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Water Resources

Alaska Region



Jago River - Arctic NWR

QUALITY ASSURANCE PLAN FOR INORGANIC WATER QUALITY ASSESSMENT IN ALASKA REFUGES

Report WRB 04-1



**QUALITY ASSURANCE PLAN
FOR
INORGANIC WATER QUALITY ASSESSMENT
IN ALASKA REFUGES**

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Report WRB 04-1

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ABSTRACT

The USFWS Water Resources Branch (WRB) in Anchorage, Alaska, collects water quality and quantity data within national wildlife refuges of Alaska to protect fish and wildlife habitat and the natural biodiversity of aquatic resources. This quality assurance plan is designed for use with all WRB hydrologic projects where physical and inorganic chemical data is obtained. Emphasis is placed on ultra-clean sampling methods that are used in natural, low ionic strength rivers and streams. Standards, policies and procedures are documented as they relate to collection, processing, analysis, data storage, and reporting of data.

BACKGROUND

Preserving water quality is one purpose of every Alaska Refuge. Land cover and use can affect the water quality of rivers, lakes and other surface waters. Potential sources of point- and nonpoint-source pollution, such as communities and resource development projects, can threaten refuges' generally pristine waters. Baseline water quality data provide a benchmark for identifying and quantifying the degree of contamination or change. On most of Alaska's refuges, there are limited or no water quality data available. The WRB designed its water quality program in 2001 to identify and protect the water quality conditions in Alaska's Refuge system.

STUDY DESIGN

The water quality program occurs in conjunction with operating stream gages which quantify the occurrence and distribution of surface water. Physical and chemical characteristics are assessed in Alaska's National Wildlife Refuge waterbodies to establish baseline data sets. Sampling sites are selected from a larger network of streamgaging stations operating on a Refuge. Larger rivers which represent the general characteristics of a watershed are chosen for sampling. Priority is also assigned to rivers and streams that are threatened with a change in water quality. Sampling sites are located far enough downstream from the confluence of streams or a point source of contamination to allow complete mixing. Cross-sectional measurements of physical parameters at various stages are conducted to verify adequate mixing. Physical properties are determined along with the occurrence and distribution of nutrients, major ions, and trace metals and their relationship to hydrologic conditions.

Measurements of pH, specific conductivity, water temperature, and salinity are recorded at all Refuge streamgaging stations when discharge measurements are made. Readings are taken at mid-depth at five or more equally spaced points in the river cross section. In addition, water samples are collected for laboratory analysis at select streamgaging sites over a range of flows. Samples are collected three or four times in open water from May to October and periodically one sample is collected in March when partial or total ice

cover may be present. Sample collection continues for a minimum of three consecutive years.

WATER QUALITY LABORATORY

Laboratories providing analytical services to the USFWS WRB must meet the requirements described in the USGS Water Resource Division Memorandum 98.03 (USGS, 1998). This memorandum describes the policy for the evaluation and approval of analytical laboratories which is a prerequisite for storing analytical data in the USGS National Water Information System (NWIS) database. The WRB stores its analytical data on NWIS and therefore is responsible for assuring that the selected laboratory meets the requirements for approval. Approved laboratories must meet the following criteria: 1) Use approved and published analytical methods, 2) Have standard operating procedures for analytical methods, 3) Have a documented and approved quality assurance plan, 4) Have documented quality control procedures and provide data that allows for continuous tracking of the bias and variability, 5) Participate in the USGS Standard Reference Sample program used to evaluate the analytical performance of the laboratory.

Consistency and comparability is necessary in order for the WRB to establish baseline data sets and to develop long-term trend analysis. The National Water Quality Laboratory (NWQL) is used by the WRB for analysis of nutrients, inorganic chemistry, and trace metals (Appendix A). NWQL is the largest water testing laboratory in the United States and is used as the primary analytical water quality laboratory for the USGS. As such, it is necessary to meet extremely high standards that support programs requiring long-term, consistent, analytical chemistry data of known quality for national assessment and trends. Performance evaluations, accreditations and external audits are used by NWQL to meet this requirement. The NWQL consistently receives overall ratings of good to excellent in performance evaluation studies. The NWQL has a detailed quality assurance program that provides analytical data of known quality. In addition, NWQL instrumentation can analyze for extremely low-detection levels, which is necessary for Alaska's natural waterbodies. It may be determined that some waterbodies may need analysis of additional parameters. The NWQL analytical services include inorganic, organic, and radio chemistry, as well as benthic invertebrates.

WATER QUALITY INSTRUMENTS AND FIELD MEASUREMENTS

Physical parameters are subject to rapid change when removed from the ir source, therefore they are measured at the field site as the samples are collected. A water quality multimeter is used to measure pH, specific conductivity, water temperature, and salinity in the field. Dissolve oxygen is only measured in rivers with slow velocities. Required instrument specifications are discussed in the USGS "National Field Manual for the Collection of Water-Quality Data" (USGS, 1997 to Present).

Instruments are maintained, operated, and calibrated according to the manufacturer's instructions (YSI, 2002). Instruments are tested and calibrated daily before and after site visits during the field trip. Multimeter pH and specific conductivity readings are acceptable within five percent of calibration standard solutions. The multimeter temperature sensor is tested semiannually against a NIST-certified thermometer and should be within 0.2 degrees Celsius. An instrument log is maintained during each field trip. At the completion of each field trip, the log entries are transferred to an electronic spreadsheet and paper copies are kept with the water quality field notes sheets in the station files. The original trip log sheet is kept in an instrument folder at the office.

In situ readings are measured mid-depth at equally spaced intervals across the river to determine representative environmental concentrations and mixing conditions. High velocities can affect the accuracy of the multimeter sensors. Under these conditions, water is withdrawn directly from the river and measured in a bottle at each station. In addition, multimeter values are recorded from the composited water after processing to compare with results of the same sample sent to the laboratory.

Changes in bicarbonate and carbonate concentrations (the major contributors to alkalinity) can occur within hours after sample collection through chemical and physical reactions. Alkalinity and concentrations of bicarbonate and carbonate determinations are made on filtered water as close as possible to the time of sample collection. Sulfuric acid is added to the sample using a digital titrator. The inflection point titration method is used to determine the equivalence point by noting the maximum change in pH divided by the change in the volume of acid added. For detailed methods, refer to "National Field Manual for the Collection of Water-Quality Data" (USGS, 1997 to Present).

