Rapid Field Test for Nitrate and Ammonia in Reclaimed Water

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ABSTRACT

Estimating the concentrations of nitrate and ammonium ions in groundwater from reclaimed water is extremely important. These determinations are usually performed in laboratories using sophisticated equipment, and turn-around time can be from 2 hours to 3 days. Many times, results are needed at the site as quickly as possible. Alternatively, the rapid determination of both nitrate and ammonium ions can be estimated using an ammonia field test kit (LaMotte, Chestertown, MD). The test makes use of the reducing capabilities of titanium chloride (TiCl\textsubscript{3}), which converts up to 15 ppm nitrate ion to ammonium ion (Braunstein, et al, 1980). Nitrate reduced by titanium chloride eliminates the possibility of coming in contact with poisonous powdered cadmium. Therefore the method is capable of determining nitrate ion and ammonium ion sequentially using the same ammonia field test kit. Field test kit concentration estimates of the combined ammonium and nitrate ions show good correlation with lab results ($R^2 = 0.85$ and 0.89 respectively), and scatter (standard deviation) between the two methods is small indicating that the test kit is an acceptable on-site method.
INTRODUCTION

Recent increased eutrophication of Florida’s surface water resources has resulted from the discharge of nutrients mainly from sewage effluent into rivers and lakes. This has lead to the active promotion of reusing reclaimed water for irrigation in agricultural areas as well as golf courses. However if the application of reclaimed water to farming areas and golf courses is not carefully managed, it has the potential to impact groundwater resources by increasing the nitrate content of water which may be extracted for potable use. Nitrates in drinking water have been linked to metheamaglobinemia in infants and stomach cancer in adults (Moss, 1988).

Estimating the concentrations of nitrogen in groundwater recharge from reclaimed water at the site is important since water samples high in nitrogen (N) can be rechecked at the lab as a priority. In reclaimed percolate water, N exists mostly as NO$_3^-$ and NH$_4^+$ and over time ammonium ion usually is oxidized to nitrite (NO$_2^-$) and then to nitrate ion. Determinations of nitrate and ammonium ions can be achieved by various field test equipment i.e., pocket colorimeters (Hach Co., Loveland, CO), and ion selective electrodes (ISE) for ammonium and nitrate respectively (Orion Res., Beverly, MA.).

A method has been developed which utilizes the Lamotte Ammonia Field Test Kit # 3315 to achieve the combined analytical estimate of nitrate and ammonium ions. This method has been tested for comparison against a certified lab procedure in a matrix of reclaimed percolate water from the Orange County National Golf Course (OCNGC), Orlando, Fl. Given the limitation that this is merely a field-test kit, the main objective of this investigation is to compare the results of this new method to that of an automated flow injection procedure.

MATERIALS AND METHODS

Materials

1. Ammonia-Nitrogen Field Test Kit (LaMotte Co. # 3315) (Test kit is all inclusive for ammonium ion with necessary reagents, sample tubes, and standardized color comparator with a range from 0-8 ppm.)
2. Disposable plastic graduated transfer pipettes, 3ml. cap. (Fisher Sci. #13-711-9A)
3. Lachat Quick-Chem Flow Injection Analysis System, for NO$_3^-$ and NH$_4^+$. (Hach Co.)

Reagents

1. Titanium Chloride (TiCl$_3$) 20% solution (Fisher Sci. # ST43-500)
   use 1 drop from a pipette (for NO$_3^-$ reduction).
Sample Preparation

All samples were diluted 5X by taking 0.5 ml sample with a disposable pipette, and transferring it to a testing tube. An additional 2.0 ml of DI water are added to the same tube. Ammonia reagent # 1 is added to the tube (2 drops) and inverted. Ammonia reagent # 2 is added (4 drops) and inverted. The NH$_4^+$ concentration is read on the comparator immediately. This measurement is referred to as [NH$_4^+$]$_{\text{initial}}$. Using a new pipette, one drop of the reducing agent, TiCl$_3$, is added to the same tube and inverted. The sample is allowed to stand for 2 minutes and settle. Once the sample has settled, it can be measured on the comparator, and this reading is referred to as [NH$_4^+$]$_{\text{total}}$.

The total ammonium measurement is related to the nitrate by the following equation,

$$[\text{NO}_3^-] = [\text{NH}_4^+]_{\text{total}} - [\text{NH}_4^+]_{\text{initial}}$$

Eq. [1]

where, [NH$_4^+$]$_{\text{total}}$ = [NH$_4^+$]$_{\text{initial}}$ + any NO$_3^-$ that is converted to NH$_4^+$
and, [NH$_4^+$]$_{\text{initial}}$ = [NH$_4^+$] that doesn’t contain any converted nitrate.

All ammonium and nitrate ion results are expressed as ppm and must be multiplied by 5 for actual estimates of concentration. Eq.1 can be used to calculate the nitrate ion estimate.

Sample Preparation for Method Comparison

This comparative study consisted of 30 samples that were split and half were analyzed for ammonium and nitrate via flow injection analysis. The data from this method was considered to be the standard. The combined ammonium and nitrate concentrations in the other half were estimated using the field test kit. All samples were from lysimeters which collected the reclaimed percolate water at the OCNGC.

Correlation, standard deviation and F-distribution data was provided by the SAS system CORR procedure (SAS, 2003)
Theory of the Combined Ammonium and Nitrate Analysis

The field test kit is specific for $[\text{NH}_4^+]$ and therefore detects $[\text{NO}_3^-]$ only by first reducing it to $\text{NH}_4^+$. This reducing step is achieved with TiCl$_3$. The following equation expresses the overall redox reaction.

\[
\text{NO}_3^- + 8\text{Ti}^{3+} + 10 \text{H}^+ \rightarrow \text{NH}_4^+ + 8\text{Ti}^{4+} + 3\text{H}_2\text{O} \quad \text{Eq. [2]}
\]

According to the above reaction, nitrate is chemically reduced to ammonium ion at the expense of trivalent titanium, which is oxidized to tetravalent titanium (Rich, et al.2006). Once the nitrate is reduced to ammonium ion it can be estimated by the test kit according to the directions.

RESULTS AND DISCUSSION

Good correlations ($R^2 = 0.89$ and 0.85) were observed for nitrate and ammonium ions respectively when comparing the test kit method to flow injection analysis. (See Fig. 1 and 2)

![Comparison of $[\text{NH}_4^+]$ results between Field Test Kit & Flow Injection Analysis](image)

Fig. 1. Comparison of $[\text{NH}_4^+]$ data between Field Test Kit & Flow Injection Analysis.
An F-distribution was used to determine confidence intervals for the variances of the ammonium and nitrate ion data. It was observed that the estimated standard deviation (SD) for the ammonium data is 0.356, and the 95% confidence level for the SD is in the range of 0.281 to 0.473. However, the estimated SD for the nitrate ion data is larger (SD = 1.55). The 95% confidence level for this SD is from 1.221 to 2.056. Although the nitrate ion SD values from samples 4, 14, 20, 23, 24, and 26 were used to obtain the estimate of the total variance, these values may be considered to be outliers since they are outside of the 95% confidence range.

![Comparison of Nitrate Results Between Field Kit & Flow Injection](image)

Fig. 2. Comparison of [NO$_3^-$] data between Field Test Kit & Flow Injection Analysis.

**CONCLUSION**

It has been shown that all ammonium ion samples were within the 95% confidence level, and all but six of the nitrate samples were within that level.

It was also shown that the ammonium field test kit is acceptable for on-site determinations of nitrate and ammonium ions in a matrix of reclaimed water.
REFERENCES


