

DIVISION S-2—SOIL CHEMISTRY

A High-Temperature Catalytic Oxidation Technique for Determining Total Dissolved Nitrogen

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ABSTRACT

A high-temperature catalytic oxidation method for determination of total dissolved N has been developed and tested on soil solution and throughfall. Unlike methods generally used for total dissolved N, this method is rapid, quantitative, and does not require use of strong acids or bases. The technique couples a commercially available chemiluminescent N detector with the combustion furnace of a commercially available C analyzer. An aqueous sample is combusted in an ultra pure oxygen environment at 680°C, converting all forms of N to nitric oxide, which then reacts with ozone. The product, metastable NO₂, is measured chemiluminescently by the N detector. The method is appropriate for samples collected in studies of forest soil solution and throughfall, having a method detection limit of 0.03 mg L⁻¹ total N, and a range from 0.03 to 10.0 mg L⁻¹. Tests of several organic and inorganic N-containing compounds showed recoveries >90% for concentrations up to 5.0 mg N L⁻¹. Urea was the only compound tested with recoveries <90%. Numerous field samples were analyzed and compared with results obtained using persulfate oxidation and high-temperature oxidation (uncatalyzed oxidation at 1100°C). Results from this high-temperature catalytic oxidation method compare well with persulfate oxidation and high-temperature oxidation.

NITROGEN occurs in various inorganic and organic forms in solutions collected from terrestrial and aquatic ecosystems. Inorganic forms of N (NO₃, NH₄, and NO₂) are quickly and easily measured by a number of methods (ion chromatography, flow injection analysis, and other wet chemistry methods). The organic N fraction cannot be measured directly but is instead measured by subtracting the inorganic N concentration from the TDN concentration. Typical methods for determining TDN in soil solution include persulfate digestion, UV oxidation, and TKN. These methods are all time consuming, tedious, use concentrated acids or bases, and in the case of TKN, generate hazardous wastes such as Hg and Se. Each of these methods also requires at least two steps, degradation of organic N to an inorganic form and analysis of the resulting digest. Because of the difficulty in measuring TDN, DON is often overlooked or estimated. However, in many forests, DON is the largest pool of dissolved N. In a hardwood forest at Coweeta Hydrologic Laboratory, Otto, NC. Qualls et al. (1991) found that 94% of total N in soil solution leaching from the forest floor was DON. Similar results were obtained by Sollins and McCorison (1981) who found that DON accounted

for 60 to 70% of total N flux in throughfall and soil solution after clearcutting an old growth coniferous forest. Dissolved organic N also can be the predominant form of N in runoff from forested basins (Hedin et al., 1995). Measurement of TDN thus is critical for accurately estimating nutrient fluxes in forested ecosystems.

Several HTO and HTOCO methods are being developed by oceanographers and marine chemists to determine total N in the open ocean (Suzuki et al., 1985; Walsh, 1989; Maita and Yanada, 1990; Hansell, 1993; Lopez-Veneroni and Cifuentes, 1994). Each of the methods reportedly converts all forms of N to NO or NO₂ by oxidizing the sample in a high-temperature furnace. The product is then trapped in a chromogenic reagent and measured spectrophotometrically (Suzuki et al., 1985; Maita and Yanada, 1990) or the NO is coupled with O₃, producing NO₂, which is measured chemiluminescently (Walsh, 1989; Hansell, 1993; Lopez-Veneroni and Cifuentes, 1994). The HTO methods involve temperatures generally around 1100°C. The HTOCO methods oxidize at lower temperatures, ≈680°C, and use a catalyst to complete the reaction.

Our objective was to develop a rapid, quantitative method of TDN measurement for use on samples of throughfall and soil solution with a wide range of TDN concentrations. A secondary objective was to develop a method that could be automated with use of a commercially available autosampler and data acquisition software. The method described here varies from the most of the marine methods because it links chemiluminescent detection and HTOCO at 680°C for measurement of TDN. Suzuki et al. (1985) also used a temperature of 680°C, but they did not use chemiluminescent detection. Walsh (1989) and Hansell (1993) used chemiluminescent detection, but their oxidation temperature was typically >680°C. Lopez-Veneroni and Cifuentes (1994) also used HTOCO at 680°C with chemiluminescent detection; however, the method was linear only to 0.48 mg L⁻¹. The seawater methods are typically used to analyze concentrations ranging from 0.0 to 0.6 mg total N. Our method incorporates several small differences from the seawater methods that allow for application to a much broader range of concentrations and is appropriate for samples collected in studies of forest soil solution and throughfall.

