UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

THE USE OF STANDARD REFERENCE WATER SAMPLES BY THE U.S. GEOLOGICAL SURVEY

By L. J. Schroder, M. J. Fishman, L. C. Friedman, and G. W. Darlington

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CONTENTS

ILLUSTRATIONS

TABLES

THE USE OF STANDARD REFERENCE WATER SAMPLES BY THE U.S. GEOLOGICAL SURVEY

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ABSTRACT

The U.S. Geological Survey has been preparing and maintaining a library of standard reference water samples for 13 years. During this period of time, 65 reference samples were prepared. The library currently contains 17 individual sets of reference samples. These samples are used routinely in a quality-assurance program to assure that water laboratories are producing analytical data of acceptable reliability for inorganic constituents. Four different samples are prepared and distributed each year to approximately 80 academic, State, and Federal laboratories. Analytical results are statistically evaluated to determine the most probable concentration of the analyzed constituents. All measured constituents, including Na, Ca, Al, As, Co, Hg, Pb, and Se have remained stable for several years in these samples. Accuracy and precision of atomic absorption spectrometric, colorimetric, titrimetric, and other analytical methods for different constituents have been determined by interlaboratory comparison.

INTRODUCTION

In 1965, the U.S. Geological Survey (USGS), Water Resources Division, began preparing standard reference water samples (SRWS) which could be made available to its laboratories. These reference samples are used to monitor a laboratory's ability to produce analytical data with an acceptable high degree of reliability. The exact composition of the reference sample is unknown; however, if the sample is analyzed by numerous laboratories using acceptable methods, it is possible to statistically determine a most-probable value for each constituent.

Sixty-five reference samples have been prepared since the program began. Initially, 400 1-liter aliquots of each sample were prepared; now 800 1-liter aliquots are prepared, to increase the usable "life-span" of a standard reference water sample. Currently, the library contains 17 individual sets of reference samples.

In 1970, the USGS began consolidating its 19 small water-analysis laboratories. The resulting two large centralized laboratories are located in Denver, Colo., and Atlanta, Ga.; they analyze over four times the number of water samples processed previously. Additional water analyses required by the USGS are provided by numerous field service units, and by State, contractor, and various cooperator laboratories, located throughout the nation. The SRWS are used routinely in quality-assurance programs to assure that these laboratories are producing analytical data of acceptable reliability for inorganic constituents (Malo and others, 1978).

Data evaluation of SRWS round-robins has produced information which can aid in laboratory evaluations and analytical methodology selection. This information, coupled with the stable reference solutions, enables the certification of new methodology that can be incorporated into the laboratories.

PREPARATION AND STANDARDIZATION

A natural water sample is collected in six 200-liter polyethylene containers, then filtered through a 0.45-m cellulose membrane filter into a 1,325-liter polyethylene container. The sample is mixed thoroughly by prolonged mechanical stirring, assuring complete homogeneity. During the mixing phase, the sample is "spiked" with additional constituents to produce samples of differing concentrations. The entire sample is again filtered through a 0.45-µm cellulose membrane filter, sterilized by passage through an ultraviolet flow-through water-sterilizer at a flow rate of less than 6 liters per minute, and then bottled in sterile Teflon[1/] 1-liter bottles (fig. 1). The bottling operation is performed in an ultraviolet hood.

Two sets of reference samples are prepared annually with each set consisting of two samples. One of these samples is analyzed for major constituents (table 1); the other is analyzed for trace metals (table 2). The trace metals samples are acidified with reagent grade nitric acid to a pH of less than 2.

[1/] The use of trade names in this report is for identification purposes only and does not imply endorsement by the U.S. Geological Survey.

