RAW SAMPLES 5.1

By **D.B. Radtke, A.J. Horowitz, Jacob Gibs, and F.D. Wilde**

Raw samples, commonly referred to as wholewater or unfiltered samples, are collected directly into the appropriate type of sample bottle from the sampling device (such as a submersible pump, sample-compositing device, peristaltic pump, or cone splitter). It is recommended that this sample collection take place within a processing chamber, especially if analyte concentrations are expected to be near the detection limit, to prevent contamination from airborne sources.

- Equipment must be clean before samples are collected and processed.
- Disposable, powderless gloves must be worn throughout sample collection and processing. In order to withstand the solvents or chemicals that could be contacted, vinyl gloves are adequate for inorganic work, but use of organic solvents for organic work requires latex or nitrile gloves.

COMPOSITES AND SUBSAMPLES 5.1.1

Surface-water samples normally are composited and processed through sample splitting (subsampling) devices (NFM 2). Ground-water samples are not composited but are pumped either directly through a splitter or through a filtration assembly (filter assembly) into sample bottles, unless a bailer or other thief-type sampler is used to collect the sample. Inorganic-constituent samples usually are composited in the plastic or fluoropolymer churn splitter; organic-compound samples commonly are composited in a fluoropolymer churn splitter or metal container, or are processed through a fluorocarbon polymer cone splitter.

Only the Clean Hands person fills sample bottles with water withdrawn from the churn or cone splitter (NFM 4).

Two types of water-sample splitters commonly used by the USGS are the polypropylene churn splitter (churn) and the fluorocarbon polymer cone splitter (cone).[5] Each splitter has specific advantages and disadvantages (NFM 2.2.1). By convention, the churn usually is used only for inorganic-constituent (and possibly for suspended organic carbon) samples. The churn is constructed of plastic materials that can potentially affect concentrations of other organic compounds. The cone is constructed of fluorocarbon polymer material and can be used for either inorganic-constituent or organic-compound samples. **Program or study protocols might dictate which equipment to use.**

- Either the churn or cone splitter can be used for splitting raw samples with suspended-sediment concentrations up to 1,000 mg/L.
- Only the cone splitter can be used for splitting raw samples with suspended-sediment concentrations up to 10,000 mg/L (Office of Water Quality Technical Memorandum 97.06).
- The splitting accuracy of the cone splitter is unknown for suspended-sediment concentrations between 10,000 to 100,000 mg/L (Office of Water Quality Technical Memorandum 97.06), but data are available that indicate the splitting accuracy of the cone is unacceptable at concentrations of 100,000 mg/L or more.

5.1.1.A Churn-Splitter Procedure

Subsamples collected from the composite sample in a churn splitter must be processed according to the specific procedures described below, using Clean Hands/Dirty Hands (CH/DH) techniques as applicable.

1. Assemble sample-processing equipment and supplies on a clean work surface.
   - Put on appropriate, disposable, powderless gloves (gloves). (Wearing multiple pairs of gloves at one time provides an efficient means of changing gloves quickly.)

[5]Consult the following references for more detailed information about the churn and cone splitters: Office of Water Quality Technical Memorandums 76.24-T, 80.17, 94.13, and 97.06; Capel and others (1995); and Capel and Larson (1996).

- If hand contact is made with a potential contaminant, remove the outer (contaminated) gloves before continuing with sample processing.
- For CH/DH techniques: Remove churn splitter and inner bag from churn carrier. Leave the churn carrier and outer bag outside the processing area (vehicle or building).

