O·I·Analytical

A New Approach for Nitrate Cadmium Reduction by Discrete Analysis

Application Note 25380206

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Nitrite Nitrogen

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Abstract

The discrete analyzer is rapidly becoming accepted as an alternative technology for procedures (i.e., analytical methods) approved for National Pollutant Discharge Elimination System (NPDES) and Safe Drinking Water Act (SDWA) compliance testing. Nitrate by cadmium reduction is one of the most important approved methods for nutrient analysis. Introducing a cadmium reduction procedure for discrete analysis is a challenging task for discrete analyzer manufacturers. Several procedures currently used by discrete manufacturers include a cadmium coil with solution delivery by a peristaltic pump, a cadmium column with solution delivery by a syringe pump, or cadmium-coated disposable cups.

This application note describes a new approach for nitrate analysis by cadmium reduction using the DA 3500 Discrete Analyzer (Figure 1).

Introduction

Procedures for determining low levels of nitrate nitrogen in water samples most often use the following reaction:

$$NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + H_2O \quad (1)$$

Figure 1. OI Analytical DA 3500 Discrete Analyzer

SYSTEM CERTIFICATION ISO 9001:2000 SGS

These procedures determine nitrite nitrogen produced by diazotization of nitrite according to the very sensitive Greiss reaction. This method determines nitrate nitrogen plus any nitrite nitrogen present before the reduction step. Using cadmium metal as a reducing agent has been found to be very quantitative. Both the pH of the sample and time of contact with the reducer must be tightly controlled. If not carefully controlled, side reactions or over-reduction of nitrite may occur. The experimentally determined optimum pH of the cadmium reduction reaction falls between 6.5 and 9.0. Nydahl determined the optimum pH to be 8.0–9.0, with a preference toward lower values to avoid precipitation of cadmium hydroxides.[1]

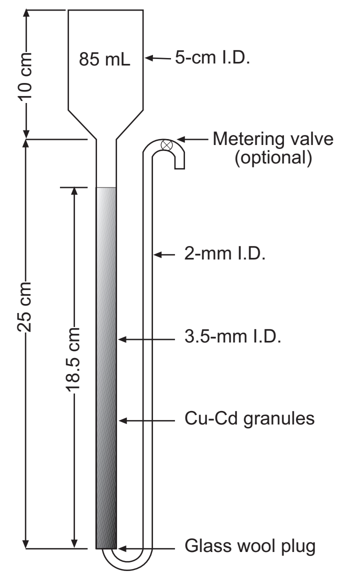

Figure 2. Cadmium reduction column for manual methods

Most USEPA accepted procedures use an ammonium chloride buffer that is adjusted to pH 8.5. This buffer contains a trace of EDTA as a complexing agent to prevent precipitation of cations and metal hydroxides. The ammonium ion also serves as a complexing agent that binds with cadmium ions produced by the reaction to prevent formation of insoluble cadmium oxides. The contact time of the sample with the cadmium is either controlled by gravity flow of a buffered sample through a bed of cadmium granules as in manual methods, or by precise flow of a peristaltic pump as in continuous flow methods. After passing through the cadmium reductor, the nitrate nitrogen that was converted to nitrite, and the nitrite nitrogen originally present in the sample are determined colorimetrically as nitrate + nitrite nitrogen.

Cadmium Reduction Manual Methods (USEPA Method 353.3 or Equivalent)

Manual methods for determining nitrate + nitrite by cadmium reduction use a 100-mL glass column containing an 18.5-cm bed of copperized cadmium metal granules (Figure 2). Samples, diluted 1:3 with a buffer solution, are added to the top of the column (Figure 3). The first ¼–½ of the sample that flows through the column is discarded, and the remaining portion of the sample is collected for analysis. Washing the column between samples is not necessary. As soon as every sample has passed through the column, the reacted samples are analyzed for nitrite nitrogen. Reduction efficiency is measured by comparing the response of a nitrite standard with the response of a nitrate standard carried through the entire process.

