SUMMARY OF THE U.S. GEOLOGICAL SURVEY NATIONAL FIELD QUALITY ASSURANCE PROGRAM FROM 1979 THROUGH 1989

by Daniel L. Stanley, William J. Shampine, and LeRoy J. Schroder

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CONVERSION FACTORS, ABBREVIATIONS, AND ACRONYMS

Multiply	*By*	*To obtain*
liter (L)	1.057	quart, liquid
milligram (mg)	0.00003527	ounce
milliliter (mL)	0.0338	ounce, fluid

Abbreviations

milligrams per liter	(mg/L)
microsiemens per centimeter at 25 degrees Celsius	(µS/cm at 25°C)
standard deviation	(SD)
most probable value	(MPV)
ultraviolet	(UV)
fourth-spread	(F-spread)
fourth-pseudosigma	(F-pseudosigma)

Acronyms

National Field Quality Assurance Program	(NFQA)
National Water Data Storage and Retrieval System	(WATSTORE)
National Water Quality Laboratory	(NWQL)
Quality Water Service Unit	(QWSU)

SUMMARY OF THE U.S. GEOLOGICAL SURVEY NATIONAL FIELD QUALITY ASSURANCE PROGRAM FROM 1979 THROUGH 1989

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ABSTRACT

Almost 38,000 pH and specific conductance measurements and almost 5,200 alkalinity measurements have been evaluated in the U.S. Geological Survey's National Field Quality Assurance Program since its inception in 1979. The measurement values were analyzed to determine the relative fourth-spread (F-spread), a measure of the width of the middle half of the data, and the fourth-pseudosigma (F-pseudosigma), a robust replacement for the standard deviation, for each of seven different specific measurement ranges. The results of the statistical analysis indicate that the vast majority of values for all three field measurements were within acceptable ranges. Levels of precision were best for pH measurements in the range between 6.00 to 6.99 units. The relative F-spread percentage was 0.4, and the F-pseudosigma was 0.02 pH units. For specific conductance and alkalinity, the percentage of the relative F-spread remains relatively constant for the different measurement ranges. The level of precision was best for specific conductance in the range between 250 to 499 microsiemens per centimeter. The relative F-spread was 2.3 percent, and the F-pseudosigma was 8.9 microsiemens per centimeter. The level of precision was best for alkalinity ranges between 150 to 199 milligrams per liter as calcium carbonate. The relative F-spread percentage was 3.1 and the F-pseudosigma was 4.6 milligrams per liter.

INTRODUCTION

Part of the mission of the Water Resources Division of the U.S. Geological Survey (USGS) is to collect water-quality information on the water resources of the Nation. Implementation of this part of the mission requires both the collection of water-quality samples for laboratory analyses and field measurements of alkalinity, pH, and specific conductance. An estimated 45,000 field measurements are made annually by USGS field analysts (hydrologists and hydrologic technicians). All USGS personnel who perform field determinations are required to participate in the National Field Quality Assurance Program (NFQA). Contract and cooperator personnel who collect these types of field data to be used in USGS reports or stored in the USGS National Water Data Storage and Retrieval System (WATSTORE) are encouraged to participate in this quality assurance program.

The formal quality assurance program to monitor the accuracy and precision of pH and specific conductance field measurements made by USGS personnel was initiated in March 1979. Initially, a set of two pH and two specific conductance proficiency samples was distributed about every 6 months to participating personnel in the USGS. The measurement of alkalinity was added as a test parameter in 1985. The frequency of distribution of the subsequent rounds of proficiency samples was changed in 1985 to two sets of proficiency samples to each participant about every 15 months. The frequency of distribution was changed to facilitate the addition of a followup or secondary sample distribution to individuals who received an unsatisfactory performance rating on any proficiency sample.

Under the NFQA, pH, specific conductance, and alkalinity proficiency samples are distributed to more than 180 USGS offices. Approximately 10 USGS offices request proficiency samples for contractor or cooperator personnel participating in the program. The most probable value (MPV) of pH, specific conductance, and alkalinity of proficiency samples is calculated from all the values submitted from the participating region (fig. 1). Contractor and cooperator data normally are not differentiated from USGS data in determining the MPV of pH, specific conductance, and alkalinity proficiency samples. The data for each proficiency sample are summarized by the NFQA manager in a report, which is then distributed to the USGS offices. All the NFQA data are stored in a computerized data base managed by the Quality Water Service Unit (QWSU) of the Florida District office of the U.S. Geological Survey.