2. Place all prelabeled wholewater or suspended-material bottles within easy reach of the churn spigot.
3. Churn the composite sample at a uniform rate by raising and lowering the disk inside the churn splitter with smooth, even strokes.
   - When churning, the disk should touch bottom on every stroke, and the stroke length should be as long as possible without breaking water surface. **Do not break the surface of the water**.
   - **The churning rate should be about 9 inches per second (in/s).** If the churning rate is significantly greater than 9 in/s, or if the disk breaks the surface of the water, excessive air is introduced into the sample and could affect dissolved gases, bicarbonate, pH, and other characteristics of the sample.
   - Inadequate churning can result in withdrawal of nonrepresentative wholewater or suspended-material samples.
4. Pre-mix the composite sample by churning for about 10 strokes to uniformly disperse suspended material before subsampling.
5. **Raw subsample.** Withdraw the raw subsamples for wholewater or suspended-materials analyses first.
   - Withdraw an adequate volume of sample water for the field rinse while continuing to churn.
   - **Withdraw the first subsample.** The first subsample withdrawn from the churn should be the largest volume required (usually a 1-L sample).
   - Do not interrupt the churning/subsampling process, if possible. If an interruption occurs, reestablish the churning rate and remix the sample by churning ten strokes before resuming subsampling.
   - As the volume of composite sample in the churn decreases, adjust the stroke length to maintain a churning rate of about 9 in/s and avoid breaking the surface of the water being sampled.

6. Check requirements for sample preservation. **For raw samples that require chemical treatment ⇨ Go to section 5.4.**
   - For raw samples that require chilling without chemical treatment(s)—Pack samples in ice or refrigerate as quickly as possible. Maintain at or below 4°C without freezing (section 5.4).
   - For raw samples that do not require chilling or chemical treatment—Set samples aside in a clean area for shipping to the laboratory (section 5.5).
7. **Filtered samples ⇨ Go to section 5.2.** After wholewater or suspended-material subsampling is complete, use the remainder of the composite sample in the churn for filtered samples.
8. Empty the churn after the required number of samples has been processed.
   - If the churn will be reused during the field trip, disassemble and field clean onsite while still wet, as described in NFM 3.
   - If the churn will not be reused during that trip, rinse with DIW before it dries out, place it in a plastic bag and in the churn carrier to be transported back to the office laboratory for cleaning.
9. Document on field forms and in field notes the types of samples collected and the splitting procedures used.

A field blank might be required after all sampling and processing equipment has been field cleaned (NFM 4.3).

TECHNICAL NOTES: Subsamples totaling 10 L and 5 L can be withdrawn from the 14-L and 8-L churn, respectively, for samples for wholewater analysis. The sample volume remaining in either churn may be used for filtered samples.

The churn splitter is used to split samples with particle sizes ≤ 250 µm and suspended-sediment concentrations ≤1,000 mg/L. Splitting accuracy becomes unacceptable at particle sizes > 250 µm and concentrations > 1,000 mg/L.

Cone-Splitter Procedure 5.1.1.B

Inorganic-constituent and organic-compound samples can be split using a fluorocarbon polymer (Teflon™) cone splitter. Although the cone splitter is used primarily for simultaneous distribution of surface-water samples into bottles, the cone also can be used similarly for a bailed or composited ground-water sample. The sample is poured into the splitter from the sampling device or transferred from a noncontaminating compositing container. If used for splitting pumped ground-water samples, the sample is pumped directly into the cone splitter.

1. Put on appropriate, disposable, powderless gloves (gloves). Remove cone splitter from protective covering.
2. Prepare a processing area that is protected from dust and fumes. Preferably, the cone splitter is installed in a processing chamber or covered with a large plastic bag.
3. Install cone splitter (see NFM 2, fig. 2-10, for a labeled diagram). **The cone splitter is built to close tolerances to achieve accurate and reliable operation and requires the following:**
   - **Use a bull's-eye level to level the cone splitter: this is critical for accurate performance.**
   - All tubes exiting the cone splitter must be the same length, as short as possible, and precleaned. Organic-compound samples require fluorocarbon polymer tubing. Carry a separate set of tubes for each site, and clean all sets on return to the office laboratory. If extra tubes are not available, do not reuse tubes for multiple sites without first cleaning them.
   - Push tubes as far as possible into the fittings on the splitter.

Minimize atmospheric contamination—Cover the cone splitter and sample bottles during the sample splitting process and when not in use.