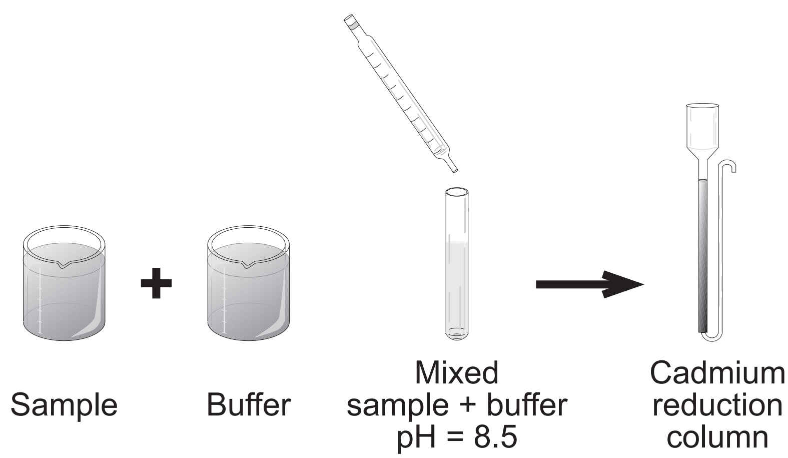

Figure 3. Processing samples for cadmium reduction using manual methods

Cadmium Reduction Automated Methods (USEPA 353.2 or Equivalent)

In continuous flow cadmium reduction methods, the sample and buffer are mixed on-line, and pass through a miniaturized cadmium column or open tubular cadmium coil (Figure 4). A peristaltic pump precisely controls the flow rates. The reacted sample merges with a color reagent, and flows through a colorimetric detector, where the nitrate + nitrite concentrations are determined. Reduction efficiency is measured by comparing the response of a nitrite standard with the response of a nitrate standard carried through the entire process. The method must be calibrated with each use to account for variability of the peristaltic tubing used to carry reagents and sample through the system.

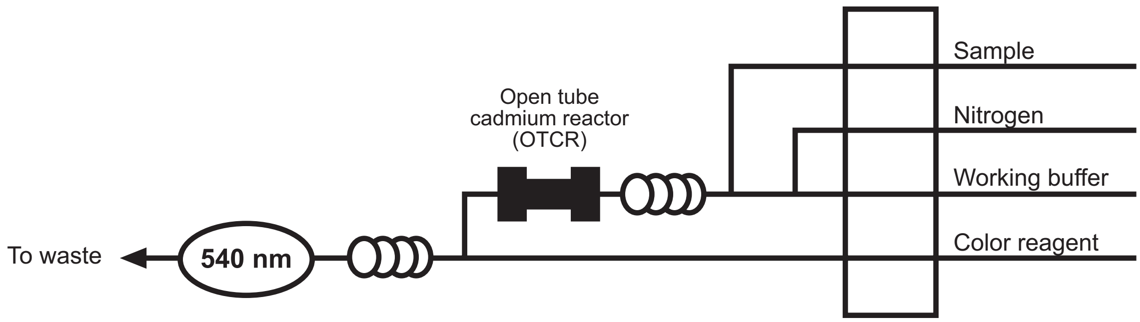

Figure 4. Flow diagram for analyzing nitrate + nitrite nitrogen and nitrite nitrogen by segmented flow analysis (SFA)

Design Options for Cadmium Reduction Methods Used with Discrete Analysis

The efforts to modify existing methodology to discrete analyzers have involved, for the most part, an attempt by manufacturers to closely imitate methodology already approved by the USEPA. In many cases, this involves a direct and simple conversion of an approved manual method to the discrete analyzer. In other cases, the adaptation requires modifications of approved flow methods to the discrete analyzer. In the analysis of nitrate nitrogen by cadmium reduction, most manufacturers have chosen to duplicate flow methods by using peristaltic pumps to mix sample aliquots with buffer solutions and carry them to a cadmium reduction coil. After reaction with the coil, the sample is pumped to a well where it is transferred to a reaction cuvette for further processing.

Another option for cadmium reduction with discrete analyzers uses a single-piece disposable cadmium cup.[2] Each individual cup is used for a single analysis. In this design, the sample mixed with buffer solution is dispensed into the cadmium cup, stirred, and allowed to react with the copperized cadmium.

The OI Analytical Approach to Cadmium Reduction with Discrete Analysis

The USEPA has defined discrete analyzers as an instrument that automates manual methodology. For this reason, OI Analytical chose to duplicate as closely as possible the manual method for analysis of nitrate + nitrite by cadmium reduction. Packed cadmium columns, cadmium wire, and open tubular cadmium coil designs were evaluated. No appreciable benefits were found for packed cadmium columns or cadmium wire over the open tubular cadmium coil. OI Analytical chose to use an open tubular cadmium coil to be able to provide consistent instrument-to-instrument reactor performance.

Using this method, the DA 3500 sample probe transfers buffer solution plus sample to well 1, where the solutions are mixed (Figure 5). The probe then aspirates the sample plus buffer mixture and forces it into the cadmium coil. The first half of the solution pushes prior solution in the coil out to well 2, where it is carried to waste. After the remaining sample plus buffer mixture reacts with the copperized cadmium walls of the coil, the probe delivers additional buffer solution to push the reacted sample into well 2. The sample in well 2 is aspirated by the sample probe and dispensed into a reaction cuvette for nitrite determination by the Greiss reaction. Between sample injections, the coil is rinsed with buffer solution and each well is rinsed with deionized water to reduce carryover.

