Checking Trace Nitrate in Water and Soil Using an Amateur Scientist's Measurement Guide

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The measurement of nitrate ion concentration in natural water bodies and tributaries is important, because the natural levels of nitrogen compounds in precipitation runoff from undisturbed land often are low. Meanwhile, pollution from a variety of human activities can lead to increased nitrate levels in natural water bodies and degradation. Elevated water nitrate levels often are traceable to non-point source pollution from agriculture, automobile-related pollution, impervious cover, suburban use of fertilizer, and so on (*1*).

Ammonium ions and organic nitrogen gradually are converted by bacterial oxidation to nitrate, typically over a matter of weeks under aerobic soil conditions. Near the surface, the nitrate ions are slowly depleted by plant growth, although this removal process becomes less efficient in winter. Once nitrate ions move underground, their concentration stabilizes. Regardless of the source, a few milligrams of nitrate nitrogen/liter (measured as the weight of atomic nitrogen) entering surface water can affect the water body. If fixed nitrogen is a major factor limiting algae growth, rapidly growing varieties of algae frequently appear in abundance followed by an oxygen depletion syndrome called eutrophication.

Due both to the stability of the ions and their biological effect as a nutrient, nitrate ions in water are a key indicator for studying non-point source pollution in developing areas. To be suitable for monitoring of water nitrate levels by amateur environmentalists, a test should use safe, inexpensive, and accessible materials. It should have a sensitivity that corresponds to natural levels. The test should be rapid and accurate. Most of these criteria can be met in a field test that can measure nitrate nitrogen ions at about 0.1 mg/L, using concentration.

Nitrate Measurement Alternatives

Nitrate ions by themselves are not very reactive, so it is a common practice to test for nitrate in two stages. In the first stage, the sample is reduced chemically to convert traces of nitrate ions into nitrite ions. Nitrite ions are then easily detected through color reactions.

The recognized authority on water analysis is *Standard Methods for the Examination of Water and Wastewater* (*2*). The most sensitive nitrate test cited begins by filtering the sample through a reduction column containing cadmium metal particles coated with copper, followed by a diazonium color reaction to detect any liberated nitrite ions.

Experimentation indicates that copper-activated zinc, like the more toxic cadmium reduction methods frequently used, can efficiently reduce nitrate to nitrite in a neutral or slightly alkaline water solution. It is possible to combine this reduction technique with the classic starch–iodine reaction, a nitrate standard, and a pocket photometer to make field measurements accurate, with practice, to ± 5%. Nitrate test kits often do not include a standard, although running one alongside an unknown tends to improve accuracy by minimizing the effect of time and temperature on slow color reactions. The end result is good sensitivity and better accuracy than most commercial nitrate test kits offer, but it is achieved using only common and relatively nontoxic materials.

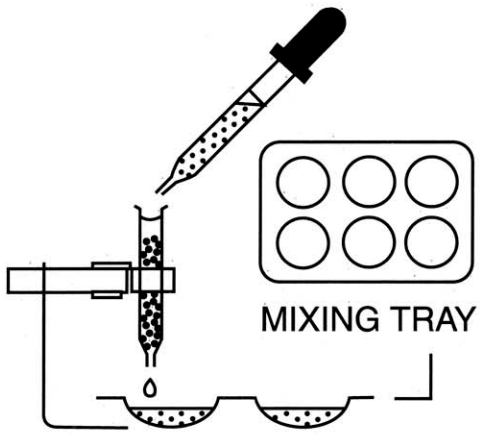

Figure 1. The reduction column and the mixing tray.

The technique originated from Feigl's description of a spot test said to detect down to 0.1 mg/L of nitrite ions in a drop of water (*3*). The starch–iodine test detects iodine by using a reaction that depends on the the ability of traces of acidified nitrite ions to oxidize iodide ions to yield free iodine (*4*); the iodine then gives a blue or purplish color reaction with starch in the presence of excess iodide ions.

A major problem with the starch–iodine reaction is that it is nonlinear, with the color rapidly disappearing below a minimum iodine level. The reason for this is still a topic of debate over whether the iodine molecules are inefficient at lining up within starch helixes to give the color (*5*) or whether iodine itself is inefficiently generated at the lowest levels (*6*). Various factors that affect the color reaction are discussed by Crouch and Lambert (*7*, *8*). The reaction is broadly sensitive to oxidants and reductants that are active in an acidic solution such as chlorine, chlorate, sulfite, and sulfide ions. Such ions do not seem to interfere in water free of industrial pollution.