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Abbreviations: TDN, total dissolved nitrogen; DON, dissolved organic nitrogen; CV, coefficient of variation; DDW, double deionized water; DIW, deionized water; EDTA, ethylenediaminetetraacetic acid; HTOCO, high-temperature catalytic oxidation; HTO, high-temperature oxidation; LTER, long-term ecological research; TKN, total Kjeldahl nitrogen; UV, ultraviolet.

MATERIALS AND METHODS

High-Temperature Catalytic Oxidation Analysis

Total N determinations with HTOC were performed using an Antek 720C chemiluminescent N detector (Antek Instruments, Inc., Houston, TX) coupled to the furnace of a Shimadzu TOC-5000 HTOC carbon analyzer (Shimadzu Scientific Instruments, Inc., Columbia, MD) (Fig. 1). The signal from the N detector was converted from analog to digital by a Waters System Interface Module (Millipore Corp., Milford, MA) and saved (1.5 Hz) and integrated using the chromatographic software program Maxima (Millipore Corp., 1990).

The combustion tube of the Shimadzu TOC-5000 was packed with 25 g of catalyst (Pt on alumina support) and topped with 8 to 9 g of CuO wire, as suggested by Sharp et al. (1993) for analysis of dissolved organic C. A small amount of quartz wool separated the copper from the catalyst. The furnace temperature was held at 680°C. Ultra Zero Oxygen (minimum purity 99.8%) was used as the carrier gas (250 mL min⁻¹) and as the supply of O₂ to the ozone generator of the N detector (40 mL min⁻¹). The sample stream was diverted to the permeation tube (membrane dryer) of the Antek 720C immediately after exiting the combustion tube of the furnace. The drying capacity of the permeation tube can be increased by supplementing the dry gas flow around the sample stream; supplementation is required for injection volumes >25 µL. Use of the dehumidifier in the Shimadzu TOC-5000 (cold trap-condensation) to remove water vapor caused a decline in area counts, leading us to conclude that some of the NO was removed with the water vapor and that use of this technique should be avoided. Cold trap-condensation is commonly used

in the chemiluminescent seawater methods (Hansell, 1993; Lopez-Veneroni and Cifuentes, 1994).

The catalyst in the TOC-5000 was conditioned prior to analysis of TDN. Conditioning was performed by running the Blank Check Program followed by injecting 2 M HCl onto the catalyst. During the blank check procedure, the catalyst is repeatedly rinsed with C- and N-free water. The procedure is more thoroughly described by Benner and Strom (1993). This step proved critical to successful analysis. Peak response and percentage recoveries deteriorate if the catalyst is not cleaned periodically. Most noticeable is the change in peak shape of the NO₃ standards and a decline in area counts when the catalyst needs to be flushed. Improved operation after flushing the catalyst could be due to the cleaning effect of rinsing the catalyst or could be due to moistening of the catalyst as reported by Hansell (1993), who found that NO standard was lost when injected onto a dry catalyst. We routinely conditioned the catalyst prior to each set of TDN analyses (autosampler run of 71 vials, 4 injections each) to ensure optimum conditions. Check standards were inserted frequently to monitor the effectiveness of the catalyst.