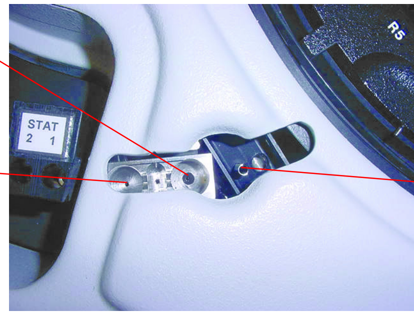

Figure 5. Nitrate module components

Nitrate reduction with the cadmium coil has been found to be repeatable over time with a wide variety of matrices. Trace metals and dissolved oxygen that can interfere with the method are compensated by the complexing and buffering ability of the buffer reagent.

Once initiated, cadmium coil activation with copper is performed entirely by the software. The activation process does not require removing the coil from the analyzer. An automated, onboard regeneration procedure can be periodically performed to rejuvenate the cadmium coil if efficiencies become low. When performed routinely, this rejuvenation procedure virtually guarantees a fresh cadmium surface reaction after reaction.

Calibration of the method is performed by contact of the calibrants with the same cadmium surface that reacts with the samples. Calibration curves are stable and need only be verified routinely by calibration verifications and efficiency check standards.

Results

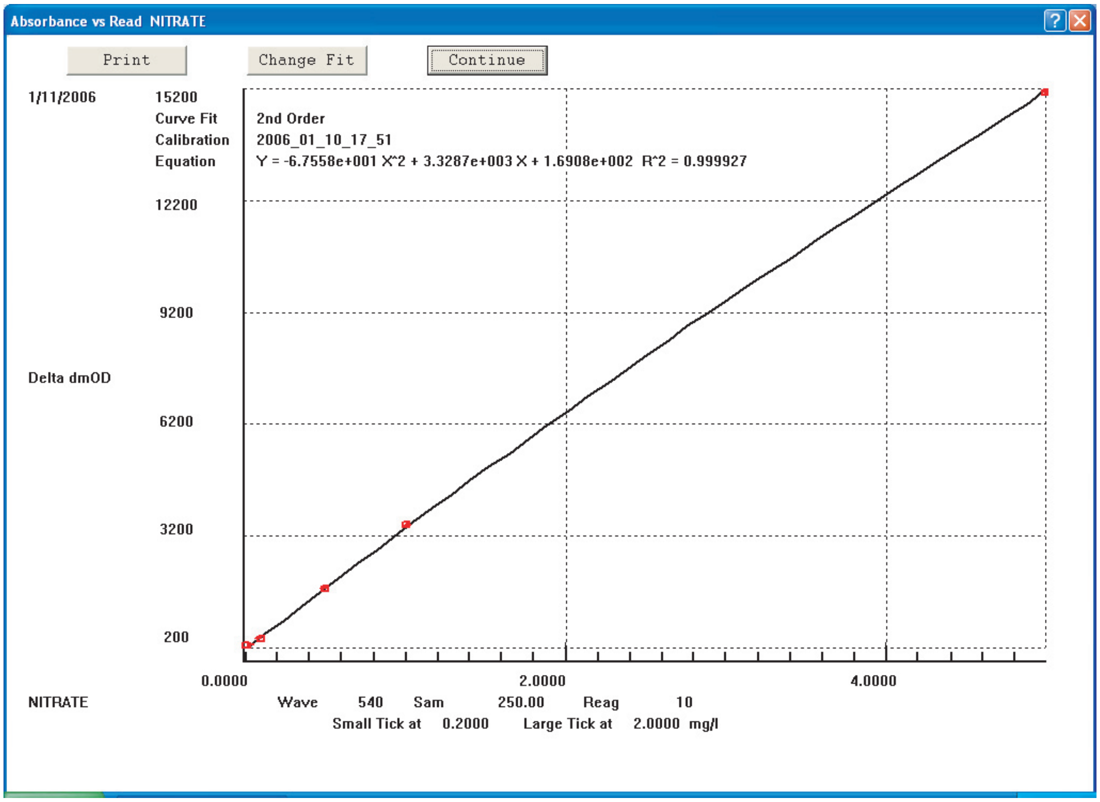

Figure 6. Nitrate + nitrite nitrogen method calibration curve (0.1–5.0 mg N/L)

Table 1. Precision study using an ERA check standard containing 3.11 mg N/L as nitrate nitrogen

