

# Standard Operating Procedures for the Collection of Water Chemistry Samples

Water Quality Control Division • Environmental Data Unit

## 1.0 Introduction

This document describes basic procedures to follow when conducting water chemistry sampling events for the Water Quality Control Division (division). It outlines standard procedures and good sampling techniques to follow for river and stream sampling in the State of Colorado.

This document describes general methods and procedures that should be followed for the collection and analysis of water quality samples for the division. It is not intended to encompass every type of sampling nor is it intended to prescribe procedures for unique situations.

The procedures prescribed in this document focus chiefly on routine sampling events that include a typical suite of water quality parameters to be analyzed. It is important to note that procedures used during field work often vary depending on the goals and objectives laid forth in Sample Analysis Plans (SAPs).

#### 2.0 Personnel Qualifications

- Sampling personnel should thoroughly read and understand this SOP before collecting samples in the field.
- Sampling must be conducted by trained personnel.
- Inexperienced samplers should work with or attend training events sponsored by qualified personnel to gain experience in this SOP.

#### 3.0 Health and Safety

- Request permission or inform landowner when collecting samples on private property.
- Use extreme caution when walking on uneven and slippery substrate in the presence of rapidly flowing waters and stop if conditions become too dangerous.
- Wear personal protective equipment (PPE) to ensure protection against environmental hazards.
- Cease field activities immediately and vacate the river/stream if lightening is observed nearby.
- Be prepared for all types of weather conditions and have appropriate clothing/gear.
- Wear disposable powder-free nitrile gloves when handling samples.
- Wear eye protection if working with acid preservatives.

#### 4.0 Equipment and Supplies

The following list of items is necessary before going out in the field. They may not be applicable to all types of sampling events so additional equipment and supplies may be required.



- Sample containers
- Barcode or sample identification labels
- 0.45 µm cellulose acetate filters
- Geofilter<sup>®</sup> 47 mm glass fiber or similar brand pre-filters
- Swinnex 47 mm filter holder
- 60 ml syringes with slip type tip
- Forceps
- Ziploc<sup>®</sup> bags
- Bucket
- 50-100'nylon rope
- Pencils
- Pens and markers with indelible ink
- Disposable powder-free nitrile gloves
- Ice
- Ice chest(s)
- Deionized laboratory water
- Chain of custody form
- Electronic or paper "field log" form
- Field notebook (optional)
- GPS unit
- Digital camera
- Sampling, field operations, and equipment Standard Operating Procedures
- Multi-parameter sonde and reader (YSI EXO1, Trimble Yuma 2 tablet, etc.), including charger and cables
- Calibration solutions
- Battery-operated air pump, plastic tubing and air stone
- Extra batteries
- Additional PPE, including waders

#### 5.0 Quality Control and Quality Assurance

Field quality control and quality assurance (QA/QC) procedures are project-specific and are outlined in the project's SAP and/or Quality Assurance Project Plan (QAPP). Standard operating procedures will be utilized as a primary tool to ensure field procedure QC. Staff performing field activities for the division will receive the training necessary to ensure that all SOPs are wholly and properly used when completing field monitoring activities. Each project-specific SAP shall describe and reference all QA/QC methods to be followed.

In the absence of a project-specific SAP, at a minimum, the following QC samples shall be taken:

- Collect one duplicate sample per 10 locations sampled.
- Collect one field blank during a field trip that results in less than 15 routine samples.
- Collect two field blanks during a field trip that results in 15 or more routine samples.

Since the intent is to ensure that equipment decontamination procedures are followed to exact specifications, the field blank shall be collected even if the field trip includes only a single routine sample. For week-long field trips that result in 15 or more routine samples then one trip blank shall be collected at the start of the week and a second field blank should



be collected at the end of the week to ensure that equipment decontamination procedures are followed to exact specifications during trips of heavy usage.

## 5.1 Blanks

The division refers to its blanks as either trip or field blanks. It is deionized water preprepared in the laboratory, taken into the field, exposed to sampling conditions, including equipment and preservatives, and returned to the laboratory for analysis.