Samples with an estimated TDN concentration >10 mg L⁻¹ TDN (based on dissolved inorganic N concentrations and past experience) were diluted prior to analysis. Each set of 71 autosampler vials contained between 5 and 11 blanks, an NH₄ standard set, an NO₃ check standard set, four check standards, and several duplicates of field samples and standards. Several sample sets included an EPA-certified TKN standard (5.0 mg L⁻¹). The four check standards were made from EDTA, urea, caffeine, and glycine. Within each sample set, check standards were the same concentration. Standards and check standards were made with DDW as the solvent. Several sample sets

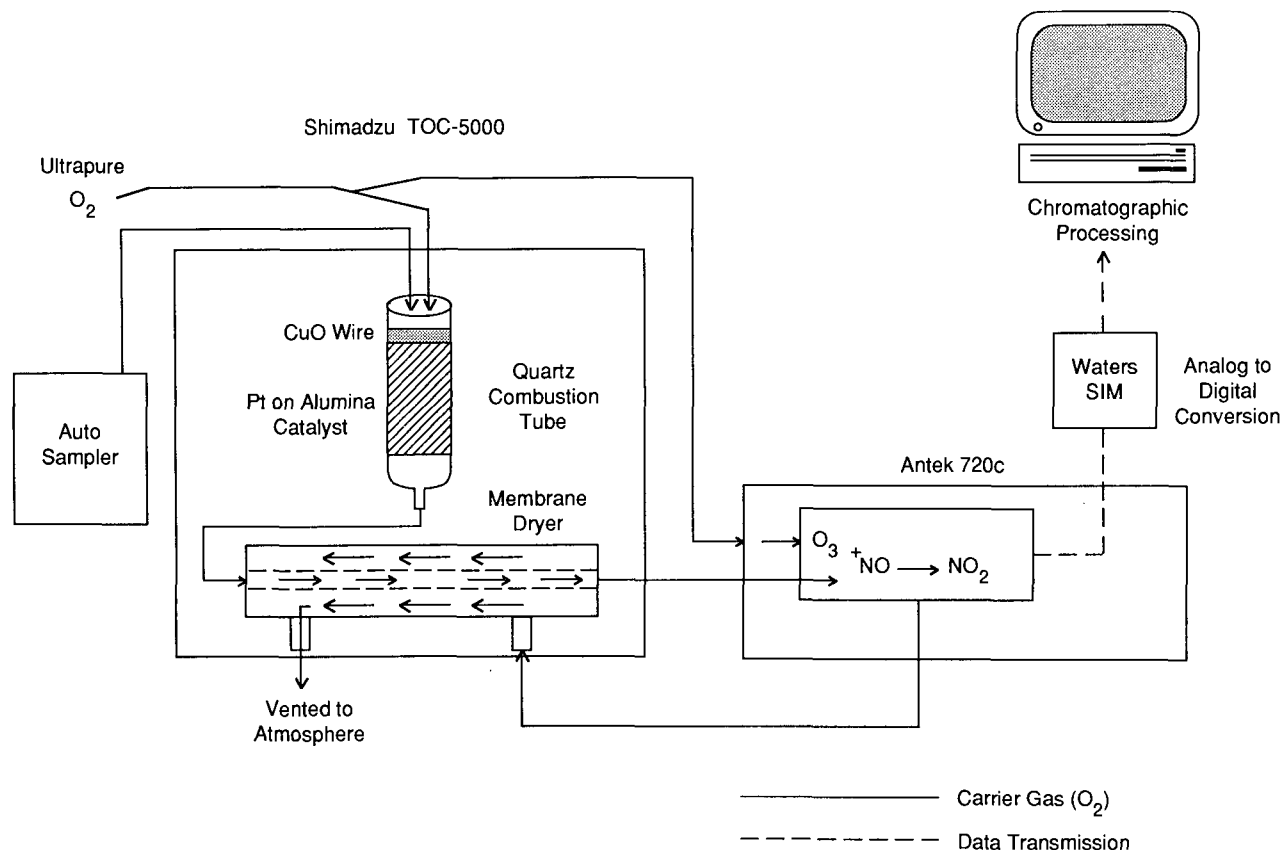


Fig. 1. Coupled Antek-Shimadzu high-temperature catalytic oxidation instrument used in this study (SIM = system interface module).

contained soil solution samples spiked with one or more of six N-containing compounds (the four listed above plus NH_4 and NO_3) to determine matrix effects.

