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A COMPARISON OF A PERSULFATE DIGESTION AND THE KJELDAHL PROCEDURE FOR DETERMINATION OF TOTAL NITROGEN IN FRESHWATER SAMPLES*

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Abstract—Precision and accuracy of the persulfate and Kjeldahl determinations of total nitrogen were assessed on 20 standards of known nitrogen concentrations and samples collected from a variety of aquatic habitats. The persulfate method was more precise than the Kjeldahl method for both sets of samples; accuracy and recovery of nitrogen from the samples were the same. Persulfate determinations should find wide application in laboratories analyzing freshwater samples for total nitrogen.

INTRODUCTION

Nitrogen determinations of aqueous samples are routinely conducted by analytical laboratories in order to establish the chemical regime of water bodies. Inorganic nitrogen is analyzed by a number of reliable methods (APHA, 1976; EPA, 1979), while total nitrogen has been determined by Kjeldahl digestions and more recently by photo-oxidation (Armstrong *et al.*, 1966). The Kjeldahl procedure yields a total Kjeldahl nitrogen (TKN) which includes most organic-N compounds and ammonia, but neither nitrate nor nitrite. This method is time-consuming, expensive, and precision is variable (APHA, 1976). Photo-oxidation is also expensive, demanding great initial investment for equipment, and some compounds are refractory to this oxidation (Henriksen, 1970).

An alternative method for total nitrogen determinations has been developed using persulfate digestion (Koroleff, 1972; D'Elia *et al.*, 1977). Alkaline persulfate oxidation of water samples yields NO_3–N as the sole product and conversion of all species to NO_3–N is complete. Thus total persulfate nitrogen (TPN) should be equivalent to TKN plus NO_3 and NO_2–N.

This study was conducted to determine if TPN adequately defines the organic and inorganic nitrogen content of a freshwater sample. Specifically, the precision and accuracy of TPN determinations were compared to those of TKN determinations and to standards of known nitrogen concentrations.

MATERIAL AND METHODS

Standard TPN

A series of 10 standard solutions (range: 0.16–2.42 mg l^{-1}) were prepared by varying, at random, concentrations of NO_3–N, NO_2–N, NH_4^+–N and sulfanilamide (organic-N). Each standard was analyzed in triplicate using the persulfate digestion technique (D'Elia *et al.*, 1977). A nitrate ion electrode (model No. 93-07, Orion Research) was used in the final determination of NO_3^- concentrations. A blank of buffer reagent was analyzed in triplicate to ascertain nitrogen contamination in the methodology.

Standard TKN

The TPN standards, minus NO_2 and NO_3–N, were used to analyze for TKN (range: 0.10–2.40 mg l^{-1}). Each standard was analyzed in triplicate using the Kjeldahl digestion and distillation (EPA, 1979). Final concentrations were determined by using Nesslerization (EPA, 1979).

Collected samples

Ten surface samples from various lotic and lentic habitats in northeast and central Missouri were analyzed for both TPN and TKN. Analysis was carried out in triplicate for each technique and methods followed those used for the standards. The sampled waters included rivers (Mississippi and Salt rivers), managed riverine marshes (Ted Shanks Wildlife Area marshes Nos 2 and 8), urban lakes (Cedar Lake and LeFevre Pond), creeks (Hinkson and Silver Fork creeks) and a creek affected by sewage effluents (Bear Creek above and below the site of sewage introduction). Samples were analyzed in an undiluted state, with the exception of the LeFevre Pond sample, which was diluted to 0.1 concentration for both techniques.

Data analysis

Precision of the analyses was evaluated by use of confidence intervals and coefficients of variation. Accuracy of standard samples was determined using a two-way analysis of variance (Snedecor & Cochran, 1967).

RESULTS AND DISCUSSION

Precision of the total N determinations are compared by examining the coefficients of variation (CV) and confidence intervals (CI) at the 95% level of significance of the samples (Tables 1 and 2). The overall CV of standard samples for TPN is 5.6 and 9.1% for TKN. A similar pattern of overall CV values is

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Table 1. Means, confidence intervals and coefficients of variation for TPN and TKN determinations of standard samples

TPN				TKN			
	Determined values				Determined values		
Known concentration	Mean ($mg\,l^{-1}$)	CI	%CV	Known concentration	Mean ($mg\,l^{-1}$)	CI	%CV
0.16	0.17	±0.025	20.05	0.10	0.11	±0.017	25.52
0.36	0.39	±0.011	4.07	0.20	0.57	±0.382	10.84
0.51	0.49	±0.008	2.22	0.30	0.36	±0.014	6.16
0.81	0.83	±0.046	7.85	0.60	0.53	±0.015	4.66
1.12	1.08	±0.033	4.24	0.80	0.66	±0.070	16.91
1.22	1.21	±0.029	3.33	1.20	1.28	±0.025	1.10
1.42	1.51	±0.033	3.04	1.40	1.30	±0.031	3.81
1.76	1.84	±0.062	4.69	1.60	1.72	±0.153	14.36
2.20	2.17	±0.031	2.02	2.00	1.88	±0.026	2.55
2.42	2.48	±0.086	4.85	2.40	2.83	±0.092	5.35

recorded for the samples collected from aquatic habitats, where overall CV for TPN is 5.6 and 12.7% for TKN. There is a significant difference in CV values between TPN and TKN for both sets of samples ($P < 0.05$). No detectable nitrogen was recorded in replicated reagent blanks.