Division sampling personnel shall use deionized water from Colorado Department of Public Health and Environment's Laboratory Services Division for all trip blanks.

It is important to store deionized water in a container that is suitable for the analysis to be conducted. For inorganic analysis it is appropriate to use a Nalgene carboy with spigot or comparable plastic cubitainer. Blank water that is to be used for microbial analyses must be autoclaved and stored in a separate storage container that is sterile.

## 5.2 Duplicates

A set of similar samples collected from the same site, at about the same time and analyzed in the same manner. Duplicate samples equate to "fraternal twins" in that they originate from one source but each sample may contain a slightly different chemical composition.

When collecting duplicates, sample the same source of water that was collected for the routine sample. This can be accomplished in several different ways as described below.

- Lower a single collection container, such as a bucket, into the water column and use the collected volume for both routine and duplicate samples.
- Lower two sample bottles side by side to the exact same depth in the water column. Do not use this technique with a bucket sample.
- If using a special sampling device such as a Van Dorn or well bailer, use half the volume collected for the routine sample and the other half for the duplicate.

#### 6.0 Grab Sample Collection

The division typically collects samples using the grab technique and the data are used to represent conditions at the exact moment sampling occurs. The grab sample shall be collected from the main channel or thalweg, which is the line of fastest flow in the stream channel and often the deepest, just below the water surface.

If stream conditions are unsafe for the sampler to wade into the thalweg, the grab sample may be collected from the stream bank where active flow occurs or where stream flow is directed along the bank, or from a bridge using a bucket.

#### 6.1 Sample Containers

The following sample containers are characteristic of a typical "bottle set" collected by the division. A bottle set is a collection of bottles to be used at a single sampling location. These containers are frequently used in routine and trend monitoring throughout the State.

• Nutrient - A 250 ml plastic container identified as "Nutrient". This container contains acid for preserving the sample and should be handled with care. Fill with source



water. Do not rinse or over-fill. Leave approximately  $\frac{1}{2}$  inch of headspace to allow for mixing and expansion.

- Neutral A 250 ml plastic container identified as "Neutral". Rinse with source water three times before collecting sample. Fill with source water. Leave approximately ½ inch of headspace to allow for mixing and expansion.
- **Dissolved metals (filtered)** A 250 ml plastic container identified as "Metals". It is important to identify this container as a filtered sample by writing "Filtered" on the container shoulder with an indelible marker.

Metals containers have been acid washed, and do not need to be rinsed with sample before filling. Samples are to be filtered through a 0.45  $\mu$ m cellulose acetate filter. Pre-filters may be used to filter out courser materials. Filters and pre-filters should be wetted with D.I. water and the first 10 ml of sample filtered to waste before final sample is collected. Leave  $\frac{1}{2}$  inch headspace to allow for mixing and expansion.

If a syringe is used to collect source water and express the sample through the filter, that syringe shall be rinsed three times with source water prior to collecting the final sample.

- Total Recoverable metals (unfiltered) A 250 ml plastic container identified as "Metals". Metals containers have been acid washed and do not need to be rinsed with sample before filling. Fill with source water. Leave approximately ½ inch of headspace to allow for mixing and expansion.
- **BD Centrifuge tube** A 50 ml plastic tube identified as "BD Falcon". Rinse with source water three times before collecting sample. Fill with source water to the <sup>3</sup>/<sub>4</sub> mark to allow for expansion because this sample is frozen upon receipt by the laboratory.
- E. coli A 100 ml hard plastic container identified as "Microbiological". These samples are grab samples. The microbiological sample containers have been washed and sterilized, so no rinsing is necessary. Fill the container to the "fill line".

#### 6.2 Instream Direct Method

Follow these procedures when collecting the routine and duplicate samples instream.

- Put on powder-free nitrile gloves or any applicable PPE.
- Remove the first non-filtered sample container from the Ziploc<sup>®</sup> bag.
- Proceed to a point within the thalweg, or other approved location, and face upstream.
- Remove the container cap and submerge the sample container into the thalweg water column.