Prior to analysis, sample vials (glass Shimadzu autosampler vials) were rinsed three times with DDW and heat treated at 475°C for 6 h. After pouring into autosampler vials, standards and field samples were covered with a small piece of Parafilm (American National Can, Neenah, WI). Samples were injected into the Shimadzu furnace using the Shimadzu ASI-5000 autosampler. Injection volume varied from 10 to 25 μL , depending on the estimated TDN concentration. Each sample was injected four times, with at least three peaks being saved and integrated by Maxima. Run time was a total of 8 min for all four injections. Attenuation on the N detector was generally set at 5.

The first three of the four injections were evaluated for each sample. If the CV of the three peaks was $<2.0\%$, the mean of the three peak areas was used. If the CV was $>2.0\%$, the two peak areas with the most similar values were used to give a mean area count. For $\approx 30\%$ of vials, we used only two peaks to calculate the mean response. Ammonium was used as the standard for calculation of unknowns and to determine the percentage recoveries of other known compounds.

Persulfate Digestions

To compare our results with a widely used method, we analyzed 160 field samples with both HTO and persulfate oxidation (Solorzano and Sharp, 1980). A sample volume of 10 mL was pipetted into a 28-mL autoclave vial, together with 16 mL of 0.22 M potassium persulfate reagent (allowing minimal head space) and the vial quickly capped and inverted several times for mixing. Methods development trials showed that this ratio of $\text{K}_2\text{S}_2\text{O}_8$ to sample volume ensured complete oxidation of the N-containing organics in our samples. All samples with TDN above 10 mg L^{-1} were individually diluted, prior to persulfate oxidation, into the range of 3 to 10 mg L^{-1} .

Each set of 60 vials contained five reagent blanks, five known standards, one independent EPA-certified check standard (4.0 mg L^{-1} TDN, consisting of 2.0 mg L^{-1} $\text{NO}_3\text{-N}$ + 2.0 mg L^{-1} $\text{NH}_4\text{-N}$), plus randomly chosen duplicate field samples. The five standards, all at 5 mg L^{-1} TDN were NH_4 , Na-nitroprusside, EDTA, and duplicate samples of NO_3 . Samples were analyzed for $\text{NO}_3\text{-N}$ by automated hydrazine reduction with a Technicon TRAACS autoanalyzer. Inorganic N (NH_4 and NO_3) in undigested samples was also measured on the TRAACS system.

The five reagent blanks were averaged within each sample set. Average reagent blanks ranged from 0.11 to 0.13 mg TDN L^{-1} , primarily due to N present in the $\text{K}_2\text{S}_2\text{O}_8$ reagent even after twice-recrystallization. Percentage recovery was calculated for each set by averaging the TDN values for the five known standards (all prepared to be 5.0 mg TDN L^{-1}), subtracting the reagent blank, multiplying the result by the expected sample/reagent dilution ($2.6\times$), dividing by 5.0, and multiplying by 100.

High-Temperature Oxidation Analysis

The HTO analysis was performed using an Antek 771C high-temperature furnace (1100°C) and the 720C N detector. The combustion tube was filled with quartz chips. Injection volume (manual injection) ranged from 2.5 to 10 μL depending on the estimated concentration of the samples. Standards were made with NH_4Cl . Each sample was injected five times, and data were saved by Maxima. All five peak areas were used to calculate a mean peak area unless an obvious outlier was

obtained. An abbreviated standard curve was run after every five samples.

Coefficients of variation for the five manual injections were commonly $>10\%$. Manual injection of 2.5-, 5.0-, and 10- μL aliquots of DDW onto an analytical balance yielded CV of 3.6, 5.4, and 1.6%, respectively. The lack of precision is most likely due to variability in the speed of injection, which has an effect on the response. Despite the poor precision, the average percentage recovery for five N-containing compounds and an EPA-certified check standard was 100%.

Sample Collection and Preservation

Throughfall and soil solution were analyzed for TDN using HTO, persulfate digestion, and HTO. Throughfall samples were collected in 30 opaque, brown 1-L polyethylene wide-mouth bottles staked in place on the forest floor, with polyethylene funnels set in the bottle mouths. Forest-floor leachate samples were collected with zero-tension lysimeters installed beneath the Oa horizon in August 1992 (Currie, 1995).