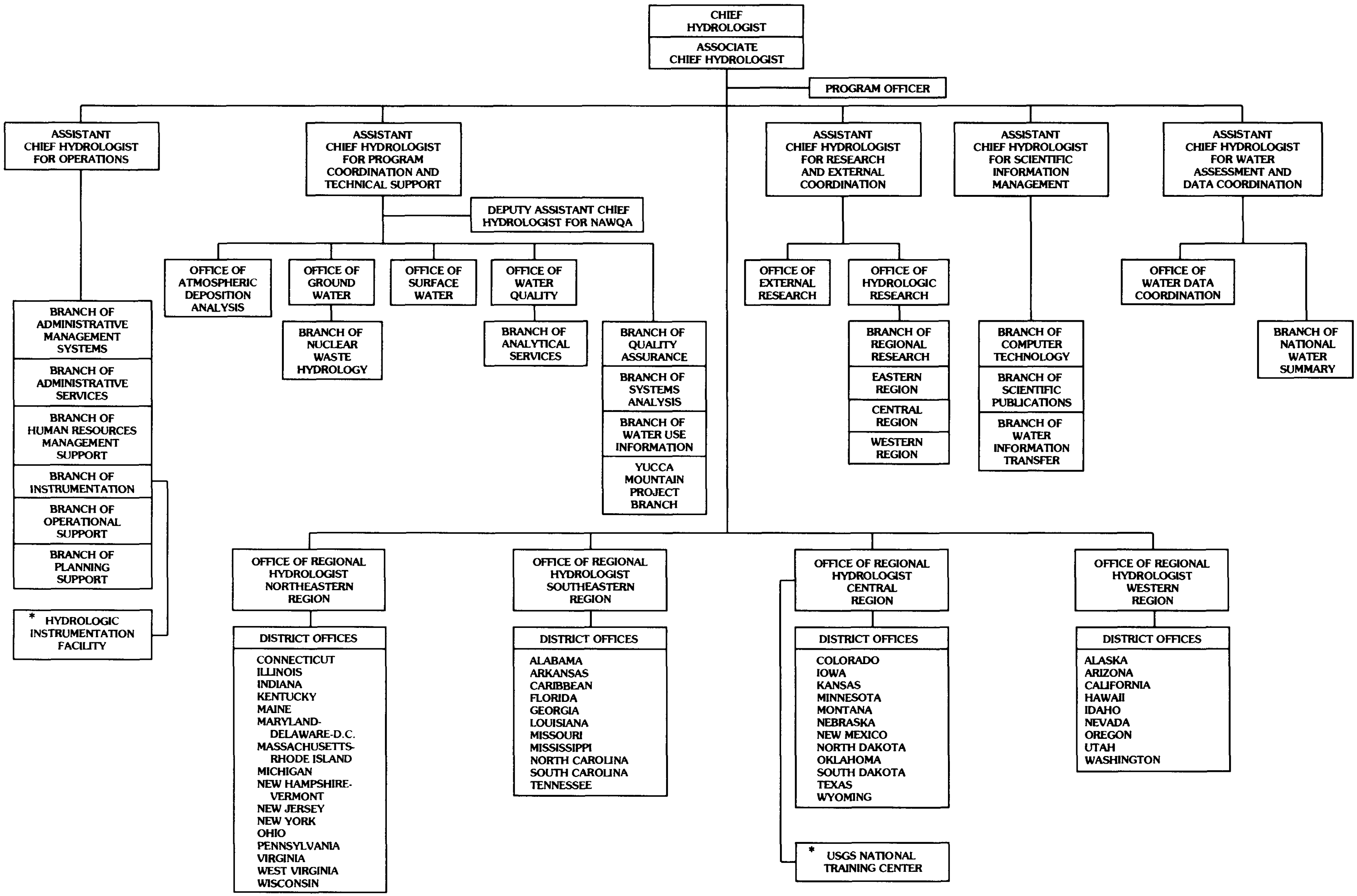
The NFQA provides documentation of the precision of the field measurements related to water quality. In addition, the NFQA provides a mechanism for identifying field personnel requiring additional training and equipment in need of calibration or repair. USGS offices in the regions and districts provide training and instrument calibration or repair as needed.

This report documents the history of the NFQA including management and technical changes in the program from 1979 through 1989. It describes the NFQA procedures used to prepare and distribute the proficiency samples and the rating process used to evaluate proficiency. Results of the statistical analysis of the quality assurance data for pH, specific conductance, and alkalinity are tabulated for various ranges of measurements. A statistical measure that describes the concentration of data about a central value is the fourth-spread or F-spread. The F-spread measures the data range of the middle 50 percent of the values. Therefore, the F-spread can be used to compare the variability and identify outlying values in data sets. The F-spread data are summarized in graphical form by year for the various measurement ranges.

PROGRAM HISTORY

The NFQA has gone through several revisions since its inception in 1979. The following summarizes some of the major events affecting the program.

March 1979	The USGS established a program to provide quality assurance proficiency samples for pH and specific conductance to field analysts. The program was managed by the USGS National Water Quality Laboratory (NWQL) in Arvada, Colo. Results were sent to the Office of Water Quality, regional office, and then to the district participants (fig. 1).
January 1981	The program was discontinued.
February 1982	The program was reinstated to provide proficiency samples for pH and specific conductance, and was managed by the NWQL in Doraville, Ga.
August 1984	Alkalinity and chloride proficiency samples were added to the program. After one shipment of proficiency samples was sent to field analysts in each region, chloride proficiency samples were discontinued (1985).
October 1985	The responsibility for managing the NFQA program was transferred from the NWQL in Doraville, Ga., to the QWSU in Ocala, Fla. The QWSU followed the existing



* National facility administered by the office shown

Figure 1.--Organization chart of the Water-Resources Division of the U.S. Geological Survey, 1991.

	protocol by sending results to the Office of Water Quality and, after review, to the regional offices for distribution to the district participants.
	The program initiated the practice of sending followup samples to field analysts whose proficiency-sample performance ratings were unsatisfactory. The frequency of distribution was changed to two initial rounds about every 15 months.
	The volume of the proficiency sample was doubled, to 250 mL, and sample bottling and labeling procedures were revised to reduce the possibility of error in sample identification.
February 1987	Procedures were changed to require that the titration method used (fixed-end point or incremental titration) is recorded and stored with the NFQA data.
October 1989	Frequency of proficiency sample distribution was again changed. It was reduced to once per year to each field analyst with a followup sample as needed. Results of the annual proficiency testing are sent to participants 2 weeks after a summary is sent to the Office of Water Quality, Branch of Quality Assurance, and regional offices.

