UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

Quality assessment program and results for the NAWQA surface water pilot studies

by

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Open-File Report 89-658

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1989

Contents

Tables

Figures

INTRODUCTION

The U.S. Geological Survey initiated a National Water-Quality Assessment (NAWQA) Program in 1986 (Hirsch and others, 1988). The goals of the program are to: (1) Provide a nationally consistent description of current water-quality conditions for a large part of the nations water resources; (2) define the trends (or lack of) in water quality that have occurred over recent decades and provide a baseline for evaluating future trends in water-quality; and (3) identify and describe the relations of both the status and the trends in water quality to the relevant natural factors and the history of land use and land and waste management practices.

The NAWQA Program is currently (1989) in the pilot phase that involves four surface water and three ground water study areas. The quality assessment program and results described in this document address the analytical component of the stream-sediment surveys for the surface-water studies. These study areas are: the upper Illinois River Basin in Illinois, Indiana, and Wisconsin; the lower Kansas River Basin in Kansas and Nebraska; the Kentucky River Basin in Kentucky; and the Yakima River Basin in Washington.

Quality assurance is a critical component of a program of the scope and duration of NAWQA. The purpose of an analytical quality assurance program is to assure the reliability (precision and accuracy) of reported laboratory data, and to provide a permanent record to assure sample integrity. Two concepts are involved: (1) quality control, which is the mechanism established to control errors, and (2) quality assessment, which is the mechanism to verify that the system is operating within acceptable limits (Taylor, 1981).

The U.S. Geological Survey, Branch of Geochemistry, has responsibility for the analysis of the stream sediment samples. Our document "Quality Assurance and Control Practices for the U.S. Geological Survey's Branch of Geochemistry pursuant to the NAWQA Program, 1988" (Arbogast and others, 1988), describes the protocols for handling samples, sample preparation, analytical methods, use of instrumentation, written documentation, etc. to be followed in the laboratory. This and an updated document are available from the Branch of Geochemistry. The updated document will be submitted for publication as a U.S. Geological Survey Open-File Report. At the inception of the NAWQA Pilot Program, the branch quality assurance program was not fully implemented. Therefore a supplemental quality assessment program was established to insure a consistent program throughout the NAWQA pilot phase and to provide confidence in the analytical results. The procedures and results of this supplemental quality assessment program are given herein.

QUALITY ASSESSMENT PROGRAM

The approach of the quality assessment program is based on traceability, through concurrent analysis of sample replicates and replicates of reference materials of similar matrix with every sample job (Gautier and Gladney, 1987). This assesses both precision and accuracy but has some limitations since the ability to achieve a good result for a reference material or sample split does not guarantee a similar result for all of the natural samples. The reference materials used in this program are well characterized for a large number of constituents, however, it should be noted that recommended or consensus values are not necessarily "true" values. The reference materials used for this study are: GXR-2, a geochemical exploration reference soil, which is a composite material of residual gray-brown loams from a mining

district which has produced lead, zinc, silver and copper (Alcott and Lakin, 1974); GSD-6, a Chinese reference stream sediment derived from clastic volcanic and basaltic rocks (Xie and others, April, 1985); and GSD-12, a Chinese reference stream sediment derived from sandstone, shale and carbonate rocks (Xie and others, October, 1985).

Samples from each study area were randomly selected and analyzed in batches (jobs) of 40 samples. Each job contained 36 NAWQA samples and 4 blind assessment materials which were placed in random positions throughout the job and were filled as follows:

(1) A sample split of a randomly chosen sample was inserted into one of the slots in each job. This provides data to assess within job precision with duplicates of actual samples.

(2) Reference material GSD-6 was inserted into one of the slots in each job for the Yakima River Basin. Reference material GSD-12 was inserted into one of the slots in each job for the upper Illinois, the lower Kansas, and the Kentucky River Basins. These materials provide data to assess accuracy based on a reference material selected to approximate the predominate matrix of the stream-sediment samples from these basins.

(3) Reference material GXR-2 was inserted into one of the slots in each job. This material has concentration levels that are above the lower limit of determination for most of the constituents determined for this program. This assures unqualified data (data that are greater than or equal to the lower limit of determination) for assessment purposes when the sample duplicate or matrix matching reference material do not have high enough concentration levels to be detected for certain constituents.

(4) A duplicate of either the GSD reference material or the GXR-2 reference material was inserted into the remaining slot in each job on an alternating basis. This provides short term precision data on reference materials.

Duplicate samples, which were part of the analysis of variance (ANOVA) sampling design, were also used as assessment materials. These materials include 30 pair of sample duplicates for each of the Illinois, Kentucky and Yakima River Basins and 20 pair of sample duplicates for the Kansas River Basin. These samples were randomized throughout all of the jobs in each basin and provide an approximation of long-term precision.

ASSESSMENT DATA

Table 1 shows the analytical protocol for the stream-sediment samples from the NAWQA Program. The table lists the constituent determined, the dissolution technique, the method of determination, and the lower limit of determination. All constituents listed were determined in all study areas except for selenium, which was determined only in the Illinois study area.

Tables 2a, 2b, and 2c are comparisons of unqualified data for reference materials GXR-2, GSD-6, and GSD-12 respectively, to literature data. The tables list arithmetic mean ($\bar{x}$, standard deviation (STD), relative standard deviation (RSD), and range data obtained from the Branch of Geochemistry (BGC); and mean, standard deviation, and number of determinations (n) from the literature. The information presented in these tables is used to evaluate the accuracy and the precision of the analysis. Boron was not determined on the reference materials due to the relatively large amount of material needed for analysis (5 gr) and the lack of characterization of the reference materials for water soluble boron.

Tables 3a, 3b, and 3c are summaries of the results of the analysis of GXR-2, GSD-6 and GSD-12 respectively. The tables list the number of times the

values from the analysis of a reference material are within 1, 2, and 3 standard deviations of the mean. The tables also list the number of L (values less than the lower limit of determination). The means and standard deviations used for these tables were calculated from the data generated from this assessment program as shown in tables 2, a-c.

