustion (HTC) method with the wet chemical digestion used in innumerable environmental investigations. An interlab comparison of several methods including the two used here was published (Elling, 1991) where TN_b was determined in only four different samples including synthetic ones. More river water and domestic wastewater samples were used by Braun *et al.* (1991) who compared TN_b values determined by a HTC N-analyser to the sum of inorganic N-species but unknown TON content. In our study a representative number of river and domestic wastewater samples were digested with K₂S₂O₈ for photometric TN_b determination. Parallel TN_b was measured simultaneously with TOC by HTC and CL-detection.

River water

Samples analysed were collected from 11 different river systems for the surveillance program of Swiss river water (Jakob *et al.*, 1994). The samples represent seasonal variations in a composition of water and TN_b concentrations varied from 0.5 to 7 N mg l⁻¹. The results of the two methods are intercalibrated in Fig. 2. Values of traditional wet chemical digestion are represented on the x-axis, assuming these values to be the correct ones, an orthogonal regression (slope: 0.966, intercept: 0.092) was calculated (Funk *et al.*, 1985). The same correlation was obtained for a linear regression (slope: 0.961, intercept: 0.099) that fits the line in x- and y-direction assuming errors occurring in both methods (Miller and Miller, 1988). Differences of paired values (*n* = 149) between the two methods were classified as not significant by a two sided *t*-test at all levels ≥90%. This documents a very good agreement of the two

Table 3. Comparison of TOC and TN_b values from particulate matter suspended in water injected direct on the catalyst (Pt(Al₂O₃)) and on a quartz wool on top of a catalyst (QW-Pt(Al₂O₃))^a

	TOC (C mg l ⁻¹)		TN _b (N mg l ⁻¹)	
	Pt(Al ₂ O ₃)	QW-Pt(Al ₂ O ₃)	Pt(Al ₂ O ₃)	QW-Pt(Al ₂ O ₃)
RNA	9.6 ± 0.5	9.1 ± 0.5	0.94 ± 0.1	1.13 ± 0.12
RNB	25.9 ± 1.4	26.9 ± 2.6	1.92 ± 0.3	2.22 ± 0.3
RHC	2.6 ± 0.5	2.6 ± 0.5	2.61 ± 0.1	2.58 ± 0.1
RHD	269 ± 43	236 ± 60	17.6 ± 3.3	22.0 ± 4.5
Ethyleneimin polym.	293 ± 7	282 ± 4	122.3 ± 1.0	164.1 ± 3.0
Humic acid	685 ± 35	663 ± 4	8.0 ± 1.2	9.5 ± 2.2

^aRN: river water at normal discharge. A, B two concentrations of resuspended particles. RH: river water at high discharge; C, slowly sedimenting particulate matter; D, resuspension of fast sedimenting particles.

methods and that HTC determination is not interfered by the river matrices. The river water used is characterised by usually low carbon and nitrogen concentration in particulate matter. On the basis of separate specific nitrate and nitrite measurements (ion chromatography) particulate N including organic bound nitrogen (TON) was estimated to be around 10–20% of TN_b because ammonium in several rivers was usually found $<10 \mu\text{mol}$ (Hydrol. Jahrbuch der Schweiz, 1991–1998). Particulate organic carbon (POC) was around 30% of TOC (calculated from TOC minus DOC). The fraction of TON and POC increased only during higher water discharge (rain events). This means if smaller differences between the two methods had been caused by particulate bound nitrogen these differences would have been missed in a comparison using river water.

Domestic wastewater

In domestic wastewater the fraction of nitrogen and carbon bound to particulate matter is much larger, so that small differences would appear if they are caused e.g. by incomplete break down of particulate matter and matrix interference. In the wastewater used the particulate fraction of nitrogen was 10–50%. From a denitrifying and a non-denitrifying sewage plant daily (24 h) composite samples were collected in the inflow and in the effluent and stored at 4°C .