PROGRAM DESCRIPTION

Currently (1992), the NFQA prepares and distributes more than 6,700 proficiency samples annually. These samples are representative of pH, specific conductance, and alkalinity ranges found in most natural waters (Hem, 1985). Almost 38,000 pH and specific conductance samples and almost 5,200 alkalinity samples have been distributed between 1979 and 1989. Sample preparation, labeling, distribution, and proficiency evaluation procedures for the NFQA are described in the following sections.

Sample Preparation

Four alkalinity, eight pH, and eight specific conductance proficiency samples are prepared for each region's annual proficiency test. A number of different proficiency samples are required to test the analytical range of the instruments and to reduce the possibility of field analysts sharing results. The need for 20 different proficiency samples for each regional test requires that twenty 100-L samples be prepared.

The following reagents are used in the proficiency-sample preparation, and the references cited are for the preparation procedures of each analyte:

1. pH--potassium hydrogen phthalate, potassium phosphate monobasic, and sodium hydroxide (Robinson and Stokes, 1959; Bates, 1964).
2. Conductivity--potassium chloride (American Public Health Association, 1989).
3. Alkalinity--sodium bicarbonate (American Public Health Association, 1989); 0.04 mg/L of thymol is added to each sample to inhibit biological activity (Fishman and Friedman, 1989).

The target value for each of the 20 proficiency samples is chosen by the NFQA program manager at the QWSU in an attempt to cover the pH, specific conductance, and alkalinity ranges commonly found in natural waters. The quantity of reagents needed to produce a 100-L proficiency sample is then

Table 1.--*Ranges of pH, specific conductance, and alkalinity target values for proficiency samples analyzed as part of the National Field Quality Assurance Program*

[μS/cm, microsiemens per centimeter; mg/L as $CaCO_3$, milligrams per liter as calcium carbonate]

Determination	Range
pH (units)	3.5 - 8.5
Specific Conductance (μS/cm)	20 - 3,200
Alkalinity (mg/L as $CaCO_3$)	15 - 300

calculated using computer algorithms. The target-value ranges of proficiency samples for the period from 1979 through 1989 are listed in table 1.

One hundred liters of water are pumped from a distilled water-holding tank into a polyethylene preparation tank (fig. 2) using a peristaltic pump and mixed with the appropriate quantity of reagents for the proficiency solution being prepared. The pH, conductivity, and alkalinity solutions are stirred continuously for 4 to 5 hours; pH and conductivity solutions are allowed to stand at least 12 hours before ultraviolet (UV) sterilization and bottling. Alkalinity solutions are allowed to stand for 5 days before sterilization and bottling because unpublished test results (Khanh K. Doan, U.S. Geological Survey, oral commun., 1985) indicate that this amount of time is necessary to allow the solution to achieve gaseous equilibrium with the atmosphere.

After the solutions have been quiescent for the appropriate amount of time, the solutions are pumped into sample bottles through clear vinyl tubing and an in-line UV radiation unit at a rate of 1.5 to 2.0 L per minute. The purpose of the UV sterilization is to prevent degradation of the proficiency samples by biological activity. The sample bottles and caps are made of high density polyethylene and are placed in a UV radiation hood for about 15 minutes prior to being filled. A minimum of 2 L of the test solution is pumped through the system before any samples are bottled. The bottling and capping process is completed under the UV radiation hood.

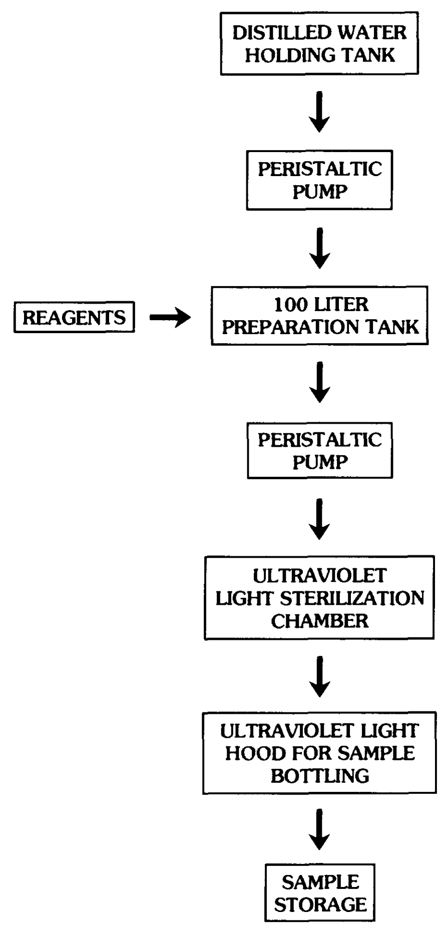


Figure 2.--Proficiency sample preparation process from holding tank to sample storage.