Tables 4a, 4b, and 4c present data to evaluate the precision of the within job duplicates of reference materials GXR-2, GSD-6 and GSD-12 respectively. The tables list the average difference between duplicates of the reference materials and the average mean for the duplicates. This information can be used to estimate the reproducibility of a determination at a given concentration level. The table also shows the number of times an L value was reported and the number of times the duplicates were both reported as L values. The reduced number of pairs of duplicates (n) for arsenic and antimony is due to an insufficient amount of material for analysis.

Table 5 presents the average relative percent difference (ARPD) and the average mean for within job sample duplicates. ARPD is a statistic often used to evaluate the precision of sample duplicates. It is calculated using the formula:

$$\frac{\Sigma \frac{r}{x} * 100}{n}$$

where: r is the difference between duplicate values,
x is the mean of the duplicates,
n is the number of pairs of duplicates.

The table also shows the number of L values and the number of times the duplicates were both reported as L values. Information in this table addresses short-term sample precision.

Table 6 presents the ARPD and average mean for the duplicates from the analysis of variance design. It is identical to table 5 in format and gives an indication of long-term sample precision.

Figure 1 is an example of $\bar{x}$ control chart which is produced for each constituent and for all three of the reference materials. The example is for copper showing concentration (ppm) plotted against time (job sequence) for duplicates of reference material GXR-2. The upper and lower warning (UWL, LWL) and control (UCL, LCL) limits are depicted as horizontal lines on the chart. The warning and control limits represent respectively 2 and 3 standard deviations from the mean.

Figure 2 is an example of an R control chart which is produced for sample duplicates for each constituent. The example is for copper, and plots R (difference between within job sample duplicates) against time (job sequence). The R horizontal line is the average value of the range (50th percentile), the warning (95th percentile) and control (99.7th percentile) limits are multiples of and are calculated using factors found in statistical tables.

The control charts are graphical presentations of data that are used to show that the system monitored is within expected limits, to signal systematic departures, shift in trends, and to identify inconsistencies in precision. Information on the use and interpretation of these charts can be found in "Quality Assurance of Chemical Measurements" (Taylor,1987). Most of the information depicted in the charts is presented here in table form. The use of these charts for this assessment program is to assess the acceptability of

