SAMPLE PRESERVATION 5.4

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Sample preservation is the measure or measures taken to prevent reduction or loss of target analytes. Analyte loss can occur between sample collection and laboratory analysis because of physical, chemical, and biological processes that result in chemical precipitation, adsorption, oxidation, reduction, ion exchange, degassing, or degradation. Preservation stabilizes analyte concentrations for a limited period of time. Some samples have a very short holding time. **Verify that time-dependent samples were received in proper condition, at the correct temperature, and that holding times were not exceeded by contacting the laboratory.**

Some samples must be preserved by filtration (section 5.3) and (or) chilling and (or) chemical treatment (Appendixes A5-A through A5-C). The preservation required for a given sample is described by the analyzing laboratory; for the NWQL, consult the laboratory for sample-preservation instructions.

- Before going to the field site and again at the field site:
  - Check the sample-designation code required for each sample.
  - Check sample requirements for chilling and chemical treatment.
  - Check with the laboratory and make note of holding time restrictions.

CHILLING 5.4.1

Immediately following sample collection and processing, samples that require chilling must be packed in ice or placed in a refrigerator and maintained at 4°C or less, without freezing, until analyzed.

- Check that there is sufficient headspace in the sample bottle to allow for sample expansion.

- Put foam sleeves around samples in glass bottles before packing them in ice.
- **Include a temperature check sample in the shipping container.**
  - Fill a polyethylene bottle with tap water, cap it securely, and label it "Temperature Check Sample," along with the site identification and the date(s) and time(s) of sampling and shipping.
  - Prepare a self-addressed, stamped postcard that is labeled "Temperature Check Sample report." The postcard should include the site information, date(s) and time(s) of sampling and shipping, and a space for the laboratory to record the arrival temperature of the check sample.
  - Put the postcard into the sealable plastic bag with the ASR form. The laboratory will record the temperature of the check sample upon arrival and will complete the card and return it to the sender.
  - Use this information to document that samples were maintained at 4°C or less.

Pack a temperature-check sample with other chilled samples.

Chilled Samples

[This list of samples that require chilling is not comprehensive—check with the analyzing laboratory. These samples must be refrigerated or placed on ice immediately and maintained at or below 4 degrees Celsius without freezing.]

Chemical classification	USGS sample-designation codes[1]
Organic compounds	VOC, GCC, TOC, DOC, SOC, RCB, LC0052, SH 2010, SH 2051, SH 2001, SH 2050
Nutrients	WCA, FCA, FCC
Chemical Oxygen Demand (COD)	LC 2144
Cyanide	LC 0880, LC 0023
$^{15}N/^{14}N$	RUS; LC 1717, LC 1718
^{14}C	RUR/RUS; LC 1199

[1]These sample-designation codes are unique to the USGS and are subject to change.

CHEMICAL TREATMENT 5.4.2

Chemicals used for sample preservation depend on the target analyte (Appendixes A5-A, A5-B, and A5-C). The most frequently used chemical preservatives by the USGS are provided in individual ampoules and contain one of the following: nitric acid (HNO_3), hydrochloric acid (HCl), sulfuric acid (H_2SO_4), nitric acid/potassium dichromate ($HNO_3/K_2Cr_2O_7$), sodium hydroxide (NaOH), or phosphoric acid/copper sulfate ($H_3PO_4/CuSO_4$). The National Water Quality Laboratory can provide a complete list of sample treatments, along with sample designations and container requirements. The preservatives are procured from QWSU and come with a quality-control certificate of analysis for selected constituents. Keep the certificate of analysis in the study data file to help with future interpretation of quality-control and environmental data.

Take steps to minimize sample contamination and maximize safety during the preservation process (Horowitz and others, 1994; Shelton, 1994; Koterba and others, 1995; Timme, 1995). Note that a chemical preservative for one sample may be a source of contamination for another. To help reduce contamination during the preservation process and ensure proper handling of chemicals:

- Work inside a preservation chamber (only the Clean Hands person works inside the chamber). **Change gloves and the cover of the portable preservation chamber each time a different type of chemical treatment is used**. Clean Hands/Dirty Hands techniques must be used for parts-per-billion levels of trace elements and are recommended for use in general and as appropriate for the study.
- Use preservatives packaged in individual ampoules for routine preservation. Be aware that preservatives dispersed from dropper-type bottles or automatic pipets could become contaminated and could result in the contamination of subsequent samples.
- Use the grade of preservative appropriate to meet data-quality requirements. (Check the certificate of analysis for the method detection limit and the concentration of the target analytes of interest.)