Sample Labeling

The proficiency sample labels are prepared using a computer program. The label identifies the District office that is to receive the samples. A participant's name and identification number also are included on the sample label. The identification number is an alpha-numeric code unique to each individual bottle assigned to a specific field-analyst.

Sample Distribution

Approximately 30 days prior to the shipment of the proficiency samples, each district office is requested to supply all participants' names, meter identification information, and method used for each sample type. The major objective of this inventory is to ensure that all personnel and instrument combinations being used to obtain on-site values for pH, specific conductance, and alkalinity data are evaluated. Because a meter might have multiple users and an individual might use multiple meters, the program strives to test all of the combinations being used. Each field analyst and meter combination is assigned a unique number, and a set of proficiency samples needed for the measurements is sent to the participant. The sample set consists of two randomly selected pH and specific conductance proficiency samples and, if requested, two randomly selected alkalinity samples.

Assessment and Report of Results

Field analysts are expected to measure the pH, specific conductance, and alkalinity of their set of samples and return their results to QWSU within 30 days. The NFQA staff immediately evaluates the results and prepares a proficiency report within 20 days of receipt of the data.

Statistical evaluation of the results from each individual proficiency sample includes a calculation of the number of results reported, the mean of the reported values, and the standard deviation. Outlying values are rejected on the basis of the T-value (Grubbs test) as described by American Society for Testing and Materials, (1969). After rejection of outliers, a new mean and standard deviation are calculated and the mean is used as the MPV (Dixon and Massey, 1969). The reporting criterion for alkalinity is two significant figures. For pH, values are reported to the nearest 0.1 pH unit. Specific conductance values less than 1,000 μS/cm are reported to the nearest 1 μS/cm and specific conductance values greater than 1,000 μS/cm are reported to the nearest 10 μS/cm.

Once the MPV for a particular proficiency sample is determined, individual results then are rated according to criteria described by Friedman and Erdmann (1982, p. 123). The specific rating criteria for pH, specific conductance, and alkalinity proficiency samples are summarized in table 2.

Prior to October 1985, unsatisfactory ratings were assigned if data were missing or received late, or if the sample concentration exceeded the capabilities of the instrument. This arbitrary rating biased the results and reduced the overall proficiency ratings for the participating offices. Since 1985, a rating of "N" is assigned to a participant who failed to send in results for whatever reason. The performance of an individual field analyst now is evaluated by a district or region using only those results that are reported.

After NFQA reports are distributed to the appropriate regional office, a follow-up proficiency sample is distributed to each field analyst who received an unsatisfactory rating, typically within 2 to 3 weeks after the NFQA report is distributed to the regional office. The follow-up samples are designed to help the field analyst find and correct the source of the error for specific determinations. Often the followup proficiency sample MPV is similar to the original MPV. A report on the results of analyses of followup samples also is prepared and sent to the appropriate regional office for review and distribution to the district office and field analyst.

Table 2.--*Rating criteria for analytical results of proficiency samples*

[MPV, most probable value; µS/cm, microsiemens per centimeter at 25 degrees Celsius; %, percent; SD, standard deviation; mg/L as $CaCO_3$, milligrams per liter as calcium carbonate; >, greater than; <, less than; ±, plus or minus]

Determination	Satisfactory	Marginal	Unsatisfactory
pH, units	MPV ± 0.1	MPV ± >0.1 to 0.2	MPV ± >0.2
Specific conductance <67 µS/cm	MPV ± 2.0	MPV ± >2 to 4	MPV ± >4
Specific conductance ≥67 µS/cm	MPV ± <4%	MPV ± 4 to 6%	MPV± >6%
Alkalinity mg/L as $CaCO_3$	MPV ± <1.5 SD	MPV ± (1.5-2.0) SD	MPV ± >2.0 SD

EVALUATION OF NATIONAL FIELD QUALITY ASSURANCE PROGRAM RESULTS

This section describes the acceptance criteria used to evaluate the performance of the field analysts. The precision data obtained from the analyses of the proficiency samples exclude unsatisfactory ratings assigned to field analysts for missing or late results.

Performance Summary

From 1979 through 1989, the NFQA developed a data base that contains the performance results of the participants, the type of field meter used in the determination, and the precision of the measurements. Performance results used by the NFQA ranks each reported value as satisfactory, marginal, or unsatisfactory. From the beginning of the program, the NFQA has used these classifications of results to rate the performance of participants. A marginal rating is used as a cautionary area between satisfactory and unsatisfactory performance. The use of the marginal ranking is intended to alert the appropriate office to the possibility of a malfunctioning meter or a field analyst who might need additional training. Response to this alert mechanism is the responsibility of the appropriate District. District water-quality specialists are asked to review results classified as marginal with field analysts even though these results are considered acceptable and within the guidelines set by Friedman and Erdmann (1982). The NFQA has continued to use the marginal rating but has treated the marginal results as acceptable when statistically evaluating the data.

The percentages of acceptable results for pH, specific conductance, and alkalinity from 1979 through 1989 are listed in table 3. The percentages of acceptable values were calculated on the basis of the total number of samples analyzed and reported by USGS personnel only. Results reported by contractors and cooperators were excluded from this analysis.