Experimental

There are many reasonable variations in technique depending on available materials, so I will describe my own methods as one alternative. I use 1- to 3-oz. dropper bottles from a pharmacy graduated in milliliters. These have polyethylene droppers that dispense drops of relatively constant volume. I use labeled bottles for 0.5% starch, 10% potassium or sodium iodide, sodium bicarbonate, and tartaric acid (formic and oxalic acid solutions also work).

Potassium iodide can be obtained through chemical supply companies such as Kodak or from high school labs. Tartaric acid is available from home brewer suppliers. One can keep a labeled bottle containing 0.722 g of weighed potassium nitrate dissolved in 1 L of water in the refrigerator. Measuring 1 mL of this solution into 100 mL of deion-

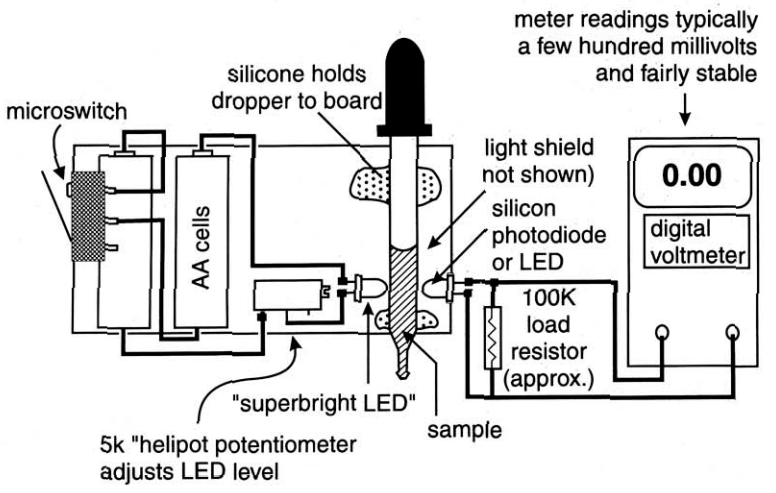

Figure 2. An easily constructed red light photometer.

ized water provides a quick, reasonably accurate standard of 1.0 mg nitrate nitrogen/L for field use.

The test requires a 0.5% starch solution. This solution is made by boiling a gram of potato starch and one aspirin tablet (as a preservative) with 200 mL of deionized water in a glass container for about 15 min. Potato starch from a health food store was used because it contains significantly less of the undesirable branched amylopectin than corn starch. This solution is stable for months at room temperature.

A medicine dropper is marked with a band of tape to reproducibly and rapidly deliver 1 mL. I prefer to shake my dropper rather than rinsing it to save time. The tests are run in a small white plastic tray used for mixing watercolors (available at Michael's craft supply chain). The tray has six hemispherical depressions holding about 5 mL each (Fig. 1).

Three depressions in a row on one side make it possible to run the 1.0-mg standard, a 0.5-mg/L solution prepared by diluting the 1.0-mg standard, and the unknown along one side of the tray. The calibrated medicine dropper is used to measure 2 mL of each sample. One drop of a 50% saturated sodium bicarbonate buffer is added to each sample before reduction. The samples are introduced into the reduction column with the dropper. They run through at a rate of several drops per second. The column can be held vertically with a holder made from coat-hanger wire and a clothespin. Each sample is run through the reduction column several times, or enough to give an obvious color at the 0.5 mg/L nitrate level. More passes increase the test sensitivity. The treated liquid is collected in the adjoining part of the tray. The column is rinsed with 2 mL of deionized water between samples.

The reduction column is made from zinc granules treated with copper and packed in a glass medicine dropper stem. One way to get zinc granules is to drill a folded sheet of zinc from a common dry cell with an electric hand drill. Drill a lot of holes, and then collect the turnings. They are stirred with a 0.5% solution of copper sulfate in white vinegar for a few minutes which coats the particles with a dark-colored electrochemically active coating of copper. The coated granules can be washed and stored dry. A small tuft of polyester wool is stuffed into the tip end of an a medicine dropper stem, the stem is packed with a layer of copper-treated zinc about 40-mm deep, and then it is sealed at the top with another tuft of the same material. The column is rinsed with rubbing alcohol and the excess blown out after use to prevent zinc oxidization. Before testing, I replace the dropper bulb and purge the column with deionized water to remove trapped gas bubbles and make the flow rate more repeatable.

