

Monroe, S. A., M. Dyer, S. Stumpf, C. Bliss, and C. Parker. 2016. Water quality monitoring protocol for streams and springs in the Southern Colorado Plateau Network. Natural Resource Report NPS/SCPN/NRR—2016/1298. National Park Service, Fort Collins, Colorado.

Standard Operating Procedure #8: Laboratory Analysis of Water Quality Samples, Version SCPN_WATER_QUALITY_ SOP08_20160901

Contents

1 Water quality laboratory analysis methods 3

2 Review of laboratory data 7

3 Revision history 8

Standard Operating Procedure #8: Laboratory Analysis of Water Quality Samples

Version SCPN_Water_Quality_SOP08_20160901				
Revision History Log				
Previous version number	Revision date	Section and paragraph	Change(s) made	Approved by

Only changes in this specific SOP will be logged here. Record the previous version number and date of revision; identify sections and paragraphs where changes were made, who approved the revision, and the new version number. More detailed descriptions of the changes made and the reason for the changes is provided at the end of this SOP.

This Standard Operating Procedure (SOP) describes laboratory analysis methods for water samples collected in SCPN parks. All samples collected in these parks are sent to a qualified contract laboratory for chemical analysis. SCPN currently sends all water quality samples to the USGS National Water Quality Laboratory (NWQL) in Denver, Colorado for analysis. Samples are collected, processed and shipped to the laboratory as prescribed in SOPs #6 and #11.

1 Water quality laboratory analysis methods

Methods of analysis used by the U.S. Geological Survey (USGS) National Water Quality Laboratory (NWQL) are published by the USGS and are available in various reports. These reports can be found on the SCPN common drive. The USGS is responsible for laboratory operations and the quality of the results produced.

The USGS has developed numerous methods for laboratory analysis of water quality samples. Specific methods used for analysis of SCPN water quality samples are presented in Table 8-1. Also included in the table are:

- Analytes, laboratory reporting levels and units. The USGS-NWQL collects quality-control data from selected analytical methods on a continuing basis to determine long-term method detection levels (LT-MDLs) and establish laboratory reporting levels (LRLs). The USGS re-evaluates these values annually based on the most current quality-control data.
- The method code and definition (see Table 8-2)
- The USGS-NWQL method number
- The specific reports where the step-by-step procedures can be found
- The sample treatment code (see Table

Table 8-1. Laboratory Analyses conducted by the USGS National Water Quality laboratory on SCPN water quality samples.

Analyte	MRL ¹	Unit	USGS NWQL Lab Code ²	USGS Method Version Code ⁴	Method Description ⁵	USGS Method Number	Reference	Sample Treatment Code	NWQL Sched- ule Number
Acid Neutralizing Capacity, as CaCO ₃	4	mg/L	70	TT040		I-2030-89	Fishman and Friedman 1989	RU	2281
Aluminum	2.2	µg/L	1784	PLM43	ICP-MS*	I-2020-05	Garbarino et al. 2006	FA	2278
Ammonia (NH ₃) as N	0.01	mg/L	3116	00048	colorimetry, DA, salicylate-hypochlorite	I-2525-89	Fishman 1993	FCC	101
Antimony	0.027	µg/L	1785	PLM43	ICP-MS	I-2020-05	Garbarino et al. 2006	FA	2278
Arsenic	0.20	µg/L	3122	PLM10	clCP-MS	I-2020-05	Garbarino et al. 2006	FA	2278
Barium	0.50	µg/L	1786	PLM43	ICP-MS	I-2020-05	Garbarino et al. 2006	FA	2278
Beryllium	0.04	µg/L	1787	PLM43	ICP-MS	I-2020-05	Garbarino et al. 2006	FA	2278
Boron	2.0	µg/L	2110	PLA13	ICP-AES	I-1472-95	Struzeski et al. 1996	FA	2278
Cadmium	0.06	µg/L	1788	PLM43	ICP-MS	I-2020-05	Garbarino et al. 2006	FA	2278
Calcium	0.022	mg/L	659	PLA11	ICP-AES	I-1472-87	Fishman 1993	FA	2281
Chloride	0.02	mg/L	1571	IC022	IC	I-2057-85	Fishman and Friedman 1989	FU	2281
Cobalt	0.05	µg/L	3124	PLM10	clCP-MS	I-2020-05	Garbarino et al. 2006	FA	2278
Copper	0.8	µg/L	3128	PLM10	clCP-MS	I-2020-05	Garbarino et al. 2006	FA	2278
Chromium	0.3	µg/L	3126	PLM10	clCP-MS	I-2020-05	Garbarino et al. 2006	FA	2278
Fluoride	0.01	mg/L	651	IC003	ISE	I-2327-85	Fishman and Friedman 1989	FU	2281
Iron	4.0	µg/L	645	PLA11	ICP	I-1472-87	Fishman 1993	FA	2278
Lead	0.04	µg/L	1792	PLM43	ICP-MS	I-2020-05	Garbarino et al. 2006	FA	2278
Magnesium	0.011	mg/L	663	PLA11	ICP-AES	I-1472-87	Fishman 1993	FA	2281
Manganese	0.40	µg/L	1793	PLM43	ICP-MS	I-2020-05	Garbarino et al. 2006	FA	2278
Mercury	0.005	µg/L	2707	CV014	CVAF	I-2494-01	Garbarino and Damrau 2001	FAM	2278
Molybdenum	0.05	µg/L	1794	PLM43	ICP-MS	I-2020-05	Garbarino et al. 2006	FA	2278
Nickel	0.20	µg/L	3130	PLM10	clCP-MS	I-2020-05	Garbarino et al. 2006	FA	2278
Nitrite + Nitrate (NO ₂ +NO ₃) as N	0.04	mg/L	3156	RED01	Colorimetry, enzymatic reduction, DA	I-2547-11	Patton and Kryskalla 2011	FCC	101
Nitrite (NO ₂) as N	0.001	mg/L	3117	00049	Colorimetry, DA	I-2545-90	Fishman and Friedman 1993	FCC	101
Orthophosphate as P	0.004	mg/L	3118	00048	Colorimetry, DA, phosphomolybdate	I-2601-90	Fishman 1993	FCC	101
pH (laboratory)	0.1	pH	68	EL006		I-2587-89	Fishman and Friedman 1989	RU	2281
Potassium	0.030	mg/L	2773	PLO03	ICP-OES	I-1630-85	Fishman and Friedman 1989	FA	2281
Residue on evaporation (ROE, aka TDS)	20	mg/L	27	ROE10	Dissolved, at 180°C	I-1750-89	Fishman and Friedman 1989	FU	2281