The percentage of acceptable results for pH, specific conductance, and alkalinity has improved significantly in the NFQA since quantitative monitoring was initiated; the most dramatic improvement occurred in the measurement of specific conductance. The percentage of acceptable specific conductance results increased from 67.7 percent in 1979 (table 3) to 92.2 percent in 1989. The percent-

Table 3.--*Proficiency results for pH, specific conductance, and alkalinity determinations made as part of the National Field Quality Assurance Program, 1979-89*

[----, no data; results from only U.S. Geological Survey personnel]

Year	pH		Specific conductance		Alkalinity	
	Samples tested	Percent acceptable	Samples tested	Percent acceptable	Samples tested	Percent acceptable
1979	3,553	93.8	2,915	67.7	----	----
1982	2,117	82.6	2,079	74.2	----	----
1983	1,654	95.5	1,812	88.0	----	----
1984	1,861	88.7	2,017	84.1	----	----
1985	1,591	88.9	1,734	82.5	573	78.6
1986	1,319	98.1	1,410	89.9	690	84.6
1987	1,849	98.6	2,048	91.5	884	89.8
1988	2,021	98.6	2,158	91.7	1,171	87.3
1989	2,001	98.6	2,060	92.2	1,142	87.6

age of acceptable pH results averaged 93.7 percent for the years 1979 through 1989 and has remained nearly constant since 1986. The percentage of acceptable alkalinity results averaged 85.6 percent for the years 1985 through 1989.

Precision

The results from the NFQA were summarized by year and tested to determine if the data were normally distributed using the Lillefors test (Inman and Conover, 1983). The data set failed the normality test, so nonparametric statistical techniques were used to describe the data set. The statistical parameters used to evaluate the scatter in the data are the Fourth-Spread (F-spread), and fourth-pseudosigma (F-pseudosigma) (Hoaglin and others, 1983). These statistical values are indicative of the precision or repeatability of the results.

$$\text{F-spread} = (\text{upper fourth}) - (\text{lower fourth}), \quad (1)$$

The F-spread is the width of the middle half of a data set. In an ordered set of data, the upper fourth is defined as the value where 25 percent of the data are equal to or greater than that value. Similarly, the lower fourth is defined as that value where 25 percent of the data are equal to or lower than that value. The relative-percent F-spread (Hoaglin and others, 1983) for a given range of data is calculated by dividing the F-spread by the maximum value in the data range.

The F-pseudosigma (Hoaglin and others, 1983), is a resistant measure of spread analogous to the standard deviation. The F-pseudosigma is calculated by dividing the F-spread by 1.349 (see eq. 2); therefore, the smaller the F-pseudosigma the more precise the determination.

$$\text{F-pseudosigma} = \frac{\text{data F-spread}}{1.349} \quad (2)$$

F-spread and F-pseudosigma values are presented in table 4. Whereas table 3 presents the percentage of acceptable results for pH, specific conductance, and alkalinity measurements recorded by USGS personnel, the data in table 4 were calculated using all data reported by USGS, contractor, and cooperator personnel.

Table 4.--*F-spread and F-pseudosigma values for pH, specific conductance, and alkalinity determinations made by U.S. Geological Survey, contractor, and cooperator personnel, 1979-89*

[μS/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L as $CaCO_3$, milligrams per liter as calcium carbonate; <, less than; >, greater than]

Determination	Range	Number of samples	F-spread	Relative F-spread percent	F-pseudosigma
pH (units)	<4.0	1,854	0.11	2.8	0.08
	4.0-4.99	2,452	.09	1.8	.07
	5.0-5.99	4,369	.06	1.0	.04
	6.0-6.99	3,483	.03	0.4	.02
	7.0-7.99	4,312	.10	1.2	.07
	8.0-8.99	1,427	.21	2.3	.15
	>9.0	251	.25	2.8	.19
Specific conductance (μS/cm)	<100	2,804	6.3	6.3	4.7
	100-249	3,608	7.8	3.1	5.8
	250-499	3,619	12	2.3	8.9
	500-749	3,819	24	3.2	18
	750-999	2,148	31	3.1	23
	1,000-1,499	2,418	48	3.2	36
	1,500-3,199	1,327	152	4.8	113
Alkalinity (mg/L $CaCO_3$)	<50	936	2.8	5.5	2.1
	50-99	1,334	3.8	3.8	2.8
	100-149	1,285	5.0	3.3	3.7
	150-199	927	6.2	3.1	4.6
	200-249	364	9.1	3.7	6.8
	250-299	103	11	5.2	8.2
	300-399	239	14	3.6	10

pH

The F-spread statistics of more than 18,000 pH proficiency measurements made for the NFQA from 1979 through 1989 are summarized in figure 3. The data are summarized by pH range and by year. The proficiency samples with a pH less than 4.0 or a pH greater than 8.0 were discontinued in October 1985. The F-spreads of pH measurements and, therefore, the relative F-spread and F-pseudosigma, vary from year to year. For example, the F-spread in years 1984 and 1987 was zero for the pH range of 6.0 to 6.99 (fig. 3). No samples in that pH range were submitted for analyses in 1983.

