STANDARD OPERATING PROCEDURE
Collection of Preserved Nitrate Samples and Safety

KEY WORDS

Safety, personal protective equipment (PPE), preservation, storage, groundwater, sampling

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1.0 INTRODUCTION

1.1 Purpose

Wells sampled by the Groundwater Protection Program (GWPP) frequently contain nitrates. High levels of nitrate in drinking water are associated with adverse health effects. Since domestic well users are encouraged to assess their well water regularly for nitrates, GWPP has provided testing for nitrates at some wells sampled for pesticides (SWRCB, 2017).

This document standardizes the procedures for safely collecting and properly storing preserved nitrate samples collected from groundwater wells for the monitoring activities conducted by GWPP staff. Refer to SOP FSWA001 for standard groundwater well sampling procedures.

1.2 Scope

Microbial presence in samples can alter the original nitrate content as microbes may utilize nitrate for metabolic processes. The preservation of nitrate samples is necessary if analysis cannot be completed within 48 hours. For preservation, samples must be acidified by the contract laboratory with sulfuric acid to achieve a pH less than 2 and refrigerated at 4 ± 2 °C prior to analysis. Properly preserved and stored samples have a maximum holding time of 28 days for combined nitrate and nitrite as nitrogen (California Laboratory Services, 2022).

Therefore, to prevent microbial interference and ensure the stability and accuracy of results upon analysis, adherence to the outlined preservation and safety protocols is necessary.

2.0 MATERIALS

2.1 Documents

2.1.1 A copy of this SOP and other appropriate SOPs:

- 2.1.1.1 FSWA001
- 2.1.1.2 FSWA018
- 2.1.1.3 QAQC005
- 2.1.1.4 ADMN006

2.1.2 A copy of the study protocol

2.1.3 Chain of Custody (COC) forms from contract laboratory

2.1.4 Well Information Sheets

2.1.5 Sulfuric Acid Safety Data Sheet

2.1.6 DPR Field Safety Manual

2.1.7 Field Safety Contact Information Sheet

2.2 Supplies (Figures 1-3)

2.2.1 Tyvek sleeves

2.2.2 Nitrile gloves (6-mil minimum thickness, in multiple sizes [S, M, L, XL])

2.2.3 Face shield (able to fit over glasses)

2.2.4 Stainless-steel measuring cup (at least 200 mL)

2.2.5 Nitrate sample bottles, provided by laboratory (125 mL bottle pre-filled with 1 mL of 95% sulfuric acid [H_2SO_4] and clear cap)

2.2.6 Sodium bicarbonate (baking soda) for neutralization and containment

2.2.7 Clean water (1 pint minimum for decontamination)

2.2.8 Plastic bags (at least 18 in. by 24 in.)

2.2.9 Ice chest with foam insert

2.2.10 Ice

2.2.11 J-Lar tape

2.2.12 Permanent markers

2.2.13 Ballpoint pens

2.2.14 Trash bags

2.2.15 Brush for cleanup

2.2.16 Paper towels for cleanup

2.2.17 DI water

Figure 1: Personal Protective Equipment (PPE) including Tyvek sleeves, 6-mil Nitrile gloves, and face shield.

Figure 2: Pre-preserved nitrate sample bottle, ice chest containing pre-preserved nitrate sample bottles in foam insert, and fill lines marked on a pre-preserved nitrate sample bottle.

Figure 3: Sodium bicarbonate (for containment and neutralization of spills) and a stainless-steel measuring cup (for sample collection).

3.0 SAFETY

3.1 Acid Risks and Properties

Sulfuric acid can cause skin irritation, severe burns, and significant eye damage. Avoid contact with skin and eyes!

3.1.1 **Skin or Hair:** If on skin or hair, immediately remove all contaminated clothing and rinse skin with clean water or water from the well (wash contaminated clothing before reuse).

3.1.2 **Eyes:** If in eyes, rinse cautiously with clean water for several minutes, remove contact lenses if present and easy to do so, then continue rinsing.

3.1.3 **Inhalation:** Do not breathe in or ingest mists, vapors, spray, or splash generated from the acid. Sulfuric acid reacts with water to release vapors of sulfuric acid and sulfur oxides that irritate the eyes, nose, and throat. Always ensure proper ventilation before opening bottles, open bottles slowly to vent vapors, and wear PPE (3.2) to avoid inhalation.
If inhaled, call a Poison Control Center, or seek medical help.

3.1.4 **Ingestion:** If the concentrated acid is accidentally swallowed, rinse the mouth, and call a Poison Control Center or 911 (do not induce vomiting).

3.1.5 **Keep Cool:** It is important to keep preserved nitrate samples cool and tightly sealed. Exposure to heat can degrade the quality of the sample, cause the sulfuric acid to discolor, and cause reactions between sulfuric acid and water to occur more readily (Flinn Scientific, 2018).

3.2 Personal Protective Equipment (PPE)

3.2.1 Always bring and wear appropriate PPE when handling and filling the nitrate sample bottles (4.2.8-4.2.13), including Nitrile gloves (6-mil minimum thickness), Tyvek sleeves, and a face shield that can fit over glasses (Figure 1) (Fong, 2024).

3.2.2 All staff should be wearing long pants and closed-toe work boots or shoes while performing nitrate sample collection.

3.2.3 Do not touch the outside of the gloves with bare hands, skin, or clothes. Do not reuse gloves. Gloves should be carefully removed after each use to avoid skin contamination, see the procedure described in the Field Safety Manual for safely removing gloves (DPR, 2019).

3.3 Handling Precautions

3.3.1 **Do not rinse** the pre-preserved nitrate sample bottles (no native rinse) before use. Rinsing can compromise sample preservation and increase risk of spilling the acid or accidental exposure.

