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Short communication

# Potential for chlorate interference in ion chromatographic determination of total nitrogen in natural waters following alkaline persulfate digestion

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**Abstract**

Determination of total nitrogen in aqueous samples after thermal potassium peroxydisulfate (persulfate) digestion is a commonly used alternative to the tedious Kjeldahl procedure. When ion chromatography is used to quantify the nitrate formed during digestion, there is a potential for interference from a chlorate peak if the digested sample initially contained chloride in concentrations close to or greater than the concentration of nitrogen. It was determined that this interference can be avoided either by using chromatographic conditions which cleanly resolve the nitrate and chlorate peaks (e.g., the Dionex AG9-HG column) or by using digestion reagent concentrations chosen to maintain a high pH throughout the digestion. The second alternative is not a viable option for investigators using a single digestion for both total nitrogen (TN) and total phosphorus (TP) analysis. 

*Keywords:* Water analysis; Environmental analysis; Nitrogen; Inorganic anions

## 1. Introduction

The dynamics of algae productivity in a waterbody are typically controlled by the concentrations of nitrogen and phosphorus present in the water column. Consequently, a reliable analytical procedure for the determination of both total nitrogen (TN) and total phosphorus (TP), using separate portions of the same digested sample, has been actively pursued for over thirty years [1–9]. A thermal acidic peroxydisulfate (''persulfate'') digestion step has been used successfully as the initial step in the determination of TP since the late 1960s [10–13].

A major goal of investigators developing methods for the determination of TN has been the elimination of the classical Kjeldahl nitrogen analysis (TKN) which requires a tedious digestion, is unresponsive to some oxidized forms of nitrogen, and generates a toxic waste stream. The first step in most of the suggested alternative procedures for TN determination is a thermal digestion of the sample using persulfate under initially alkaline conditions [2,14–25]. These conditions promote efficient hydrolysis and oxidation of most nitrogenous compounds, resulting in nitrate ions.

Simultaneous determination of TN and TP using a

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single digestion has been shown to be possible if the initial ratio of hydroxide ion to persulfate ion is selected carefully [2,4,5,7]. Under such conditions, the pH of the digestate will progressively decrease from highly alkaline to highly acidic, in response to the release of hydrogen ion which accompanies the thermal decomposition of excess persulfate. At the initially alkaline conditions, most nitrogenous compounds are hydrolyzed and oxidized to nitrate. As acidic oxidizing conditions develop, phosphorus compounds are efficiently hydrolyzed and oxidized to phosphate ions. Total phosphorus can then be determined using time-tested colorimetric methodology.

Determination of TN by measurement of nitrate in digested samples has been most commonly carried out using the cadmium reduction colorimetric technique [2–5,7–9,14–16,18,21,22], although other colorimetric [6,20,24], ultraviolet [23,25], and specific ion electrode [17,19] methods have been described. Recently, the use of ion chromatography (IC) has been reported for measurement of nitrate in the digestates [26–28]. IC is fast, has a relatively low detection limit, and is generally not subject to interferences from the sample/digestate matrix.

In attempting to adapt IC methodology to persulfate-digested samples, we have made some observations which are relevant to analysts using IC for nitrate determination. There is clear evidence that hot persulfate can oxidize chloride present in samples to chlorate ($ClO_3^-$) if the pH becomes highly acidic during the course of the digestion. Depending on IC column conditions, chlorate can co-elute with nitrate. This is particularly a concern to investigators determining both TP and TN. If the initial ratio of hydroxide to persulfate ion is too high, the digestate will not experience a change to strongly acidic pH, a condition deemed essential for efficient conversion of combined phosphorus to orthophosphate.

As we evaluated the unbuffered alkaline persulfate digestion method for total nitrogen determination using IC to quantify the resulting nitrate (TPN-IC method), we initially observed large overestimates of TN, particularly in aquatic samples taken from waters of high ionic strength (e.g., Onondaga Lake, Syracuse, NY, USA). In contrast, TN results on samples from low ionic strength waters (e.g., Lake George, NY, USA) compared favorably with TN values obtained using the Kjeldahl method. For these initial experiments, a Dionex 4000i ion chromatograph fitted with an AS4A separator column was used for nitrate determination. The AS4A column, which is commonly used for the analysis of anions in natural waters, did not resolve the nitrate and chlorate peaks.

In this report, we establish that the above disparities are a consequence of partial conversion of chloride to chlorate during the persulfate digestion. Using modified chromatographic conditions, we have been able to resolve the nitrate and chlorate peaks. A preliminary study of the effect of changing the composition of the digestion reagent on the extent of chloride oxidation has also been carried out.