The statistical summaries of the pH measurements, given in table 4 and shown in figure 3, indicate that the most precise measurement of pH was in the range 6.0 to 6.9. In that range, the F-pseudosigma is only 0.02 pH units. The weighted F-pseudosigma is 0.04 pH units for the entire pH range tested, from less than 4.0 to greater than 9.0 pH units. This indicates that the precision of the measurement of field pH is ± 0.04 pH units.

Specific Conductance

The F-spread statistics for almost 20,000 specific conductance proficiency measure-

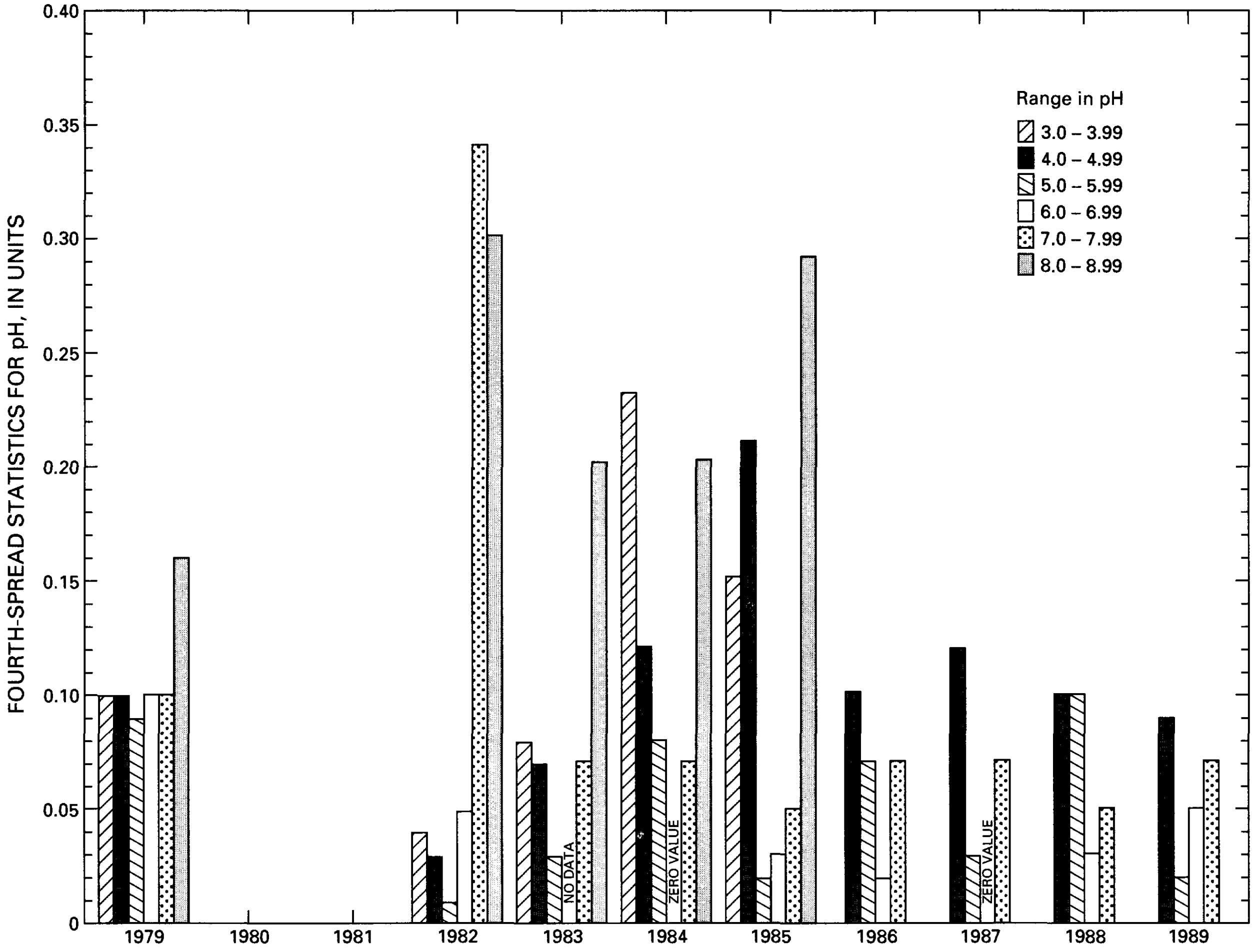


Figure 3.--Fourth-spread statistics for selected pH ranges, 1979-89.

ments made for the NFQA from 1979 through 1989 are summarized in figure 4. The data are summarized by year and by specific conductance range. Proficiency samples with a specific conductance greater than 1,500 µS/cm only were distributed in 1979 and 1982. The F-spread of the specific conductance measurements vary from year to year within a specific conductance range. Also, the seven specific conductance ranges shown in figure 4 have different F-spreads. The magnitude of the F-spread increases as the magnitude of the specific conductance ranges increases. In contrast, the relative F-spread percent remains nearly constant for the five specific conductance ranges covering the interval from greater than 100 µS/cm to 1,499 µS/cm (table 4).

Although the F-pseudosigma statistic is 8.9 µS/cm for the specific conductance range from 250 to 499 µS/cm (table 4), the relative F-spread of 2.3 percent indicates that measurements in this range are the most precise. Hem (1985) reports that the specific conductance of natural water can range from 50 to greater than 50,000 µS/cm, which is larger than the specific conductance range tested by the NFQA. Districts polled by the NFQA, indicated that most of the specific conductance values reported by the USGS range from 100 to 1,500 µS/cm. The average relative F-spread for specific conductance values ranging from 100 to 1,500 µS/cm is 3.0 percent compared to an average relative F-spread of 3.7 percent for all the reported specific conductance values.