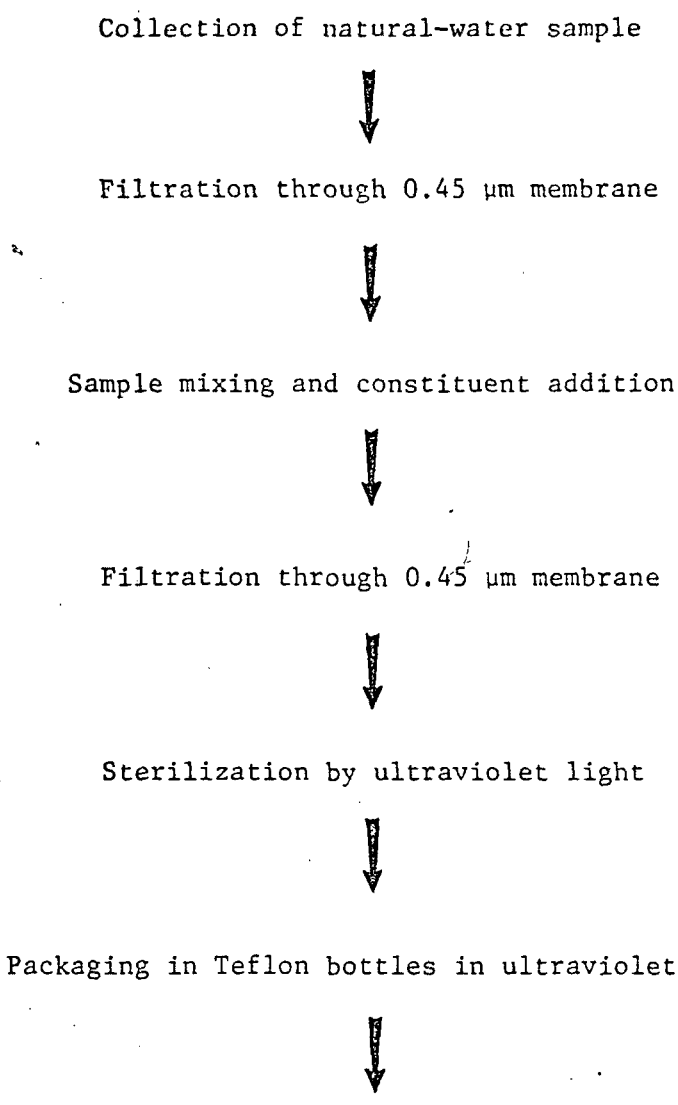


Figure 1.--Standard reference water sample sequence from collection to certification.

Table 1.--Major chemical constituents determined in SRWA

Silica (SiO_2)	Iodide (I)
Calcium (Ca)	Nitrate as N
Magnesium (Mg)	Nitrite as N
Sodium (Na)	Phosphorus, total (P)
Potassium (K)	Dissolved solids, 180°C
Bicarbonate (HCO_3)	Specific conductance
Sulfate (SO_4)	pH
Chloride (Cl)	Boron (B)
Fluoride (F)	Strontium (Sr)
Bromide (Br)	Vanadium (V)

Table 2.--Trace metals determined in SRWS

Aluminum (Al)	Lithium (Li)
Iron (Fe)	Mercury (Hg)
Manganese (Mn)	Molybdenum (Mo)
Arsenic (As)	Nickel (Ni)
Barium (Ba)	Selenium (Se)
Beryllium (Be)	Silver (Ag)
Cadmium (Cd)	Strontium (Sr)
Chromium (Cr)	Zinc (Zn)
Cobalt (Co)	Antimony (Sb)
Copper (Cu)	Thallium (Tl)
Lead (Pb)	

One set of reference samples is prepared each 6 months and an announcement letter is sent to approximately 80 academic, State, and Federal laboratories. Upon their reply, a code number is assigned to each participating laboratory; each laboratory is identified only by its code number in the final report. The two USGS centralized laboratories are identified by name. An analytical data-report form, a list of suggested analytical methods to be used for the determinations, and appropriate samples are distributed to each laboratory. A laboratory is not obligated to use methods that are listed; however, if other methods are used, a description of the method or reference to a published procedure is requested.

A statistical analysis of the data is used to obtain the most reliable estimate of the true value for each of the constituents determined (Skougstad and Fishman, 1974). The mean, average deviation, percent deviation from the mean, standard deviation, total range, and 95 percent confidence interval for the mean are calculated for each constituent. Reported values of "less than" are not used in computations. Outlying values are rejected on the basis of statistical tests as outlined in "Recommended Practice for Dealing with Outlying Observations" (ASTM, 1969).

A frequency distribution graph is plotted for every constituent present in the SRWS (see fig. 2). The number of laboratories reporting values for each determination and the percentage of values rejected are tabulated. An overall summary tabulating the number of reporting laboratories, rejected values, percentages of unrejected values falling within the 95-percent confidence interval, and the standard deviation by method is sent to all round-robin participants.

LEAST SQUARE EQUATIONS

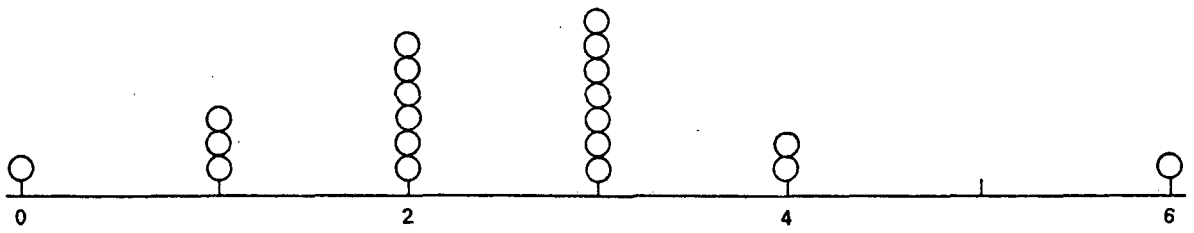
Least square equations were calculated for all constituents monitored by the SRWS, except thallium. The equation may be expressed as follows:

$$y = mx+c$$

where

y is the overall precision,
m is the slope of the line,
c is the zero concentration intercept, and
x is the concentration determined in milligram or microgram per liter (ASTM, 1978).