## 2. Experimental

### 2.1. Persulfate digestion procedure

The alkaline persulfate digestion reagent, 0.22 *M* $K_2S_2O_8$ in aqueous NaOH, was prepared by dissolving 15 g of low-nitrogen potassium persulfate ($K_2S_2O_8$) in 250 ml of NaOH solution and gently heating to dissolve the $K_2S_2O_8$. Aqueous solutions of NaOH were prepared at concentrations of 0.125 *M*, 0.25 *M*, 0.40 *M* and 0.50 *M*. All water used in preparation of reagents, standards, eluent and regenerant solution was doubly deionized. All reagents and standards were certified ACS grade unless otherwise specified.

A 7-ml aliquot of digestion reagent was added to 35 ml of sample or standard in a digestion tube. The digestion tube was capped and placed in an autoclave at 204 kPa and 121°C for 30 min.

Standard solutions for TPN-IC were prepared by dilution of a 0.20% N (as urea) stock solution and a 0.50% chloride (as NaCl) stock solution.

### 2.2. Instrumentation

Following persulfate digestion, undiluted portions of each digested sample or standard were analyzed by IC for nitrate, chloride and chlorate using a Dionex 4000i ion chromatograph equipped with a Dionex autosampler. A Dionex AS9-HC separation column with a Dionex AG9-HC guard column

installed immediately upstream was used with an eluent of 9 m*M* $Na_2CO_3$ at a flow-rate of 1.0 ml/min. A 100 m*M* solution of $H_2SO_4$ was used with a Dionex ASRS-I anion micromembrane conductivity suppressor at a flow of 15 ml/min. Peak integration was performed by a Dionex Peaknet software system installed on an Optiplex Gs Dell computer.

### *2.3. Kjeldahl procedure*

The macro-Kjeldahl procedure for the determination of organic nitrogen (TKN), as described in the Standard Methods for the Examination of Water and Wastewater [29] was used for samples and standards. A 250-ml sample of lake water or standard was mixed with 50 ml of digestion reagent (10 ml concentrated sulfuric acid, 6.7 g $K_2SO_4$ and 1.25 ml of saturated $HgSO_4$ solution) and a few PTFE boiling chips and boiled in a hood until the volume was approximately 50 ml or less, and copious white fumes were observed. The digestion was continued with heating for an additional 30 min. After the digestion the flask was cooled, 300 ml of water were added and the solution was mixed. Hydroxide–thiosulfate reagent was then added, and the mixture was distilled and collected below 50 ml of 0.02 *M* $H_2SO_4$. The phenate colorimetric method [29] was then used to determine the concentration of ammonia.

## 3. Results and discussion

### *3.1. Determination of total nitrogen by persulfate digestion and ion chromatography (TPN-IC) in the presence of chloride*

Since a range of NaOH concentrations has been used by previous workers employing the peroxydisulfate digestion procedure, the percent yields for both oxidized nitrogen (as nitrate) and oxidized chloride (as chlorate) were investigated as a function of initial NaOH concentrations. Standard solutions of 2 mg/kg N (as urea) in 50 mg/kg Cl (as NaCl) were digested at three different NaOH concentrations and then analyzed for nitrate, chlorate and chloride using a AS9-HC separation column. The results, including the percent chloride retained as chloride and the percent chloride converted to chlorate are given in Table 1. As shown in Fig. 1, the nitrate and chlorate peaks are well resolved, and the large sulfate peak provides no interference, even with undiluted samples.

Table 1
Percent oxidation of nitrogen and chlorine at various NaOH concentrations (2 mg/kg N; 50 mg/kg Cl initially)

| [NaOH] (*M*) | % N recovered as nitrate | % Chloride unreacted | % Cl converted to $ClO_3^-$ |
|---|---|---|---|
| 0.125 | 107, 137 | 55, 44 | 53, 52 |
| 0.250 | 88, 97 | 71, 68 | 22, 24 |
| 0.500 | 95, 102 | 95, 98 | 0, 0 |