Important Notes:

- Metals containers have already been acid washed and do not need to be rinsed with sample before filling.
- Nutrient containers are pre-preserved ahead of time do not rinse.

If a rinse is required then fill the container ¼ full, re-cap, shake forcefully, and then discard the rinsate downstream from the sample point. Repeat two more times. It is important to also rinse the cap since it is part of the "container".

- Fill the container to the desired level, cap, and return container to the Ziploc<sup>®</sup> bag.
- Repeat the above steps for the remaining non-filtered containers.
- Proceed to the filtering phase.
- Open the Swinnex 47 mm filter holder by unscrewing the upper half from the bottom half. See Figure 1. Using forceps, center a 0.45 µm cellulose acetate filter onto the lower half. Do not handle the filter with bare hands.
- Wet the cellulose acetate filter with deionized water. If necessary, add a pre-filter on top so the two filters stick together. Screw the upper half of the filtering apparatus to the bottom half ensuring that the two orange-colored O-rings remain fixed in place.



Figure 1. Swinnex 47 mm Filter Holder

- Remove the filtered "Dissolved Metals" container from the Ziploc<sup>®</sup> bag. Make certain that "Filtered" is written on the container shoulder using an indelible marker. Take the container, the pre-loaded filter holder and a 60 ml syringe to the same point within the thalweg or other approved location. Face upstream.
- Submerge the syringe into the thalweg and draw 60 ml of source water into the syringe. Discard rinsate downstream. Repeat two more times.
- To rinse filter media, draw source water into the syringe. Insert the syringe tip into the top of the filter holder. Force 10 ml of sample water through the filter into the stream in a downstream direction.
- Remove the container cap and snugly fit the filter holder over the container opening.
- Begin filling the container by successively filling the syringe and forcing sample through the filter.
- Replace the filter(s) if they become clogged.
- Complete filling the container to the desired level, cap, and return the container to the Ziploc<sup>®</sup> bag.
- Remove the filter(s) from the filter holder and properly dispose of.



Triple rinse with deionized water any sample collection device, such as a bucket, filter • holder or syringe that is to be reused from site to site.

#### 6.3 Bucket Direct Method

Bridge sampling can be performed on the upstream or the downstream side of a bridge if access to the stream bank is hazardous or if property access was unobtainable. However, be cognizant of the exact location of the station. Some station descriptions are specific as to whether it is located upstream or downstream of the bridge.

Follow these procedures when collecting the routine and duplicate samples from a bridge.

- Put on powder-free nitrile gloves or any PPE.
- Based on the site description and established coordinates, approach the upstream or downstream side of the bridge. In the absence of a directional descriptor or if the coordinates fall directly on the bridge, default to the upstream side of the bridge.
- From the bridge, position yourself directly over the thalweg and lower the bucket down into the water column.
- Fill the bucket.
- Raise the bucket back to the bridge.

For upstream side sampling, discard the bucket rinsate to the downstream side of the bridge. If the bridge is heavily traveled by motor vehicles do not attempt to cross the road to discard the rinsate. While on the bridge, laterally move to one side of the thalweg and dump the bucket rinsate back into the stream away from the sample point.

For downstream side sampling, laterally move to one side of the thalweg and dump the bucket rinsate back into the stream away from the sample point.

- Repeat the bucket rinsing procedure twice more.
- On the fourth bucket, fill with stream water up to the <sup>3</sup>/<sub>4</sub> quarter point of the bucket and raise the bucket back up to the bridge. This is your sample.
- For non-filtered samples, remove the container cap and pour water from the bucket directly into the sample containers to the prescribed levels. Do not dip the sample containers into the bucket.

Note: Metals containers have already been acid washed and do not need to be rinsed with sample before filling. Nutrient containers are pre-preserved ahead of time - do not rinse.

Note: If a rinse is required then fill the container ¼ full, re-cap, shake forcefully, and then discard the rinse water downstream from the sample point. Repeat two more times. It is important to rinse the cap since it is part of the "container".