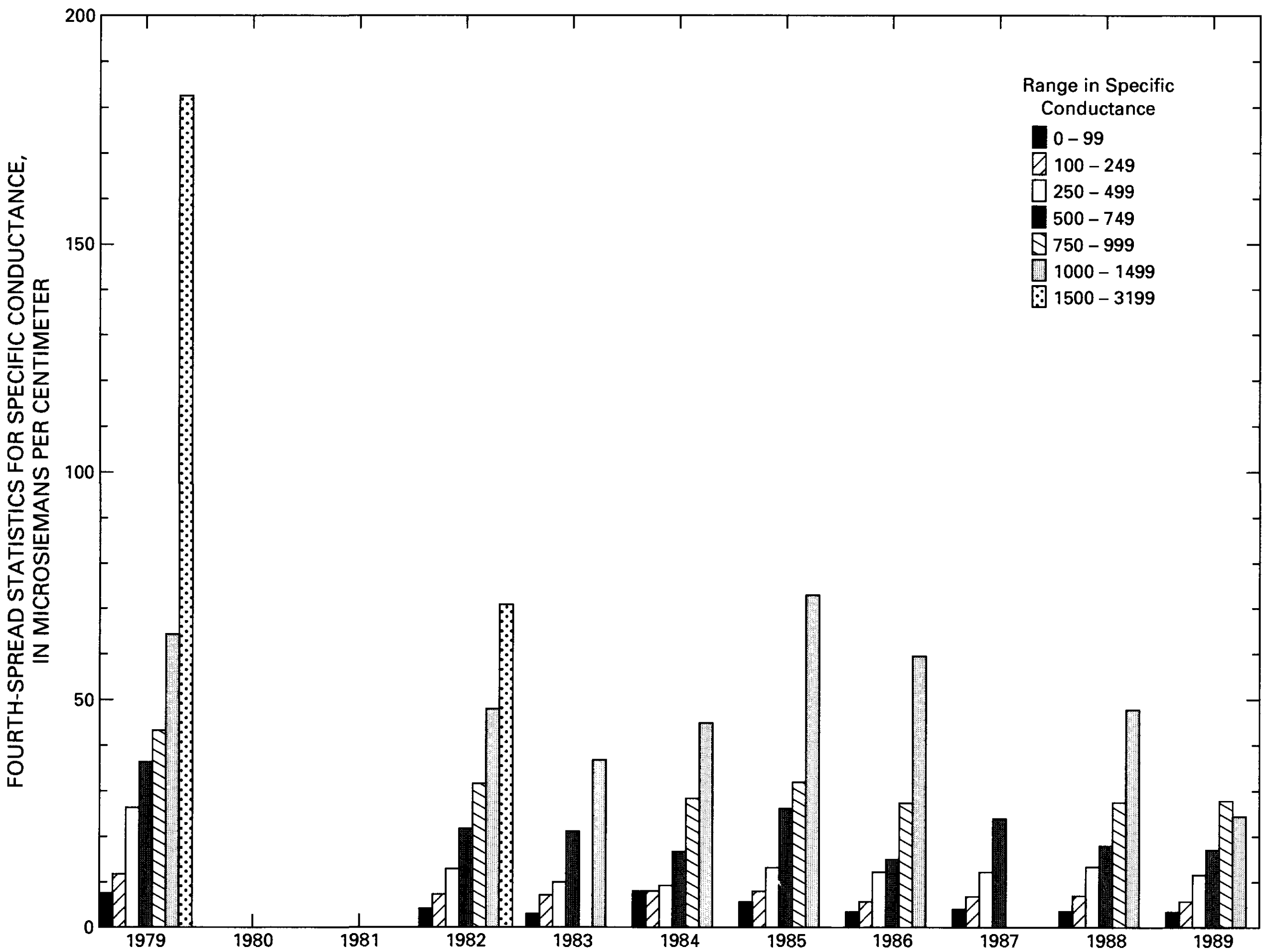


Figure 4.--Fourth-spread statistics for selected specific conductance ranges, 1979-89.

Hem (1985) states that carefully operated conductance instruments can measure specific conductance with a precision of ±2 to ±5 percent. The NFQA statistical evaluations infer that the measurement of specific conductance by district personnel is probably as precise as possible when using the conductance meters.

Alkalinity

Alkalinity measurements were added to the proficiency testing program in 1985 (table 3); therefore, the data set is smaller than either the pH or specific conductance data sets. The procedure used by USGS personnel to determine alkalinity is described by Fishman and Friedman (1989) and presents the option of performing a titration to a fixed end point of pH 4.5 or an incremental titration where the end point is that volume at which there occurs a maximum rate of change of pH per volume of titrant added. The results from either titration procedure are considered equivalent; and, for the purpose of this evaluation the results of the two methods were combined.