Equations (table 3) were derived using all applicable results submitted for SRWS samples 27 through 65 and are updated each 6 months. Analysts in the USGS centralized laboratories examine the SRWS which are submitted as "unknowns." These analytical results are compared with the reported SRWS means and must be within 1.5 standard deviations of that mean, as determined by the applicable least-square equation. Values which exceed 1.5 standard deviations are considered to be outside the desired confidence limit (Malo and others, 1978).



Arsenic reported in micrograms per liter (µg/L), 20 laboratories.

Figure 2.--Frequency distribution of reported arsenic values.

Table 3.--Least squares equations for constituents determined in the SRWS

Determination	Equation
SiO_2	y = 0.0357x + 0.536
Ca	y = 0.0390x + 0.306
Mg	y = 0.0340x + 0.328
Na	y = 0.0381x + 0.0463
K	y = 0.101x + 0.0211
HCO_3	y = 0.0407x + 1.34
SO_4	y = 0.0313x + 2.49
Cl^4	y = 0.0365x + 0.310
F	y = 0.0745x + 0.0424
Sp. cond.	y = 0.0197x + 2.61
pH	y = 0.0778x + 0.781
B	y = 0.178x + 20.2
Sr	y = 0.0821x + 14.4
NO_3+NO_2(<3.0 mg/L)	y = 0.139x + 0.046
DSRD[1]	y = 0.0350x + 3.88
As	y = 0.246x + 0.927
Al	y = 0.0913x + 24.1
Fe	y = 0.0749x + 7.67
Mn	y = 0.0802x + 4.21
Cu	y = 0.0724x + 4.83
Zn	y = 0.0724x + 4.86
Cr	y = 0.214x + 1.97
Pb	y = 0.206x + 2.86
Cd	y = 0.192x + 0.27
Ni	y = 0.255x + 1.47
Hg	y = 0.126x + 0.11
Co	y = 0.105x + 0.57
Ba	y = 0.040x + 50.2
Li	y = 0.0431x + 2.29
Mo	y = 0.1226x + 0.63
Se	y = 0.216x + 1.83
Ag	y = 0.283x - 0.19
Be	y = 0.169x + 1.84

[1]Solids, residue at 180°, dissolved.

ACCURACY AND PRECISION

Determination of the concentration of a constituent by many laboratories, often using two or more entirely different analytical techniques giving essentially the same values, reasonably assures that the true concentration value lies very close to the determined value. Using this premise, concentration means or "most probable" values, with a corresponding confidence interval of the SRWS estimates the true or known value. Table 4 is a statement sent to requesting laboratories listing the constituent analyzed, mean concentration, standard deviation, and the number of reporting laboratories.

Data obtained from the SRWS round-robin are coded by methodology which allows methods to be compared. For example, comparison of the data obtained for SRWS No. 64 for sulfate indicates that gravimetric determinations have the highest precision of the four most-used methods, and turbidimetric, the lowest (table 5). Colorimetric determination of sulfate by automated analysis appears to have adequate accuracy and sufficient precision to be the method of choice for laboratories performing large numbers of aqueous sulfate analyses. Information from these comparisons can aid in the selection of methodology to meet a laboratory's mission.

Round-robin data can also be used to evaluate newer methodology or instrumentation, such as plasma emission spectroscopy. For example, data shown in table 6 indicates that plasma emission spectrometry compares favorably with atomic absorption spectrometry for analysis of cadmium at the 10-µg/L concentration level. This favorable correlation and the fact that plasma emission spectrometry is a multielement analysis technique indicates this method of analysis will compliment current techniques in water-analysis laboratories.

SAMPLE STABILITY

Sample stability is a requirement for all SRWS. Samples prepared in 800-liter batches are available to USGS laboratories for approximately 5 years at the current rate of use. SRWS stability is reviewed by comparing the mean obtained from the round-robin to the mean obtained from subsequent analyses of the samples by USGS laboratories. In table 7, examples are given for a number of constituents determined during a recent 6 month period. The means and standard deviations in columns four and five, respectively, represent 40 replicates or more. Most dissolved constituents have been stable for up to 42 months. Mercury at the 3-µg-per-liter concentration has been stable for 38 months in a natural water matrix preserved by nitric acid acidification to a pH<2 and stored in sterile Teflon bottles. Slight differences in the round-robin "most probable values" and the USGS laboratory mean value are within the reported uncertainties.