- Always store preservatives in separate, sealed containers, preferably away from each other, and away from environmental and quality-control samples.
- Store spent preservative ampoules, containers, and supplies separately in closed and labeled containers (such as screw-cap bottles) until they can be disposed of properly. Refer to OWQ Technical Memorandum 92.11 on the return of spent $HNO_3/K_2Cr_2O_7$ ampoules to the laboratory.
  - Use a separate ampoule-waste container for each type of chemical preservative.
  - Store used gloves and chamber covers in a closed container, such as a pail with a lid, until proper disposal can be arranged.
- Follow a prescribed order in which samples are to be preserved (the recommended order is described in the steps below).

CAUTION: Before handling any chemical, refer to the Material Safety Data Sheet (MSDS) for safety precautions. Wear appropriate gloves, safety glasses, and apron when working with corrosive or oxidizing solutions.

For chemical treatment and handling of samples, follow the recommended sequence and procedure described in the steps that follow:

1. Put on appropriate disposable, powderless gloves.
2. Set up preservation chambers and assemble equipment and solutions in the order in which they will be used. If nitric acid is the only chemical preservative being used, the processing chamber can be used as a preservation chamber after all the filtered samples have been removed from the chamber.
3. Rinse the outside of each preservative ampoule with DIW and dry with a laboratory-grade, lint-free paper towel (for example, Kimwipe™).
4. For organic-compound samples:
   a. Change gloves.

b. Place inside the preservation chamber the required organic-compound samples, chemical preservatives (treatments), and ampoule-waste containers. Common treatments include hydrochloric acid, sulfuric acid, or phosphoric acid/copper sulfate. **(VOC samples that are to be chemically treated can have the acid preservative added to the sample within the processing chamber as long as subsequent samples are not contaminated (section 5.1.2 and Appendix A5-A).**

c. Change gloves.

d. Uncap the sample bottle and dispense the appropriate chemical treatment into the sample. Place any spent ampoule into the appropriate ampoule-waste container.

e. Immediately recap the sample bottle and invert the bottle about five times to mix. **Vials with septum-lined caps for VOC must have no headspace.**

f. Repeat steps b, c, and d for each type of chemical treatment, if necessary, changing gloves and chamber cover each time. Make sure there is headspace in all glass bottles except for the vials for volatile organic compounds (VOC).

g. Chill all organic samples (treated and untreated) immediately and maintain them at 4°C during storage and shipment to the laboratory (section 5.5).

5. For inorganic-constituent samples:

a. Change gloves.

b. Change the chamber cover. Set up additional preservation chambers, if practical. (For example, one chamber for nitric acid treatments and a separate one for potassium dichromate treatment.)

- Transfer samples requiring chemical treatment to the preservation chamber.
- Place the first preservative and its waste container inside the chamber.
- Change gloves.

c. Add chemical treatments to samples in the following order:

i. Major, minor, and trace cation samples: Add contents of the HNO_3 ampoule to samples designated RA or FA (Appendix A5-B). Place spent ampoule into the HNO_3 ampoule waste container.

ii. Mercury sample(s): Add contents of the $HNO_3/K_2Cr_2O_7$ ampoule to the sample(s) designated RAM or FAM (Appendix A5-B). Place the spent ampoule into the $HNO_3/K_2Cr_2O_7$ ampoule waste container.

iii. Change chamber cover and change gloves.

iv. Nutrient samples designated WCA or FCA (Water Quality Technical Memorandum 99.04):

- Place sample bottles into chamber.
- Add contents of the 1-mL 4.5-normal H_2SO_4 ampoule to 125-mL samples designated as WCA or FCA (Appendix A5-B). Place the spent ampoule into the H_2SO_4 ampoule waste container.
- Chill samples to 4°C or below without freezing immediately after adding the sulfuric acid.

v. Change chamber cover and gloves. Place bottles requiring other acid treatments into the chamber, along with the necessary chemicals and chemical-waste containers. Add the hydrochloric or other acid treatments to the samples. Place spent ampoules in appropriate waste containers.

vi. Remaining samples (Appendixes A5-B and A5-C): Change the chamber cover and change gloves for each type of treatment (for example, zinc acetate, sodium hydroxide, copper sulfate).

d. Tighten the cap on the bottle immediately after adding the chemical treatment and invert about five times to mix.

- Chilled samples must be put on ice and shipped to the laboratory immediately.
- Emptied ampoules must be stored in designated waste or recycle containers.

6. Disassemble and clean the chamber frame.

a. Remove the disposable cover from the chamber and the work area.

- Collapse the plastic cover while outside of the field vehicle.
- Tie a knot in the cover to close it.
- Dispose of the cover as regulations require.

b. Clean the chamber frame, if necessary.

7. Document in field notes the preservation procedures and chemical treatments used.

8. Spent ampoules should be collected and, at the end of each field trip, disposed of according to Federal, State, and local regulations. (The District safety officer and water-quality specialists can be consulted for proper ampoule-disposal methods.)