



Simultaneous determination of total nitrogen and total phosphorus in environmental waters using alkaline persulfate digestion and ion chromatography



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ABSTRACT

An ion chromatography (IC) method was developed for the simultaneous determination of total nitrogen and total phosphorus after alkaline persulfate digestion. This study takes advantage of advances in construction of high-resolution, high-capacity anion-exchange columns that can better tolerate the matrices typically encountered when a determination of total nitrogen and total phosphorus is required. Here, we used an electrolytically generated hydroxide eluent combined with a high-capacity, hydroxide-selective, anion-exchange column for the determination of total nitrogen (as nitrate-N) and total phosphorus (as phosphate-P) in environmental samples by IC. This method yielded LODs for nitrate-N and phosphate-P of 1.0 and 1.3 $\mu\text{g/L}$, respectively. The LOQs determined for these analytes were 3.4 and 4.2 $\mu\text{g/L}$, respectively. Due to the dilution factor required and the blank nitrate-N concentration after the persulfate digestion, the quantification limits increased for nitrate-N and phosphate-P to 171 and 63 $\mu\text{g/L}$, respectively. The suitability of the method was evaluated by determining the nitrogen and phosphorus concentrations from known concentrations of organic-containing nitrogen and phosphorus compounds. In addition, environmental samples consisting of six different wastewaters and 48 reservoir samples were evaluated for total nitrogen and phosphorus. The recoveries of nitrogen and phosphorus from the organic-containing compounds ranged from 93.1 to 100.1% and 85.2 to 97.1%, respectively. In addition, good correlation between results obtained by the colorimetric method and IC was also observed. The linearity, accuracy, and evaluation of potential interferences for determining TN and TP will be discussed.

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1. Introduction

Nitrogen and phosphorus are essential nutrients for all living organisms that are required to support the growth of plants, feed animals, and ultimately provide adequate nutrition for an expanding global population. The proper balance of environmental nutrients is critical for maintaining a healthy ecosystem. However, in several developed and rapidly developing regions of the world, the excess use of nutrients has caused significant water quality and health issues. Over the last 50 years, the use of nitrogen fertilizers on a global scale increased 9-fold, while phosphorus use has tripled. Over the next 40 years, the global mineral fertilizer consumption for nitrogen and phosphorus is expected to increase substantially, about 40–50%, to feed a growing world population [1].

Similar to other parts of the globe, the impact of nutrient pollution in the U.S. has been identified as one of the most widespread, costly, and challenging environmental problems in the 21st century [2]. Nutrient pollution causes excess algae growth (i.e., algal blooms) over large bodies of water, resulting in a significant impact on the environment, human health, and the economy. Algal blooms consume significant amounts of oxygen and therefore deprive fish, shellfish, and other aquatic organisms of the oxygen needed to survive. In addition, algae can have a negative impact on human health by emitting toxins that can cause stomach aches, rashes, and more serious health issues. In terms of the economic impact, it is estimated that the U.S. tourism industry loses about \$1 billion annually due to decreases in fishing and recreational activities [3]. About 80% of the assessed U.S. coastal waterways are currently experiencing eutrophication [4]. Excess nutrients in bodies of water are primarily caused by fertilizer runoff, animal manure, sewage treatment plant discharges, storm water runoff, and auto and power plant emissions [3].

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The standard U.S. Environmental Protection Agency (EPA) method for determining TN is based on the determination of TKN plus the sum of nitrite and nitrate. The TKN procedure converts organic nitrogen such as amino acids, proteins, and peptides into ammonia [5]. The sample is digested for 2.5 h in a sulfuric-acid/mercuric-sulfate/potassium-sulfate solution to convert the organic nitrogen forms to inorganic ammonium. To determine nitrite and nitrate, the EPA provides several approaches such as IC, potentiometric, and colorimetric methods [6–8]. Although TKN is approved under the National Pollution Discharge Elimination System (NPDES) and Safe Drinking Water Act (SDWA) for compliance monitoring, the method has a number of drawbacks. For example, the method poses environmental and safety hazards by using toxic reagents (e.g., mercury) at high temperatures. In addition, the environmental impact and associated costs for disposing mercury raises serious concerns. Environmental waters with levels of nitrate greater than the TKN ammonia will give a negative bias and in some cases NO_x can be measured as TKN giving a positive bias to the TKN measurement. Finally, some U.S. states require the determination of TN without defining TN.

An alternative method for determining TN and TP is the alkaline persulfate digestion technique. This is a well established approach that provides an environmentally safer alternative to Kjeldahl digestion without the positive and negative bias. The 22nd edition of the American Public Health Association's Standard Methods for the Examination of Water and Wastewater describes a protocol for determining TN and TP after alkaline persulfate digestion [9]. To demonstrate alkaline persulfate digestion for determining TN and TP, the U.S. Geological Survey (USGS) conducted a large scale and geographically diverse study over a 12-month period on 2100 surface and ground water samples. The samples were analyzed independently for TN and TP using alkaline persulfate digestion [10]. The USGS concluded that the alkaline persulfate digestion technique was more sensitive, accurate, and uses less toxic reagents than the Kjeldahl digestion method. In addition, TKN values can be determined by subtracting the nitrate-N concentrations in undigested samples from the TN concentrations determined after alkaline persulfate digestion.