FIGURE 2

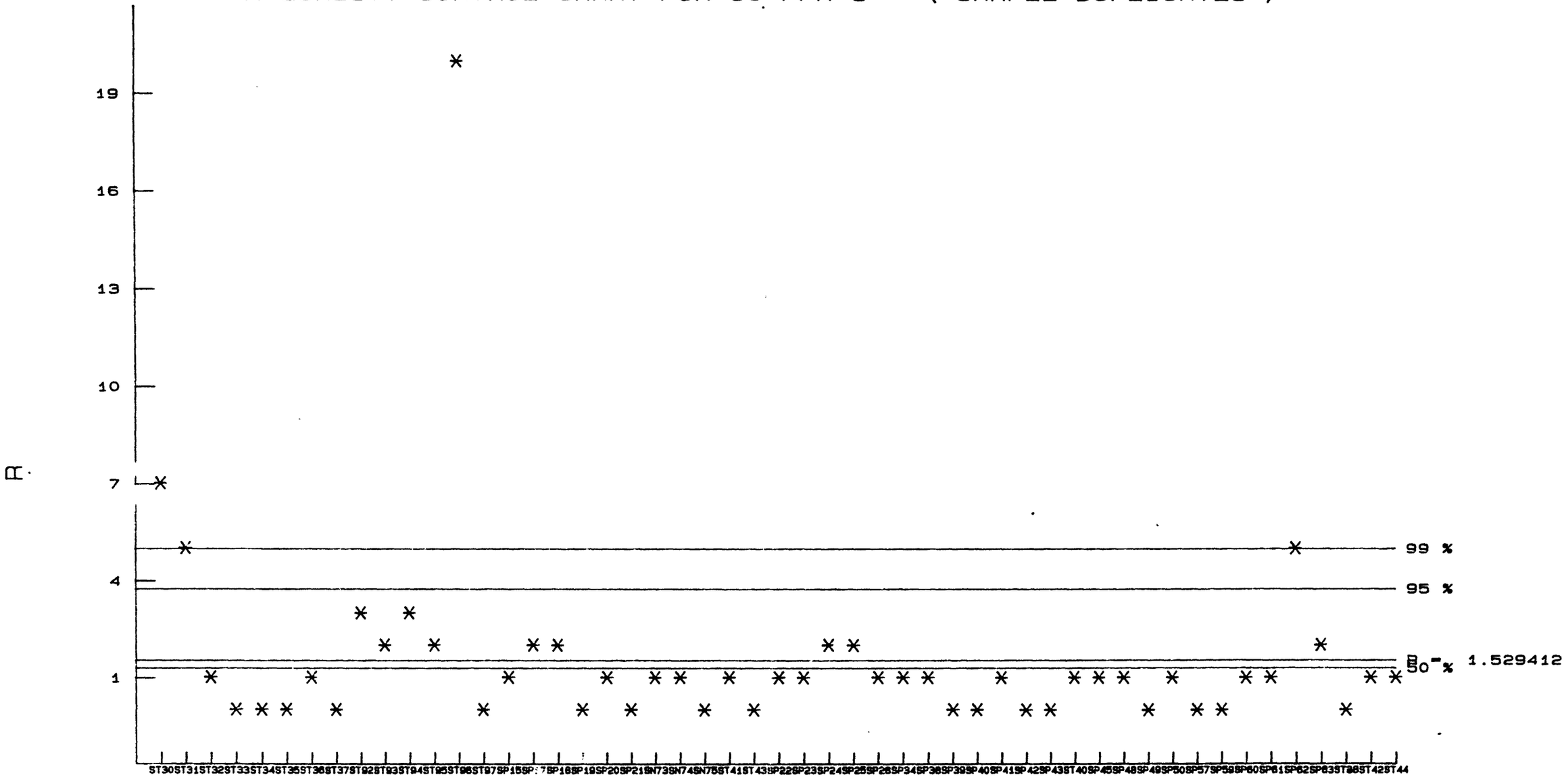
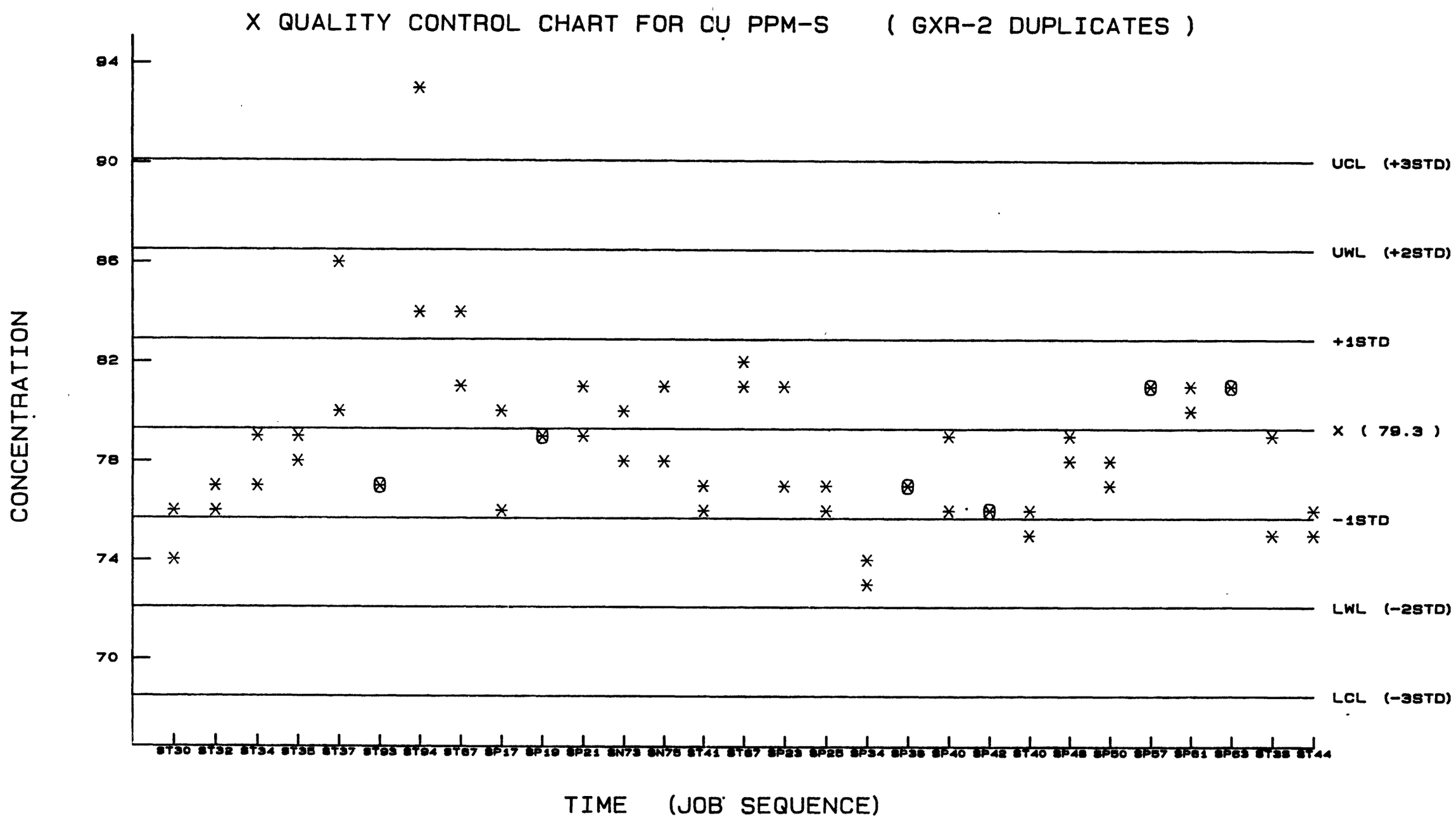

R QUALITY CONTROL CHART FOR CU PPM-S (SAMPLE DUPLICATES)
19
16
13
10
7
4
1
R
99 %
95 %
R̄o=% 1.529412
TIME (JOB SEQUENCE)

FIGURE 1


X QUALITY CONTROL CHART FOR CU PPM-S (GXR-2 DUPLICATES)
CONCENTRATION
94
90
86
82
78
74
70
UCL (+3STD)
UWL (+2STD)
+1STD
X (79.3)
-1STD
LWL (-2STD)
LCL (-3STD)
ST30 ST32 ST34 ST35 ST37 ST93 ST94 ST87 SP17 SP19 SP21 SN73 SN75 ST41 ST87 SP23 SP25 SP34 SP36 SP40 SP42 ST40 SP48 SP50 SP57 SP61 SP63 ST38 ST44
TIME (JOB SEQUENCE)

the data and for the detection of drift. Control charts are prepared for all constituents determined and are maintained within the U.S. Geological Survey, Branch of Geochemistry.

ACCEPTANCE CRITERIA

The acceptability of the data was evaluated using control charts. Control charts for the duplicate reference material and the second reference material ($\bar{x}$ charts) and the sample duplicates (R chart) were evaluated for each job. If more than one result for reference materials and sample duplicates was found to be outside of the upper or lower control limit for a particular constituent then the job was reanalyzed. (R charts were scrutinized to establish if an outlier was a actual precision problem or the result of an anomalously high concentration level) (Taylor, 1987). The use of this criteria resulted in the repeat analysis of three jobs for boron, two jobs for mercury, two jobs for antimony and one job for sulfur. None of the jobs were reanalyzed for more than 1 constituent. The problem in all cases of reanalysis was traced to a mixup in sample order.

SUMMARY

The scientific reliability of the reported data is critical to a program of the scope, complexity and duration of NAWQA. We believe the QA program of the Branch of Geochemistry along with the supplemental quality assessment program presented in this document provide adequate information on the protocols and procedures as well as the precision and accuracy of the assessment materials to evaluate the reliability of the reported data.