AQUISITION OF SUPPLIES AND EQUIPMENT

The quality of data can be significantly affected by the type of supplies and equipment used. The quality control related supplies used to process and preserve inorganic water samples are generally purchased from the NWQL. The NWQL assure products to the microgram per liter level required for trace metals sampling. Most of the collection equipment is produced by the Federal Interagency Sedimentation Project (FISP) in Vicksburg, Mississippi and purchased from the USGS Hydrologic Instrumentation Facility (HIF) at the Stennis Space Center, Mississippi. Appendix B provides a list of water sampling and processing equipment and identifies sources to contact to acquire them.

COLLECTION AND PROCESSING

Guidelines for sampling can be found in the USGS "National Field Manual for the Collection of Water-Quality Data" (USGS, 1997 to Present) and the EPA "Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels" (EPA, 1996). Additional sources for water quality field techniques include USGS

publications by Horowitz (1994) and Shelton (1994). Specific WRB field techniques and modifications are detailed in Appendix D.

Equipment Cleaning and Preparation

Powderless latex gloves are used during each cleaning step. All equipment that contact the sample are cleaned by rinsing with potable water to remove any dirt and particles picked up while in the field. If equipment is new or excessively dirty, a 0.2-percent solution of phosphate-free soap is used for washing followed by rinsing with potable water. All equipment is then cleaned in a 5% hydrochloric acid solution followed by a thorough rinse with deionized water. Cleaned equipment is placed in sealed plastic bags for transport and/or storage.

Sample bottles are pre-rinsed 3 times with deionized water and stored 1/4th full in a clean, sealable plastic bag within a few days of collecting samples.

Sample Collection, Filtration, Preservation, and Shipping

Samples are collected through the entire depth of the water column and at multiple verticals across the river using the equal-width increment (EWI) method during the open water period. This method results in a flow-weighted, depth and width integrated representative sample. The EWI method is used with a minimum of five stations if multimeter measurements indicate a well mixed cross section. Ten verticals are used if the cross section is poorly mixed. Sampling equipment consists of a DH81 sampler with shrink-wrapped rod or a DH95 sampler with suspension cable, D77 cap, Teflon nozzle, and 1 liter plastic bottle (refer to FISP, Undated and FISP, 2000).

When ice cover is present, a sample is collected at one to three ice holes depending on conditions. A US WHB-96 weighted bottle sampler, fitted with a 1 liter plastic bottle and bottle transfer/vent cap is lowered through ice holes when ice cover is present. The sampling method through the ice does not allow for a velocity integrated sample, however a depth integrated sample is obtained by using the transfer cap with the sampler and lowering and raising it through the water column at an equal transit rate.

The use of non-standard methods are occasionally necessary due to environmental conditions or safety concerns. In these instances, detailed documentation of the equipment and methods used is required.

Sample water is composited in a churn splitter. Sample bottles are filled with well-mixed water from the churn splitter spigot for some laboratory analysis requiring unfiltered water. Filtered samples are removed from the churn splitter using a peristaltic pump with C Flex hosing, and either a capsule or a disk filter with a 0.45 μm membrane. Nitric acid (HNO_3) is used to preserve water for cation and trace metals analysis and sulfuric acid

(H₂SO₄) is used for the preservation of nutrients for analysis. Sample bottle requirements are listed in Appendix A.

Samples are processed in the field just after collection. To reduce/eliminate potential contamination: the work surface is covered with plastic sheeting; a processing chamber frame with disposable plastic cover is used to process samples; and powderless latex gloves are worn during each step.

Samples are shipped, overnight delivery, in ice-filled coolers to the NWQL as soon as possible after collection. Due to logistical constraints, this usually occurs at the conclusion of the field trip, upon returning to the office. Sample temperature is verified on arrival at NWQL and should be within a range just above freezing to 6°C (Maloney, 2004). NWQL Analytical Services Requests (ASR) forms are completed and mailed with the samples. Copies of the ASRs are retained with the water quality field forms in the office station folders.

QUALITY CONTROL REQUIREMENTS

Quality Control samples include field blanks, equipment blanks, split replicates, and concurrent replicates. At a minimum, one set of quality control samples should be collected at every water quality site during the project.

Quality assured inorganic blank water (IBW) is used to test for contamination arising from collection, processing, preservation, and shipping procedures (Mueller, 1997; Horowitz, 1994). Field blanks are obtained at the field site before processing a stream sample. Field blanks are collected two to three times at each water quality station during the project. If contamination is identified, additional field blanks may be necessary to aid in eliminating the source and to validate subsequent data. Equipment blanks are performed in a clean, non-field environment once a season prior to the collection of samples or when equipment will be used for the first time.

Quality control replicate samples are collected to produce statistically meaningful evaluations of data. Split replicate samples are used to determine variability introduced during sample processing and analysis (Mueller, 1997; Horowitz, 1994). A split replicate is a single, large volume of sample water that is divided into identical subsamples (a primary and duplicate). Split samples are collected one or two times at each water quality station. Concurrent replicate samples comprise the maximum imprecision of the data by incorporating variability measured from split replicates and variability introduced by sample collection. A concurrent replicate is two separate samples collected closely together in time at the same location. Concurrent samples are collected one or two times at each water quality station.

WATER QUALITY DATA MANAGEMENT

Water quality data is documented on paper and in electronic formats. Physical and chemical data are measured and recorded during field trips on standardized water quality and water quantity field forms and stored in station file folders. Analytical data is received electronically from the laboratory. Water quality data associated with quality assurance and water samples are stored on the USGS NWIS database and the EPA STORET database. Other analytical data from the field are entered into the SIM-DE database and transferred into STORET.

Analytical Data Review

The WRB project hydrologist is responsible for complete and accurate field notes, initial data entry, edits, and analysis of continuous water temperature data. Records are validated by another WRB hydrologist. It is the responsibility of the WRB hydrologist specializing in water quality to oversee the data entry and data management.

It is the responsibility of the project hydrologist to check the field notes, field measurements, and calibration logs for completeness. Laboratory analytical results are checked for anomalies as soon as results are received, so requests for re-testing can be made before holding times are exceeded. The NWIS-QWDATA generates a WATLIST for each sample record that reports several validation checks, which are reviewed by the hydrologist responsible for oversight of water quality data. Comparisons are made between the field measurements and laboratory analyses. Comparisons are also made between current and past sample results for the site. All comparisons and notes are written on the WATLIST and stored in the station file.

Quality assurance samples (blanks and replicates) are checked for inaccuracies or bias. Corrective actions are taken based on unacceptable results.

Data Storage

All original data on paper (including field notes, NWQL Analytical Services Requests (ASR) and calibration notes) are permanently retained in station field folders at the WRB Anchorage office. Unmodified, original electronic data from the laboratory and are permanently retained in computerized water quality files (Hubbard, 1992).