Samples were collected from experimental forest plots at the Harvard Forest LTER site in Petersham, MA. Two forest stands were sampled, the first an even-aged red pine (*Pinus resinosa* Aiton) stand ≈ 65 yr old, the second a mixed hardwood stand ≈ 80 yr old. Experimental N amendments have been made in both of these stands each year since 1988 in an ongoing effort to study ecosystem response to chronically elevated N inputs (Aber et al., 1993). Nitrogen additions in the form of NH_4NO_3 are sprayed directly onto the forest floor six times per year at rates of 50 and 150 $\text{kg N ha}^{-1} \text{ yr}^{-1}$. Control plots receive no N amendments. Samples used for the present analyses were taken from control, low-N addition, and high-N addition treatments in both forest stands. The TDN in these samples ranged from $<0.5 \text{ mg N L}^{-1}$ to $>110 \text{ mg TDN L}^{-1}$.

Collections reported here were made during late summer and fall 1994. Samples were kept on ice upon retrieval from the field and transported the same day to our laboratories at the Univ. of New Hampshire, Durham. Within 36 h of collection, samples were filtered through precombusted (1 h at 450°C) Whatman GF/F glass-fiber filters (Whatman International Ltd., Maidstone, England) and frozen for up to 4 mo. After thawing, subsamples were stored at 4°C in the dark until analysis. Subsamples were oxidized (persulfate oxidation method) the same day the samples were thawed, analyzed for total organic C using HTO the second day, and analyzed for TDN using HTO the third day. Samples were refrozen after analysis. A subset of these samples was thawed at a later date and analyzed using HTO.

RESULTS AND DISCUSSION

Persulfate Oxidation

Average percentage recoveries ranged from 86 to 95%, with a CV of 2% for the set of five known standards within a given run. All samples were corrected for the reagent blank and the percentage recovery. We analyzed NO_3 , NH_4 , EDTA, Na-nitroprusside, and standard humic acid in various concentrations and combinations in DDW and in field samples. We showed that the percentage recovery correction worked quantitatively and repeatably with CV of 6% or less.

Random paired duplicate analyses of field samples during the persulfate-oxidation sets reported here were measured with CV within 2%. Measured EPA-certified

check standards included with each run reported here were quantified with CV of <2% from the certified value.

Detection Limits and Blanks using the Antek-Shimadzu High-Temperature Catalytic Oxidation

The method detection limit (American Public Health Association, 1989, p. 1-18) was 0.03 mg L⁻¹ using an injection volume of 15 µL and an attenuation setting of 5 on the Antek detector (the conditions we most commonly used). The sensitivity of the instrument can be increased by increasing the injection volume and/or decreasing the attenuation; however, this would also decrease the range of the analysis.

The mean of the two blanks at the beginning of each sample set ranged from 0.00 to 0.15 mg L⁻¹ and averaged 0.04 mg L⁻¹. Blanks were sometimes greater later in the run due to a small amount of carryover. Carryover was most likely due to a residual amount of NO or NO₂ that was not swept out of the N analyzer or the permeation tube by the gas stream. Carryover was limited but measurable (e.g., immediately following a 10 mg L⁻¹ standard, the blank was calculated to be 0.14 mg L⁻¹). The mean of all blanks across 10 sample sets was 0.09 mg L⁻¹. Walsh (1989) used a vacuum pump to lower the ambient pressure in the system, minimizing background luminescence and presumably carryover as well. For applications with a very wide range of concentrations, vacuum extraction of the drying tube may be required.

Replicates using the Antek-Shimadzu High-Temperature Catalytic Oxidation

Replicates of standards had a mean CV of 4.2% and ranged from 0 to 16.6%. Average CV of replicate field

samples was 1.7%, with a minimum and maximum of 0.2 and 5.3%, respectively.

Recovery of Known Compounds using the Antek-Shimadzu High-Temperature Catalytic Oxidation

Percentage recoveries were generally >90% for seven N-containing compounds; urea recovery averaged only 78.4 to 91.3% (Table 1). Generally, there was a slight decline in percentage recovery as concentration increased. This decline may be due to the limited ability of the combustion tube and catalyst to oxidize higher concentrations of N, possibly because of the decline in the ratio of catalyst surface area to N compound. Despite this decline, the recovery is >90% at 5 mg L⁻¹ for most of the N-containing compounds tested.