Sample	Concentration (mg/L)
Standard 1	2.8606
Standard 2	2.8421
Standard 3	2.7713
Standard 4	2.8548
Standard 5	2.8985
Standard 6	2.9272
Standard 7	2.7982
Standard 8	2.863
Standard 9	2.8585
Standard 10	2.8951
Average	**2.85693**
Standard Deviation	**0.046166**
% RSD	**1.62**

Table 2. MDL study using an ERA check standard containing 0.15 mg N/L as nitrate nitrogen

Sample	Concentration (mg/L)
Standard 1	0.14
Standard 2	0.14
Standard 3	0.14
Standard 4	0.14
Standard 5	0.14
Standard 6	0.17
Standard 7	0.14
Standard Deviation	0.009476
MDL	0.03
ML	0.09

Table 3. Wastewater and seawater samples fortified with 2 mg/L of nitrate nitrogen

Sample	Spike Amount (mg/L)	Nonspiked Concentration (mg/L)	Spiked Concentration (mg/L)	Percent Recovery
ERA QC sample	—	3.110	—	97.04
Wastewater 1	2.0	3.599	5.063	73.30
Wastewater 2	2.0	0.413	2.344	96.55
Wastewater 3	2.0	0.114	2.158	102.2
Wastewater 4	2.0	0.279	2.253	98.70
Wastewater 5	2.0	1.937	3.822	94.25
ERA check standard	—	2.999	—	96.43
Wastewater 6	2.0	2.012	3.755	87.15
Seawater	2.0	0	1.951	97.55

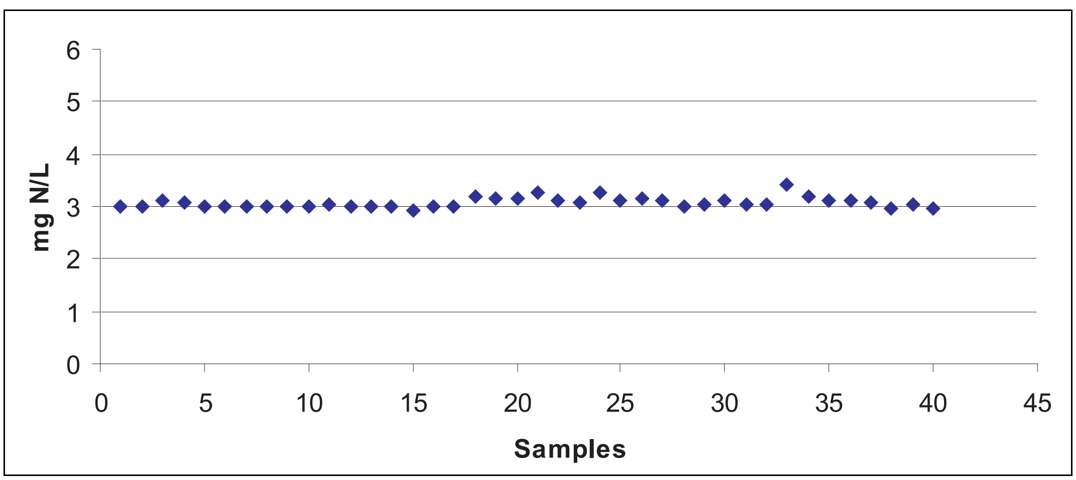

Figure 7. Long-term reliability study for nitrate nitrogen by cadmium reduction using an 3.11-mg/L ERA QC sample. Even after analyzing 40 samples, no signs of cadmium coil degradation appear.

Conclusions

- The new approach to nitrate analysis by cadmium reduction using the DA 3500 Discrete Analyzer eliminates the peristaltic pumping of reagents and sample, reducing maintenance and calibration frequency.

- The solution for nitrate analysis by cadmium reduction avoids the generation of potentially toxic solid waste with each test when using disposable cadmium reaction cups.

- The DA 3500 automatically performs cadmium coil regeneration.

- The DA3500 simulates the manual USEPA Method 353.3 by employing the same cadmium reduction procedure. The new approach is truly equivalent to the USEPA manual method.

- Software functions of the DA 3500 automatically calculate nitrate values (subtracting nitrite nitrogen from nitrate plus nitrite nitrogen) to facilitate sample reporting.

References

1. Nydahl, F. On the Optimum Conditions for the Reduction of Nitrate to Nitrite by Cadmium. *Talanta*, **1976**, *23*, 349–357.

2. Bogren, K. and Harbridge, J. Nitrate Reduction by Discrete Analysis. *American Laboratory*, February **2005**, 24–25.

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