Water quality field measurements associated with sample collection are entered into the NWIS database by WRB staff with the assistance of the Anchorage USGS water quality specialist. Electronic data from the NWQL is transferred by the USGS water quality specialist to the NWIS database. Two NWIS databases are used to store water quality data: NWIS-QWDATA 01 (environmental samples) and NWIS-QWDATA 02 (quality assurance data). Hard copies of sample results are stored in the station folders. Data

entered into NWIS-QWDATA is transferred periodically into the EPA STORET database when data has been reviewed and finalized.

Not all water quality data collected are entered into NWIS. Observational data, such as cross-sectional measurements of physical water quality parameters, are entered into the Microsoft Access based software called Dassler X. This is a user-friendly database which also creates export files of water quality data that can be loaded into the STORET database. The STORET (STOrage and RETrieval) is a repository of water quality data used by government agencies, universities, and others and it is maintained and upgraded by the Environmental Protection Agency. WRB will periodically transfer non-NWIS information into STORET when data has been reviewed and finalized.

PUBLICATION OF WATER QUALITY DATA

Water quality data are published after the conclusion of each Refuge hydrologic investigation. The report contents include introduction and background information; review of historical data from each site; discussion of sampling design, procedures, and methods; review of quality assurance protocols and results; tables of collected data; graphs used for representing analysis; discussion of identifiable trends; and conclusions. Reports will be made available in paper and electronic media.

Reports must be internally and externally reviewed before meeting approval. Uninterpreted data may be made available to the public before publication if it has undergone preliminary review for accuracy. Interpretive results are only available after final approval to avoid releasing conclusions that may be subject to change during the review process.

WATER QUALITY TRAINING AND REVIEWS

Adequate training in methods and procedures is necessary to improve knowledge, avoid potential error, ensure the quality of the data, and lend legal credibility to the data. Employee training includes self education, work experience, in-house instruction, and formal courses. Individuals must be fully trained in the proper protocols before collecting water quality data.

An informal audit of collection procedures is conducted for each employee in the field by the water quality hydrologist as part of on-going quality assurance. Corrective actions are taken when problems are identified.

REFERENCES CITED

- EPA. 1996. Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels. U.S. Environmental Protection Agency, Office of Water, Washington, D.C. EPA 821-R-95-036. 33 p.
- FISP. (n.d.). Operator's Manual for the US DH-81 Depth-Integrating Suspended-Sediment Sampler. Federal Interagency Sedimentation Project, Vicksburg, Mississippi. 23 p.
- FISP. 2000. Sampling with the U.S. DH-95 Depth-Integrating Suspended-Sediment Sampler. Federal Interagency Sedimentation Project, Vicksburg, Mississippi. 15 p.
- Horowitz, A.J., C.R. Demas, K.K. Fitzgerald, T.L. Miller, and D.A. Rickert. 1994. U.S. Geological Survey Protocol for the Collection and Processing of Surface-Water Samples for the Subsequent Determination of Inorganic Constituents in Filtered Water. U.S. Geological Survey Open File Report 94-539. 57 p.
- Hubbard, E.F. 1992. Policy Recommendations for Management and Retention of Hydrologic Data of the USGS. U.S. Geological Survey Open File Report 92-56. 32 p.
- Maloney, T.J. 2004. Quality Management System. U.S. Geological Survey, National Water Quality Laboratory, Water-Resources Investigations Report uncontrolled copy, version 1.1, 119 p.
- Mueller, D.K., J.D. Martin, and J.T. Lopez. 1997. Quality-Control Design for Surface-Water Sampling in the National Water-Quality Assessment Program. U.S. Geological Survey Open File Report 97-223. 17 p.
- Shelton, L.R. 1994. Field Guide for Collecting and Processing Stream-Water Samples for the National Water-Quality Assessment Program. U.S. Geological Survey Open File Report 94-455. 42 p.
- USGS. 1997 to Present. National Field Manual for the Collection of Water-Quality Data. U.S. Geological Survey Techniques of Water-Resources Investigations, Book 9, chapter A1-A6, 2 volumes. v.p.
- USGS. 1998. *Technical Memorandum 98.02 (Revised)*. Memorandum from Janice R. Ward, Acting Chief, U.S. Geological Survey Office of Water Quality, April 16, 1998, re: Policy for the evaluation and approval of production analytical laboratories. 13 p.
- YSI. 2002. Operator's Manual Model 63. YSI Incorporated, Yellow Springs, Ohio. 43 p.

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APPENDIX A

Laboratory Analysis, Sampling Requirements, Methods, and Holding Times

Major ions and Nutrients, Schedule 1833

Analyzing Laboratory: USGS-NWQL, Denver, CO

<u>Analyte</u>	<u>Lab Code</u>	<u>*Parameter/ Watstore/ STORET Code</u>	<u>Method</u>	<u>CAS Number</u>	<u>Reporting Limit</u>	<u>Unit</u>	<u>**Reporting Limit Type</u>	<u>Bottle Type Bottle</u>
Alkalinity, lab	2109	29801	A	471-34-1	2	mg/L	mrl	FU
Calcium	659	00915	D	7440-70-2	0.012	mg/L	lrl	FA
Chloride	1571	00940	J	16887-00-6	0.20	mg/L	lrl	FU
Inductively coupled plasma (ICP) setup	2002	L2002				unsp	lrl	FA
magnesium	663	00925	C	7439-95-4	0.008	mg/L	lrl	FA
nitrogen, ammonia	1980	00608	H	7664-41-7	0.015	mg/L	lrl	FCC
nitrogen, ammonia + organic nitrogen	1985	00623	D	17778-88-0	0.10	mg/L	lrl	FCC
nitrogen, ammonia + organic nitrogen	1986	00625	D	17778-88-0	0.10	mg/L	lrl	WCA
nitrogen, nitrite	1977	00613	H	14797-65-0	0.0023	mg/L	lrl	FCC
nitrogen, nitrite + nitrate	1979	00631	G		0.022	mg/L	lrl	FCC
pH, laboratory	68	00403	A		0.1	pH	mrl	RU
phosphorus	2331	00666	G	7723-14-0	0.0044	mg/L	lrl	FCC
phosphorus, phosphate, ortho	1978	00671	I	14265-44-2	0.007	mg/L	lrl	FCC
phosphorus, total	2333	00665	G	7723-14-0	0.0037	mg/L	lrl	WCA
potassium	54	00935	B	7440-09-7	0.11	mg/L	lrl	FA
residue, 180 degrees Celsius	27	70300	A		10	mg/L	mrl	FU
Silica	667	00955	D	7631-86-9	0.04	mg/L	lrl	FA
Sodium	675	00930	C	7440-23-5	0.09	mg/L	lrl	FA
specific conductance, laboratory	69	90095	A		2.6	uS/cm	mrl	RU
Sulfate	1572	00945	G	14808-79-8	0.18	mg/L	lrl	FU

***Parameter Code and Method**

The Parameter, Watstore and STORET code are all the same. The parameter code identifies what the compound/analyte is and the method code describes how the sample was analyzed. To track data shifts, the Method Code is changed any time the method is modified or changed to the point where it might impact the data.