- Return the container(s) to the Ziploc<sup>®</sup> bag
- Proceed to the filtering phase.
- Open the Swinnex 47 mm filter holder by unscrewing the upper half from the bottom half. Using forceps, center a 0.45 µm cellulose acetate filter onto the lower half. Do not handle the filter with bare hands.
- Wet the cellulose acetate filter with deionized water. If necessary, then add the prefilter on top so the two filters stick together. Screw the upper half of the filtering apparatus to the bottom half ensuring that the two orange-colored O-rings remain fixed in place.
- Submerge the syringe into the bucket and draw 60 ml of source water into the syringe. Discard rinsate. Repeat two more times.
- To rinse filter media, draw source water into the syringe. Insert the syringe tip into the top of the filter holder. Force 10 ml of sample water through the filter into the stream in a downstream direction.
- Remove the filtered "Dissolved Metals" container from the Ziploc<sup>®</sup> bag. Make certain that "Filtered" is written on the container shoulder using an indelible marker.
- Remove the container cap and snugly fit the filter holder over the container opening.
- Begin filling the container by successively filling the syringe and forcing sample through the filter.
- Replace the filter(s) if they become clogged.
- Complete filling the container to the desired level, cap, and return the container to the Ziploc<sup>®</sup> bag.
- Remove the filter(s) from the filter holder and properly dispose of.
- Triple rinse with deionized water any sample collection device, such as a bucket, filter holder or syringe that is to be reused from site to site.

A meter reading should be performed last on the bucket volume. See Section 7.0 for further details.

## 6.4 Sample Preservation

Various analytical procedures require different preservation techniques. Some preservatives may include acids or bases, but others may only require cooling to less than 4 °C.

For purposes of this procedure, default to cooling all sample containers to less than 4 °C with ice. Place each Ziploc<sup>®</sup> bag or bottle set in an ice chest with an ample amount of cubed ice for the duration of the field trip. Refresh quantity of cubed ice throughout the field trip, as necessary. Remove from ice only when samples are to be submitted to laboratory personnel.



Important Notes:

- The only sample container that comes pre-preserved is the 250 ml nutrients container. It is pre-preserved with  $H_2SO_4$  and labeled accordingly.
- Total recoverable and dissolved metals containers are preserved with HNO<sub>3</sub> after receipt at the laboratory. For that reason, metals containers do not necessarily need to be cooled to 4 °C or less in the field. However, be sure to inform laboratory personnel when metals bottles are not preserved in the field and when laboratory personnel are required to add the preservative.
- Do not use snow as a surrogate for ice. Snow could potentially introduce unknown • contaminants to the sample collection process.

# 7.0 Field Measurements

Field measurements for temperature, pH, dissolved oxygen and specific conductance will be made at the same time when water chemistry samples are collected. These measurements can be made directly from the stream or from a discreet sample collected in a bucket at the same time the water chemistry samples are collected.

These measurements are recorded with a handheld, multi-parameter sonde. Please refer to the division's Standard Operating Procedures for operation and calibration of YSI EXO1 and In-Situ Troll 9500 multi-parameter sondes.

Standard Operating Procedure for the Operation and Calibration of the YSI EXO1 Multi-Parameter Sonde. Water Quality Control Division, Environmental Data Unit.

Standard Operating Procedures for the Operation of the In-Situ Multi-Parameter TROLL 9500. Water Quality Control Division, Environmental Data Unit.

# 8.0 Documentation

# 8.1 Monitoring "Field Log" Form

Sampling metadata is documented on a Microsoft Excel<sup>®</sup> form (spreadsheet), which is preloaded onto ruggedized field tablets. The form utilizes a series of drop down menus and is macro-enabled. This function allows for consecutively saving form data during a field trip and resetting the form in between sites. A separate entry on the form will be made for each sample. This also includes blanks and duplicates. Include an entry for visits where no sample is collected at the time of the site visit.