Table 8-1. (continued) Laboratory Analyses conducted by the USGS National Water Quality laboratory on SCPN water quality samples.

Analyte	MRL ¹	Unit	USGS NWQL Lab Code ²	USGS Method Version Code ⁴	Method Description ⁵	USGS Method Number	Reference	Sample Treatment Code	NWQL Sched- ule Number
Selenium	0.05	µg/L	3132	PLM10	cICP-MS	I-2020-05	Garbarino et al. 2006	FA	2278
Silica	0.018	mg/L	667	PLA11	ICP-MS	I-1472-87	Fishman 1993	FA	2281
Silver	0.02	µg/L	1796	PLM43	ICP-MS	I-2020-05	Garbarino et al. 2006	FA	2278
Sodium	0.06	mg/L	675	PLA11	ICP-AES	I-1472-87	Fishman 1993	FA	2281
Specific conductance	5	µS/cm	69	WHT03		I-2781-85	Fishman and Friedman 1989	RU	2281
Sulfate	0.02	mg/L	1572	IC022	IC	I-2057-85	Fishman and Friedman 1989	FU	2281
Uranium	0.014	µg/L	1797	PLM43	ICP-MS	I-2020-05	Garbarino et al. 2006	FA	2278
Vanadium	0.08	µg/L	3134	PLM10	cICP-MS	I-2020-05	Garbarino et al. 2006	FA	2278
Zinc	2.0	µg/L	3138	PLM10	cICP-MS	I-2020-05	Garbarino et al. 2006	FA	2278

¹ Reporting Limit – The minimum concentration reported by the Laboratory.

² USGS-NWQL Lab Code – Specific Laboratory analysis as requested from the USGS National Water Quality Laboratory Schedule of Analyses.

³ USGS-NWIS Parameter Code – Parameter identifier under which results will be reported to the USGS National Water Information System (water quality database).

⁴ USGS Method Code – Unique method identifiers, which change when methodologies are updated. Identical codes indicate the same method is used for different analytes.

⁵Method abbreviations:

ICP-MS: Inductively coupled plasma mass spectrometry

IC: Ion chromatography

cICP-MS: Collision/reaction cell inductively coupled plasma mass spectrometry

ISE: Ion-selective electrode

ICP-AES: Inductively coupled plasma atomic emission spectrometry

CVAF: Cold vapor-atomic fluorescence spectrometry

ICP-OES: Inductively coupled plasma optical emission spectrometry

DA: automated discrete analyzer

Table 8-2. USGS Method Codes and Definitions.