****Reporting Limit Type**

The Laboratory Reporting Level (LRL) is generally equal to twice the yearly determined Long-Term Method Detection Levels (LT MDL). The LRL controls false negative error. The probability of falsely reporting a non-detection for a sample that contained an analyte at a concentration equal to or greater than the LRL is predicted to be less than or equal to 1 percent. The value of the LRL will be reported with a "less than" remark code for samples in which the analyte was not detected. The National Water Quality Laboratory collects quality-control data from selected analytical methods on a continuing basis to determine long-term method detection levels (LT-MDL's) and establish laboratory reporting levels (LRL's). These values are re-evaluated annually based on the most current quality-control data and may, therefore, change.

The Minimum Reporting Level (MRL) defines the smallest measured concentration of a constituent that may be reliably reported by using a given analytical method. MRLs are determined from statistical data gathered from analysis over time. For analytes where spiking solutions are not available, such as pH and total dissolved solids, the detection limit used by NWQL is the MRL.

Reference:

Childress, C.J.O., W.T. Foreman, B.F. Conner, and T.J. Maloney. 1999. New Reporting Procedures Based on Long-Term Method Detection Levels and Some Considerations for Interpretations of Water-Quality Data Provided by the U.S. Geological Survey National Water Quality Laboratory. U.S. Geological Survey Open File Report 99-193. 24 p.

Schedule 1833 Sampling Requirements

Sample bottle type: FA

Minimum sample volume: 100 mL

Bottle description: 250 mL polyethylene bottle, acid-rinsed

Treatment and preservation: Filter through 0.45-um filter, use filtered sample to rinse containers and acidify sample with nitric acid (HNO₃) to pH < 2

Sample bottle type: FCC

Minimum sample volume: 125 mL

Bottle description: 125 mL Brown polyethylene bottle

Treatment and preservation: Filter through 0.45-um filter, use filtered sample to rinse containers before filling, chill and maintain at 4 deg C, ship immediately

Sample bottle type: FU

Minimum sample volume: 250 mL

Bottle description: 250 or 500 mL polyethylene bottle

Treatment and preservation: Filter through 0.45-um filter, use filtered sample to rinse containers before filling

Sample bottle type: RU

Minimum sample volume: 50 mL

Bottle description: 250 or 500 mL polyethylene bottle

Treatment and preservation: Use unfiltered sample to rinse bottles

Sample bottle type: WCA

Minimum sample volume: 125 mL

Bottle description: 125 mL Plain (translucent) polyethylene bottle,

Treatment and preservation: Use unfiltered sample to rinse bottles before filling, acidify with 1 mL of 4.5N (4.5 normal) sulfuric acid (H₂SO₄), chill and maintain at 4 deg C, ship immediately.

Schedule 1833 References:

1. **OFR 93-125**

Fishman, M.J., ed., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory--Determination of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open-File Report 93-125, 217 p.

Method ID: I-1472-87 , I-2525-89 , I-2542-89 , I-2546-91 , I-2606-89

2. OFR 00-170

Patton, C.J., and Truitt, E.P., 2000, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory-- Determination of ammonium plus organic nitrogen by a Kjeldahl digestion method and an automated photometric finish that includes digest cleanup by gas diffusion: U.S. Geological Survey Open-File Report 00-170, 31 p.

Method ID: I-2515-91, I-4515-91

3. OFR 93-125

Fishman, M.J., ed., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory--Determination of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open-File Report 93-125, 217 p.

Method ID: I-1472-87, I-2525-89, I-2542-89, I-2546-91, I-2606-89

4. TWRI B5-A1/89

Fishman, M.J., and Friedman, L.C., 1989, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, 545 p.

Method ID: I-1630-89, I-1750-89, I-2030-89, I-2057-89, I-2587-89, I-2700-89, I-2781-89

Trace Metals, Schedule 1916

Analyzing Laboratory: USGS-NWQL, Denver, CO

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<u>Analyte</u>	<u>Lab Code</u>	<u>Parameter/ Watstore/ STORET Code</u>	<u>Method</u>	<u>CAS Number</u>	<u>Reporting Limit</u>	<u>Unit</u>	<u>Reporting Limit Type</u>	<u>Bottle Type</u>
<u>Aluminum</u>	1784	01106	G	7429-90-5	1.6	ug/L	lrl	FA
<u>arsenic</u>	2503	01000	D	7440-38-2	0.2	ug/L	lrl	FA
<u>barium</u>	1786	01005	G	7440-39-3	0.2	ug/L	lrl	FA
<u>Cadmium</u>	1788	01025	G	7440-43-9	0.04	ug/L	lrl	FA
<u>chromium</u>	1936	01030	I	7440-47-3	0.8	ug/L	lrl	FA
<u>copper</u>	1791	01040	G	7440-50-8	0.4	ug/L	lrl	FA
<u>ICP Mass Spectrometry (ICPMS) setup</u>	2181	L2181				unsp	mrl	FA
<u>Inductively coupled plasma (ICP) setup</u>	2002	L2002				unsp	lrl	FA
<u>iron</u>	645	01046	D	7439-89-6	6.4	ug/L	irl	FA
<u>lead</u>	1792	01049	G	7439-92-1	0.08	ug/L	lrl	FA
<u>manganese</u>	1793	01056	G	7439-96-5	0.2	ug/L	lrl	FA
<u>nickel</u>	1795	01065	G	7440-02-0	0.06	ug/L	lrl	FA
<u>Selenium</u>	2506	01145	C	7782-49-2	0.4	ug/L	lrl	FA
<u>silver</u>	1796	01075	G	7440-22-4	0.20	ug/L	lrl	FA
<u>Strontium</u>	2507	01080	I	7440-24-6	0.4	ug/L	lrl	FA
<u>zinc</u>	1798	01090	G	7440-66-6	0.6	ug/L	lrl	FA

Schedule 1916 Sampling Requirements

Sample bottle type: FA

Minimum sample volume: 100 mL

Bottle description: 250 mL polyethylene bottle, acid-rinsed

Treatment and preservation: Filter through 0.45-um filter, use filtered sample to rinse containers and acidify sample with nitric acid (HNO₃) to pH < 2

Schedule 1916 References:

1. **OFR 99-093**

Garbarino, J.R., 1999, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory -- Determination of dissolved arsenic, boron, lithium, selenium, strontium, thallium, and vanadium using inductively coupled plasma-mass spectrometry: U.S. Geological Survey Open-File Report 99-093, 31 p.