ACKNOWLEDGEMENT

The authors wish to thank Stu McKenzie for his valuable input into the design of the assessment program and Barb Chazin for her help in developing the control charts.

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Table 1.--Analytical protocol for NAWQA stream sediment samples

Constituent	Decomposition	Method of determination	Lower limit of determination
Al	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	0.05%
Ca	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	0.05%
Fe	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	0.05%
K	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	0.05%
Mg	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	0.005%
Na	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	0.005%
P	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	0.005%
Ti	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	0.005%
Ag	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	4 ppm
Au	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	8 ppm
Ba	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	1 ppm
Be	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	1 ppm
Bi	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	10 ppm
Cd	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	2 ppm
Ce	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	4 ppm
Co	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	1 ppm
Cr	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	1 ppm
Cu	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	1 ppm
Eu	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	2 ppm
Ga	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	4 ppm
Ho	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	4 ppm
La	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	2 ppm
Li	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	2 ppm
Mn	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	4 ppm
Mo	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	2 ppm
Nb	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	4 ppm
Nd	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	4 ppm
Ni	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	2 ppm
Pb	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	4 ppm
Sc	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	2 ppm
Sn	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	10 ppm
Sr	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	2 ppm
Ta	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	40 ppm
Th	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	4 ppm
V	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	2 ppm
Y	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	2 ppm
Yb	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	1 ppm
Zn	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	4 ppm
Hg	($HNO_3/Na_2Cr_2O_7$)	Cold vapor-AAS	0.02 ppm
U	(partial, HNO_3)	Fluorimetry	0.05 ppm
Total C	(combustion)	Infrared	0.01%
Crbnt C	($HCLO_4$)	Titration	0.01%
Orgnc C		By difference	0.01%
S	(combustion)	Titration	0.01%
B	hot water soluble	ICP-AES	0.4 ppm
As	(HF, HNO_3, $HClO_4$)	Hydride-AAS	0.1 ppm
Sb	(HF, HNO_3, $HClO_4$)	Hydride-AAS	0.1 ppm
Se	(HF, HNO_3, $HClO_4$)	Hydride-AAS	0.1 ppm

ICP-AES = Inductivedly Coupled Plasma-Atomic Emission Spectrometry
AAS = Atomic Absorption Spectrometry

Table 2a.--Comparison of data (for unqualified values) for reference material GXR-2 to literature concensus data (N=114 samples)

[All values ppm except * in %]

	BGC values				Concensus values[1]		
Constituent	$\bar{x}$	STD	RSD	Range	$\bar{x}$	STD	N
Ag	19.3	1.0	5.2	15-21	18	3	9
Al*	6.60	0.32	4.8	5.8-7.5	18.57	0.06	3
Au	X	--	--	--	0.046	0.019	5
Ba	2120	80	3.8	2000-2300	2210	160	7
Be	2.0	0.2	10.0	1.0-2.0	1.6	--	1
Bi	X	--	--	--	0.44	0.10	4
Ca*	0.91	0.02	2.2	0.85-0.98	0.88	0.04	4
Cd	3.4	0.5	14.7	3.0-4.0	4.1	0.04	7
Ce	51.0	1.9	3.7	43-55	50	--	2
Co	11.1	0.5	4.5	10-12	9.0	1.3	10
Cr	36.3	2.8	7.7	32-45	34	4	7
Cu	79.3	3.6	4.6	72-93	70	6	11
Eu	X	--	--	--	0.77	--	2
Fe*	1.90	0.06	3.2	1.8-2.0	1.84	0.05	10
Ga	18.3	1.2	6.6	13-22	37	--	2
Ho	X	--	--	--	No data available		
K*	1.35	0.06	4.4	1.2-1.5	1.36	0.04	4
La	26.7	1.1	4.1	25-29	25	3	3
Li	61.0	2.3	3.8	55-70	48	--	2
Mg*	0.82	0.03	3.7	0.74-0.91	0.88	0.02	4
Mn	1015	41	4.0	970-1100	980	40	7
Mo	X	--	--	--	1.5	0.2	4
Na*	0.57	0.02	3.5	0.53-0.65	0.54	0.08	5
Nb	7.1	1.5	21.1	4L-15	9.0	--	1
Nd	21.5	1.4	6.5	12-24	No data available		
Ni	17.3	0.8	4.6	15-20	20	4	8
P*	0.07	0.004	5.7	0.06-0.08	0.068	--	2
Pb	696	57	8.2	590-900	670	50	9
Sc	6.1	0.3	4.9	6.0-7.0	7.2	--	2
Sn	X	--	--	--	1.2	0.4	3
Sr	160	6.1	3.8	15-17	152	16	4
Ta	X	--	--	--	0.78	--	2
Th	8.3	1.0	12.0	6L-13	8.6	0.2	6
Ti*	0.27	0.01	3.7	0.23-0.29	0.29	0.01	6
V	48.2	1.9	3.9	44-53	61	9	6
Y	14.3	0.5	3.5	13-15	19	--	2
Yb	2.0	0.2	10.0	1.0-2.0	2	--	2
Zn	545	22.2	4.1	490-600	460	30	12
Hg	3.1	0.2	6.5	2.4-3.9	2.7	0.6	3
U	1.9(P)	0.3	15.8	1.3-2.8	1.98(P)	1.25	--

Table 2a.--Comparison of data (for unqualified values) for reference material GXR-2 to literature concensus data (N=114 samples)--Continued

	BGC values				Consensus values[1]		
Constituent	$\bar{x}$	STD	RSD	Range	$\bar{x}$	STD	N
Total C*	2.88	0.09	3.1	2.30-3.13	2.50	0.24	3
Inor. C*	0.02	0.007	35.0	0.01L-0.04	No data available		
Org. C*	2.87	0.10	3.5	2.30-3.12	No data available		
S*	0.03	0.008	26.6	0.01L-0.05	.0315	--	1
B	Not determined			--	No data available		
As	22.2	3.1	14.0	14-32	21	4	14
Sb	34.1	10.1	29.6	11-82	47	4	10
Se (N=24)	0.7	0.2	28.5	0.2-0.9	0.57	0.17	10