The pH was monitored before and after the samples entered the autoclave. In each case the initial pH was approximately 13. The samples with 0.25 *M* NaOH and 0.125 *M* NaOH gave final pH values of 2 whereas the 0.50 *M* NaOH sample had a final pH of 11. While the oxidation reactions of both nitrogen and chloride consume hydroxide ion, the bulk of the pH drop is expected to be the result of the thermal decomposition of the persulfate. The overall reaction for the thermal decomposition of persulfate is:

$$S_2O_8^{2-} + 2OH^- \rightarrow 2SO_4^{2-} + \tfrac{1}{2}O_2 + H_2O \quad (1)$$

$$S_2O_8^{2-} + H_2O \rightarrow 2SO_4^{2-} + \tfrac{1}{2}O_2 + 2H^+ \quad (2)$$

The final pH values are consistent with expectations since the concentration of $K_2S_2O_8$ used was 0.22 *M*, and two hydroxide ions are consumed for each persulfate decomposed. Although most, but not all, of the NaOH was consumed in the trials using 0.50 *M* NaOH, the $K_2S_2O_8$ was present in great excess in the trials 0.125 *M* and 0.25 *M* NaOH, resulting in dramatic drops in the pH.

The fraction of chloride converted to chlorate decreased sharply as the initial NaOH concentration was increased. The overall reaction for the oxidation of chloride is expected to be:

$$3S_2O_8^{2-} + Cl^- + 6OH^- \rightarrow 6SO_4^{2-} + ClO_3^- + 3H_2O \quad (3)$$

Since hydroxide ion is consumed in this reaction,

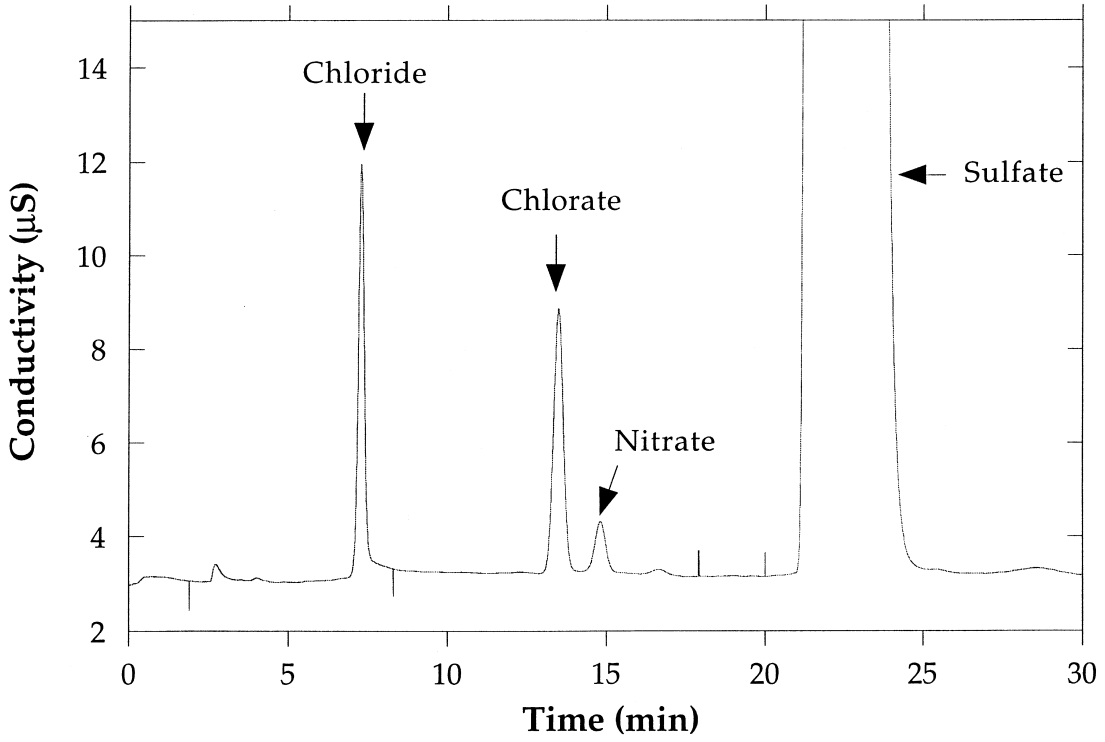


Fig. 1. Ion chromatogram of digested standard solution of 2 mg/kg N (as urea) in 50 mg/kg Cl (as NaCl). A 7-ml aliquot of digestion reagent (0.22 *M* $K_2S_2O_8$ in 0.125 *M* NaOH) was added to 35 ml of the standard and digested for 30 min at 121°C. A chlorate peak appears as a result of the oxidation of chloride during digestion. An eluent of 9 m*M* $Na_2CO_3$ at a flow-rate of 1.0 ml/min was used with a Dionex 4000i ion chromatograph equipped with a Dionex AS9-HC separation column and a Dionex AG9-HC guard column. A 100 m*M* solution of $H_2SO_4$ was used with a Dionex ASRS-I anion micromembrane conductivity suppressor at a flow of 15 ml/min.

the significant decrease in oxidation with increasing NaOH concentration is not what would be expected from thermodynamic considerations. Consequently, we conclude that the fraction of chloride oxidized is, under these circumstances, kinetically controlled and acid catalyzed. The thermal decomposition of $K_2S_2O_8$ is generally agreed to be acid catalyzed in aqueous solution [4]. Since the dramatic drop in pH during the digestion only occurs when the $K_2S_2O_8$ is present in significant excess relative to hydroxide, the formation of chlorate during digestion is expected to be related to the initial ratio of $K_2S_2O_8$ to sodium hydroxide rather than to the absolute concentration of either reagent.