Method ID: I-2477-92

2. **OFR 92-634**

Faires, L.M., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory--Determination of metals in water by inductively coupled plasma-mass spectrometry: U.S. Geological Survey Open-File Report 92-634, 28 p.

Method ID: I-2477-92

3. **OFR 93-125**

Fishman, M.J., ed., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory--Determination of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open-File Report 93-125, 217 p.

Method ID: I-1472-87

4. **OFR 93-449**

McLain, Betty, 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory--Determination of chromium in water by graphite furnace atomic absorption spectrophotometry: U.S. Geological Survey Open-File Report 93-449, 16 p.

Method ID: I-1233-93

Method holding times used by the National Water Quality Laboratory (Maloney, 2004).

Procedure	Lab code /schedule	Description	Holding time (time from sampling to preparation or analysis, in calendar days)	Reference and source of holding time
70300A	27	gravimetric, residue on evaporation at 180° C, solids, filtered	180	National Water Quality Laboratory (NWQL)
955C	56	colorimetry, ASF, molybdate blue, silica as SiO ₂	180	NWQL
403A	68	Electrometric electrode, pH, lab	30	NWQL
90095A	69	Wheatstone bridge, specific conductance, lab, whole-water recoverable	30	NWQL
915D	659	ICP, calcium, filtered water	180	U.S. Environmental Protection Agency (2002a), table II, p. 27-29 (EPA)
925C	663	ICP, magnesium, filtered water	180	EPA
930C	675	ICP, sodium, filtered water	180	EPA
935C	2773	ICP, potassium, filtered water	180	NWQL
940J	1571	ICP, chloride, filtered water	180	NWQL
945G	1572	ICP, sulfate, filtered water	180	NWQL
613H	1977	colorimetry, ASF, nitrite as N, low level, filtered water	30	Patton and Gilroy (1999)
671I	1978	colorimetry, ASF, phosphomolybdate, orthophosphate as P, low level, filtered water	30	Patton and Gilroy (1999)
631G	1979	colorimetry, ASF, cadmium reduction-diazotization, nitrite + nitrate as N, low level, filtered water	30	Patton and Gilroy (1999)
608H	1980	colorimetry, ASF, salicylate-hypochlorite, ammonia as N, low level, filtered water	30	Patton and Gilroy (1999)
623D	1985	colorimetry, ASF, microkjeldahl digestion, ammonia + organic nitrogen as N, low level, filtered water	30	Patton and Gilroy (1999)
625D	1986	colorimetry, ASF, microkjeldahl digestion, ammonia + organic nitrogen as N, whole-water recoverable, acidified	30	Patton and Gilroy (1999)
29801A	2109	Titration, alkalinity as CaCO ₃ , lab value, filtered water	30	NWQL
666G	2331	low-level total phosphorus, filtered water	30	Patton and Gilroy (1999)
665G	2333	low-level total phosphorus, whole-water recoverable, acidified	30	Patton and Gilroy (1999)

Method holding times used by the National Water Quality Laboratory -- Continued

Procedure	Lab code /schedule	Description	Holding time (time from sampling to preparation or analysis, in calendar days)	Reference and source of holding time
1046D	645	ICP, iron, filtered water	180	EPA
1106G	1784	ICPMS, aluminum, filtered water	180	EPA
1005G	1786	ICPMS, barium, filtered water	180	EPA
1025G	1788	ICPMS, cadmium, filtered water	180	EPA
1040G	1791	ICPMS, copper, filtered water	180	EPA
1049G	1792	ICPMS, lead, filtered water	180	EPA
1056G	1793	ICPMS, manganese, filtered water	180	EPA
1065G	1795	ICPMS, nickel, filtered water	180	EPA
1075G	1796	ICPMS, silver, filtered water	180	EPA
1090G	1798	ICPMS, zinc, filtered water	180	EPA
1030I	1936	GFAA, chromium, filtered water	180	EPA
1000D	2503	ICPMS, arsenic, filtered water	180	EPA
1145C	2506	ICPMS, selenium, filtered water	180	EPA
1080I	2507	ICPMS, strontium, filtered water	180	EPA

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NWQL relies on studies to determine holding times for a method. When studies have not been conducted, NWQL relies upon its analytical experience or uses established USEPA holding times from similar analytical methods.

References:

Maloney, T.J. 2004. Quality Management System. U.S. Geological Survey, National Water Quality Laboratory, Water-Resources Investigations Report uncontrolled copy, version 1.1, 119 p.

Patton, C.J. and Gilroy, E.J. 1999. U.S. Geological Survey Nutrient Preservation Experiment – Experimental Design, Statistical Analysis, and Interpretation of Analytical Results. U.S. Geological Survey Water-Resources Investigations Report 98-4118, 73 p.

U.S. Environmental Protection Agency. 2002. Guidelines Establishing Test Procedures for Analysis of Pollutants. U.S. Code of Federal Regulations, Title 40. 136 p.

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APPENDIX B

Equipment and Supply List for Sampling and Processing Inorganic Water Samples

EQUIPMENT AND SUPPLY LIST FOR SAMPLING AND PROCESSING INORGANIC WATER SAMPLES

*Sources for some items are listed to maintain quality standards (NWQL, National Water Quality Lab; FISP, Federal Interagency Sedimentation Project)

Cleaning Equipment and Supplies:

- Gloves, powderless, large (NWQL Q449FLD), extra large (NWQL Q450FLD)
- Acid, HCL 5% solution
- Water, deionized (FWS Regional office laboratory)
- Bag, sealable plastic (1 gal.)
- Trashbags, Med. (30 gal.)
- Trashbags, Large
- Tubing connectors
- Wash basins, plastic (soap wash, acid wash, DIW rinse)
- Scrub brush, nonmetallic
- Acid waste container
- Marble chips
- Detergent, phosphate free, Liqui-Nox
- Safety glasses
- Safety smock
- Paper towels

Water Sampling Equipment:

- Teflon nozzles (3/16 in.) (FISP)
- Teflon nozzles (1/4 in.) (FISP)
- Teflon nozzles (5/16 in.) (FISP)
- D-77 Cap (FISP)
- DH-81 Adapter for 1 L bottle (FISP)
- WQ Wading rod, plastic shrink wrapped (FISP)
- WQ Extension rod, plastic shrink wrapped (FISP)
- DH-95 Sampler [used with cable suspension from reel or hand line] (FISP)
- US WBH-96 Sampler [used with a hand line] (FISP)
- 3 L Plastic bottles (FISP)
- 1 L Plastic bottles (FISP)
- Churn Splitter, 8 L
- Churn Splitter, 4 L