4. Field rinse cone splitter and the appropriate sample bottles with the water to be sampled. **Do not field rinse laboratory-cleaned and baked glass bottles.**
   a. Open cover to access cone-splitter reservoir. (Flap or access slots for hands can be cut into the plastic bag covering the splitter.)
   b. Transfer 2 to 4 L of the sample into the cone-splitter reservoir. Some splitter reservoirs may be retrofitted with a funnel to ease pouring.
   c. Close cover and lightly tap splitting system to dislodge adhering water drops. Discard rinse water.
   d. Field rinse bottles for raw samples (RA, RU, and so on) with wholewater sample. Do not use the water sample previously processed through the cone splitter; follow directions in table 5-2.
5. Place bottles for raw samples under outlet tubes. Complete splitting procedure first with bottles for organic-compound samples, next with bottles for inorganic-constituent samples.
   - Place outlet tubes into sample bottles to prevent spilling. **Outlet tubes should not extend beyond the neck of the sample bottle. Do not submerge the ends of outlet tubes in the sample.**
   - Outlet tubes can be combined to collect various combinations of volumes of the original sample. Make sure no back pressure results from restrictions of water and air flow if combining outlet tubes into a single bottle.
   - Direct sample discharge from unused outlet tubes to waste.
6. Pour (or pump) sample into cone splitter. If hand contact is made with a potential contaminant while using CH/DH techniques, remove outer contaminated glove(s) or put on a new pair of gloves before transferring sample to cone splitter.
   a. Gently shake or agitate sample for at least 10–15 seconds to resuspend any particulate matter present in sampler bottle or discrete sampler (such as a bailer).

b. Transfer sample to cone-splitter reservoir (some splitter reservoirs may be retrofitted with a funnel to ease filling).

- Open cone-splitter cover and invert sampler or compositor containing sample over splitter reservoir. (If using a bailer, empty through bottom-emptying device. If using a pump, hold sample line over the cone-splitter reservoir and pump sample directly into the cone splitter.)
- First, collect organic-compound samples into clean, baked glass bottles (Appendix A5-A).
- Next, collect inorganic-constituent samples into cleaned and field-rinsed polyethylene bottles or as designated (Appendix A5-B or A5-C).

c. Maintain a head of water above the splitter standpipe to prevent air from entering the splitting block while rapidly transferring the sample. **Do not spill any of the sample when pouring or pumping it into the cone splitter.**

d. For proper operation, the splitter standpipe must be discharging at full-flowing capacity.

- **Never overfill sample bottle.**
- **Always transfer the entire composite sample into cone splitter** for thorough distribution into the sample bottles.

7. **When splitting the samples, avoid exposing samples to direct sunlight or freezing conditions.** During sample splitting, the temperature of samples from the cone splitter should remain constant.
8. Close cone-splitter cover.
9. After flow has stopped, lightly tap the cone splitter to dislodge adhering drops.
10. Remove sample bottles and cap them immediately.
11. **To obtain smaller subsample volumes**, position bottles at cone outlet ports and pour a sample from the preceding set of split samples into the cone splitter. **For inorganics only, remember to rinse each new set of polyethylene sample bottles with DIW and sample as previously directed** (sections 5.0.1 and 5.0.3).

12. If multiple passes through the cone are required, randomize the ports selected. This minimizes bias from differences in ports caused by manufacturing processes.
13. Check requirements for sample preservation. **For samples that require chemical treatment ⇨ Go to section 5.4.**
    - For raw samples that require chilling without chemical treatment(s)—Pack samples in ice or refrigerate as quickly as possible. Maintain samples at or below 4◦C without freezing (section 5.4).
    - For raw samples that do not require chilling or chemical treatment—Set samples aside in a clean area for shipping to the laboratory (section 5.5).
14. **Filtered samples ⇨ Go to section 5.2.** Remember to use only sample filtrate for the bottle field rinse.
15. Clean cone splitter, following instructions in NFM 3.
    - Disassemble and clean in the field before reusing. Field cleaning between sites must be done onsite while the cone splitter is still wet.
    - If the cone splitter will not be reused immediately, rinse with DIW and place in a plastic bag for transporting back to the office laboratory for cleaning.
16. Document on field forms and in field notes the types of samples collected and the splitting procedures used.

A field blank might be required after sampling and processing equipment has been field cleaned (NFM 4.3).