[1]Gladney and Burns, 1984;
(P) = Partial dissolution
X = Insufficient unqualified data
L = Less than the lower limit of determination

Table 2b.--Comparison of data (for unqualified values) for reference material GSD-6 to literature recommended data (N=20 samples)

[All values ppm except * in %]

	BGC values				Recommended values[1]		
Constituent	$\bar{x}$	STD	RSD	Range	$\bar{x}$	STD	N
Ag	X	--	--	--	0.36	0.04	26
Al*	7.48	0.20	2.7	7.2-7.9	7.49	--	--
Au	X	--	--	--	No data available		
Ba	310	11	3.5	300-340	330	40	31
Be	2.0	0	--	2.0	1.7	0.4	26
Bi	X	--	--	--	5	0.6	30
Ca*	2.82	0.10	3.5	2.6-3.0	2.77	--	--
Cd	X	--	--	--	0.43	0.04	20
Ce	64.2	2.1	3.3	60-67	68	8	15
Co	25.8	1.4	5.4	23-28	24.4	3	53
Cr	199	12	6.0	170-220	190	24	49
Cu	395	15	3.8	370-420	383	18	56
Eu	X	--	--	--	1.5	0.13	11
Fe*	4.03	0.12	3.0	3.8-4.3	(4.12)	--	--
Ga	17.1	0.9	5.3	16-20	16.7	0.8	15
Ho	X	--	--	--	(0.78)	0.17	7
K*	2.02	0.08	4.0	1.9-2.2	2.03	--	--
La	34.0	1.6	4.7	32-37	39	8	32
Li	42.9	2.0	4.7	40-48	40	2	22
Mg*	1.80	0.05	2.8	1.7-1.9	1.81	--	--
Mn	959	22.7	2.4	900-1000	970	60	64
Mo	6.0	0.7	11.7	5-7	7.7	1.2	37
Na*	1.78	0.10	5.6	1.7-2.0	1.71	--	--
Nb	5.9	2.1	35.6	4L-12	12	4.6	30
Nd	30.6	1.7	5.6	27-33	33	6	14
Ni	75.2	2.5	3.3	69-79	78	7	47
P*	0.10	0.006	6.0	0.10-0.12	0.10	0.07	37
Pb	28.4	2.5	8.8	24-34	27	5	49
Sc	16.1	0.7	4.3	15-17	17	1.6	11
Sn	X	--	--	--	2.8	1.0	21
Sr	280	7.6	2.7	270-300	266	28	34
Ta	X	--	--	--	0.72	0.07	5
Th	8.2	0.9	11.0	6.0-9.0	9.0	2.0	18
Ti*	0.41	0.02	4.9	0.37-0.44	0.46	0.02	45
V	137	4.7	3.4	130-140	142	12	49
Y	16.4	1.4	8.5	15-19	20.2	2.4	34
Yb	2.0	0	0	2.0	2.1	0.4	19
Zn	137	6.7	4.9	120-150	144	10	44
Hg	X	--	--	--	0.045	0.008	12
U	1.0(P)	0.13	13.0	0.8-1.3	2.4	0.5	24

Table 2b.--Comparison of data (for unqualified values) for reference material GSD-6 to literature recommended data (N=20 samples)--Continued

	BGC values				Recommended values[1]		
Constituent	$\bar{x}$	STD	RSD	Range	$\bar{x}$	STD	N
Total C*	0.97	0.06	6.2	0.89-1.10	(1.17)	Not available	
Inorg. C*	0.54	0.008	1.5	0.53-0.56	(.55)	Not available	
Org. C*	0.43	0.06	14.0	0.35-0.60	(.62)	Not available	
S*	0.07	0.01	14.3	0.02-0.09	(.08)	Not available	
B	Not determined			----	No data available		
As	13.0	3.2	24.6	4.1-17	13.6	1.5	30
Sb	1.2	0.3	25.0	0.5-1.5	1.25	0.33	23

[1]XueJing and others, April 1985
( ) = Values do not meet criteria for recommended values
(P) = Partial dissolution
X = Insufficient unqualified data
L = Less than the lower limit of determination

Table 2C.--Comparison of data (for unqualified values) for reference material GSD-12 to literature recommended data (N=68 samples)

[All values ppm except * in %]

	BGC values				Recommended values[1]		
Constituent	$\bar{x}$	STD	RSD	Range	$\bar{x}$	STD	N
Ag	--	--	--	--	1.15	0.16	24
Al*	4.69	0.13	2.8	4.4-5.0	4.92	0.09	31
Au	X	--	--	--	(5.6 ppb)	2.3	5
Ba	193	6.6	3.4	180-210	206	23	45
Be	6.8	0.4	5.9	6.0-7.0	8.2	1.1	40
Bi	10.2	1.4	13.7	10L-20	10.9	1.3	32
Ca*	0.85	0.03	3.5	0.80-0.96	0.83	0.05	39
Cd	3.8	0.3	7.9	3.0-4.0	4.0	0.4	28
Ce	54.1	4.1	7.6	45-62	61	5	24
Co	9.0	0.4	4.4	8.0-10	8.8	1.1	67
Cr	38	2.5	6.6	32-45	35	4	59
Cu	1240	62	5.0	1200-1400	1230	51	52
Eu	X	--	--	--	0.61	0.04	19
Fe*	3.40	0.08	2.3	3.3-3.6	3.41	0.13	43
Ga	13.8	0.7	5.1	12-15	14.1	0.7	20
Ho	X	--	--	--	0.94	0.09	15
K*	2.3	0.08	3.5	2.2-2.5	2.41	0.05	37
La	28.7	2.5	8.7	24-35	32.7	2.2	32
Li	39.5	1.1	2.8	37-42	39.0	1.5	28
Mg*	0.25	0.008	3.2	0.24-0.28	0.28	0.07	38
Mn	1420	41	2.9	1400-1500	1400	73	60
Mo	6.6	0.9	13.6	3.0-8.0	8.4	0.9	34
Na*	0.31	0.007	2.3	0.29-0.32	0.33	0.03	41
Nb	7.9	1.7	21.5	5.0-15.0	15.4	1.6	39
Nd	22.7	1.8	7.9	20-27	25.6	3.6	18
Ni	12.0	0.6	5.0	11-14	12.8	1.9	65
P*	0.02	0.002	10.0	0.02-0.03	0.024	0.003	43
Pb	292	22	7.5	250-360	285	16	41
Sc	4.9	0.3	6.1	4.0-5.0	5.1	0.6	24
Sn	20.6	2.9	14.1	10-30	54	7	25
Sr	23.7	0.7	3.0	22-26	24.4	4.1	41
Ta	X	--	--	--	3.2	0.3	11
Th	20.7	1.3	6.3	18-24	21.4	1.7	25
Ti	0.13	0.007	5.4	0.12-0.14	0.151	0.007	45
V	42.3	1.6	3.8	39-46	46.6	5.3	56
Y	20.0	1.0	5.0	19-23	29.3	4.0	51
Yb	2.9	0.3	10.3	2.0-3.0	3.7	0.5	33
Zn	508	21	4.1	470-560	498	27	52
Hg	0.10	0.04	40.0	0.02L-0.22	0.06	0.01	18
U	5.9(P)	1.0	16.9	4.2-8.1	7.8	1.0	20