Processing Equipment and Supplies:

- Pump, peristaltic and pump head
- Battery, 12 Volt
- Tubing, C-Flex
- Capsule filter, Whatman, 0.45 μm (NWQL Q398FLD)
- Disk filter, Gelman Aquaprep Groundwater sampling device, 0.45 μm (NWQL Q460FLD)
- Sample bottle, Poly., Plain, 8 oz (250ml) (NWQL Q34FLD)
- Sample bottle, Poly., Plain, 4 oz (125ml) (NWQL Q407FLD)
- Sample bottle, Poly., Acid Rinsed, 8 oz (250ml) (NWQL Q32FLD)
- Sample bottle, Poly., Amber, 4 oz (125ml) (NWQL Q405FLD)
- Sample bottle Cap, Plastic, 28mm (NWQL Q26FLD)
- Labels, bottle

Processing Equipment and Supplies--Continued

Processing Chamber frame
Plastic sheeting
Processing Chamber Bag, Clear, disposable (NWQL Q52FLD)
Acid, Vial (PP), HNO₃, 7.5N – 7.7N, 2ml, Ultrex, Trace Metal Preservative (NWQL Q436FLD)
Acid, Vial (PP), H₂SO₄, 4.5N (1:7), 1ml, Whole Water (WCA) Nutrient Preservative (NWQL Q438FLD)
Water, Inorganic Blank (NWQL Q386FLD)
Water, deionized (FWS Regional office laboratory)
Gloves, powderless, large (NWQL Q449FLD), extra large (NWQL Q450FLD)
Markers, permanent
Cooler, Small
clean wipes

Field Analysis and Supplies:

Multimeter (pH, Specific Conductivity, Temperature)
AA batteries, spare
Buffers, pH 4 (NWQL Q 125FLD)
Buffers, pH 7 (NWQL Q 127FLD)
Buffers, pH 10 (NWQL Q 123FLD)
Standards, specific conductance, 50uS (NWQL Q42FLD)
Standards, specific conductance, 100uS (NWQL Q43FLD)
Thermometer

Alkalinity Titration Equipment

pH meter
9 volt batteries, spare
Titrator, digital
Acid, sulfuric titrator cartridge, 0.16N (NWQL Q142FLD)
Cartridge delivery tube (NWQL Q388FLD)
Stirrer, portable magnetic
Stir bars, Teflon magnetic, small size
Ring stand and 3 prong clamps
Pipet, volumetric, 50 ml, class A "To Deliver"
Pipet squeeze bulb
Beaker, glass, 100 ml or 150 ml

Miscellaneous Supplies:

WQ field forms
Alkalinity forms
WQ field calibration log sheets
WRB Field Guide for Collecting & Processing Inorganic Surface-Water Quality Samples

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APPENDIX C

Water Quality Field Forms



**U.S. FISH AND WILDLIFE SERVICE, WATER RESOURCES BRANCH
SURFACE-WATER QUALITY FIELD NOTES**

Refuge/Project: _____ FWS Station No. _____ USGS Station No. _____
 River: _____ Date: _____
 Sampled By: _____ Photos Taken? _____
 Collection Start Time: _____ Collection End Time: _____ Collection Mean Time: _____ Time Datum: AKDT AKST

Samples Collected

NWIS Record No. _____ Analysis: Physical: _____ Chemical: Major Ions & Nutrients _____ Trace Metals (filtered) _____
 Lab Schedule: 1833 (Major ions, nutrients) _____ 1916 (Trace metals) _____
 Filter Type: GELMAN ACRO DISC 50A Lot# _____ GELMAN CAPSULE Lot# _____ OTHER _____
 Preservative Lot Numbers: 7.5N HNO3 (cations & metals) _____ 4.5N H2SO4 (raw nutrients) _____
 Sample Filtering Location: ON-SITE _____ OTHER _____
 Quality Control Information:
 Field Blank _____ NWIS Record No. _____ Inorganic Blank Water Lot Number _____
 Equipment Blank _____ NWIS Record No. _____ Duplicate (Split) _____ NWIS Record No. _____
 Source Solution Blank _____ NWIS Record No. _____ Duplicate (Concurrent) _____ NWIS Record No. _____
 QC Sample Lab Schedules: 1833 (Major ions, nutrients) _____ 1916 (Trace metals) _____
 Filter Type: GELMAN ACRO DISC 50A Lot# _____ GELMAN CAPSULE Lot# _____ OTHER _____
 Preservative Lot Numbers: 7.5N HNO3 (cations & metals) _____ 4.5N H2SO4 (raw nutrients) _____
 Comments: _____

Meters

Meter Make/Model _____ S/N _____ pH Electrode No. _____
 Cond. Sensor type: DIP OTHER _____ Cond. Temperature Compensation: AUTO MANUAL corr factor= _____
 Calibration or test date: Before _____ After _____ (See Meter Log for details)
 Meter Make/Model _____ S/N _____ pH Electrode No. _____
 Cond. Sensor type: DIP OTHER _____ Cond. Temperature Compensation: AUTO MANUAL corr factor= _____
 Calibration or test date: Before _____ After _____ (See Meter Log for details)

Field Measurements

Corrected Gage Height _____ ft Q, inst. _____ cfs MEASURED RATING ESTIMATED
 Water Temp _____ °C (mean / composite) pH _____ units (mean / composite) Cond. _____ μ S/cm @ 25°C (mean / composite)
 Salinity _____ ppt (mean / composite) Alkalinity _____ mg/L as CaCO₃ Bicarbonate _____ mg/L as HCO₃
 (note: convert pH values to a logarithm before calculating mean value)

NOTES: _____

**U.S. GEOLOGICAL SURVEY – NATIONAL WATER QUALITY LABORATORY
ANALYTICAL SERVICES REQUEST**

THIS SECTION MANDATORY FOR SAMPLE LOGIN

NWIS RECORD NUMBER		User Code	Project Account	LAB USE ONLY	
SAMPLE TRACKING ID				NWQL LABORATORY ID	
STATION ID	2 0	Begin Date (YYYYMMDD)	Begin Time	Medium Code	Sample Type
District Contact Phone Number	End Date (YYYYMMDD)	End Time	District Contact Email		

SITE / SAMPLE / SPECIAL PROJECT INFORMATION (Optional)

State	County	Geologic Unit Code	Analysis Status*	Analysis Source*	Hydrologic Condition*	Hydrologic Event*	Chain of Custody	Sample Set
NWQL Proposal Number	NWQL Contact Name		NWQL Contact Email		Program/Project			