All samples obtained during 1 week were first homogenised before equal aliquot were taken for separate analysis. Without homogenising it would be very difficult to subdivide the raw sample into two identical test portions. This can be done more accurately and reproducibly from a homogenised sample containing smaller particles of a narrower size distribution. Otherwise, if a systematic difference in one step of the sample splitting occurs it is assigned falsely to the subsequent chemical transformation step of one method. TN_b of samples

from several weeks (total $n = 99$) were determined by the two methods. For HTC $20 \mu\text{l}$ of undiluted wastewater was injected. The paired values are intercalibrated in Fig. 3. Obviously the values strayed much more compared to river water due to a higher concentration of particulate matter. However linear and orthogonal regression analysis revealed no deviation between the two methods, and a two sided t -test on the differences gave no significant deviation at all levels $>80\%$. It can be concluded that particulate bound nitrogen in wastewater injected on quartz wool on top of a $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst did not reduce N-recovery rates.

CONCLUSIONS

For the simultaneous determination of carbon and nitrogen by high temperature catalytic combustion the sample pre-treatment for direct TOC measurement is ideal for determination of TN_b as well as for DOC and TDN. However, as we and others have demonstrated, the usual practise of direct injection of the sample solution onto the hot Pt-coated catalyst reduces N-recovery rates of dissolved and particulate N-components higher than $1 \text{ mg l}^{-1} \text{ N}$ to a non-acceptable level. By investigating the hot zone filling evidence was gathered that the evaporation step is decisive for quantitative recovery rates. This step can be improved by increasing the oven temperatures, but still suffers from insufficient recovery rates and fast break down of expensive parts. These drawbacks were eliminated by an oven temperature of 690° and a minimal change in the hot zone filling, that does not affect C-recovery and which can be implemented on any existing carbon combustion instrument. Only a NO-detection is needed instead of labour-intense wet chemical digestion or an additional N-analyser instrument.

Our extensive method comparison proved that TN_b values obtained by the HTC-CLD are identical to those obtained by wet chemical digestion. This demonstrates that also for higher concentrations

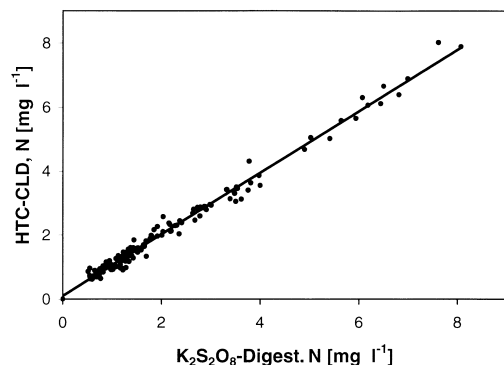


Fig. 2. Intercalibrated river water TN_b values ($n = 149$) obtained from wet chemical digestion ($\text{K}_2\text{S}_2\text{O}_8$) and from high temperature combustion with CL-detection (HTC-CLD). The line drawn is the calculated linear regression line ($y = 0.961x + 0.098$, $R^2 = 0.9876$).

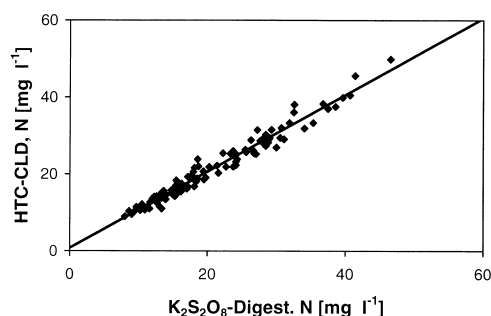


Fig. 3. Intercalibrated domestic wastewater TN_b values ($n = 99$) obtained from wet chemical digestion ($\text{K}_2\text{S}_2\text{O}_8$) and from high temperature combustion with CL-detection (HTC-CLD). The line drawn is the calculated linear regression line ($y = 0.9956x + 0.795$, $R^2 = 0.9643$).

and particulate matter containing samples a common pyrolytic treatment exists that allows high efficient determination of total carbon and total nitrogen in one sample.

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