Table 4.--Statement of analysis for SRWS no. 64

Constituent	Mean concentration (mg/L)	Standard deviation (mg/L)	Reporting laboratories
SiO_2	16.6	1.1	25
Ca	166	6	33
Mg	64.6	4.3	36
Na	160	4	37
K	8.27	1.01	34
HCO_3	38.9	3.4	26
SO_4	621	24	31
Cl	245	8	33
F	1.00	.08	29
Br[1/]	------	------	--
I[2/]	------	------	--
NO_2-N	.039	.008	22
NO_3-N	3.29	.52	31
P, total	.474	.034	27
DSRD 180°C	1395	31	29
Sp. cond.	1904	87	34
pH	7.29	.20	35
B	.319	.088	11
Sr	1.670	.090	12
V	.0068	.0016	5

[1/] Insufficient data, mean approximately 0.90 mg/L.
[2/] Insufficient data, mean approximately 0.10 mg/L.

Table 5.--Sulfate data from SRWS no. 64 grouped by methodology

Method used	Mean (mg/L)	Standard deviation (mg/L)	Reporting laboratories
Volumetric, thorin	628	31.1	5
Gravimetric, barium chloride	622	11.1	7
Turbidimetric, barium chloride	614	36.2	17
Autoanalyzer, methyl thymol blue	619	25.1	11
Other[1/]	623	15.3	3
All methods combined	619	28.2	43

[1/] Methods could not be adequately documented.

Table 6.--Cadmium data from SRWS no. 65 grouped by methodology

Method used	Mean (µg/L)	Standard deviation (µg/L)	Reporting laboratories
Atomic absorption, chelation extraction	10.6	1.0	7
Atomic absorption, direct	12.7	1.8	14
Atomic absorption, flameless	11.6	2.4	12
Emission, plasma excitation	10.3	.6	3
Other[1/]	13.2	3.3	4
All methods combined	11.9	2.1	40

[1/] Methods could not be adequately documented.

Table 7.--SRWS stability data for selected constituents

Constituent	Roundrobin		Elapsed time (months)	USGS laboratories	
	Mean	Standard deviation		Mean	Standard deviation
Na	15.4 mg/L	0.9 mg/L	39	15.7 mg/L	0.5 mg/L
Ca	61.7 mg/L	2.8 mg/L	42	61.7 mg/L	1.6 mg/L
As	9.8 µg/L	3.4 µg/L	42	10.1 mg/L	2.2 µg/L
Hg	3.32 µg/L	.61 µg/L	38	3.22 µg/L	.49 µg/L
Pb	47.5 µg/L	6.8 µg/L	38	46.8 µg/L	2.3 µg/L
Co	9.1 µg/L	3.2 µg/L	22	9.8 µg/L	1.5 µg/L
Se	15.5 µg/L	10.9 µg/L	31	15.8 µg/L	2.6 µg/L
SiO_2	10.7 mg/L	1.0 mg/L	31	10.3 mg/L	.5 mg/L
SO_4	68.9 mg/L	2.6 mg/L	31	68.5 mg/L	1.9 mg/L

SUMMARY

The SRWS library currently contains 17 unique reference samples that are used by USGS laboratories to assure that laboratories are producing data of acceptable reliability for inorganic constituents. These SRWS are stable for long periods of time even for constituents such as mercury.

Interlaboratory comparisons are used to determine a statistically valid, most-probable value for each SRWS constituent determined. Comparison of data obtained from the round-robins allows analytical methods to be evaluated for both accuracy and precision.

REFERENCES

American Society for Testing and Materials, 1969, Annual book of ASTM standards, Part 30: Philadelphia, American Society for Testing and Materials, p. 429-435.

_____1978, Annual Book of ASTM standards, Part 31: Philadelphia, American Society for Testing and Materials, p. 12-14.

Malo, B. A., Beetem, W. A., Friedman, L. C., and Erdmann, D. E., 1978, The quality assurance program of a national laboratory system, *in* Proceedings, 4th Joint Conference on Sensing of Environmental Pollutants, New Orleans, La.: p. 345-347.

Skougstad, M. W., and Fishman, M. J., 1974, Standard reference water samples, *in* Proceedings of the American Water Works Association, Water Quality Technology Conference, Dallas, Tex.: p. XIX-1-6.

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