GROUND WATER: PUMPED AND BAILED SAMPLES 5.1.2

Steps for filling bottles with raw sample pumped from water-supply wells and monitoring wells are described in this section (refer also to section 5.6 and Appendixes A5-A, A5-B, and A5-C). The equipment needed and the procedures required to purge a well and withdraw the sample are described in NFM 2 and NFM 4, respectively, and are only briefly described below.

The recommended method for withdrawing ground-water samples from conventional supply or monitoring wells is to use a submersible or peristaltic pump and to pump the sample directly to a processing chamber (or to a glove box filled with inert gas).[6] Ground-water samples collected using a bailer or other discrete sampling device can be processed either as described under 5.1.1 (composites and subsamples) or within a processing chamber (or glove box), as described later in this section.

Only the Clean Hands person fills the sample bottle inside of the sample-processing chamber (NFM 4).

Collect/process equipment blanks, field blanks, replicates, and other types of quality-control (QC) samples periodically (NFM 4.3 and Appendix A4-B of NFM 4). The frequency, number, types, and distribution of QC samples are determined ahead of time according to the study workplan. Nevertheless, in the event of unforeseeable field conditions (for example, dust storms, new point source(s) of contamination, or application of agricultural or other chemicals), **field personnel must judge whether to process additional QC samples**.

- Replicates of environmental samples—Fill bottles one after the other (NFM 4.3).
- Field blanks—Process according to the study quality-assurance plan or as needed (NFM 4.3).

[6]Wells or devices constructed to obtain samples under natural flow gradient (passive) conditions are not addressed in this report.

Processing of samples

The steps listed below for processing raw ground-water samples are based on the assumption that both organic-compound and inorganic-constituent samples will be collected. Before proceeding, check section 5.6 for analyte requirements.

- Prelabel bottles with site identification, sample designation, date, and time (section 5.5 and NFM 1).
- Process samples in the order recommended for sample collection listed on table 5-1. This helps to limit overpurging of volatile compounds, reduce airborne contamination and cross contamination among samples and sites, and minimize discrepancies in the ionic mass balance.
- When pumping the sample, do not stop the pump or interrupt flow to the processing chamber during sampling. The rate of flow during sampling should remain constant throughout processing and be the same as the rate of flow while making final field measurements at the end of purging (NFM 4, NFM 6).

To process ground-water samples for organic-compound analyses:

1. Put on appropriate (latex or nitrile), disposable, powderless gloves (gloves). Cover bench or table with a sheet of aluminum foil to make a clean work surface.
2. Assemble necessary equipment and supplies on the clean work surface, and remove aluminum foil wrapping from precleaned equipment. Attach processing chamber cover. (Processing of organic-compound samples within a chamber is not mandatory but is recommended.)
3. Check requirements for treatment of the sample(s) collected.
   - If collecting a VOC sample that will be acidified—Test for the number of drops of HCl needed to lower sample pH to ≤ 2 using 40 mL of the final purge water. Dispense the HCl from a dropper bottle.
   - All samples processed for organic-compound analysis are to be chilled to 4°C or below without freezing.
4. Place bottles and other equipment needed for processing raw samples into processing chamber. If collecting samples for VOCs, place only VOC vials and VOC equipment in the chamber.

5. Withdraw samples from the well.

If using a pump—

a. Purge wells first, preferably with the same pump to be used for withdrawing the samples. Consult NFM 4.2 for purging procedures.

b. Check that the discharge end of sample line from the pump or manifold is secured in the processing chamber.

c. Direct sample flow through the sample line into the processing chamber (NFM 4.2).

- Waste initial sample through chamber drain for the sample-line rinse; do not let sample spray onto chamber cover—change chamber cover if this happens.
- Check for air bubbles in the sample line; tap the line or make adjustments to remove any air from the line.
- Flow should appear smooth and uniform (with no splashing) and should not exceed 150 mL/min when filling 40-mL VOC vials or 500 mL/min for larger bottles.