Station Name: _____ Field ID: _____

Comments to NWQL: _____

Hazard (please explain): _____

ANALYTICAL WORK REQUESTS: SCHEDULES AND LAB CODES (CIRCLE A=add D=delete)

SCHED 1: _____ SCHED 2: _____ SCHED 3: _____ SCHED 4: _____ SCHED 5: _____ SCHED 6: _____

Lab Code: _____ A D					
Lab Code: _____ A D					
Lab Code: _____ A D					

SHIPPING INFORMATION (Please fill in number of containers sent)

ALP	COD	FA	PCN	IQE	IRM	RA	RU	SUR	TPCN
BGC	CRB	FAM	FU	IQL	MBAS	RAM	RUR	SUSO	UAS
C18	CU	FAR	FUS	IQM	OAG	RAR	RURCT	TBI	WCA
CC	CUR	FCA	GCC	IRE	PHE	RCB	RURCV	TBY	
CHY	DOC	FCC	GCV	IRL	PIC	RCN	RUS	TOC	

NWQL Login Comments: _____

Collected by: _____ Phone No. _____ Date Shipped: _____

FIELD VALUES

Lab/P Code	Value	Remark	Lab/P Code	Value	Remark	Lab/P Code	Value	Remark
21/00095			51/00400			2/39085		
<small>Specific Conductance at 25 deg C</small>			<small>pH Standard Units</small>			<small>Alkalinity - IT eq/L as CaCO3</small>		
/			/			/		

Field Comments: _____

*MANDATORY FOR NWQL

Form 9-3094
(August 2000)

APPENDIX D

Field Guide for Collecting & Processing Inorganic Surface-Water Quality Samples

Field Guide for Collecting & Processing Inorganic Surface-Water Quality Samples

Revised: 08/2003

Equipment Cleaning

The 1 L collection bottle, cap and nozzle, 3 L composite bottle, churn splitter, tubing, and any other equipment that will contact the sample are cleaned as follows:

1. a) Put on clean latex gloves and rinse equipment with potable water to remove any dirt and particles picked up while in the field. Fill wash basin with water and soak then, rinse tubing.

or

- b) If equipment is new or excessively dirty, fill washbasin with a 0.2-percent solution of phosphate-free soap and scrub with a nonmetallic brush, then put on clean latex gloves and rinse with potable water.

2. Wash equipment with a 5% HCL solution. Pour used HCL solution into a neutralization container with marble chips covering the bottom. The solution can be discarded when narrow range pH indicator strips show a reading greater than 6.0.

- a) Put both tubing ends into the 1 L HCL bottle filled with a third of solution. Connect the tubing to the peristaltic pump and circulate the HCL solution for several minutes. Drain the tubing, disconnect from the pump and rinse exterior of tubing with HCL solution from squirt bottle.

- b) Rinse all inside surfaces of the churn splitter and run HCL through the spigot. Use a small container filled with the HCL solution to soak the cap and nozzle or use a squirt bottle containing HCL to rinse them.

- c) For 1 L and 3 L bottles, fill the bottles to one tenth full with HCL solution, close the lid, and shake for 1 minute. Rinse inside of lid, threads and bottle neck with the HCL solution from the squirt bottle.

3. Place tubing into a cleaned washbasin and change gloves. Pour enough deionized water (DIW) into the basin to rinse the exterior of the tubing. Put one end of the tubing into a rinse bottle filled with DIW and pump through tubing. Rinse the bottles, lids, churn splitter, cap and nozzle three times with DIW.

4. Place all cleaned equipment in sealed plastic bags for transport and/or storage.

Field Preparation

- 1) Water quality multimeter calibration:
 - a) Chill pH buffers as close to temperatures expected to encounter in the field to maximize accuracy. Refer to page 37 in YSI manual for a table listing the values of the buffers at various temperatures.
 - b) Keep conductance standards as close to 25C to maximize accuracy. Calibrate using standard closest to that expected in the field. The YSI cannot not be calibrated below 50uS. Use 100uS standard to calibrate, then check against the 49 uS standard. Should be within 2% accuracy for the YSI. Conductivity standards are good for approximately 30 days once bottles are opened.
 - c) WQ meter calibration log sheets are to be saved and the results entered into the Water Quality Calibration spreadsheet (WQ calibration.xls) at the completion of each trip.
- 2) Pre-rinse bottles 3 times with DIW and store 1/3rd filled with DIW. This should be done within a few days of collecting samples. Store bottles in a clean, sealable plastic bag.

Field Measurements and Collection Methods

In Situ Measurements with the Multimeter:

Divide stream width by 6 to determine the 5 sample stations. Measure pH, temperature, specific conductance, and salinity at each sample station. If mixing is poor as noted by large variations in the above measurements, double the number of stations by dividing the stream width by 11, and take additional measurements with the meter. In addition, record the multimeter values from the remaining composite sample after processing.

Velocity affects the pH sensor and to a lesser extent, the specific conductivity sensor on the multimeter. In high velocity conditions, fill the 1 L bottle at or near the centroid and compare pH and specific conductivity readings in the 1 L bottle with those observed in the cross section. Record the water temperature in the bottle after collecting the all the subsamples to avoid contamination.

Sample Collection:

Use the Equal-Width-Increment (EWI) sampling method to collect samples.

- 1) Select the number of equally separated verticals in the cross section. A minimum of five stations can be used if the cross section is well mixed as determined from the multimeter measurements. A minimum of ten verticals is necessary if the cross section is poorly mixed.

- 2) Calculate the equal width intervals by dividing the stream width by the desired number of verticals. The first and last sampling stations should be ½ the width interval from the bank.
- 3) Anyone handling bottles and samplers must wear clean, powderless latex gloves. Assemble the sampling rod, adapter, cap, nozzle, and 1 L bottle and rinse them in the stream.
- 4) To determine the transit rate, lower and raise the sampler at the fastest/deepest station at a constant rate that fills the bottle no more than 0.9 L. Discard the water into the composite bottle or churn splitter as part of the field rinse.
- 5) This transit rate should be used at all stations. The amount of water collected at each station will vary according to the velocity and depth of the water.
- 6) Move to the first station from the stream bank and collect the water sample. When additional stations cannot be sampled without overfilling the bottle (more than 0.9 L), empty the collection bottle into the 3 liter composite bottle or churn splitter. Tilt the bottle and pour to minimize aeration. Swirl the last portion of sample water before emptying the bottle to maximize the transfer of suspended particles. Continue sampling in the same manner until all the stations have been sampled.
- 7) Disassemble sampler. Seal all used equipment in plastic bags for transport. Do not allow “dirty” equipment to dry out prior to cleaning.