Third party samplers, who collect water chemistry samples under this SOP, may not have field tablets at their disposal. Therefore, the conventional paper "field log" form is provided in Appendix A. It is recommended to print this form on waterproof Rite-in-the-Rain<sup>®</sup> paper.

All fields should be completed for each log entry and general observations recorded on this form. Barcodes distinguishing routine, duplicate, and blank samples will be noted on this form; not on the chain of custody (COC) form.



The saved form data or the original paper form is the official documentation of the site visit and sample collection.

#### 8.2 Chain of Custody

Samples are tracked by means of a chain of custody form. The COC describes the location sampled, the date/time, the sample matrix collected, the test panels to be analyzed, and the preservative used. It also identifies the individual responsible for collection and tracks physical possession of the samples from field to laboratory. Additionally, a space is provided to record the receiving temperature of the sample ice chest. The COC shall accompany all the samples from the time of their collection to the time of their receipt by laboratory personnel.

The COC used by the division is provided in Appendix B. It is available in a Microsoft Word<sup>®</sup> format and can be prepared and preprinted on regular or waterproof paper before conducting field work or it can be filled out entirely while in the field. Simply leave the date and time blank.

The procedure is as follows:

- An indelible marker may be used on waterproof COCs whereas a pen with indelible ink may more appropriate for non-waterproof COCs.
- Write legibly. If a mistake is made, cross out the error with a single line, then write in the correction. Date and initial close to the cross out/correction.
- Apply the sample barcode or unique identifying number in the upper right hand corner of the form. This is the same barcode or identifier that is affixed to each sample container and the field log form.
- Record the station ID, stream name, and description under "Sample Site". Check the box if the station is new.
- Record the collection date and time, the initials of the individual who collected the sample, and the sample matrix under "Specimen Information".
- Record the number and types of bottles collected per sample under "Bottle Information". This will vary based on specific projects. Tally the total number of bottles to be submitted to the laboratory on the last line under the column "Number".
- Check the appropriate test panel under "Test Order". The most common test panels are WQCD Routine Panel or WQCD Trend Panel.

**Note:** Do not indicate whether the sample is routine, blank, or duplicate on the COC. Quality control samples are intentionally submitted to the laboratory using an identification scheme (e.g. barcodes) such that the laboratory doesn't know that they are blanks or duplicates.

• When relinquishing custody of the samples, sign and date the first "Relinquished by" box and have the individual receiving the samples to sign and date on the first "Recv by" box. Ask the individual receiving the samples to record the receipt temperature in the "Temperature at Receipt" box.



## 9.0 Document Version

2.0\_042116

# 10.0 Approval Signatures

4/21/2016

4/21/2016

X Andrew Ross

Andrew Ross Environmental Data Unit Acting Manager

X Christopher Theel

Christopher Theel Environmental Data Unit QA Officer



Sample Bar Code Label						
Start Time:hrs Sample Time:hrs End Time:hrs	DAD					
Site No Sample Collection Date: Stream / Site Name Location Description	CODE LABEL					
GPS: TypeNo	BLANK					
Map Datum Sat Status						
Sampling Location: Bridge Directream Other Direct Bank Directory Right Bank						
Collection Method:    From bridge w/bucket    Instream w/bucket    Instream direct						
Filtering Equipment: Geo Tech Pump Syringe Other						
Filter Holder: 142 mm Geo Tech 47mm Swinnex Other	BAR					
Filter Paper Type: 142 mm Geo Tech 47mm Geo Tech Other	CODE					
Filtering Method:  Instream direct From bucket From sample container Filters Used - Total Count: Roughing Final	LABEL					
	DUDE					
De-Ionized Water: Source Date//	DUPE					
QA / QC Samples: Yes / No Type: Duplicate Spike						
FIELD MEASUREMENTS:						
Instruments Used: In-situ I Quanta I YSI Other Other						
Instruments Calibrated at this site? Yes / No Meter Index No.						
Measurement Method: From bridge w/bucket Instream w/bucket Instream direct						
Measurements: Stream Temp °C Spc uS/cm DO mg/L	BAR					
pHsu@°C T. Alk mg/L Air Temp°C	CODE					
Winkler DO mg/L Other Other Other	LABEL					
1 ofai Aikaimity calculation:						
Other Field Activity (Check all that apply):           Habitat         RBP         Macroinvertebrate         Flow         Other	SPIKE					
Field/Weather Observations and Comments						
Pretor weather Observations and Comments:						
Samples Collected (Check all bottles that amply):						
Metals (250 ml) Metals, Filtered (250 ml) Metals (1 L) Metals, Filtered (1 L)						
Nutrient (250 ml)         Nutrient (1 L)         Neutral (1 L)         Neutral (250 ml)         Micro						
Other						
Maps, Drawings, or Additional Comments on BACK						





#### Appendix B - Chain of Custody Form



Laboratory Services Division 8100 Lowry Boulevard, Denver, CO 80230-6928 Phone: (303) 692-3090 Fax (303) 344-9989

Sample barcode here

#### REQUEST FOR ANALYTICAL SERVICES

Note: This form to be used from 7/1/15-6/30/16

CUSTOMER		SPECIMEN INFORMATION				
Customer ID: Name:	00000372 CDPHE – WQCD – [Unit name here]	Collected:	M-D-Y Time:			
Address: City/State/Zip: Contact Name: Contact Phone: Contact Email:	4300 Cherry Creek Drive South Denver, CO 80246 [your name here] [your phone # here] [your email address here]	Collected by:	Matrix: Surface Water			
SAMPLESITE			BOTTLE INFORMATION			
Station ID:		BOTTLE         M         PM         Next           250 ml         1         1         1         1           500 ml         1         1         1         1           50 ml         1         1         1         1           50 ml         1         1         1         1	eck each box that applies Not TN* was avac BC BIO HB Number			
Description:	Check if new station	1 Liter Amber Micro Other				
	TEST ORDER (Check appropriate box)					
METALS	NUTRIENTS	OTHER	MICROBIOLOGY			
	m 🛛 Nitrate/Nitr	ite 🗆 DOC	Total Coliform, PA			
C      Antimor	y 🛛 Nitrogen, A	mmonia 🛛 TOC	Fecal Coliform, MT			
C C Arsenic	<ul> <li>Nitrogen, Kj</li> </ul>	jeldahl Cyanide, Direct	E. coli, MPN			
C C Cadmiur	n 🗆 Nitrogen, To	otal 🛛 Sulfide	•			
	Im LI Phosphoru:	s, lotal LI UV @ 254				
Hardnes	s, Total Alkalinity, T	otal 🛛	-			
	BOD/COD		TEST PANELS			
Lead	Chloride	RADIOCHEMISTRY	WQCD Routine Panel			
O O O Magnes	ium 🗆 Conductivit	y 🗆 Radium 226	WQCD Trend Panel			
U D D Mangan	ese 🛛 Fluoride	Radium 228	CPW Panel			
	Descenter	Ortho	WOCD - Mine Impact Surface Water Pkg*     WOCD - Mine Impact Sediment Pkg*			
	im 🗌 Solids. Dissi	olved	WQCD - Mine Impact DW Wells Pke*			
C      Seleniur	n 🛛 Solids, Total	Suspended	WQCD - Mine Impact Fish Pkg*			
Solids, Total		-	Mining - Metals & Minerals			
	Culture .		Mining - Nutrients			
			C mining mounting			

DEPOSITION CHAIN OF CUSTODY					
RELINQUISHED BY:	DATE/TIME:	RECV BY:	DATE/TIME:		
RELINQUISHED BY:	DATE/TIME:	RECV BY:	DATE/TIME:		
RELINQUISHED BY:	DATE/TIME:	RECV BY:	DATE/TIME:		
TEMPERATURE AT RECEIPT: C	LSD Internet Address: http://www.cdphe.state.co.us/lr/ Form #251 - Revised: 03/16/2016				