If using a bailer—

a. Purge wells first, using a pump (NFM 4.2). Do not purge wells with a bailer unless absolutely necessary.

b. Set up holding stand, as appropriate.

c. Lower the sampler (after field rinse) smoothly into the well; cause as little disturbance to the water column as possible. Follow analogous directions as those for sampler field rinsing (NFM 4.0.2.A).

d. After reaching the sampling depth within the screened or open interval, collect sample by raising the sampler smoothly (minimizing disturbance to water column). Keep the deployment line clean and untangled as sampler is lowered and raised.

e. Place sampler into holding stand and insert sample-delivery tube/device.

> TECHNICAL NOTE: Sampling from wells with a bailer or other discrete sampling device is not recommended if target analytes (such as trace elements and hydrophobic organic compounds) are those that typically associate or partition to particulates because deployment of bailers or other point-source samplers usually stirs up or otherwise mobilizes particulates. Fine-grained and colloidal-sized particulates can persist in the water column, causing a potential for bias.

6. Collect all raw organic-compound samples into designated bottles.
   a. Fill VOC vial from bottom of vial to overflowing without entraining air bubbles. Leave a convex meniscus. If sample will not be acidified, cap vial securely, invert, and check for air bubbles. **Follow directions in section 5.6.1.A.**
   b. If acidification of the sample is required,
      - The preservative can be added to VOC samples while samples are inside the processing chamber as long as the chemical treatment will not affect any subsequent samples to be collected for analysis of organic compounds. Otherwise, acidify VOC samples in a preservation chamber.
      - Add 1 to 5 drops of HCl to the sample (sections 5.4 and 5.6). Usually two drops of HCl are sufficient to lower the pH of the VOC sample to ≤ 2. Cap vial securely, invert, and check for air bubbles. If air bubbles are present, discard the vial and start again.
      - Change cover of processing chamber and change gloves.
   c. Place remaining raw organic-compound sample bottles into processing chamber. Fill bottles directly from the sample line to the shoulder of each bottle (section 5.6.1.B).
7. For filtered organic-compound samples:
   a. Place aluminum plate-filter assembly into chamber for pesticides and other filtered organic-compound samples. Change gloves.
   b. Load the filter, connect the plate-filter assembly, and field rinse the filter as directed in section 5.2.2.A.
   c. After following filtration directions in section 5.2.2.A, pass bottles out of chamber for DH handling.
8. After processing raw and filtered organic-compound samples:
   a. Fill sample bottle with DIW and label "temperature-check sample" to accompany chilled organic-compound samples.
   b. Remove the equipment used to process the samples and pass to DH.
   c. Discard chamber cover.
   d. Remove aluminum foil covering from work bench.
9. **Sample preservation ⇨ Go to section 5.4.**

Process ground-water samples for inorganic-constituent and remaining analyses:

1. Direct flow of pumped sample away from the processing chamber. Change to vinyl or latex, disposable, powderless gloves (gloves).
2. Cover bench or table with a plastic sheet to make a clean work surface. Change processing chamber cover. Assemble equipment and supplies needed on the clean work surface. Remove plastic wrapping from pre-cleaned equipment. Change gloves.
3. **For filtered inorganic-constituent, nutrient, radiochemical, and isotope samples**:
   a. Place filtration equipment, sample bottles (prelabeled), and other supplies and equipment for filtered inorganic-constituent samples into processing chamber. Change gloves.
   b. Connect filtration equipment as directed in section 5.2.1.
   c. Resume sample flow to the chamber.
      - Check for air bubbles in the sample line; tap line or make adjustments to remove air from the line.
      - Flow should be smooth and uniform—about 500 mL/min to fill sample bottles without splashing.
   d. Collect all filtered inorganic-constituent samples first, as directed in section 5.2.1.
4. Disconnect the filter assembly. Change gloves.
5. **Raw inorganic-constituent, nutrient, radiochemical, and isotope samples:**
   a. Place prelabeled bottles for raw samples into the processing chamber. Change gloves.
   b. Field rinse bottles with raw sample (section 5.1, table 5-1).
   c. Collect samples into designated bottles.
   d. Place bottles outside of chamber. Change gloves.
6. Remove equipment, discarding chamber cover appropriately.
7. **Sample preservation ⇨ Go to section 5.4.**
8. **Radon and CFC samples ⇨ Go to section 5.6.**