Sample Processing and Preservation

- 1) Put on powderless gloves.
- 2) Spread clean plastic tarp or sheeting over the work surface (such as the helicopter skid). Set up sample processing chamber frame and clip the plastic bag to the interior of the frame **rather than surrounding it**. (The processing chamber is intended to reduce/eliminate potential atmospherically-derived contaminant inputs). Set up peristaltic pump.
- 3) Fill out bottle labels. **Round the mean sample collection time to the nearest 10 minute interval** (for example, 1320 or 1330 hrs). To separate results for split, concurrent, and field blank samples, change the time as follows:

Site A ---	StaID = 591638160115500, Date = 09/21/03, Time = 1330
Site A split ---	StaID = 591638160115500, Date = 09/21/03, Time = 1331
Site A concurrent ---	StaID = 591638160115500, Date = 09/21/03, Time = 1332
Site A field blank ---	StaID = 591638160115500, Date = 09/21/03, Time = 1333
Site A source blank ---	StaID = 611056149515100, Date = 09/21/03, Time = 1334

Each time will have its own set of bottles with that information on them.

- 4) **Raw samples** for whole water analysis should be withdrawn first starting with the largest volume required. (RU 250 mL then WCA 125mL plain bottle). If duplicate samples are being collected, fill the same bottle types of one set then the other before

continuing with the next bottle type (ie. fill RU bottle of both sets before filling the WCA bottles).

- a) Ideally a churn splitter should be used to obtain a well mixed, unfiltered sample.
- Churn the composite sample at a uniform rate of 9 inches per second for about 10 strokes before withdrawing the subsample. The disk should touch bottom on every stroke and the stroke length should be as long as possible without breaking the water surface.
 - Discard DIW from the pre-rinsed sample bottle then use the spigot to rinse once with the water to be sampled (10% of the volume). Continue mixing the sample while pre-rinsing and withdrawing the subsamples.
 - When all the unfiltered subsamples are collected, a minimum volume of 3 L of water should remain in the 8 L churn splitter or 1.5 L in the 4 L churn splitter.

or

- b) Occasionally the 3 L bottle is used for compositing then withdrawing the subsample with the pump and tubing (without the filter). Document on the field form when this method is used.
- Follow the procedures in the first two bullets of step 5 below then disconnect the filter and set it aside in the chamber bag.
 - Keep the pump tubing submerged in the sample and gently swirl the 3 L composite bottle without breaking the surface of the water for approximately one minute before removing sample. Discard DIW from the pre-rinsed sample bottle then rinse once with the water to be sampled (10% of the volume). Continuously swirl the sample while pre-rinsing bottles and withdrawing the unfiltered subsamples.

5) Filtered samples:

- Place filter and sample bottles into chamber. Run tubing into the top of the chamber through a hole in the plastic bag. Rinse the outside of the other end of tubing with DIW and place into the DIW bottle. Then connect tubing to pump head.
- Run DIW through tubing, then attach the filter (this will avoid excessive pressure in the filter). Pre-rinse capsule filters with 1 L of DIW and disk filters with 500 ml of DIW. Remove tubing from the DIW source and continue pumping until residual liquid is removed from the filter. Rinse the outside of

the intake tubing with composite sample before placing it in the 3 L bottle or churn splitter.

- Run 25 mL of sample water through filter and then field rinse sample bottles. To remove trapped air in the filter when pumping, hold the filter so that the outlet is pointing upward and slowly start the pump. When water starts coming out, turn the device over and continue to flush the system.
 - Discard DIW from the pre-rinsed sample bottle then rinse once with the water to be sampled (10% of the volume). Filter samples in the following order: FA (major cations and trace metals), FU (major anions), field alkalinity, and FCC (nutrients).
- 6) Remove sample bottles from chamber that do not need acid preservation. Place together in a ziplock bag.
 - 7) If there is enough water remaining after filtering, take a multimeter measurement of the composite sample and record values on the data sheet.
 - 8) Seal all used equipment in plastic bags for transport. Do not allow “dirty” equipment to dry out prior to cleaning.

Acid Preservation:

Remove filtered samples from chamber that do not need acid preservation. Then add acids to the FA and WCA bottles inside the chamber in the following order:

- 1) Add HNO₃ ampoule to FA bottle (cations and trace metals) and dispose ampoule in a ziplock waste bag. (Caution: Nitric acid preservation for cation samples can be a potential contaminant for nutrient determinations. Sulfuric acid preservation for nutrients can be a potential contaminant for major anions. Therefore, gloves should be changed after the use of each acid preservative to limit potential cross-sample contamination.)
- 2) Add H₂SO₄ ampoule to WCA bottle (undissolved total nutrients) and dispose ampoule in a ziplock waste bag.

Field Analysis of Alkalinity:

Within several hours after sample collection, chemical and physical reactions can change concentrations of bicarbonate and carbonate ions (the major contributors to alkalinity). Therefore, determination of alkalinity will need to take place as soon after sample collection as possible. Refer to the photocopy from the USGS National Field Manual for the Collection of Water-Quality Data, Chapter 6.6. for instructions on the incremental method using the Hach digital titrator.

Sample Shipment

The minimum information required for each bottle is the USGS site identification number, the date, the time, the sample designation code (RU, WCA, FA, FU, FCC), and the schedule number 1833 and 1916.

Include a NWQL Analytical Services Request Form (Log-In Sheet) for each sample sent to the laboratory. Fill in the appropriate sections of the form; remember to retain a copy. The Request Forms must be shipped together with the appropriate samples. To prevent damage to the forms (soaking due to sample spillage or melting ice), place them inside a sealable plastic bag taped to the inside of the lid of the cooler along with the return address label.

Include a temperature check sample in shipping container. Fill bottle with tap water and label it "Temperature check sample" along with the project name, date and time of shipping. Prepare a self addressed, stamped postcard labeled "Temperature check sample report." The postcard should include the project name, date and time of shipping, and space for arrival temperature, date, and time. Include the postcard in the sealable plastic bag with the ASR lab forms and return address label.

Mark the inside lid of the cooler with the WRB return address and telephone number. Double line coolers with two heavy duty trash bags, add ice, and securely seal it (do not use "blue-ice"). The volume of ice should be equal to or greater than the volume occupied by the samples. Use twice the volume of ice during warm months. Group all the sample bottles from one station in a ziplock bag and place them on top of the ice bag.

Ship samples using FedEx to:

National Water Quality Laboratory
U.S. Geological Survey
P.O. Box 25608, MS 407
Building 95, Entrance E3
Denver Federal Center
Denver, CO 80225-0608
303.236.3707