A low CV of 5.8% was determined by D'Elia *et al.* (1977) for TPN determinations in sea-water. A technical inspection of several Swedish analytical laboratories revealed a CV of 29.6% ($n = 21$) for TPN using cadmium reduction and 16.8% ($n = 6$) using automated systems (Ekedahl *et al.*, 1975). That same investigation reported Kjeldahl + NO_3–N determinations to have an overall CV of 30.8% ($n = 22$), while Nesslerization had an overall CV of 64.4% ($n = 15$). The overall CV values presented here for TPN tend to agree with findings by D'Elia *et al.* (1977), while the findings of Ekedahl *et al.* (1975) may reflect interlaboratory variance, rather than within the techniques.

Electrochemical analysis (nitrogen ion probe), rather than cadmium reduction, may reduce variance with replication, although no definitive data are presented here. The nitrate-specific ion electrode has previously been shown to yield very good precision and recovery values (Yu and Berthouex, 1977).

Narrower confidence intervals of TPN, compared to TKN, also reflect the greater precision of TPN determinations (Tables 1 and 2, Fig. 1). The average CI of standard samples for TPN is ±0.036 and is significantly less than the CI for TKN, ±0.083 ($P < 0.05$). Samples collected from various aquatic habitats yield a similar relationship, where average CI for TPN is ±0.143 and for TKN is ±0.216. The less time-consuming, less expensive TPN method also lends itself to additional improvements in precision through greater replication.

Accuracy of both methods is determined for the standard samples, using the two-way analysis of variance with the known concentration as a control. Because TKN does not include NO_3–N and NO_2–N, TPN concentrations were adjusted to exclude these forms. The results of the statistical test ($F_{2,18} = 1.52$) indicate that there was no difference between the ac-

Table 2. Means, confidence intervals, and coefficients of variation for TPN and TKN determinations of collected samples. TPN values are approximately TKN plus NO_3 and NO_2–N

	Empirical values					
	TKN			TPN		
Sample sites	Mean ($mg\,l^{-1}$)	CI	%CV	Mean ($mg\,l^{-1}$)	CI	%CV
Bear Creek above site	0.18	±0.039	10.65	0.22	±0.025	5.72
Silver Fork Creek	0.36	±0.140	19.29	0.41	±0.054	6.49
Mississippi River	0.55	±0.064	5.79	0.80	±0.101	6.22
Salt River	0.59	±0.305	25.31	0.76	±0.050	3.23
Hinkson Creek	0.61	±0.122	9.90	0.69	±0.062	4.46
Ted Shanks Marsh No. 8	0.61	±0.313	25.25	1.05	±0.048	2.28
Bear Creek below site	0.72	±0.108	7.37	0.82	±0.157	9.44
Ted Shanks Marsh No. 2	0.75	±0.171	11.24	1.20	±0.124	5.11
Cedar Lake	0.87	±0.051	2.89	1.10	±0.135	6.04
LeFevre Pond	4.39	±0.845	9.49	4.83	±0.674	6.88

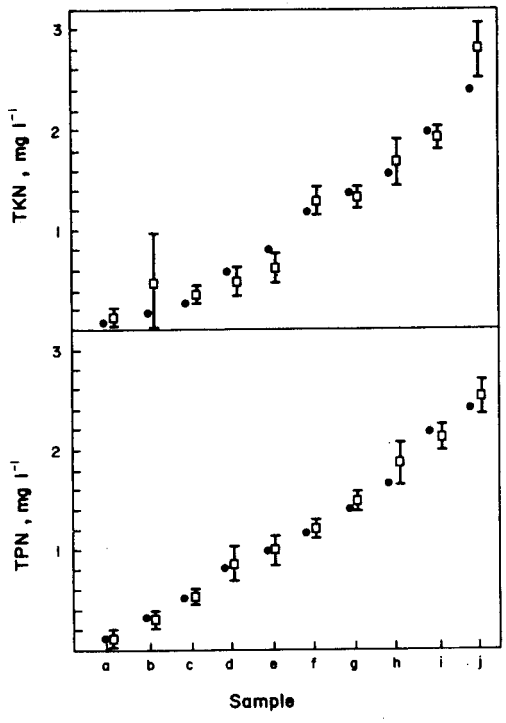

Fig. 1. Comparison of the precision of standard samples for the TPN and TKN methods. The dots represent the known amount of nitrogen contained in a sample, the open squares represent the mean concentration recovered by each method and the vertical lines indicate the 95% CI for each mean.

curacy of TPN and TKN. No significant difference is found between TPN and the control, and between TKN and the control. No difference exists among TPN, TKN, and the known concentrations (control), indicating complete recovery of nitrogen by both methods.

Kjeldahl determination requires an initial investment for digestion and distillation apparatus. A spectrophotometer is necessary for Nesslerization. Persulfate determination requires an autoclave and either cadmium reduction columns or a nitrate probe. In this study, chemical costs were approx. 8 times greater for TKN determinations than for TPN. Persulfate digestion is a reliable method and it should be a substantial improvement over Kjeldahl and photo-oxidation with respect to time, expense, precision and inclusion of all N-containing compounds for analysis.

This investigation presents the first comparison of TKN and TPN determinations within one analytical laboratory using a wide range of nitrogen concentrations in freshwater samples. The study further presents determinations of standard and collected samples, where precision is greater for TPN rather than TKN in both sets. Although EPA (1979) recommends that Kjeldahl-Nesslerization procedure for samples with less than 1 mg l^{-1} N, our results indicate a persulfate digestion technique is more precise. Because of the numerous advantages of TPN determination, it should be considered as an alternative method to TKN in aquatic analytical laboratories.

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