3.3.2 **Work slowly** to avoid contact with your body or clothing, and work in well-ventilated areas when handling and filling the nitrate bottles to minimize spills, cross-contamination, and acid vapor exposure.

3.3.3 **To prevent sample contamination**, it is crucial to ensure a clean environment during sampling and transport. All equipment and containers mentioned here should be clean before use and stored in a clean environment. It is mandatory to wear proper gloves and to dispose of disposable supplies according to SOP FSWA018 and SOP FSWA001.

3.4 Spills

3.4.1 **Alert and inform** all nearby sampling staff about the spill location to prevent accidental slipping, contact, or inhalation of vapors.

3.4.2 **Contain and neutralize spills** by pouring sodium bicarbonate (baking soda) onto the spill to contain and neutralize the acid. If not available, use sand or another inert absorbent material (Flinn Scientific, 2018).

3.4.3 **Clean up and dispose** of neutralized spill by collecting the residue using a brush. Place the collected material into a plastic bag (2.2.8), use tape or tie a knot at the end of the bag to seal it. Dispose of this waste at the nearest appropriate public location (DPR, 2019).

3.5 Training

3.5.1 All staff will be trained during onboarding; thereafter, all staff will review this SOP annually. Supervisors will maintain a record of training and SOP reviews.

4.0 PROCEDURES

4.1 Pre-Study Considerations

4.1.1 **Samples and COCs:** Estimate the number of wells and nitrate samples to collect for the trip and bring extra nitrate bottles. COCs can be filled at the time of sample collection or ahead of time with the study number, sample numbers (4.1.2), chemicals to be analyzed, and the contracting laboratory's ID number. SOPs QAQC005 and ADMN006 may be helpful.

4.1.2 **Labeling:** Pre-label nitrate bottles with printed sample and study number labels. Attach labels with J-Lar tape to cover the entire label so it does not get wet. Alternatively, write the sample number directly on the bottle using a permanent marker.

4.1.3 **Ice:** Bag ice the day before leaving. Bring enough ice or replenish as necessary to keep the nitrate samples cool during sampling and transportation. Retrieve the nitrate bottles from the walk-in refrigerator and secure the bottles with the foam insert inside the ice chests to prevent them from floating in the water when the ice melts.

4.2 Collecting the Sample

4.2.1 Refer to SOP FSWA001 to complete the groundwater sampling procedure.

4.2.2 **Important:** Do not fill the nitrate bottle at the well, as it must remain in the ice chest throughout the groundwater sampling procedure (U.S. EPA, 2016). Only take the nitrate bottle out (4.2.8-4.2.12) and place it on a plastic bag (2.2.8) in the van when you are ready to fill the bottle, then immediately reseal it and return it to the ice chest after filling (Fong, 2024).

4.2.3 Set a plastic bag in the van where you will be filling the well sample into the nitrate bottle.

4.2.4 Rinse the stainless-steel measuring cup with DI water before sampling.

4.2.5 Conduct a native rinse by filling the stainless-steel measuring cup with groundwater directly from the well you are sampling, swirling the water, and then pouring it out as specified in SOP FSWA001.

4.2.6 Collect groundwater from the well by filling the stainless-steel measuring cup enough to adequately fill the nitrate bottle (at least 200 mL). Return to the van with the filled stainless-steel measuring cup and set it on the plastic bag.

4.2.7 Suit up with **all required PPE** at this point in the procedure (See Figure 1, section 3.2, and materials list 2.2.1-2.2.3) before handling nitrate bottles.

4.2.8 Remove the nitrate bottle from the ice chest with your gloved hand and place it on the plastic bag next to the stainless-steel measuring cup.

4.2.9 Open the cap on the nitrate bottle slowly. If the bottle has warmed, there may be some pressure released and possibly droplets. Place the cap on the plastic bag.

4.2.10 Pick up both the stainless-steel measuring cup and the nitrate bottle, and carefully turn so that you are facing away from the van. Slowly pour the water from the stainless-steel measuring cup into the nitrate bottle, taking care to avoid spills and splashes. Do not fill the nitrate bottle completely. Fill to the 125 mL line to leave air space (Fong, 2024).

4.2.11 After filling the nitrate bottle, face the van again and place both containers back on the plastic bag. Securely seal the nitrate bottle with its cap. Place the sealed nitrate bottle in the foam insert inside the ice chest. Ensure the nitrate bottle is secured inside the ice chest before returning to the well.

4.2.12 Store the stainless-steel measuring cup in the purging bucket and do not store it with clean tools and supplies. You may discard of any water that is leftover inside of the stainless-steel measuring cup by pouring it out on the ground at the site of the well you sampled from.

4.2.13 **Carefully remove your PPE. If any acid or acidified sample water contacts the PPE, dry it off with a paper towel. Do not touch it with your bare hands. If you do, rinse your hands with clean water immediately! You may not feel the acid on your fingertips; however, your eyes, skin and mucous membranes are very sensitive to sulfuric acid if it transfers from your hands to these body parts. Regardless of exposure, always rinse your hands with clean water after removing PPE.**

4.2.14 After returning from the field, clean the stainless-steel measuring cup according to SOP FSWA018.

4.2.15 Store any unused bottles in the walk-in refrigerator until they are used. If the project is finished, neutralize the acid in the bottles with baking soda and then dispose of the bottles.

4.3 Preparing Sample Documentation

4.3.1 Complete a COC form to go with each nitrate sample and note the sample numbers on the Well Information Sheet as described in SOP ADMN006 and SOP FSWA001.

4.3.2 Upon completion, the COC and nitrate samples can be delivered to the contracted laboratory in an ice chest with ice.

5.0 REFERENCES

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