Table 2C.--Comparison of data (for unqualified values) for reference material GSD-12 to literature recommended data (N=68 samples)--Continued

	BGC values				Recommended values[1]		
Constituent	$\bar{x}$	STD	RSD	Range	$\bar{x}$	STD	N
Total C*	0.50	0.03	6.0	0.38-0.57	(0.45)	Not available	
inorg. C*	0.04	0.01	25.0	0.01L-0.09	(0.05)	0.03	13
org. C*	0.46	0.03	6.5	0.35-0.53	(0.40)	0.06	8
S*	0.09	0.009	10.0	0.08-0.13	.094	.006	12
B	Not determined		---	----	No Data Available		
As	112	18	16.1	22-170	115	9	35
Sb	20.6	4.8	23.3	12-34	24.3	3.8	34
Se (N=21)	0.36	0.07	19.4	0.2-0.5	0.25	0.04	15

[1]XueJing and others, October 1985
( ) = Values do not meet criteria for recommended value
(P) = Partial dissolution
X = Insufficent unqualified data
L = Less than the lower limit of determination

Table 3a.--Summary of results of analysis of reference material GXR-2 (N=114 samples)

Constituent determined	No. of samples <= 1STD	No. of samples <= 2STD	No. of samples <= 3STD	No. of L values
Ag	91	112	112	0
Al	81	111	114	0
Au	---	---	---	114
Ba	58	109	114	0
Be	111	111	111	0
Bi	---	---	---	114
Ca	84	111	113	0
Cd	64	114	114	0
Ce	66	108	113	0
Co	85	108	114	0
Cr	90	106	113	0
Cu	86	109	113	0
Eu	---	---	---	114
Fe	65	114	114	0
Ga	78	112	112	0
Ho	---	---	---	114
K	109	109	114	0
La	74	104	114	0
Li	88	109	113	0
Mg	76	108	114	0
Mn	92	93	114	0
Mo	---	---	---	114
Na	93	112	113	0
Nb	73	99	101	12
Nd	78	112	112	0
Ni	95	107	113	0
P	92	92	114	0
Pb	90	109	112	0
Sc	101	101	114	0
Sn	---	---	---	114
Sr	72	114	114	0
Ta	---	---	---	114
Th	89	109	112	1
Ti	95	109	112	0
V	83	112	114	0
Y	73	112	114	0
Yb	110	110	110	0
Zn	63	109	114	0
Hg	88	112	112	0
U	74	111	114	0
Total C	91	109	113	0
Orgnc C	94	110	113	0
Crbnt C	X	X	X	X
Total S	57	104	111	3
As	78	109	112	0
Sb	91	110	112	0
Se (N=24)	14	23	24	0

L = Less than the lower limit of determination
X = insufficent unqualified data

Table 3b.--Summary of results of analysis of reference material GSD-6 (N=20 samples)

Constituent determined	No. of samples <= 1STD	No. of samples <= 2STD	No. of samples <= 3STD	No. of L values
Ag	0	0	0	20
Al	16	18	20	0
Au	--	--	--	20
Ba	18	19	20	0
Be	20	20	20	0
Bi	--	--	--	19
Ca	16	18	20	0
Cd	--	--	--	20
Ce	13	20	20	0
Co	15	20	20	0
Cr	16	19	20	0
Cu	15	20	20	0
Eu	--	--	--	20
Fe	14	19	20	0
Ga	14	19	19	0
Ho	--	--	--	20
K	16	18	20	0
La	11	20	20	0
Li	15	18	20	0
Mg	15	20	20	0
Mn	16	19	20	0
Mo	10	20	20	0
Na	17	18	20	0
Nb	12	13	14	6
Nd	14	19	20	0
Ni	16	18	20	0
P	12	19	19	0
Pb	15	19	20	0
Sc	10	20	20	0
Sn	--	--	--	20
Sr	12	19	20	0
Ta	--	--	--	20
Th	16	19	20	0
Ti	18	20	20	0
V	14	20	20	0
Y	9	20	20	0
Yb	20	20	20	0
Zn	12	19	20	0
Hg	X	X	X	12
U	14	19	20	0
Total C	15	19	20	0
Orgnc C	15	19	20	0
Crbnt C	11	19	20	0
Total S	17	19	19	0
As (N=16)	13	15	16	0
Sb (N=16)	15	15	16	0

L = Less than the lower limit of determination
X = Insufficient unqualified data

Table 3c.--Summary of results of analysis of reference material GSD-12 (N=68 samples)