The F-spread statistics for almost 5,200 alkalinity measurements made for the NFQA, from 1979 through 1989, are summarized in figure 5. The data are further summarized by year and by alkalinity range. The proficiency samples with an alkalinity greater than 200 mg/L as calcium carbonate were discon-

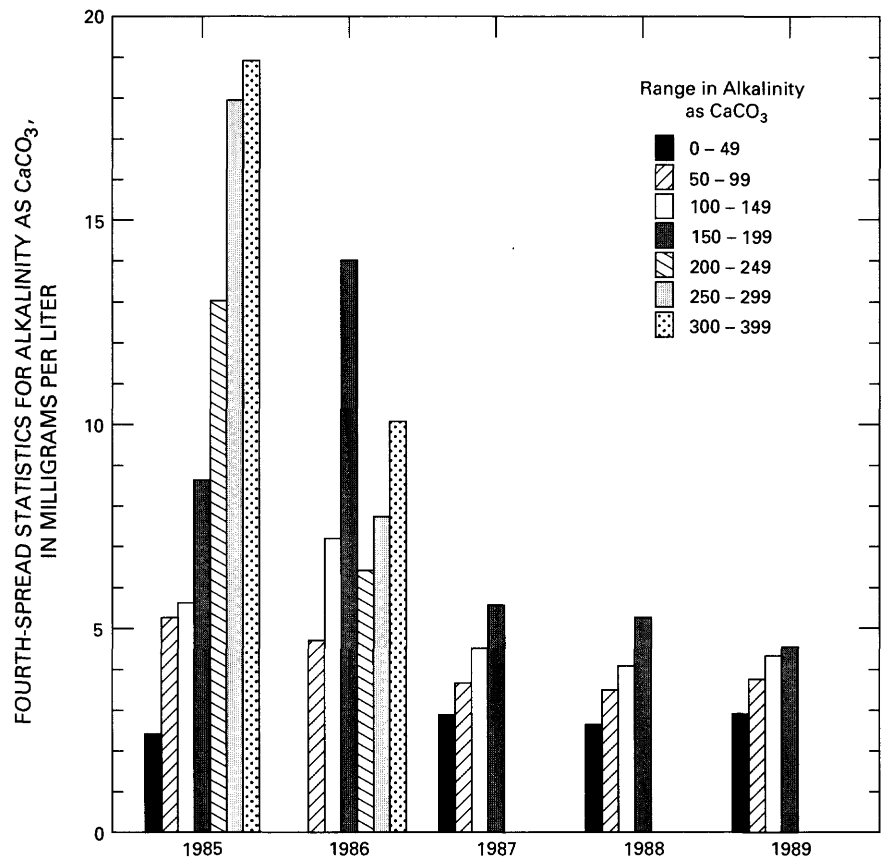


Figure 5--Fourth-spread statistics for selected alkalinity ranges, 1985-89.

tinued after 1986. For each of the four alkalinity ranges 0-49, 50-99, 100-149, and 150-199 mg/L as calcium carbonate, the F-spreads have remained nearly constant for 3 years (1987-89) (fig. 5). More than one-half of the alkalinity values reported were in the range from 50 to 149 mg/L as calcium carbonate (table 4). This range was tested more frequently because most natural waters have an alkalinity in this range. The weighted F-pseudosigma for the entire range of alkalinity measurements is 5.6 mg/L as calcium carbonate. Fishman and Friedman (1989) reported a weighted average relative standard deviation of about 10 percent for alkalinity values ranging from 56.7 to 316 mg/L as calcium carbonate. Therefore, the NFQA data infer that the field measurement of alkalinity proficiency samples is as precise as the laboratory determinations.

SUMMARY

In March 1979, the U.S. Geological Survey began the National Field Quality Assurance Program which is still operating today (1992). The program was designed to monitor the proficiency of U.S. Geological Survey field analysts. Initially, the program assessed the performance of pH and specific conductance measurements; alkalinity was added to the program in 1985.

The two specific objectives of the National Field Quality Assurance Program are to provide precision data for the field measurements and to identify field analysts who might need additional training. Proficiency samples are currently distributed annually to all individuals who determine pH, specific conductance, and alkalinity in the field. After the proficiency samples are analyzed and the results reported, a proficiency report is prepared by the NFQA manager and submitted to the appropriate U.S. Geological Survey offices for their review. The report contains satisfactory, marginal, or unsatisfactory ratings for the field analysts' measurement results. Since 1985, follow-up round of proficiency samples is sent to any field analyst receiving an unsatisfactory rating. A proficiency report for the follow-up round also is prepared and submitted to the participating offices for review and distribution to the field analysts.

Since 1979, almost 38,000 measurements of pH and specific conductance and almost 5,200 measurements of alkalinity have been made for the NFQA. The acceptance rate for all measurements has improved significantly since the inception of the program, but the acceptance rate seems to be nearly level for the past several years. Since 1986, measurements that are rated as acceptable average about 99 percent for pH, 92 percent for specific conductance, and 87 percent for alkalinity.

The relative F-spread and F-pseudosigma values, which are indicative of the precision or repeatability of the results, are small for the various value ranges. The relative F-spread ranged from 0.4 to 2.8 percent for pH, 2.3 to 6.3 percent for specific conductance, and 3.1 to 5.5 percent for alkalinity. The F-pseudosigma ranged from 0.02 to 0.19 units for pH, 4.7 to 113 μS/cm for specific conductance, and 2.1 to 10 mg/L as calcium carbonate for alkalinity.

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