At higher concentrations, NO₃ peaks tended to overlap slightly, although peak areas were reproducible and equivalent to NH₄ peak areas. Slopes for NO₃ standards were identical to NH₄ standard curves (NO₃ = 0.996 × NH₄ - 0.049; r² = 0.996). Ammonium and NO₃ showed good linearity at least up to 30 and 20 mg N L⁻¹, respectively.

Similar peak area counts were produced by standards and check standards. However, as an analysis progressed, NO₃ peaks began to shorten and broaden. This is presumably due to the catalyst becoming unconditioned. This emphasizes the need to run frequent check standards and the necessity of reconditioning the catalyst prior to each analysis set. Despite the catalyst's declining condition during a run, area counts of check standards showed no consistent trends during a run (Fig. 2).

Percentage recoveries of most compounds were comparable with other published data for HTO and HTO methods. Recoveries of caffeine were reported to be >95% at 30 µg L⁻¹ dissolved N (Maita and Yanada,

Table 1. Average percentage recovery of N using the high-temperature catalytic oxidation method (standard error of the mean in parentheses).

Compound	N recovery							
	Concentration							
	0.5 mg L ⁻¹	1.0 mg L ⁻¹	2.0 mg L ⁻¹	2.5 mg L ⁻¹	3.0 mg L ⁻¹	5.0 mg L ⁻¹	10.0 mg L ⁻¹	Average
	%							
NaNO ₃	106.1 (3.4)	99.3 (1.4)	100.6 (2.2)	96.3 (2.7)	98.0 (1.0)	97.3 (1.3)	94.8 (2.0)	99.2 (0.8)
EDTA	92.6 (4.2)	103.1 (2.6)	95.7 (1.2)	93.8 (1.5)	92.0 (1.1)	92.1 (1.5)	86.0 (1.9)	94.6 (1.0)
NED	-†	97.1	-	-	96.7	95.5	89.6 (5.0)	95.7 (0.5)
Caffeine	94.1 (3.8)	96.0 (1.8)	92.2 (2.2)	91.1 (0.3)	94.0 (1.1)	92.4 (0.7)	91.1 (3.8)	93.6 (0.7)
Glycine	108.1 (3.4)	101.2 (1.9)	96.7 (3.0)	96.4 (0.6)	97.1 (1.4)	95.9 (1.5)	94.0 (2.8)	98.5 (0.9)
Urea	89.4 (5.4)	91.3 (2.6)	88.8 (3.6)	78.4 (3.1)	89.5 (1.4)	86.4 (2.8)	84.0 (3.8)	88.4 (1.1)
Sulfanilamide	-	102.3	-	-	90.6	85.7	90.6	90.9 (2.7)
5.0 EPA TKN‡ Standard	-	-	-	-	-	97.6 (2.2)	-	97.6 (2.2)
Average	99.9 (2.1)	98.4 (0.9)	94.9 (1.2)	90.9 (1.9)	94.2 (0.6)	94.3 (0.7)	91.1 (1.3)	

† - = not determined.

‡ EPA = Environmental Protection Agency; TKN = total Kjeldahl N.