IC is a well established technique for the determination of inorganic anions in environmental samples. The application of IC for the determinative step after alkaline persulfate digestion has primarily focused on TN [11–14]. TP determination by IC after persulfate digestion is typically excluded due to the high sulfate concentration produced after decomposition of persulfate, which can interfere with phosphate determinations [15]. To overcome this challenge, some authors have implemented hydrogen peroxide as the oxidizing reagent as an alternative to persulfate [16,17] or have used column-switching techniques after alkaline persulfate digestion [18]. However, significant advances in IC stationary phases [19] have enabled the simultaneous and direct determination of TN and TP after alkaline persulfate digestion.

Currently, there are no known previous reports of the simultaneous determination of TN and TP by IC after alkaline persulfate digestion. IC offers several advantages for this analysis, such as its simplicity, relatively low detection limits, and minimal interferences from the digestion matrix when using higher capacity anion-exchange columns. In this study, we demonstrate the simultaneous determination of TN and TP by IC with suppressed conductivity detection after alkaline persulfate digestion. The digestion procedure was adopted from the USGS [10]. The dynamic range, detection limits, precision, and recovery of nitrate-N and phosphate-P from quality control standards after alkaline persulfate digestion are reported. In addition, to determine method robustness and its application to brackish waters, we investigated the performance in high chloride concentration samples.

2. Experimental

2.1. Instrumentation

A Thermo Scientific™ Dionex™ ICS-2100 Reagent-Free™ IC (RFIC™) System (Thermo Fisher Scientific, Sunnyvale, CA, USA) was used in this study. The Dionex ICS-2100 system integrates an ion chromatograph with an electrolytic eluent generator, a dual-piston pump with vacuum degas, a six-port injection valve fitted with a 5 μL injection loop, a heated conductivity cell, and a column heater set at 30 °C. A Thermo Scientific Dionex AS-AP Autosampler was used for sample processing. A Thermo Scientific™ Dionex™ IonPac™ AG19 Guard Column (50 \times 2 mm i.d.) and Dionex IonPac AS19 Analytical Column (250 \times 2 mm i.d.) were used for all analytical separations, along with a Thermo Scientific Dionex CR-ATC Continuously Regenerated Anion Trap Column. The KOH eluent was electrolytically generated with the Thermo Scientific Dionex EGC III KOH Eluent Generator Cartridge to produce the following conditions: 20 mM KOH from 0 to 10 min, 20–50 mM from 10 to 12 min, 50 mM from 12 to 20 min. TN as nitrate-N and TP as phosphate-P were detected by suppressed conductivity with a Thermo Scientific™ Dionex™ AERS™ 500 Anion Electrolytically Regenerated Suppressor (2 mm) operating at 38 mA current in the recycle mode. Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System software version 7.2 was used for system control and data processing.

2.2. Reagents and standards

All solutions were prepared in deionized (DI) water with a specific resistance of at least 18 $\text{M}\Omega\text{-cm}$ (Millipore, Billerica, MA, USA). All reagents were ACS grade. Stock solutions were prepared at 1000 mg/L for nitrite and nitrate as nitrogen from the sodium salts and phosphate was prepared as phosphorus from the potassium salt (Fisher Scientific, Pittsburgh, PA, USA). To evaluate the potential interference from chloride, a stock solution of 10,000 mg/L chloride from the sodium salt (Fisher Scientific) was prepared. Glucose was purchased from VWR (J.T. Baker® brand, Radnor, PA, USA). Urea, nicotinic acid, adenosine-5'-triphosphate, glucose-1-phosphate, ammonium chloride, phytic acid, glycine, and glycerophosphate were purchased from Sigma-Aldrich (St. Louis, MO, USA). ACS reagent-grade potassium persulfate with a purity specification of $\geq 99\%$ (Fluka, Sigma-Aldrich) was found to contain low nitrogen content, and therefore was used in this study. Sodium hydroxide was purchased from Fisher Scientific.

2.3. Inorganic and organic nitrogen standards

Nitrogen standards were prepared from urea, nicotinic acid, glycine, and ammonium chloride by dissolving the appropriate amounts in DI water for a final stock solution concentration of 1000 mg/L. Glycine was used as a continuous-digest check solution, and therefore was included in each sample analysis batch. The other solutions were used to check the robustness of the optimized digestion procedure.

2.4. Organic phosphorus standards

Phosphorus standards were prepared from phytic acid, glycerophosphate, glucose-1-phosphate, and adenosine-5'-triphosphate (ATP) by dissolving the appropriate amounts in DI water for a final stock solution concentration of 1000 mg/L. Glycerophosphate was combined with glycine (described in the previous section) as a continuous-digest check solution and therefore was included in each sample analysis batch.

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