Constituent determined	No. of samples <= 1STD	No. of samples <= 2STD	No. of samples <= 3STD	No. of L values
Ag	--	--	--	68
Al	51	65	68	0
Au	--	--	--	68
Ba	41	65	68	0
Be	53	68	68	0
Bi	53	53	53	14
Ca	49	64	67	0
Cd	56	56	68	0
Ce	42	67	68	0
Co	59	59	68	0
Cr	48	65	68	0
Cu	63	63	68	0
Eu	--	--	--	68
Fe	27	66	68	0
Ga	43	66	68	0
Ho	0	0	0	68
K	56	64	68	0
La	45	67	68	0
Li	47	63	68	0
Mg	40	61	67	0
Mn	54	68	68	0
Mo	57	65	67	0
Na	34	63	68	0
Nb	46	65	66	1
Nd	50	66	68	0
Ni	45	67	67	0
P	65	65	65	0
Pb	54	65	66	0
Sc	61	61	68	0
Sn	62	62	62	0
Sr	59	66	67	0
Ta	--	--	--	68
Th	53	64	68	0
Ti	30	68	68	0
V	43	63	68	0
Y	61	67	68	0
Yb	60	60	68	0
Zn	43	67	68	0
Hg	42	66	67	1
U	42	67	68	0
Total C	53	65	67	0
Orgnc C	51	65	67	0
Crbnt C	59	63	65	2
Total S	64	67	67	0
As (N=67)	61	65	65	0
Sb (N=54)	39	52	54	0
Se (N=21)	19	21	21	0

L = Less than the lower limit of determination

Table 4a.--Average range and average mean of values (unqualified) for within job duplicates of reference material GXR-2
(N=45 pairs of duplicates)

Constituent determined	Average range of duplicates	Average mean	No. of L's (total)	No. of L (pairs)
Ag	0.4	19.3	0	0
Al*	0.19	6.6	0	0
Au	X	--	90	45
Ba	42	2115	0	0
Be	0.04	2.0	0	0
Bi	X	--	90	45
Ca*	0.02	0.91	0	0
Cd	0.16	3.4	0	0
Ce	1.4	51	0	0
Co	0.3	11.2	0	0
Cr	0.8	36.3	0	0
Cu	2.2	79.3	0	0
Eu	X	--	90	45
Fe*	0.04	1.9	0	0
Ga	0.8	18.3	0	0
Ho	X	--	90	45
K*	0.04	1.35	0	0
La	0.5	26.7	0	0
Li	1.1	61.0	0	0
Mg*	0.02	0.83	0	0
Mn	22	1015	0	0
Mo	X	--	90	45
Na*	0.01	0.57	0	0
Nb	1.0	7.1	11	3
Nd	1.1	21.5	0	0
Ni	0.5	17.3	0	0
P*	0.002	0.07	0	0
Pb	13	696	0	0
Sc	0.04	6.1	0	0
Sn	X	--	90	45
Sr	2.7	160	0	0
Ta	X	--	90	45
Th	0.8	8.3	1	0
Ti*	0.01	0.27	0	0
V	0.9	48.2	0	0
Y	0.3	14.3	0	0
Yb	0.07	2.0	0	0
Zn	11	545	0	0
Hg	0.13	3.1	0	0
U	0.3	1.9	0	0
Total* C	0.06	2.88	0	0
Orgnc* C	0.06	2.87	0	0
Crbnt* C	0.004	0.02	41	16
Total* S	0.01	0.03	3	0
As	1.7	22.0	0	0
Sb	3.9	35.3	0	0
Se (N=9)	0.16	0.71	0	0

All values in ppm except * in percent.
L = Less than the lower limit of determination
X = Insufficient unqualified data

Table 4b.--Average range and average mean of values (unqualified) for within job duplicates of reference material GSD-6
(N=5 pairs of duplicates)

Constituent determined	Average range of duplicates	Average mean	No. of L's (total)	No. of L (pairs)
Ag	X	--	10	5
Al*	0.08	7.48	0	0
Au	X	--	10	5
Ba	6	310	0	0
Be	0	2.0	0	0
Bi	X	--	10	5
Ca*	0.02	2.82	0	0
Cd	X	--	10	5
Ce	1.4	64.2	0	0
Co	0.6	25.8	0	0
Cr	4.0	199	0	0
Cu	4.0	395	0	0
Eu	X	--	10	5
Fe*	0.02	4.03	0	0
Ga	0.8	17.1	0	0
Ho	X	--	10	5
K*	0.02	2.02	0	0
La	0.4	33.9	0	0
Li	0.4	42.9	0	0
Mg*	0.02	1.80	0	0
Mn	10	959	0	0
Mo	0.6	6.0	0	0
Na*	0	1.78	0	0
Nb	2.7	5.9	4	2
Nd	1.4	30.6	0	0
Ni	0.8	75.2	0	0
P*	0	0.10	0	0
Pb	2.8	28.4	0	0
Sc	0.2	16.1	0	0
Sn	X	--	10	5
Sr	2.0	280	0	0
Ta	X	--	10	5
Th	1.4	8.2	0	0
Ti*	0.012	0.41	0	0
V	0	137	0	0
Y	0	16.4	0	0
Yb	0	2.0	0	0
Zn	2.0	137	0	0
Hg	X	--	9	4
U	0.1	1.0	0	0
Total* C	0.01	0.97	0	0
Orgnc* C	0.02	0.43	0	0
Crbnt* C	0.01	0.54	0	0
Total* S	0.01	0.07	0	0
As (N=3)	1.1	14.8	0	0
Sb (N=3)	0.2	1.1	0	0

All values in ppm except * in percent
L = Less than the lower limit of determination
X = insufficient unqualified data

Table 4c.--Average range and average mean of values (unqualified) for within job duplicates of reference material GSD-12
(N=17 pairs of duplicates)