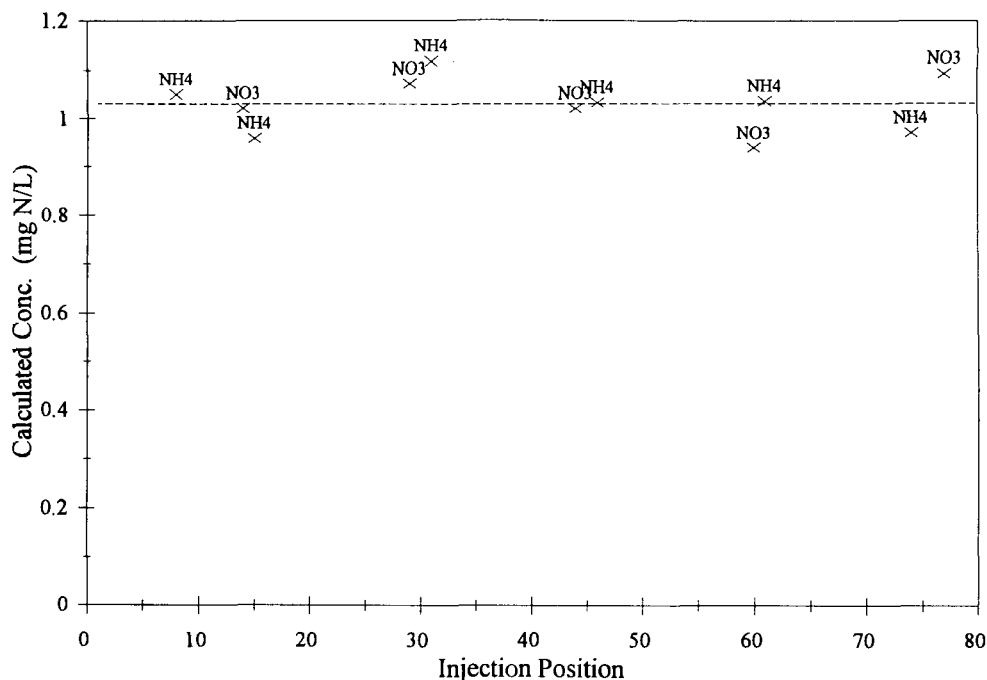


Fig. 2. Calculated concentration of replicate samples of $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ during a run. The mean calculated concentration was 1.03 mg L^{-1} total dissolved N for both $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$.

1990) using a furnace temperature of 650°C . Suzuki et al. (1985) used a furnace temperature of 680°C and reported recoveries of 95, 98, and 101% for caffeine concentrations of 0.2 to $1.0 \mu\text{g L}^{-1}$ TDN, respectively. Walsh (1989) used a furnace temperature of 1100°C and reported recoveries of 100% or slightly greater for NH_4 , NO_3 , glycine, EDTA, and urea at $560 \mu\text{g L}^{-1}$ dissolved N. Walsh (1989) reported 96% recovery of NED (*N*-1-naphthylendiamine dihydrochloride).

At concentrations similar to those used in earlier studies (0.5 mg L^{-1}), our recoveries are similar. Urea was the only compound tested here that gave recoveries $<90\%$ when concentrations were 3.0 mg L^{-1} or less. Other studies report recoveries near 100% for urea (Maita and Yanada, 1990; Walsh, 1989). The reason for the lower recovery is not known, although Walsh (1989) reported recoveries of 73 and 83% for concentrations of 560 and $140 \mu\text{g L}^{-1}$, respectively, using a UV oxidation method, indicating that urea can be recalcitrant.

Matrix effects were not apparent. Soil solution was increased by 1.0 and 3.0 mg L^{-1} TDN using NO_3 , NH_4 , EDTA, urea, caffeine, and glycine. A paired *t*-test showed that percentage recovery was not significantly different between compounds dissolved in DDW and compounds dissolved in soil solution ($P < 0.01$). Average recovery of all compounds in soil solution was 96.6%.