After all three 2-mL samples have all been reduced to nitrite in this fashion, I add the other reagents. First I add two drops of 10% iodide solution and two drops of starch solution to all three samples. Then I stir in five drops of saturated tartaric acid to start the reactions. The 1.0 mg/L nitrate standard should start to turn blue in seconds. A 10-min period is sufficient for color development. By trial and error involving the successive dilution of the standard or unknown with the calculated dropperfuls of water, I can judge the unknown by sight to ± 10%. The higher nitrate level always gives the deeper color. If a sample is suspected of having initial nitrite or other redox interferences, this can be determined by comparing the result given without using the reduction step.

For amateurs who want the best accuracy, it is easy to build a pocket-sized medicine dropper photometer (Fig. 2). Red light is strongly absorbed by the starch–iodine reaction. Glue a "superbright" red LED (Radio Shack) to one side of a glass medicine dropper stem with clear silicone rubber and glue a photodiode to the opposing side. I use a silicon photodiode, but a second superbright LED also can be used as the detector. Spray black enamel over this assembly to block stray light, especially near the light-sensing region of the dropper stem.

I load the photodiode with a resistor, typically between 10 kilohms and 10 megohms, to reduce sensitivity to stray light. Then I use a 5-kilohm helipot resistor, initially set midway, to give an adjustable red light set to correspond to the meter's full millivolt range with pure water. I use two AA alkaline dry cells, and a microswitch in series with the LED. I measure the resulting photovoltage to more or less three-digit accuracy with a pocket digital ohmmeter (Radio Shack; about $25). This simple arrangement has some drift, but it is slow and does not interfere much with the accurate comparison of successive samples.

Starch–iodine photometry is nonlinear for two reasons. As stated earlier, the reaction is very weak below about 0.5

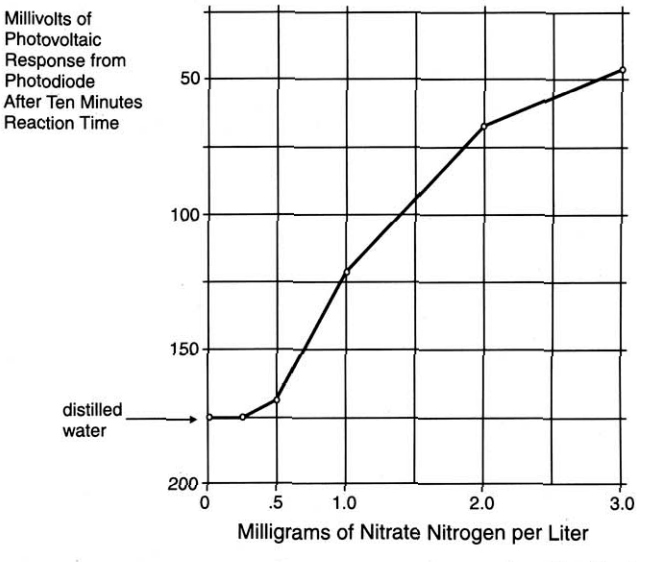

Figure 3. A graph of the photometer response to various levels of nitrate nitrogen.

mg per L. At higher nitrate levels, measurements become non-linear in accord with Beer's law, the photovoltage measurements showing less relative change as the nitrate levels increase and the color becomes deeper. Therefore, the photometric graph is a curve with a flat bottom that will give the accurate results when the unknown is above 0.5 mg per liter of nitrogen but not too much higher (Fig. 3). The 0.5 mg and 1.0 mg/L standards are reference points to achieve a best fit to a graph. The unknown should be concentrated to reach the 0.5 mg/L level if necessary. If the unknown is much above 1.0 mg/L, it can be estimated directly or else diluted and remeasured more precisely. The exact graph results will depend on reduction technique and photometer construction.

To increase substantially nitrate test sensitivity, nitrate ions are stable enough that we can boil away most of an accurately measured 20-mL volume in a Pyrex container, dilute it back to 2 mL with deionized water, and rerun the test with the sample concentrated by 10 to surpass the 0.5 mg/L lower detection limit. This method is sensitive enough that contamination may become a problem, making it important to run a blank for comparison.

We may sometimes wish to measure soil nitrate levels for agricultural purposes. Because nitrates are highly soluble, it is sufficient to weigh out a gram of soil and to stir it with 10 mL of deionized water. The soil is allowed to settle and the clear liquid is tested.

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