The recovery of nitrogen as nitrate and the conversion of chloride to chlorate were further investigated at several concentrations of urea and also using glycine and nitrate as sources of nitrogen. For standards in which nitrogen was present as urea nitrogen concentrations varied from 0.5 mg/kg N to 4.0 mg/kg N, while for glycine and nitrate standards concentrations were 1.0 mg/kg N and 2.3 mg/kg N, respectively. In all of these preliminary investigations, using 0.50 *M* NaOH and 0.22 *M* $K_2S_2O_8$, nitrogen was essentially quantitatively converted to nitrate while little or no chloride was oxidized to chlorate.

### *3.2. Determination of total nitrogen in natural waters by TPN-IC: a comparison with the Kjeldahl method*

Unfiltered samples taken from Loughberry Lake, Saratoga Springs, NY, USA in April 1998 were analyzed for organic nitrogen by TKN, nitrate by IC and total nitrogen by the TPN-IC method under

Table 2
A comparison of the TPN-IC method and the Kjeldahl method for organic nitrogen (TKN) in natural waters and for a 1 mg/kg standard (mg/kg N)

| Analysis method | Inlet stream 1 | Inlet stream 2 | Loughberry Lake | Urea standard |
|---|---|---|---|---|
| TKN | 0.34 | 0.32 | 0.58 | 0.95 |
| Nitrate by IC | 1.18 | 1.18 | 0.77 | – |
| Sum of TKN and nitrate | 1.52 | 1.50 | 1.35 | 0.95 |
| TPN-IC | 1.46 | 1.53 | 1.14 | 1.10 |

investigation. The sum of the nitrate measured on undigested lake samples by IC and organic nitrogen from the Kjeldahl method was compared with the total nitrogen by TPN–IC. The same procedure was also conducted on a nominal 1 mg/kg N (as urea) standard. The results (Table 2) show that the TPN-IC method can be used in natural water analysis as an alternative to the Kjeldahl method, if the nitrate concentration is subtracted from the total nitrogen by TPN-IC.

## 4. Conclusions

During the unbuffered thermal digestion of aqueous samples, the reaction of peroxydisulfate with any chloride present will result in the formation of chlorate if $K_2S_2O_8$ is present in excess relative to NaOH. This is potentially problematic since, depending on the chromatographic conditions and column used, chlorate and nitrate can coelute. If the digested sample is to be used for TPN-IC only, this chlorate interference can be avoided in either of two ways. The formation of chlorate does not interfere with nitrogen determination if the chromatographic conditions and column used clearly resolve the nitrate and chlorate peaks (e.g., Dionex AG9-HG). Alternatively, if digestion reagent concentrations are chosen to maintain a high pH throughout digestion, chlorate will not be formed under typical TPN-IC conditions. For example, an initial NaOH concentration of at least twice the initial $K_2S_2O_8$ concentration will result in a highly alkaline solution throughout the digestion period. If the digestion sample is to be used for both TPN-IC analysis and a TP analysis, the literature suggests [4] that a pH drop during digestion is necessary for the quantitative hydrolysis of phosphorus compounds to phosphate. In addition, Ebina [4] suggests that for some organic compounds the recovery of nitrogen can be more complete with a variable pH digestion than with the buffered alkaline digestion.

When a pH drop during digestion is desired, the potential for chlorate interference can be avoided by the use of chromatographic conditions which clearly resolve chlorate and nitrate peaks. The Dionex AG9-HG column not only resolves the chlorate and nitrate peaks but also cleanly resolves both of these peaks from the very large sulfate peak, even in undiluted samples.

The TPN-IC method for determination of nitrogen in natural aqueous samples has many advantages over the Kjeldahl method. It is much simpler and generates less toxic waste. In addition, the unbuffered persulfate digestion can be used for TP analysis as well. Chlorate interference should be considered by investigators using TPN-IC but it can be avoided by using appropriate chromatographic or digestion conditions.

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