Constituent determined	Average range of duplicates	Average mean	No. of L's (total)	No. of L (pairs)
Ag	X	--	34	17
Al*	0.07	4.69	0	0
Au	X	--	34	17
Ba	2.9	193	0	0
Be	0.1	6.8	0	0
Bi	0.8	10.2	6	2
Ca*	0.02	0.86	0	0
Cd	0.2	3.8	0	0
Ce	1.6	54.2	0	0
Co	0.2	9.0	0	0
Cr	0.5	38.1	0	0
Cu	17	1238	0	0
Eu	X	--	34	17
Fe*	0.04	3.40	0	0
Ga	0.3	13.8	0	0
Ho	X	--	34	17
K*	0.07	2.33	0	0
La	1.1	28.7	0	0
Li	0.6	39.5	0	0
Mg*	0.004	0.25	0	0
Mn	17	1421	0	0
Mo	0.5	6.6	0	0
Na*	0.004	0.30	0	0
Nb	0.9	7.9	0	0
Nd	0.8	22.7	0	0
Ni	0.5	12.0	0	0
P*	0	0.02	0	0
Pb	2	292	0	0
Sc	0.2	4.9	0	0
Sn	0.6	20.6	0	0
Sr	0.4	23.7	0	0
Ta	X	--	34	17
Th	0.7	20.7	0	0
Ti*	0.002	0.13	0	0
V	0.6	42.3	0	0
Y	0.2	20.0	0	0
Yb	0.2	2.9	0	0
Zn	7.1	508	0	0
Hg	0.03	0.10	1	0
U	0.7	5.9	0	0
Total* C	0.03	0.50	0	0
Orgnc* C	0.03	0.46	0	0
Crbnt* C	0.01	0.04	1	0
Total* S	0.01	0.09	0	0
As (N=16)	11.7	112	0	0
Sb (N=12)	2.0	19.9	0	0
Se (N=6)	0.07	0.37	0	0

All values in ppm except * in percent
L = Less than the lower limit of determination
X = insufficient unqualified data

Table 5.--Average relative percent difference and average mean (for unqualified values) for within job sample duplicates (N = 66 pairs of duplicate samples)

Constituent determined	Average relative percent difference	Average mean	No. of L's (pairs)	No. of L values (total)
Ag	X	--	121	60
Al	1.8	6.20*	0	0
Au	X	--	132	66
Ba	3.7	530	0	0
Be	2.0	1.8	0	0
Bi	X	--	132	66
Ca	2.8	2.59*	0	0
Cd	X	--	120	59
Ce	4.0	69.1	0	0
Co	3.8	16.5	0	0
Cr	4.3	70.5	0	0
Cu	6.5	35.1	0	0
Eu	X	--	129	64
Fe	2.6	3.49*	0	0
Ga	4.9	15.3	0	0
Ho	X	--	132	66
K	2.2	1.87*	0	0
La	3.0	35.7	0	0
Li	3.1	34.4	0	0
Mg	2.5	1.01*	0	0
Mn	1.1	905	0	0
Mo	X	--	106	52
Na	3.0	0.87*	0	0
Nb	16.8	8.0	37	13
Nd	6.2	33.1	0	0
Ni	3.3	29.7	0	0
P	3.6	0.12*	0	0
Pb	9.5	52.5	2	0
Sc	2.8	11.2	0	0
Sn	X	--	121	60
Sr	2.1	173	0	0
Ta	X	--	132	66
Th	9.1	10.1	2	0
Ti	6.6	0.39*	0	0
V	3.0	93.3	0	0
Y	2.7	21.2	0	0
Yb	6.3	2.6	0	0
Zn	3.6	139	0	0
Hg	31.8	0.33	51	19
U	25.1	1.4	0	0
Total C	2.0	2.77*	0	0
Orgnc C	6.1	2.20*	0	0
Crbnt C	14.3	0.67*	14	4
Total S	39.4	0.11*	12	3
B (N=57)	48.9	1.9	1	0
As	10.6	13.1	0	0
Sb	14.2	0.8	0	0
Se(N=15)	18.5	1.9	0	0

All values in ppm except * in percent.
L = Less than the lower limit of determination
X = insufficient unqualified data

Table 6.--Average relative percent difference and average mean (for unqualified values) for sample duplicates from the analysis of variance design
(N = 110 pairs of duplicate samples)

Constituent determined	Average relative percent difference	Average mean	No. of L's (pairs)	No. of L values (total)
Ag	X	--	219	109
Al	3.1	6.23*	0	0
Au	X	--	220	110
Ba	5.6	519	0	0
Be	6.4	1.8	17	8
Bi	X	--	219	119
Ca	5.1	2.59*	0	0
Cd	X	--	216	108
Ce	8.3	63.2	0	0
Co	7.2	17.2	0	0
Cr	8.5	55.2	0	0
Cu	9.2	24.6	0	0
Eu	X	--	204	98
Fe	4.4	3.70*	0	0
Ga	7.1	15.6	1	0
Ho	X	--	220	110
K	5.8	1.73	0	0
La	7.8	33.6	0	0
Li	4.2	31.0	0	0
Mg	5.0	1.05*	0	0
Mn	7.2	931	0	0
Mo	X	--	192	93
Na	5.2	0.94*	0	0
Nb	22.5	8.6	48	12
Nd	8.5	31.2	0	0
Ni	6.3	26.3	0	0
P	7.6	0.09*	0	0
Pb	12.1	38.4	0	0
Sc	4.6	11.7	0	0
Sn	X	--	218	108
Sr	4.3	172	0	0
Ta	X	--	220	110
Th	14.9	9.4	7	1
Ti	8.9	0.43*	0	0
V	5.3	101	0	0
Y	4.9	20.8	0	0
Yb	7.3	2.6	2	1
Zn	6.6	95.3	0	0
Hg	40.6	.06	69	24
U	21.1	1.7	0	0
Total C	9.4	3.13*	0	0
Orgnc C	12.0	2.69*	0	0
Crbnt C	23.8	0.70*	32	12
Total S	31.6	0.09	21	3
B (N=98)	43.2	1.3	19	3
As	16.3	9.0	0	0
Sb	20.2	0.7	0	0
Se (N=30)	24.5	0.9	0	0

All values in ppm except *in percent.
L = Less than the lower limit of determination
X = insufficient unqualified data