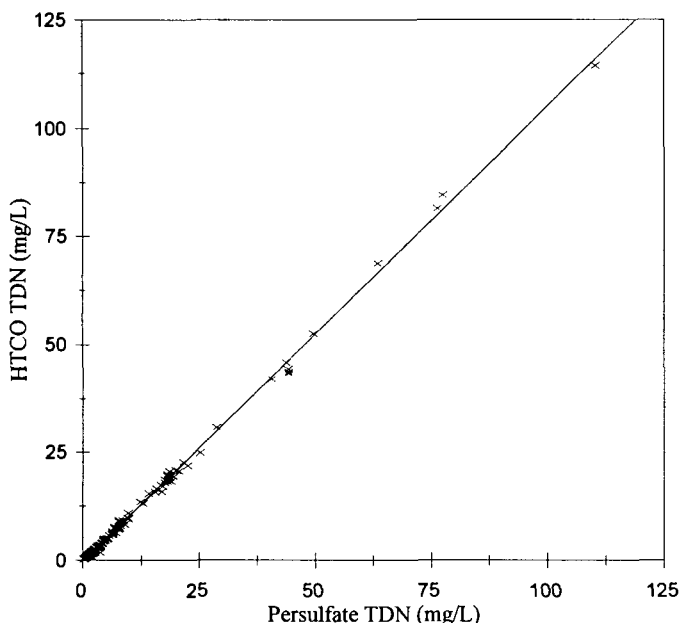


Fig. 3. Comparison of total dissolved N (TDN) measured by high-temperature catalytic oxidation (HTCO) and persulfate digestion [HTCO = $-0.26 + 1.052$ (persulfate); $r^2 = 0.998$; $n = 204$].

Comparison of High-Temperature Catalytic Oxidation with Persulfate Digestion and High-Temperature Oxidation

The HTCO and persulfate digestion produced similar results for TDN. Concentrations of TDN ranged from <0.5 to $>110 \text{ mg L}^{-1}$. Throughout this concentration range, we observed good agreement between HTCO and persulfate digestion (Fig. 3). The slope of this regression is significantly different from 1.0 ($P < 0.05$), indicating that the HTCO method produces slightly higher TDN values than does persulfate digestion. This may be due to a more complete oxidation of dissolved N by the HTCO method. Maita and Yanada (1990) compared an HTCO method (650°C using spectrophotometric determination of NO_2) with persulfate oxidation at concentra-

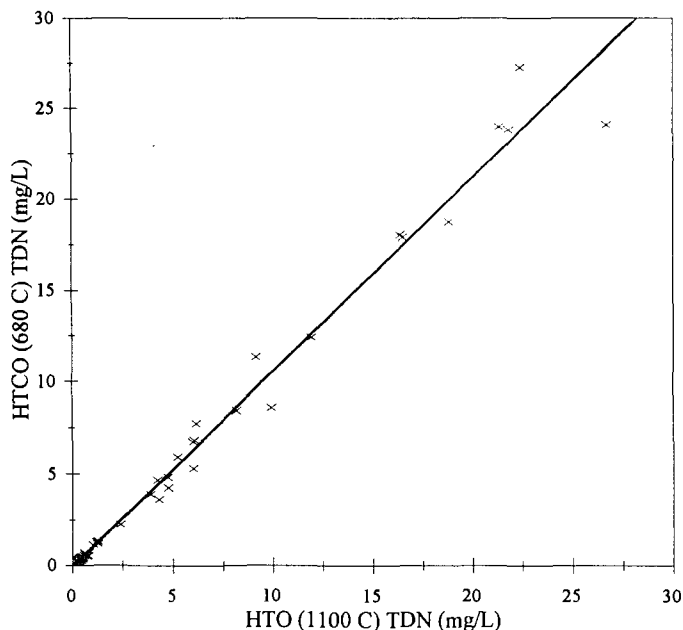


Fig. 4. Comparison of total dissolved N (TDN) measured by high-temperature catalytic oxidation (HTCO) and high-temperature oxidation (HTO) [$HTCO = -0.03 + 1.060(HTO)$; $r^2 = 0.982$; $n = 39$].

tions from 0 to 50.0 $\mu\text{g L}^{-1}$ TDN and also found that the HTCO method gave slightly higher TDN values than persulfate oxidation.

Despite lower percentage recoveries of standard solutions, HTCO and HTO produced similar results for TDN in field samples (Fig. 4). Thirty-nine field samples were analyzed using HTO and HTCO, with concentrations ranging from 0.25 to ≈ 25 mg L^{-1} TDN. There was greater variability around the regression line than was evident in the comparison with the persulfate oxidation, which we attribute to the poor precision of the manual injections using HTO. The slope of the regression line was not significantly different from one, indicating that HTCO gives results similar to HTO for the field samples measured here.

In summary, the automated HTCO method described here gives accurate and precise measurement of TDN without using concentrated acids or bases, without generating hazardous wastes, and without the necessity of a separate analysis of a digest to determine concentration. This method is applicable to the relatively high concentrations of TDN found in soil solution and throughfall.

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