Method code	Method definition
00048	Nutrients in filtered water, colorimetric, by discrete analyzer
00049	Nutrients in filtered water by enzymatic reductase colorimetry by discrete analyzer
CL048	Nutrients, filtered water, cadmium-reduction, colorimetric
CV014	Mercury in Filtered Water by Cold Vapor-Atomic Fluorescence Spectrometry
EL006	pH, lab, by automated glass electrode
IC022	Anions, filtered water, ion chromatography
ISE05	Anions, filtered water, ion-selective electrode
PLA11	Metals, filtered water, Inductively coupled plasma-atomic emission spectrometry (NWQL)
PLA13	Metals, filtered water, add, Inductively coupled plasma-atomic emission spectrometry
PLM10	Elements in filtered water using collision/reaction cell inductively coupled plasma-mass spectrometry
PLM43	Metals, filtered water, Inductively coupled plasma-mass spectrometry
PLO03	Potassium in filtered water by ICP-OES
RED01	Nitrate plus nitrite, colorimetric determination in water by enzymatic reduction, automated discrete analyzer
ROE10	Residue on evaporation at 180°C of filtered water, by weight
TT040	Alkalinity by automated electrometric titration to pH 4.5 (NWQL)
WHT03	Specific conductance, lab, automated, by Wheatstone bridge

Table 8-3. Water quality sample bottles and treatments required for different analyses. Different laboratory analyses require different treatments for samples and different types of sample bottles.

Analysis	Bottle type	Bottle volume	Treatment code ¹	Rinse	Treatment and preservation	Max hold time(days)	NWQL Schedule #
Trace metals	Clear Polyethylene, clear cap	250 ml	FA	No; these are pre-rinsed and capped	Filter through 0.45-µm filter, use filtered sample to rinse containers and acidify sample with nitric acid (HNO ₃) to pH < 2.	180	2278
Mercury	Clear glass	250 ml	FAM	Yes	Filter through 0.45-µm filter, use filtered sample to rinse containers and acidify sample with hydrochloric acid (HCl) to pH <2.	180	2278
Nutrients	Brown Polyethylene	125 ml	FCC	Yes	Filter through 0.45-µm filter, use filtered sample to rinse containers, chill and maintain at 4 °C, ship within 1 week.	30	101
Major elements	Clear Polyethylene, black cap #2	250 ml	FU	Yes	Filter through 0.45-µm filter, use filtered sample to rinse containers.	180	2281
pH, specific conductance, and Acid neutralizing capacity	Clear Polyethylene, black cap #1	250 ml	RU	Yes	Use unfiltered sample to rinse bottles.	180	2281

¹ FA: Filtered, acidified; FAM: Filtered, acidified, mercury; FCC: Filtered, chilled; FU: Filtered, unchilled; RU: Raw, untreated

8-3)

- NWQL schedule number – this is a number that designates a group of analyses

2 Review of laboratory data

Data are received from the NWQL in Excel spreadsheets. Once received, the lead technician should briefly review the results for completeness and for data anomalies; comparing the new results to older data may be helpful with this. If necessary, re-runs of the samples may be requested. The lab keeps samples for 180 days after samples are received for this purpose. To allow for the time to re-run the samples, it is important to send samples to the lab as quickly as possible so that the hold times are not exceeded.

The spreadsheet of results contains a value qualifier column, which occasionally contain characters to qualify the data. Normally, no action is needed, but some of these qualifiers may need to be noted in SCPN annual reports. These qualifiers are defined below:

b - value is below the lowest calibration standard, so the numeric result was extrapolated.

n - value was between LTMDL and 2× LTMDL. The NWQL sets their reporting levels at 2× LTMDL. The “n” qualifier indicates that the analyte was detected, but was not detected above the reporting level.

@c - sample exceeded holding time. Because it is an unstable parameter, results for acid neutralizing capacity will always have this qualifier.

d - sample was diluted.

***** - sample was >4°C when received by the lab. This message will only show up for

chilled samples.

The results also contain a tab summarizing the error checks performed by the NWQL prior to releasing the data. The most common error messages concern ion balances, total dissolved solids to specific conductance ratios, and ions to specific conductance ratios. The cations used in the ion balance calculation are calcium, magnesium, potassium, and sodium. The anions include alkalinity/acid neutralizing capacity, sulfate, and chloride. The ratio of cations to anions in milliequivalents should be similar. Additionally, the lab looks at the ratio of dissolved solids to specific conductance and the ratios of cations and anions to specific conductance. A large difference in the ion ratios or an out-of-range dissolved solid to conductance ratio could indicate something is wrong with the samples. Any of these will prompt additional actions by the NWQL analysts, such as checking for bottle mix-ups, re-analyzing the samples to confirm the results, or looking at previous results from the site prior to releasing the results. These actions are summarized in the error checks tab. For more information on these types of quality assurance monitoring, see Friedman and Erdmann (1982).

3 Revision history

Provide the following information for each revision made to SOP #8.

New version:

SCPN_WATER_QUALITY_SOP08_YYYYMMDD

Date:

Author:

Sections affected:

Changes & reasons: