M. J. Fishman

REPORT OF
ANALYTICAL EVALUATION PROGRAM
STANDARD REFERENCE WATER SAMPLES NUMBERS 16 AND 17

Standard Chemical Analysis

U. S. GEOLOGICAL SURVEY
WATER RESOURCES DIVISION
Denver, Colorado
1966

Contents

Standard Reference Water Samples Numbers 16 and 17

PURPOSE AND PLAN

In order to provide an independent and objective program for the statistical evaluation of the accuracy of analytical data published by Survey laboratories, standard reference water samples are prepared and distributed at regular intervals. This report summarizes the analytical data submitted by 23 laboratories for Standard Water Samples Nos. 16 and 17 distributed on October 18, 1965.

These samples differ from previous ones in that they are natural waters. Thus, they represent concentrations and conditions commonly found in many samples analyzed routinely by water quality laboratories throughout the country. Man can never duplicate nature with artificially prepared standards, and it is for this reason that this type of testing program was initiated. The preparation of natural standard samples presents certain problems but, with the preparation of these samples, a beginning has been made in determining their practicality and in eliminating some of the problems.

Water samples collected in conventional containers may change in chemical composition during storage. Such changes, when observed, may be attributed to photosynthetic action of algae, nitrogen-fixing bacteria, other bacteria such as sulfate-reducing and iron-devouring organisms, precipitation, ion adsorption, contamination, and gaseous exchange between sample and atmosphere. Alkalinity and pH values are especially subject to alteration by the latter factor.

Sterilization by ultraviolet radiation was investigated as a means of preserving samples against chemical changes due to photosynthetic and bacteriological action. Four-mil polyethylene bags which transmit about 30-40% of the incident UV light were selected for packaging. Tests proved that heat sealing samples in these bags and exposing them to UV light destroyed all living organisms present.

There has been concern over the porosity of polyethylene film and the possibility of gaseous exchange. Thus far, no problems have been encountered. It has not been determined whether ion adsorption of trace elements will significantly alter stored samples. Other plastic films are currently under investigation.

The standard reference program, while evaluating the data and methods of individual laboratories, will at the same time aid greatly in determining the feasibility of indefinite storage of water samples by this method and the most practical containers for storage and shipping. Several samples in this series have been retained and will be analyzed periodically to accumulate further data and determine whether changes in chemical composition are actually taking place.

PREPARATION OF SAMPLES

Each sample was collected in bulk volume, filtered through a 0.45μ membrane filter into a 55-gallon drum and mixed with a motor driven stirrer for approximately twelve hours. Individual 1.5-liter portions were then withdrawn and heat-sealed in 4-mil thickness polyethylene bags. Each sample was then sterilized by exposure to ultraviolet (2537Å) radiation from a germicidal lamp. The sterilized sample was then sealed inside a second bag, and packaged for shipping.

Samples were selected at random and analyzed in duplicate at three different times over a period of about two months. None of the samples showed any change in concentration of the constituents and properties determined over the two-month period of storage.

The dissolved solids contents of samples 16 and 17 were approximately 150 and 55 ppm, respectively. While these represent fairly dilute waters, future samples will include waters containing higher concentrations of dissolved material, so that eventually standard reference water samples of a considerable range of concentrations of dissolved material will be available.

DETERMINATIONS

Detailed instructions for analysis and reporting of results were provided at the time the samples were shipped. The following determinations were requested for each sample: pH, alkalinity, specific conductance, silica, aluminum, iron, manganese, calcium, magnesium, sodium, potassium, sulfate, chloride, fluoride, nitrate, and phosphate. Each laboratory was requested to perform the pH and alkalinity determinations immediately after opening the sample container. The order for performing the other determinations was not specified. Each determination was performed in duplicate and each laboratory was requested to provide a copy of the analytical procedure, or a reference to the procedure if an unmodified published procedure was used. As in the past, participating laboratories are identified by code number only.

PARTICIPATING LABORATORIES

U. S. Geological Survey

Alabama, Tuscaloosa

Alaska, Palmer

California, Sacramento

Colorado, Denver

D. C., Washington

Florida, Ocala

Louisiana, Baton Rouge

Nebraska, Lincoln

New Mexico, Albuquerque

New York, Albany

North Carolina, Raleigh

Ohio, Columbus

Oklahoma, Oklahoma City

Oregon, Portland

Pennsylvania, Philadelphia

Puerto Rico, San Juan

Texas, Austin

Utah, Salt Lake City

Wyoming, Worland

Other

Kansas, Topeka, State Department of Health, Sanitary Engineering Lab

North Dakota, Bismarck, State Laboratories Department

Ohio, Cincinnati, U. S. Public Health Service, Water Quality Section

Wyoming, Laramie, State Department of Agriculture

MATHEMATICAL TREATMENT OF DATA

Since these samples are natural waters rather than synthetic standards, the true value of each of the various constituents and properties measured is not known. However, a reliable estimate of the true value can be obtained by a statistical and mathematical evaluation of the analytical data supplied by many laboratories, each analyzing the sample independently.

In the process of data analysis and evaluation, the following terms and definitions are used:

N -- The number of observations on which the calculations are based.

Mean ($\bar{X}$) -- The average or measure of the central tendency obtained by adding the replicate results and dividing by the number of those results.

$$\bar{X} = \frac{X_1 + X_2 + \cdots + X_N}{N} \tag{1}$$

Deviation (x_i) -- The difference between a measurement and the mean.

$$x_i = X_i - \bar{X} \tag{2}$$

Percent Deviation from the Mean -- The percent difference between a measurement and the mean.

$$\% \text{ Deviation} = \frac{x_i}{\bar{X}} \times 100 \tag{3}$$

Average Deviation ($\bar{x}$) -- The average of the individual deviations, taken without regard to sign.

$$\bar{x} = \frac{|x_1| + |x_2| + \cdots + |x_N|}{N} \tag{4}$$

Average Percent Deviation -- The average of the individual percent deviations from the mean.

Standard Deviation (s) -- The calculated standard deviation; the best estimate of the true standard deviation (σ) that may be made from a finite set of measurements.

$$s = \sqrt{\frac{x_1^2 + x_2^2 + \cdots + x_N^2}{N-1}} \tag{5}$$

Total Range -- The difference between the highest and lowest value reported. In this report both extreme values are listed.

Most Probable Value (μ) -- The best estimate of the true value obtainable from available data;

$$\mu = \bar{X} \pm t \, (s/\sqrt{N}) \qquad (6)$$

where t is the distribution coefficient for N measurements at a given confidence level, obtainable from statistical tables.

Confidence Level -- The percentage probability that the true value (μ) lies within a given interval about the mean ($\bar{X}$). A confidence level of 90% is used in this report.

Confidence Interval -- The interval about the mean within which the true value may be expected to lie with a certain degree of confidence.

On examining the data it is obvious that several reported values are considerably in error. If the mean is to be a reliable estimate of the true value, those values which can be justifiably rejected should be omitted from the calculations. To determine whether any individual doubtful result could be omitted, the mean and average deviation for that constituent was calculated, omitting the most doubtful value. If the deviation of the doubtful value was then greater than 2.5 times the average deviation, the value was rejected from the set. This process was repeated until all extraneous values were rejected.

After eliminating discordant data, an attempt was made to establish the true value or most probable value from the available data. Assuming a normal distribution of values, standard deviations were calculated according to equation (5). This assumption is approximately true in all cases except for the reported values for Al, Fe, Mn, NO_3, PO_4, and Cl on sample no. 17, in which cases the concentrations are extremely low and the methods used obviously lack the sensitivity needed for these very low concentrations. In these cases, neither the standard deviations nor the confidence limits about the mean could be calculated.

The mean, the average deviation, and the total range were calculated for each determination. The average percent deviation and the percent deviation from the mean were calculated for each determination except for those of very low concentrations where the ratio of deviation to mean made such calculations appear meaningless.

When possible, confidence limits about the mean were calculated from equation (6). There is a 90% probability that the true value lies within this interval.

RESULTS

Tabulated in Appendix A are the average results for each determination by individual laboratory code number. Many reported results are enclosed in brackets [ ] which indicate that they have been rejected from the calculations of the mean, average deviation, average percent deviation, standard deviation and most probable value for that determination. Only the total range was calculated using all reported results. The statistical values, when calculated, are shown at the bottom of the page for each determination.

Reported results for each determination are shown graphically in Appendix B. Each reported value and the frequency of occurrence of each value is shown.

The two tables in Appendix C summarize the results obtained in this analytical program. Since the actual concentrations of the constituents are unknown, the most reliable estimate of the true value can be obtained only after discarding those values which can justifiably be excluded from the set as pointed out in the previous section. The percentage of excluded or rejected results is shown for each determination.

Where possible, the percentage of laboratories that reported values within the 90% confidence interval is shown. The percentage of results falling within one standard deviation ($\bar{X} \pm s$), and within two standard deviations ($\bar{X} \pm 2s$) of the mean was calculated. These calculations are based only on the acceptable or unrejected values. Thus, many of the statements concerning accuracy and precision in the following sections are based not on the performance of all laboratories reporting, but rather on what may be expected under normal conditions assuming that the unrejected values alone represent the normal for water quality laboratories.

CONCLUSIONS

Silica

The high percentage of rejected values, 28 to 33%, indicates that many laboratories are not determining silica with satisfactory accuracy at concentration levels of less than 10 ppm. Assuming that the remaining values represent the typical silica determination, an accuracy of not more than ±0.2 ppm or 3 percent can be expected at such concentrations.

Aluminum, Iron, Manganese

No statistical quantities were calculated for these ions because of the extremely small concentrations present. However, it is apparent from the data that aluminum can probably be determined to within ±0.1 ppm, iron to within ±0.02 ppm, and manganese to within ±0.02 ppm. The comparatively low number of rejected values indicates that most laboratories determined these elements with satisfactory accuracy.

Calcium

Calcium was determined with satisfactory accuracy by most laboratories reporting. The lower percentage of rejected values for sample no. 17 indicates that some laboratories performed the determination better at the 11 ppm level than at 21 ppm. Indications are that it is possible to determine calcium to within an accuracy of from 3% to 5% over this concentration range.

Magnesium

Reported results for magnesium were somewhat less satisfactory than for calcium. This may be partially attributed to the fact that most laboratories determined magnesium by difference between the titrations for hardness and calcium. The fact that only 5 percent of the unrejected results for sample no. 17 fell within the range for most probable value is due to the clustering of data points on each side of the mean. No laboratory reported a value equal to the respective means of 6.9 and 3.3, probably because of the generally accepted practice of rounding off to even-numbered values. The high standard deviation indicates that the accuracy of this determination is probably not greater than ±0.4 ppm and accuracies of 5 to 10% may be expected in this concentration range.

Sodium

Sodium at the 19 ppm level was one of the most accurate analyses reported. The small range and absence of rejected values indicate that all laboratories determine this concentration to within ±1 ppm. At lower concentrations the accuracy is less satisfactory and some laboratories tend to report high values. Assuming that the unrejected values represent the best sodium analysis, the method may approach an accuracy of ±0.1 ppm, but is more likely in the order of ±0.2 ppm. The fact that only two laboratories reported the mean of 1.7 ppm reflects the practice of reporting even-numbered results, since values of 1.6 and 1.8 occurred in much greater abundance.

Potassium

The accuracy of the potassium determination is similar to that of sodium at low concentrations. Under carefully controlled conditions, an accuracy of ±0.1 ppm may be possible.

Bicarbonate

The wide range of reported results and the high percentage of rejected values indicate that many laboratories are not determining alkalinity with satisfactory accuracy. The abundance of 66 ppm and 68 ppm values for sample no. 16 reflects the tendency to report even rather than odd values. The deviations of the unrejected values indicate that, with care, an accuracy of ±1 ppm or 1 to 2% can be attained in the 40 to 70 ppm concentration range.

Sulfate

The sulfate determination is accurate to within ±2 ppm at the 33 ppm level. The low percentage of rejections indicates that most laboratories are determining concentrations of this magnitude satisfactorily. Fewer laboratories reported acceptable results at the 10 ppm level, but from these results, it appears that the precision and accuracy is about ±1 ppm.

Chloride

Chloride was determined satisfactorily by all laboratories at the 24 ppm level. The data and calculations indicate that the method is probably accurate to within ±1 ppm at this concentration. Chloride results below 1 ppm are less satisfactory, and it seems that, at best, a precision of about ±0.3 ppm is possible.

Fluoride

Results for fluoride indicate that the accuracy of this determination is within ±0.1 ppm at concentrations less than 1.0 ppm.

Nitrate and Phosphate

No attempt was made to define statistical quantities about the mean for these determinations because of the very low concentrations present. However, it is readily apparent from the data that nitrate cannot be determined to within ±0.1 ppm.

Specific Conductance

The wide range and high percentage of rejected values indicates that many laboratories are not determining specific conductance with a high degree of accuracy. Although the total range was as great as 20 micromhos, it seems probable from the acceptable values that an accuracy of ±2 micromhos should be attainable in this concentration range.

pH

There were relatively few rejected pH values, indicating that most laboratories perform this determination satisfactorily. Analysis of the data indicates that the reliability of the pH determination as routinely performed is probably no better than ±0.2 pH unit.

RECOMMENDATION

Each laboratory which reported a result for any determination which deviated considerably from the mean, especially those having rejected values, should examine its methods carefully to determine the source of error.

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APPENDIX A

Reported Results
Calculated Means and Measures of Dispersion

Silica (SiO_2)

Method	Percent deviation from mean	PPM SiO_2
USGS WSP 1454, D:34a-1	3.1	6.6
"	[9.4]	[5.8]
"	0.0	6.4
"	4.7	6.7
"	3.1	6.6
"	0.0	6.4
Colorimetric Molybdosilicate, APHA Standard Methods, 1960	[11]	[7.1]
USGS WSP 1454, D:34a-1	0.0	6.4
Not specified	3.1	6.2
USGS WSP-1454, D:34a-1	4.7	6.1
"	3.1	6.6
"	[9.4]	[7.0]
"	7.8	5.9
"	1.6	6.3
"	3.1	6.2
"	0.0	6.4
"	[20]	[5.1]
"	0.0	6.4
Not specified	[20]	[7.7]
Colorimetric Molybdosilicate, APHA, Standard Methods, 1960	[9.4]	[5.8]
USGS WSP-1454, D:34a-1	6.2	6.8

Total Range----------5.1-7.7
Mean ($\bar{X}$), PPM---------- 6.40
Standard Deviation(s), PPM- 0.24

Average Deviation($\bar{x}$), PPM-------0.17
Average Percent Deviation,%-----2.7
Most Probable Value (μ), PPM----6.40±0.11
(for 90% confidence level)

Aluminum (Al)

Method	PPM Al
USGS WSP-1454, D:3a-1	0.20
"	0.2
"	[0.0]
"	0.1
Eriochrome Cyanine RC	0.11
APHA Standard Methods, 10th edition, p. 38-40	0.10
Aluminon, APHA Standard Methods, 1960;	0.09
Not specified	0.2
USGS WSP-1454, D:3a-1	0.2
"	0.2
"	0.2
"	0.1
"	0.2
Not specified	0.2
Aluminon, APHA Standard Methods, 1960	0.05
USGS WSP-1454	0.2

Total Range----------0.0-0.2
Mean ($\bar{X}$), PPM---------- 0.16
Average Deviation ($\bar{x}$), PPM-------0.05
Most Probable Value(μ), PPM------0.16

Iron (Fe)

Method	PPM Fe
USGS WSP-1454, D:19a-1	0.01
Atomic Absorption, P.E. Model 303	.02
USGS WSP-1454, D:3a-1 and D:19a-1	.03
"	.01
" D:19a-1	[.05]
" "	.00
Phenanthroline, APHA Standard Methods, 1960	.00
USGS WSP-1454, D:19a-1	.01
Not specified	.02
USGS WSP-1454, D:3a-1	.01
" D:19a-1	.00
" "	.01
" D:3a-1	.01
"	.02
" D:19a-1	.01
"	.01
" "	.00
Phenanthroline, APHA Standard Methods, 1960	[.06]
USGS WSP-1454, D:19a-1	.00
Not specified	.02
Phenanthroline, APHA Standard Methods, 1960	[.06]
USGS WSP-1454	.00

Total Range----------0.00-0.06 Average Deviation($\bar{x}$), PPM-----0.01
Mean ($\bar{X}$), PPM---------- 0.01 Most Probable Value (μ), PPM--0.01

Manganese (Mn)

Method	PPM Mn
USGS WSP-1454, D:24a-2	0.00
Atomic Absorption, P.E. Model 303	.02
" "	.00
"	.00
" "	.03
Persulfate, APHA Standard Methods, 1960	[.04]
Not specified	.00
USGS WSP-1454, D:24a-1	.0
Atomic Absorption, P.E. Model 303	.00
USGS WSP-1454, D:24a-2	.01
"	.00
"	.02
Periodate, APHA Standard Methods, 1960	[.6]
Atomic Absorption	.00
Not specified	.02
Persulfate, APHA Standard Methods, 1960	.02
USGS WSP-1454	.00

Total Range----------0.00-0.6 Average Deviation ($\bar{x}$), PPM-----0.01
Mean ($\bar{X}$), PPM---------- 0.01 Most Probable Value (μ), PPM---0.01

Method	Percent deviation from mean	PPM Ca
USGS WSP-1454, D:8a-1, EDTA	[14]	[24]
"	4.8	22
Atomic Absorption, P.E. Model 303 and USGS WSP-1454, D:8a-2	4.8	22
USGS WSP-1454	4.8	20
Atomic Absorption	4.8	20
" , P.E. Model 303	4.8	20
USGS WSP-1454, D:8a-1, EDTA	4.8	20
" "	4.8	22
Not specified	4.8	20
USGS WSP-1454, D:8a-1, EDTA	0.0	21
"	0.0	21
" "	0.0	21
" "	4.8	20
"	4.8	22
"	0.0	21
" "	0.0	21
" "	0.0	21
USGS WSP-1454, D:8a-1, and Atomic Absorption	4.8	20
Not specified	[9.5]	[23]
APHA Standard Methods, 1960, EDTA	[14]	[24]
USGS WSP-1454	0.0	21
Not specified	[9.5]	[19]

Total Range----------19-24
Mean ($\bar{X}$), PPM---------- 20.8
Standard Deviation(s), PPM- 0.80

Average Deviation($\bar{x}$), PPM---------0.61
Average Percent Deviation,%-------2.9
Most Probable Value(μ), PPM-------20.8±0.3
(for 90% confidence level)

Magnesium (Mg)

Method	Percent deviation from mean	PPM Mg
USGS WSP-1454, D:23a-1	[25]	[5.2]
" "	1.4	7.0
Atomic Absorption, P.E. Model 303 and USGS WSP-1454, D:23a-1	[16]	[8.0]
USGS WSP-1454	8.7	7.5
Atomic Absorption	[16]	[8.0]
" , P.E. Model 303	1.4	6.8
USGS WSP-1454, D:23a-1	4.3	6.6
" "	1.4	6.8
Not specified	5.8	7.3
USGS WSP-1454, D:23a-1	7.2	7.4
"	2.9	6.7
" "	5.8	7.3
" "	[13]	[7.8]
"	8.7	6.3
"	2.9	6.7
" "	2.9	6.7
" "	2.9	6.7
USGS WSP-1454, D:23a-1, and Atomic Absorption	7.2	7.4
Not specified	8.7	6.3
APHA Standard Methods, 1960, Calc. by difference	4.3	6.6
USGS WSP-1454	4.3	7.2
Not specified	1.4	6.8

Total Range----------5.2-8.0
Mean ($\bar{X}$), PPM---------- 6.89
Standard Deviation(s), PPM-- 0.37

Average Deviation ($\bar{x}$), PPM-----0.32
Average Percent Deviation,%----4.6
Most Probable Value(μ), PPM----6.89±0.15
(for 90% confidence level)

Sodium (Na)

Method	Percent deviation from mean	PPM Na
Flame Photometric	5.3	18
Flame, Beckman Model B	0.0	19
Flame, Beckman Model DU	0.0	19
Flame, Beckman Model 4100	0.0	19
Flame Photometric	0.0	19
Atomic Absorption, P.E. Model 303	0.0	19
Flame Photometric	5.3	20
Atomic Absorption	5.3	20
Not specified	5.3	18
Flame, Beckman Model B	0.0	19
Flame Photometric	5.3	18
Beckman Model 41 Direct Reading	0.0	19
Flame Photometric	0.0	19
"	5.3	18
"	0.0	19
Flame Photometry and Atomic Absorption	5.3	18
Not specified	0.0	19
Flame, Beckman Model B	5.3	18
Flame, Beckman Model DU	5.3	18
Not specified	5.3	18

Total Range----------18-20
Mean ($\bar{X}$), PPM---------- 18.7
Standard Deviation(s), PPM----- 0.73

Average Deviation ($\bar{x}$), PPM--------0.50
Average Percent Deviation,%--------2.6
Most Probable Value(μ), PPM-------18.7±0.3

Potassium (K)

Method	Percent deviation from mean	PPM K
Flame Photometric	12	1.5
Flame, Beckman Model B	5.9	1.8
Flame, Beckman Model DU	12	1.5
Flame, Beckman Model 4100	5.9	1.6
Flame Photometric	[53]	[2.6]
Atomic Absorption, P.E. Model 303	5.9	1.6
Flame Photometric	[35]	[2.3]
Atomic Absorption	5.9	1.6
Not specified	0.0	1.7
Flame, Beckman Model B	[18]	[2.0]
Flame Photometric	5.9	1.8
Beckman Model 41 direct reading	5.9	1.8
Flame Photometric	0.0	1.7
"	[24]	[1.3]
Atomic Absorption	0.0	1.7
Not specified	0.0	1.7
Flame, Beckman Model B	[35]	[2.3]
Flame, Beckman Model DU	5.9	1.8
Not specified	[41]	[2.4]

Total Range----------1.3-2.6
Mean ($\bar{X}$), PPM---------- 1.68
Standard Deviation(s), PPM-- 0.11

Average Deviation ($\bar{x}$), PPM-------0.08
Average Percent Deviation,%------5.0
Most Probable Value(μ), PPM------1.68±0.05
(for 90% confidence level)

Bicarbonate (HCO_3)

Method	Percent deviation from mean	PPM HCO_3
USGS WSP-1454, D:2a-1	1.5	66
"	0.0	67
"	1.5	68
"	1.5	66
"	1.5	68
"	1.5	68
"	[7.5]	[62]
"	1.5	68
Not specified	[6.0]	[63]
USGS WSP-1454, D:2a-1	1.5	68
"	1.5	68
"	1.5	66
"	4.5	64
"	[15]	[57]
"	1.5	68
"	0.0	67
"	1.5	68
"	0.0	67
"	1.5	66
Not specified	1.5	68
APHA Standard Methods, 1960, Methyl Orange Indicator	[13]	[76]
USGS WSP-1454, D:2a-1	1.5	66
Not specified	[21]	[53]

Total Range----------53-76
Mean ($\bar{X}$), PPM---------- 67.0
Standard Deviation(s), PPM-- 1.16

Average Deviation($\bar{x}$), PPM-------0.9
Average Percent Deviation,%-----1.4
Most Probable Value(μ), PPM-----67.0±0.5
(for 90% confidence level)

Sulfate (SO_4)

Method	Percent deviation from mean	PPM SO_4
Instrumental Thorin	3.0	32
USGS WSP-1454, D:38a-1	3.0	32
Instrumental Thorin	0.0	33
USGS WSP-1454, D:38a-2	3.0	34
Thorin	3.0	34
USGS WSP-1454, D:38a-2	0.0	33
" D:38a-3	3.0	32
" D:38a-2	3.0	34
Not specified	6.1	35
USGS WSP-1454, D:38a-2	6.1	35
"	3.0	32
" "	0.0	33
" "	[12]	[37]
"	6.1	35
"	[9.1]	[30]
" "	6.1	31
" D:38a-1	3.0	34
" D:38a-2	0.0	33
Not specified	3.0	34
Gravimetric, APHA Standard Methods, 1960	6.1	31
USGS WSP-1454	6.1	35
Not specified	6.1	35

Total Range----------30-37
Mean ($\overline{X}$), PPM---------- 33.4
Standard Deviation(s), PPM-- 1.40

Average Deviation ($\bar{x}$), PPM------1.2
Average Percent Deviation,%-----3.5
Most Probable Value(μ), PPM-----33.4±0.5
(for 90% confidence level)

Method	Percent deviation from mean	PPM Cl
Spectrophotometric Mercurimetric	8.3	22
USGS WSP-1454, D:10a-1	0.0	24
" "	0.0	24
" "	0.0	24
" "	0.0	24
Spectrophotometric Mercurimetric	4.2	23
USGS WSP-1454, D:10a-1	0.0	24
" "	0.0	24
Not specified	4.2	25
USGS WSP-1454, D:10a-1	4.2	23
" "	8.3	26
Mercurimetric	0.0	24
USGS WSP-1454, D:10a-1	0.0	24
" "	4.2	23
" "	8.3	26
" "	4.2	23
" "	0.0	24
Potentiometric, Ag-AgCl electrodes	8.3	22
Visual and Spectrophotometric Mercurimetric	0.0	24
Not specified	0.0	24
Mohr, APHA Std. Methods, 1960	4.2	25
USGS WSP-1454, D:10a-1	4.2	23
Not specified	8.3	22

Total Range----------22-26
Mean ($\bar{X}$), PPM---------- 23.8
Standard Deviation(s), PPM-- 1.11

Average Deviation($\bar{x}$), PPM-------0.7
Average Percent Deviation,%-----3.1
Most Probable Value(μ), PPM-----23.8±0.4
(for 90% confidence level)

Fluoride (F)

Method	Percent deviation from mean	PPM F
USGS WSP-1454, D:16a-1	14	0.6
" "	0.0	.7
" "	14	.8
" D:16a-2	14	.8
"	14	.6
" D:16a-1	0.0	.7
Spadns Method, APHA Standard Methods, 1960	0.0	.7
USGS WSP-1454, D:16a-1	14	.6
Not specified	14	.6
USGS WSP-1454, D:16a-1	14	.8
"	14	.6
" "	0.0	.7
" "	14	.8
"	[43]	[1.0]
"	0.0	.7
" "	14	.8
Spadns Method, APHA Standard Methods, 1960, p. 130-131	0.0	.7
USGS WSP-1454, D:16a-1	14	.8
Not specified	14	.6
Scott-Sanchis Method, APHA Standard Methods, 1960,	14	.6
USGS WSP-1454	0.0	.7
Not specified	14	.6

Total Range----------0.6-1.0
Mean ($\bar{X}$), PPM---------- 0.69
Standard Deviation(s), PPM--- 0.08

Average Deviation($\bar{x}$), PPM-------0.07
Average Percent Deviation,%-----9.3
Most Probable Value(μ), PPM-----0.69+0.03
(for 90% confidence level)

Nitrate (NO_3)

Method	PPM NO_3
USGS WSP-1454, D:25b-1	0.0
" "	0.2
" "	0.1
" "	0.0
" "	0.1
Hydrazine-Reduction	0.0
USGS WSP-1454, D:25b-1	0.3
" "	0.0
Not specified	0.1
USGS WSP-1454, D:25b-1	0.2
" "	0.1
" "	0.2
" "	0.2
" "	0.2
" "	0.0
" "	0.0
" "	[1.5]
" "	0.3
Not specified	0.1
Phenyldisulfonic Acid, APHA Standard Methods, 1960	[0.8]
USGS WSP-1454, D:25b-1	0.2

Total Range----------0.0-1.5 Average Deviation($\bar{x}$), PPM-------.08
Mean ($\bar{X}$), PPM---------- .12 Most Probable Value(μ), PPM-----0.12

Phosphate (ortho) (PO_4)

Method	PPM PO_4
USGS WSP-1454, D:31a-1	0.00
" "	.00
" "	.00
" "	.00
USGS Proposed Method, March 1964	.00
$SnCl_2$ Method, APHA Standard Methods, 1960	.00
USGS WSP-1454, D:31a-1	.00
Not specified	.00
USGS WSP-1454, D:31a-1	.00
" "	.02
" "	.00
" "	.0
" "	.0
" "	.00
" "	[.10]
USGS Proposed Method, March 1964	.00
Not specified	.01
$SnCl_2$ Method, APHA Standard Methods, 1960	[.06]
USGS WSP-1454, D:31a-1	.00
Not specified	[<.1]

Total Range----------0.00-0.1 Average Deviation($\bar{x}$), PPM-------0.00

Mean ($\bar{X}$), PPM---------- 0.00 Most Probable Value(μ), PPM-----0.00

Method	Specific conductance: Percent deviation from mean	Specific conductance: Sp.cond. µmhos
Not specified	0.4	262
"	[5.0]	[274]
Serfass Conductivity Bridge RCM15B1, USGS WSP-1454, D:37a-1	[3.8]	[271]
USGS WSP-1454, D:37a-1	0.8	259
Not specified	0.4	262
Wheatstone Bridge USGS Mod., WSP-1454, D:37a-1	0.8	263
USGS WSP-1454, D:37a-1	1.1	264
Not specified	0.4	262
"	0.4	262
USGS WSP-1454, D:37a-1	0.4	260
" "	0.4	262
Not specified	0.4	260
USGS WSP-1454, D:37a-1	[2.3]	[267]
" "	0.0	261
" " , Ind. Instruments, Solu Bridge RD-R104	[1.9]	[256]
" "	0.0	261
" "	1.1	264
" "	1.1	258
Not specified	0.4	262
Industrial Instruments Bridge	[2.3]	[255]
USGS WSP-1454, D:37a-1	[2.7]	[268]
Not specified	[5.4]	[275]

Total Range----------255-275
Mean ($\bar{X}$), µmhos---------- 261.4
Standard Deviations(s)µmhos- 1.71

Average Deviation($\bar{x}$), µmhos------1.4
Average Percent Deviation,%------0.5
Most Probable Value(µ) µmhos-----261.4±0.7
(for 90% confidence level)

pH Sample No. 16

Method	Percent deviation from mean	pH	Code No.	Date Mo., Yr.
USGS WSP-1454, D:2a-1	3.8	8.1	001	12-65
"	2.6	8.0	002	11-65
"	0.0	7.8	003	11-65
"	3.8	7.5	004	12-65
"	2.6	8.0	005	11-65
"	2.6	8.0	006	11-65
" D:29a-1	[6.4]	[7.3]	007	11-65
" D:2a-1	5.1	7.4	008	11-65
Not specified	1.3	7.7	009	12-65
USGS WSP-1454, D:2a-1	3.8	8.1	012	11-65
"	0.0	7.8	013	10-65
"	3.8	7.5	015	10-65
"	5.1	7.4	016	11-65
"	[12]	[6.9]	017	11-65
" D:29a-1	0.0	7.8	018	11-65
" D:2a-1	2.6	8.0	019	11-65
"	0.0	7.8	021	11-65
"	0.0	7.8	024	12-65
" D:29a-1	0.0	7.8	025	11-65
Not specified	0.0	7.8	026	11-65
APHA Standard Methods , 1960	3.8	8.1	027	11-65
USGS WSP-1454	[10]	[7.0]	028	11-65
Not specified	0.0	7.8	030	11-65

Total Range----------6.9-8.1
Mean ($\bar{X}$)---------- 7.81
Standard Deviation(s)------ 0.22

Average Deviation ($\bar{x}$)------- 0.16
Average Percent Deviation--- 2.0
Most Probable Value (μ)-----7.81± 0.09
(for 90% confidence level)

Silica (SiO_2)

Method	Percent deviation from mean	PPM SiO_2
Same as reported analyses for Sample No. 16 except as specified.	0.0	5.4
	[9.3]	[4.9]
	3.7	5.6
	5.6	5.7
	[11]	[6.0]
	3.7	5.2
	7.4	5.8
	3.7	5.2
	0.0	5.4
	5.6	5.1
	1.9	5.3
	7.4	5.8
	3.7	5.2
	1.9	5.3
	1.9	5.3
	[15]	[4.6]
	[17]	[4.5]
	1.9	5.5
	[20]	[6.5]
	[17]	[4.5]
	5.6	5.7

Total Range----------4.5-6.5
Mean ($\bar{X}$), PPM---------- 5.43
Standard Deviation(s), PPM-- 0.24

Average Deviation(x), PPM-------0.19
Average Percent Deviation,%-----3.6
Most Probable Value(μ), PPM-----5.43±0.11
(for 90% confidence level)

Aluminum (Al)

Method	PPM Al
Same as reported analyses for Sample No. 16 except as specified.	0.06
	.1
	.0
	.0
	.01
	.00
	.00
	.0
	.1
	.1
	.0
	.0
	.1
	.0
	.00
	.0

Total Range----------0.0-0.1 Average Deviation($\bar{x}$), PPM------0.03
Mean ($\bar{X}$), PPM---------- 0.03 Most Probable Value(μ), PPM-----0.03

Method	PPM Fe
Same as reported analyses for Sample No. 16 except as specified.	0.01
	.02
	.02
	.01
	.03
	.02
	.01
	.02
	.02
	.01
	.01
	.02
	.01
	.03
	.01
	.03
	.00
	[.11]
	.02
	.00
	.04
	.00

Total Range----------0.00-0.11 Average Deviation($\bar{x}$), PPM-------0.01
Mean ($\bar{X}$), PPM 0.02 Most Probable Value(μ), PPM-----0.02

Method	PPM Mn
USGS WSP-1454, D:24a-1	0.00
	.02
	.00
All other methods same as reported analyses for Sample No. 16 except as specified.	.00
	.03
	.03
	.00
	.0
	.00
	.02
	.00
	.02
	[.4]
	.00
	.01
	[.06]
	.00

Total Range----------0.0-0.4 Average Deviation($\bar{x}$), PPM-------0.01
Mean ($\bar{X}$), PPM---------- 0.01 Most Probable Value(μ), PPM-----0.01

Calcium (Ca)

Method	Percent deviation from mean	PPM Ca
Same as reported analyses for Sample No. 16 except as specified.	[27]	[14]
	9.1	12
	9.1	12
	0.0	11
	0.0	11
	9.1	10
	9.1	12
	9.1	12
	0.0	11
	0.0	11
	9.1	12
	0.0	11
	0.0	11
	9.1	10
	0.0	11
	0.0	11
	9.1	10
	9.1	10
	9.1	12
	9.1	12
	9.1	10
	9.1	10

Total Range----------10-14
Mean ($\bar{X}$), PPM---------- 11.0
Standard Deviation(s), PPM------- 0.81

Average Deviation($\bar{x}$), PPM-------0.62
Average Percent Deviation,%-----5.6
Most Probable Value(μ), PPM-----11.0±0.3
(for 90% confidence level)

Magnesium (Mg)

Method	Percent deviation from mean	PPM Mg
Same as reported analyses for Sample No. 16 except as specified.	[42]	[1.9]
	12	2.9
	9.1	3.0
	9.1	3.6
	3.0	3.2
	6.1	3.1
	9.1	3.0
	6.1	3.1
	9.1	3.6
	6.1	3.5
	18	2.7
	9.1	3.6
	3.0	3.4
	[30]	[4.3]
	9.1	3.0
	9.1	3.0
	[30]	[4.3]
	12	3.7
	12	2.9
	3.0	3.4
	15	3.8
	3.0	3.4

Total Range----------1.9-4.3
Mean ($\bar{X}$), PPM---------- 3.26
Standard Deviation(s), PPM-------- 0.32

Average Deviation ($\bar{x}$), PPM-----0.28
Average Percent Deviation,%----8.6
Most Probable Value(μ), PPM----3.26±0.13
(for 90% confidence level)

Sodium (Na)

Method	Percent deviation from mean	PPM Na
Same as reported analyses for Sample No. 16 except as specified.	12	1.5
	5.9	1.6
	5.9	1.8
	5.9	1.8
	[47]	[2.5]
	5.9	1.6
	18	1.4
	[47]	[2.5]
	5.9	1.6
	5.9	1.8
	5.9	1.6
	5.9	1.8
	0.0	1.7
	0.0	1.7
	[35]	[2.3]
	5.9	1.6
	5.9	1.8
	[82]	[3.1]
	18	2.0
	[24]	[1.3]

Total Range----------1.3-3.1
Mean ($\bar{X}$), PPM---------- 1.69
Standard Deviation(s), PPM-- 0.15

Average Deviation($\bar{x}$), PPM-------0.12
Average Percent Deviation,%-----7.1
Most Probable Value(μ), PPM-----1.69±0.07
(for 90% confidence level)

Method	Potassium (K) Percent deviation from mean	PPM K
Same as reported analyses for Sample No. 16 except as specified.	33	0.4
	0.0	0.6
	33	0.8
	17	0.5
	[100]	[1.2]
	17	0.5
	0.0	0.6
	17	0.5
	0.0	0.6
	0.0	0.6
	17	0.5
	33	0.4
	17	0.5
	33	0.8
	0.0	0.6
	0.0	0.6
	0.0	0.6
	17	0.7
	0.0	0.6

Total Range----------0.4-1.2
Mean ($\bar{X}$), PPM---------- 0.58
Standard Deviation(s), PPM-- 0.11

Average Deviation ($\bar{x}$), PPM---------0.08
Average Percent Deviation,%---------13.0
Most Probable Value(μ), PPM---------0.58±0.05
(for 90% confidence level)

Bicarbonate (HCO_3)

Method	Percent deviation from mean	PPM HCO_3)
Same as reported analyses for Sample No. 16 except as specified.	[7.0]	[40]
	0.0	43
	2.3	44
	0.0	43
	2.3	44
	0.0	43
	2.3	42
	0.0	43
	0.0	43
	0.0	43
	2.3	42
	2.3	44
	[4.7]	[41]
	[9.3]	[39]
	2.3	44
	0.0	43
	2.3	44
	2.3	42
	2.3	42
	2.3	44
	[12]	[48]
	2.3	42
	[16]	[36]

Total Range----------36-48
Mean ($\bar{X}$), PPM---------- 43.1
Standard Deviation(s), PPM-- 0.80

Average Deviation($\bar{x}$), PPM------0.61
Average Percent Deviation,%----1.4
Most Probable Value(μ), PPM----43.1±0.3
(for 90% confidence level)

Sulfate (SO_4)

Method	Percent deviation from mean	PPM SO_4
Same as reported analyses for Sample No. 16 except as specified.	0.0	10
	2.0	9.8
	6.0	9.4
	10	11
	0.0	10
	0.0	10
	2.0	9.8
	10	11
	0.0	10
	10	11
	[14]	[8.6]
	2.0	9.8
	10	11
	10	11
	8.0	9.2
	[16]	[8.4]
	[30]	[13]
	3.0	9.7
	0.0	10
	[24]	[7.6]
	[20]	[12]
	10	9.0

Total Range----------7.6-13
Mean ($\bar{X}$), PPM---------- 10.1
Standard Deviation(s), PPM-- 0.71

Average Deviation(x), PPM-------0.47
Average Percent Deviation,%-----4.7
Most Probable Value(μ), PPM-----10.1±0.30
(for 90% confidence level)

Chloride (Cl)

Method	PPM Cl
Same as reported analyses for Sample No. 16 except as specified.	0.5
	0.2
	0.0
	0.1
	0.0
	0.4
	0.0
	0.4
	0.2
	0.0
	0.6
	0.3
Visual Mercurimetric	0.5
	[1.0]
	[2.2]
	0.4
	0.1
	0.0
	0.4
	0.4
	[1.5]
	0.3
	[<1.0]

Total Range----------0.0-2.2
Mean ($\bar{X}$), PPM---------- 0.25
Average Deviation($\bar{x}$), PPM-------0.17
Most Probable Value(μ), PPM-----0.25

Fluoride (F)

Method	Percent deviation from mean	PPM F
Same as reported analyses for Sample No. 16 except as specified.	50	0.2
	0	0.4
	25	0.5
	25	0.5
	0	0.4
	25	0.3
	25	0.3
	25	0.3
	25	0.3
	0	0.4
	0	0.4
	25	0.3
	0	0.4
	25	0.5
	25	0.3
	25	0.5
	0	0.4
	0	0.4
	50	0.6
	25	0.3
	0	0.4
	0	0.4

Total Range----------0.2-0.6
Mean ($\bar{X}$), PPM---------- 0.39
Standard Deviation(s), PPM-- 0.10

Average Deviation($\bar{x}$), PPM-----0.07
Average Percent Deviation,%---17
Most Probable Value(μ), PPM---0.39±0.03
(for 90% confidence level)

Nitrate (NO_3)

Method	PPM NO_3
	0.0
	0.4
	0.1
	0.1
	0.1
	0.5
	0.0
	0.4
	0.1
	0.3
	0.3
	0.5
	0.2
	0.4
	0.2
	0.0
	[0.7]
	0.4
	0.2
	[0.9]
	0.3

Total Range----------0.0-0.9
Mean ($\bar{X}$), PPM---------- 0.24
Average Deviation($\bar{x}$), PPM--------0.14
Most Probable Value(μ), PPM------0.24

Phosphate (ortho) (PO_4)

Method	PPM PO_4
Same as reported analyses for Sample No. 16 except as specified	0.00
	.00
	.00
	.00
	.00
	.00
	.00
	.00
	.03
	.00
	.00
	.00
	.0
	.0
	.01
	.00
	.02
	[.04]
	[.12]
	.00
	[<.1]

Total Range----------0.0-0.12 Average Deviation($\bar{x}$), PPM-----0.00
Mean ($\bar{X}$), PPM---------- 0.00 Most Probable Value(μ), PPM---0.00

Specific Conductance

Method	Percent deviation from mean	Sp.Cond. µmhos
Same as reported analyses for Sample No. 16 except as specified.	1.1	95
	[4.3]	[98]
	[3.2]	[97]
	1.1	93
	1.1	93
	0.0	94
	[5.3]	[99]
	1.1	95
	[9.6]	[85]
	1.1	93
	1.1	93
	1.1	93
	[3.2]	[97]
	2.1	92
	[9.6]	[85]
	1.1	93
	0.0	94
	1.1	95
	0.0	94
	0.0	94
	1.1	95
	2.1	96
	[7.4]	[101]

Total Range----------85-101
Mean ($\bar{X}$), µmhos---------- 93.9
Standard Deviation(s), µmhos---------- 1.10
Average Deviation($\bar{x}$), µmhos-----0.88
Average Percent Deviation,%----1.0
Most Probable Value(µ), µmhos--93.9±0.5
(for 90% confidence level)

pH Sample No. 17

Method	Percent deviation from mean	pH	Code No.	Date Mo., Yr.
Same as reported analyses for Sample No. 16 except as specified.	1.3	7.6	001	12-65
	1.3	7.6	002	12-65
	1.3	7.4	003	11-65
	[5.3]	[7.1]	004	12-65
	4.0	7.8	005	11-65
	1.3	7.6	006	11-65
	1.3	7.6	007	11-65
	[6.7]	[7.0]	008	11-65
	1.3	7.4	009	12-65
	2.7	7.7	012	11-65
	4.0	7.8	013	10-65
	[9.3]	[6.8]	015	10-65
	4.0	7.2	016	11-65
	1.3	7.4	017	11-65
	2.7	7.3	018	11-65
	0.0	7.5	019	11-65
	2.7	7.3	021	11-65
	0.0	7.5	024	12-65
	1.3	7.6	025	11-65
	1.3	7.6	026	11-65
	4.0	7.8	027	11-65
	[11]	[6.7]	028	11-65
	1.3	7.6	030	11-65

Total Range----------6.7-7.8
Mean ($\bar{X}$),---------- 7.54
Standard Deviation(s),------ 0.18

Average Deviation($\bar{x}$),-------0.15
Average Percent Deviation,%-2.0
Most Probable Value(μ)------7.54±0.07
(for 90% confidence level)

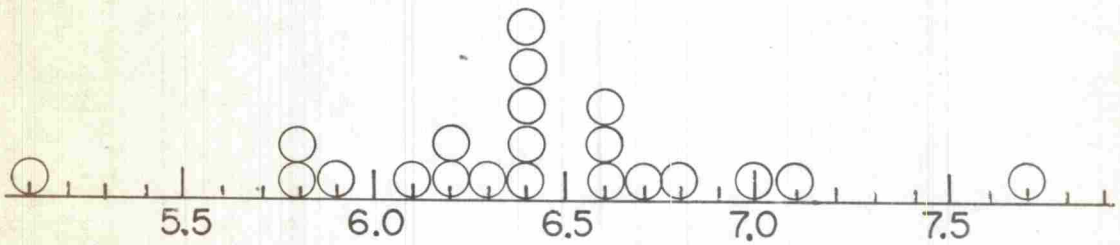
M. J. Fishman

REPORT OF
ANALYTICAL EVALUATION PROGRAM
STANDARD REFERENCE WATER SAMPLES NUMBERS 16 AND 17

APPENDIX B

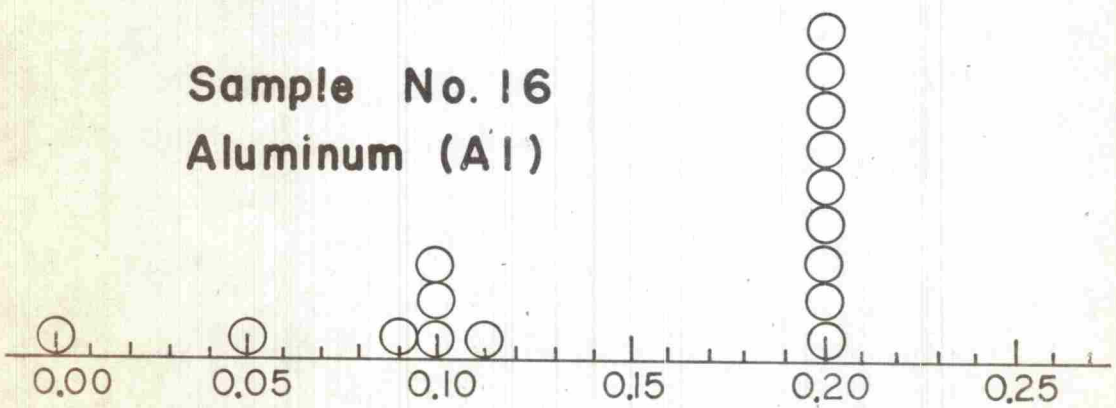
Graphical Presentation of Data

Sample No. 16
Silica (SiO_2)



Silica concentration, ppm

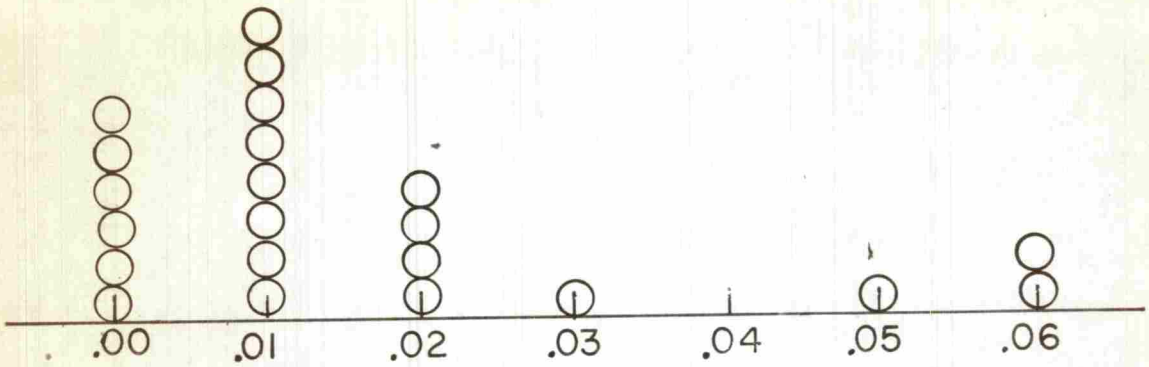
Sample No. 16
Aluminum (Al)



Aluminum concentration, ppm

Sample No. 16

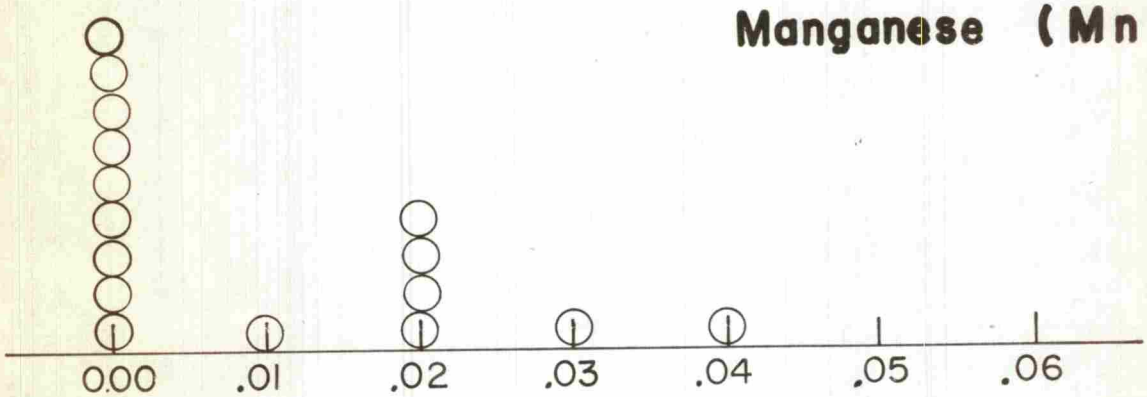
Iron (Fe)



Iron concentration, ppm

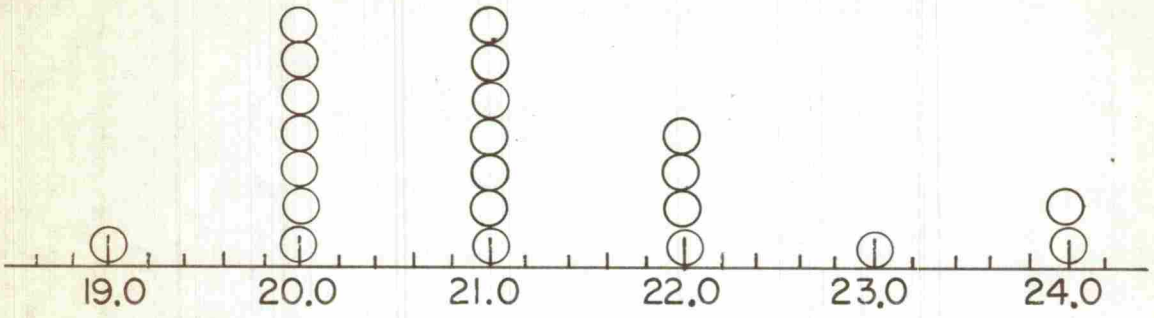
Sample No. 16

Manganese (Mn)



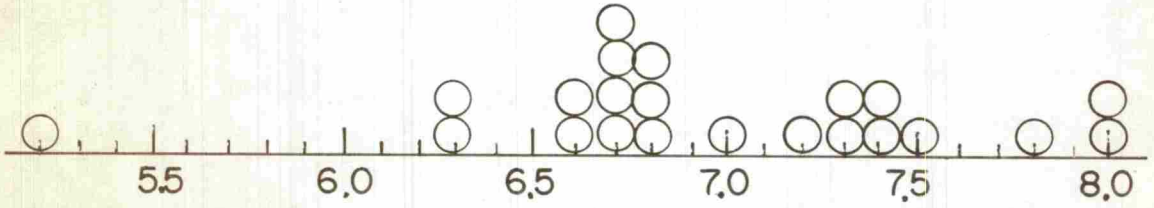
Manganese concentration, ppm

Sample No. 16
Calcium (Ca)



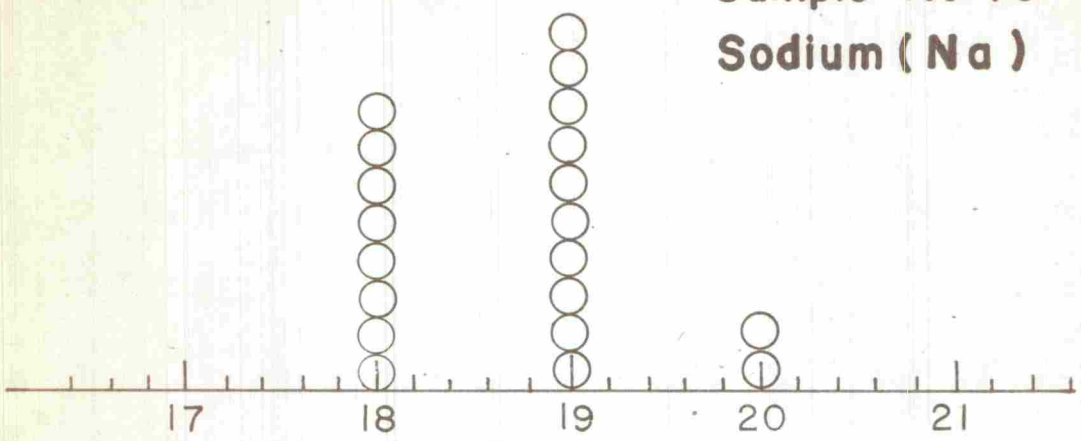
Calcium concentration, ppm

Sample No. 16
Magnesium (Mg)



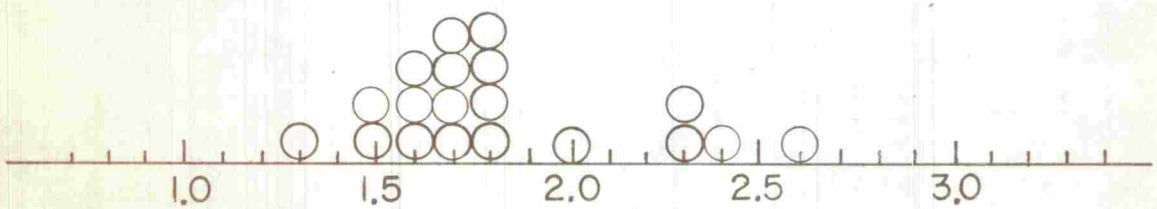
Magnesium concentration, ppm

Sample No 16
Sodium (Na)



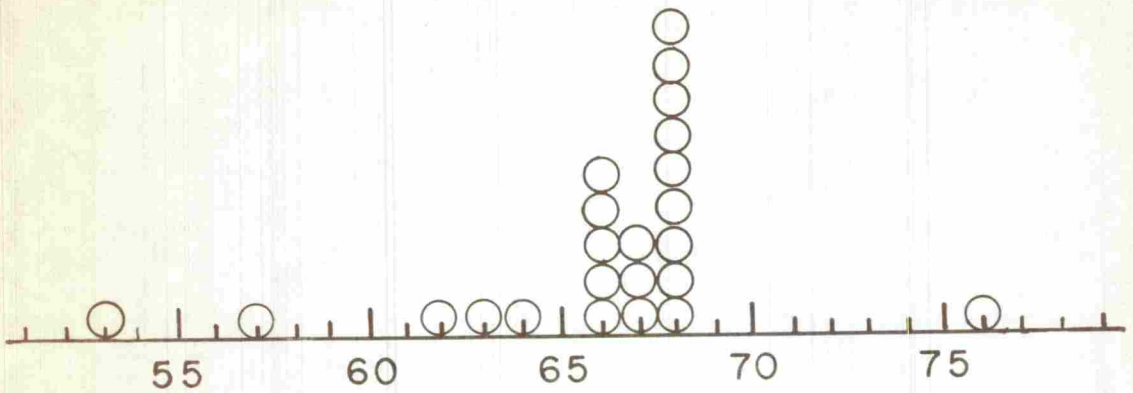
Sodium concentration, ppm

Sample No. 16
Potassium (K)



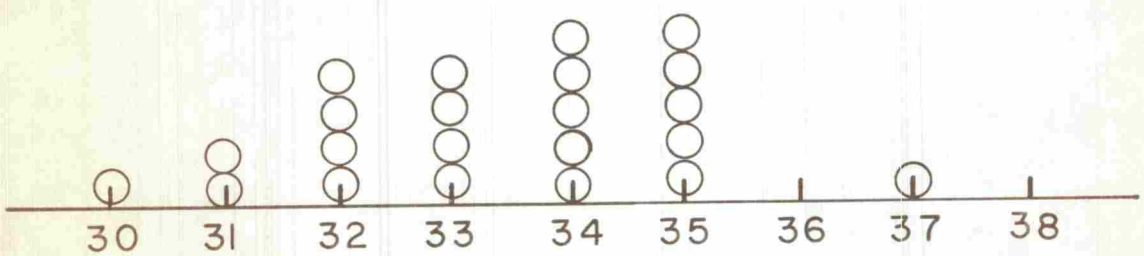
Potassium concentration, ppm

Sample No. 16
Bicarbonate (HCO_3)



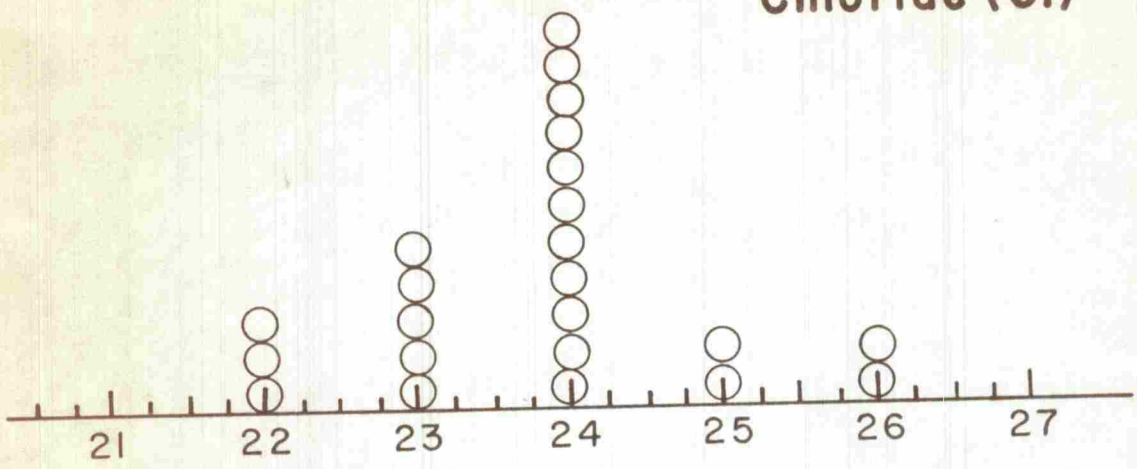
Bicarbonate concentration, ppm

Sample No. 16
Sulfate (SO4)



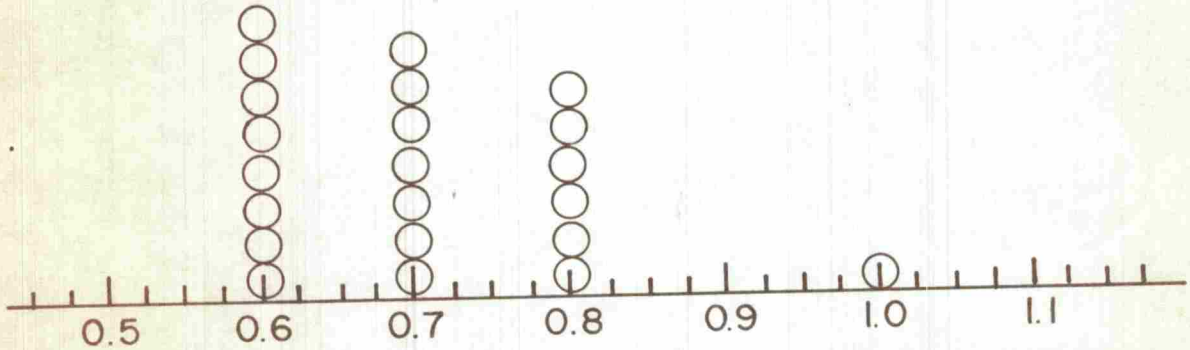
Sulfate concentration, ppm

Sample No. 16
Chloride (Cl)



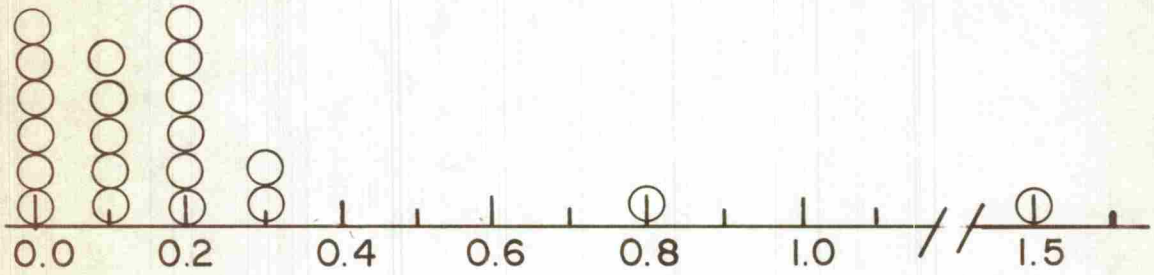
Chloride concentration, ppm

Sample No. 16
Fluoride (F)



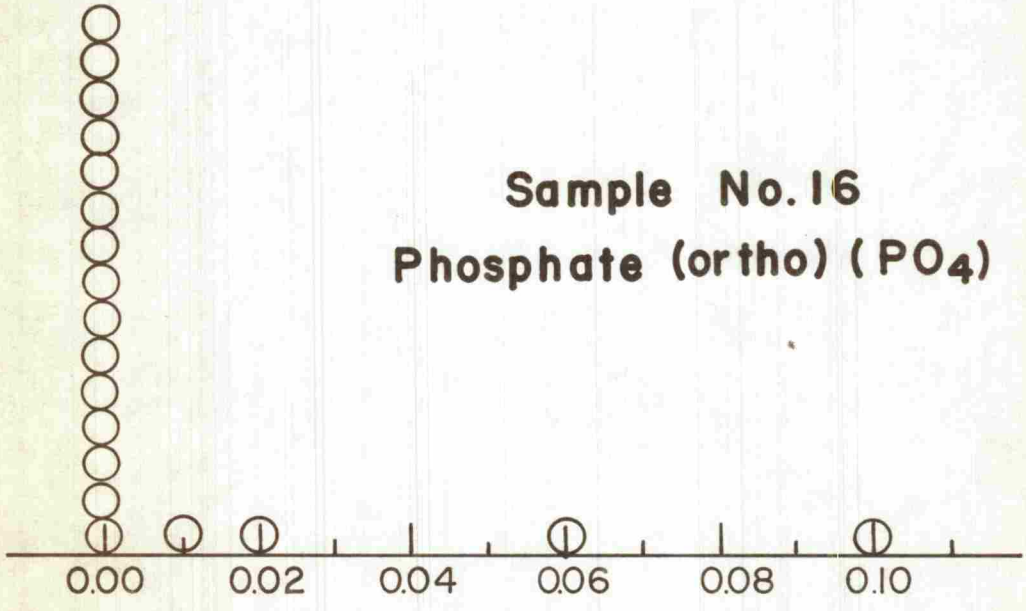
Fluoride concentration, ppm

Sample No. 16
Nitrate (NO_3)



Nitrate concentration, ppm

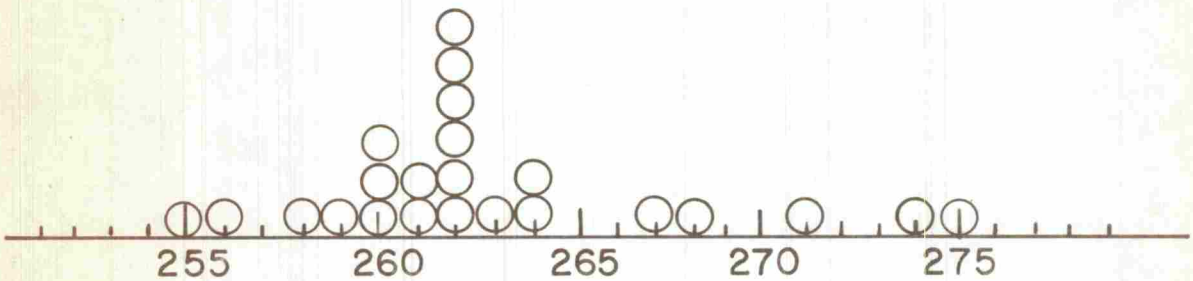
Sample No. 16
Phosphate (ortho) (PO_4)



Phosphate (ortho) concentration, ppm

Sample No. 16

Specific conductance



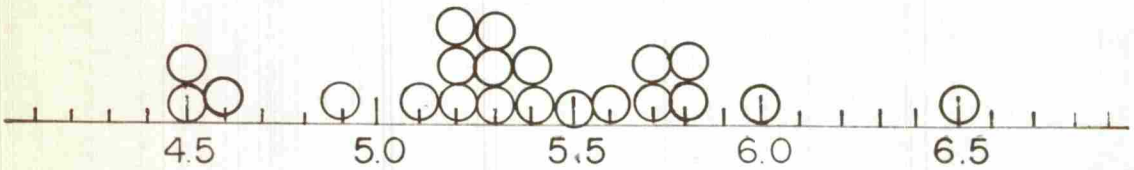
Specific conductance, micromhos (25°C)

Sample No. 16

pH

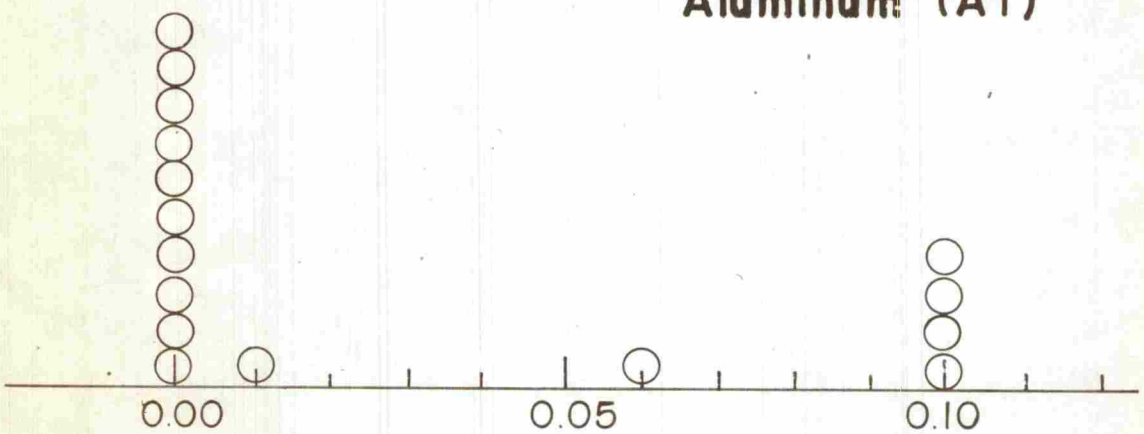
pH

Sample No. 17
Silica (SiO_2)



Silica concentration, ppm

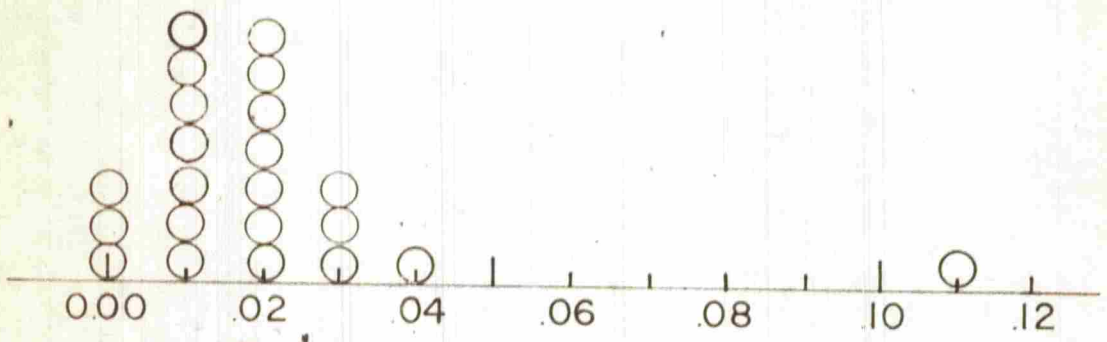
Sample No. 17
Aluminum (Al)



Aluminum concentration, ppm

Sample No 17

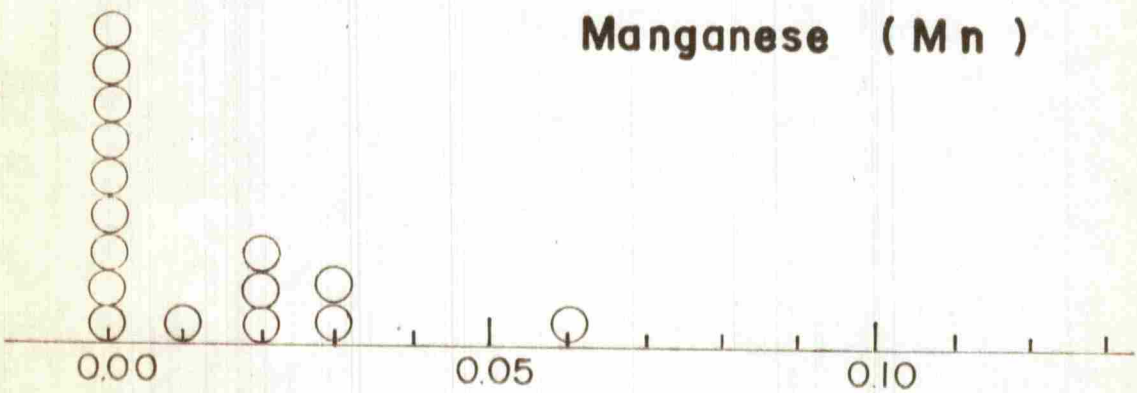
Iron(Fe)



Iron concentration, ppm

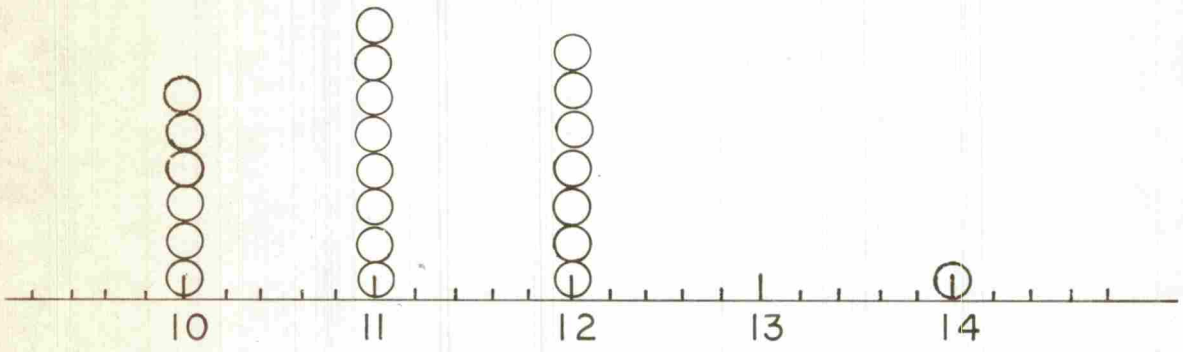
Sample No. 17

Manganese (Mn)



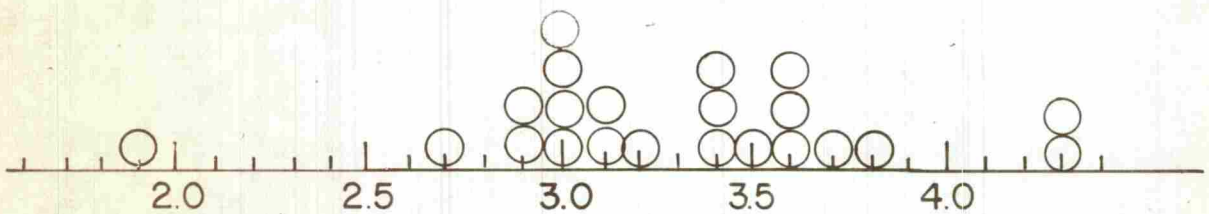
Manganese concentration, ppm

Sample No. 17
Calcium (Ca)



Calcium concentration, ppm

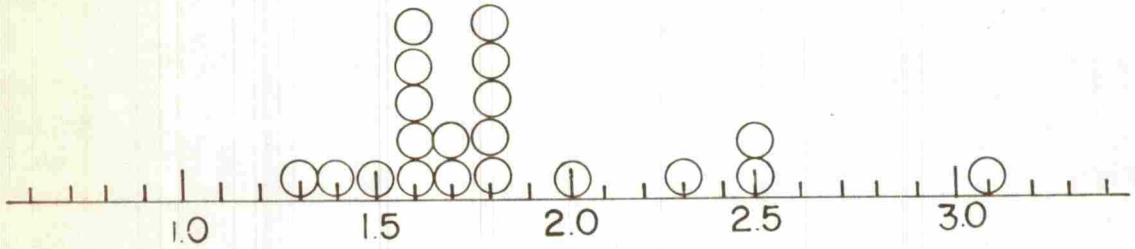
Sample No. 17
Magnesium (Mg)



Magnesium concentration, ppm

Sample No 17

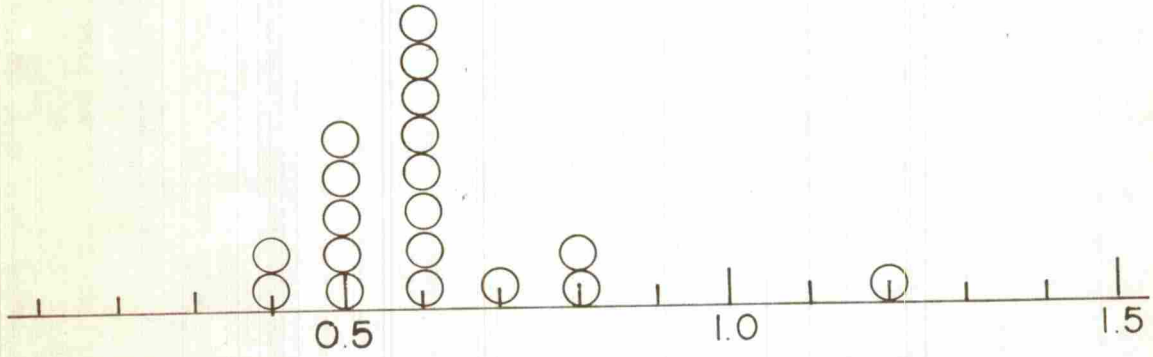
Sodium (Na)



Sodium concentration, ppm

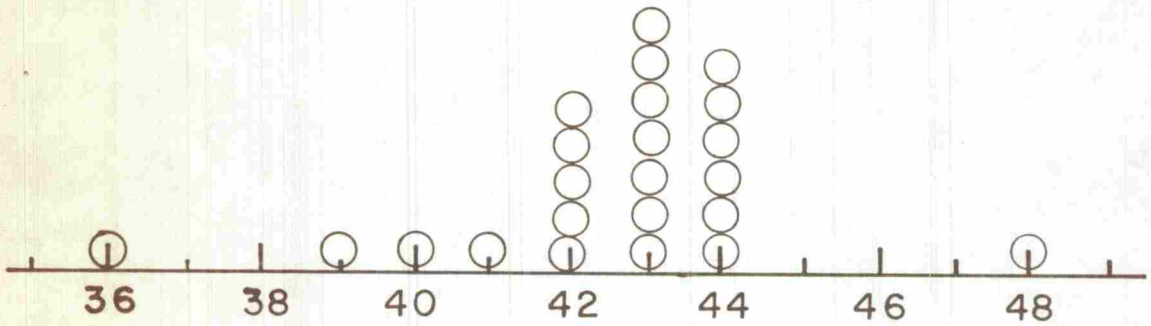
Sample No. 17

Potassium (K)



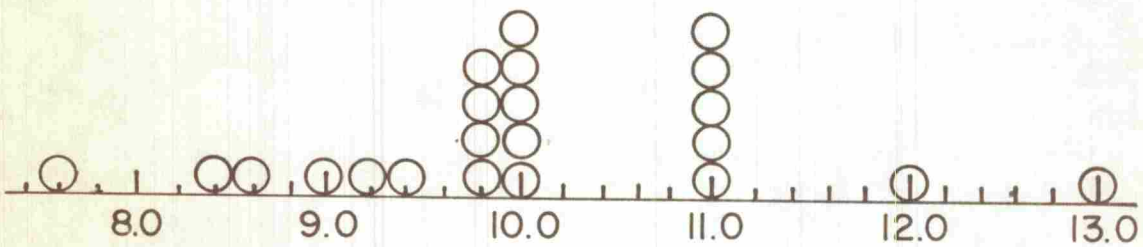
Potassium concentration, ppm

Sample No. 17
Bicarbonate (HCO_3)



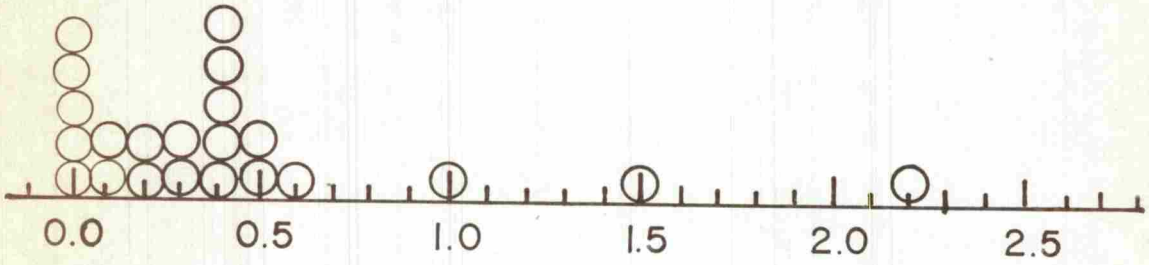
Bicarbonate concentration, ppm

Sample No. 17
Sulfate (SO4)



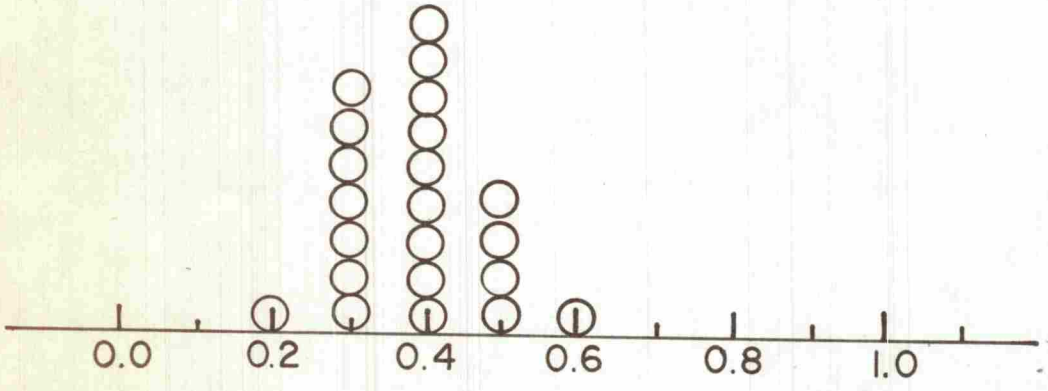
Sulfate concentration, ppm

Sample No. 17
Chloride (Cl)



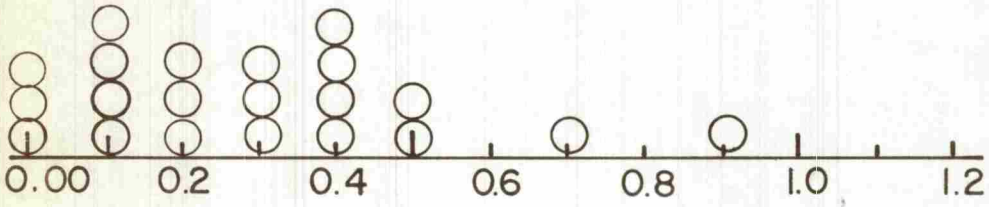
Chloride concentration, ppm

Sample No. 17
Fluoride (F)



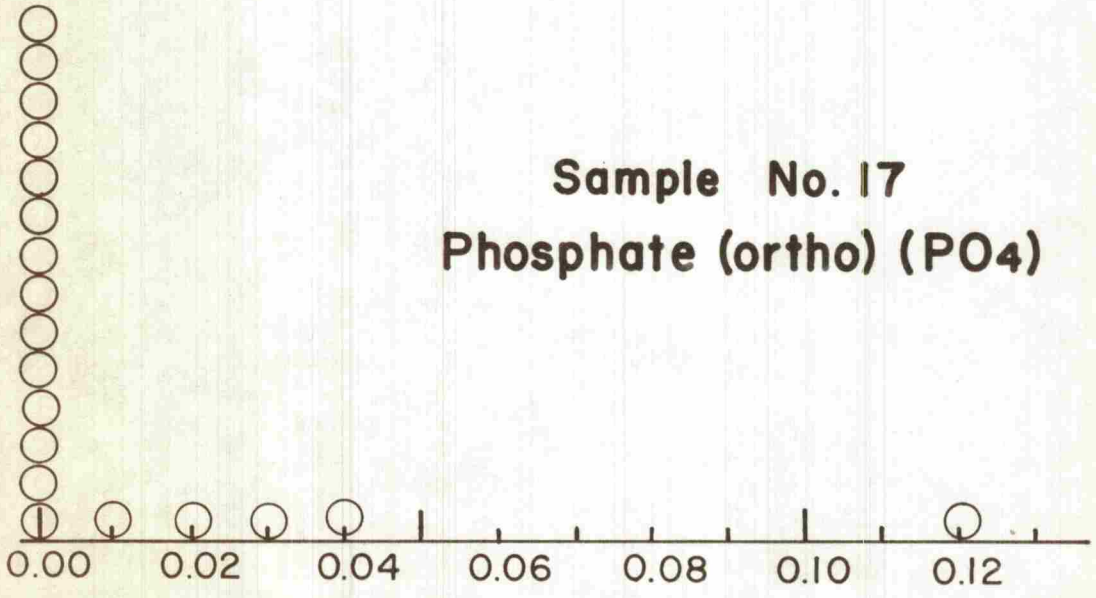
Fluoride concentration, ppm

Sample No. 17
Nitrate (NO_3)



Nitrate concentration, ppm

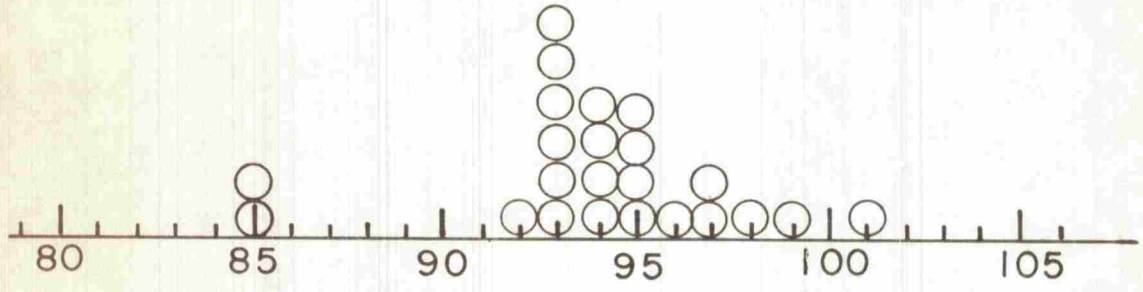
Sample No. 17
Phosphate (ortho) (PO_4)



Phosphate (ortho) concentration, ppm

Sample No. 17

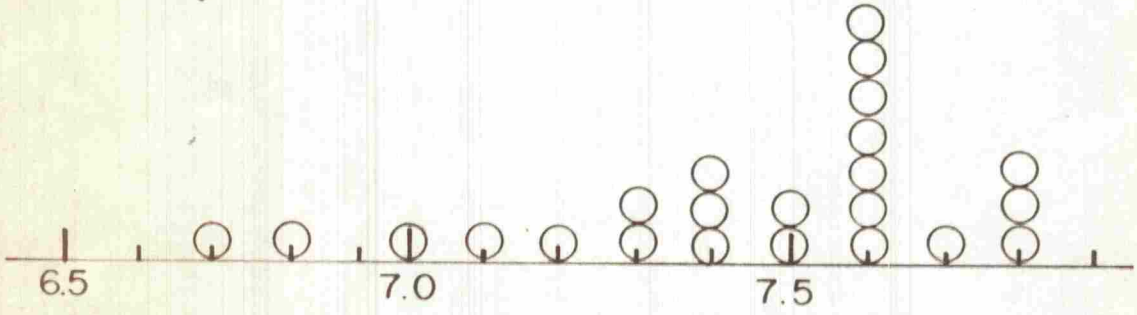
Specific conductance



Specific conductance, micromhos (25°C)

Sample No. 17

pH



pH

M. J. Fishman

REPORT OF

ANALYTICAL EVALUATION PROGRAM

STANDARD REFERENCE WATER SAMPLES NUMBERS 16 AND 17

APPENDIX C

Laboratories reporting

Percentage of rejected values

Percentage distribution about the mean

STANDARD SAMPLE NUMBER 16

Determination	Number of labs reporting	Percentage of values rejected	Percentage of unrejected values lying within:		
			90% CI	$\bar{X} \pm s$	$\bar{X} \pm 2s$
SiO_2	21	33	43	79	100
Al	16	6	--	--	--
Fe	22	14	--	--	--
Mn	17	12	--	--	--
Ca	22	18	39	78	100
Mg	22	18	22	61	100
Na	20	0	50	90	100
K	19	32	31	54	100
HCO_3	23	22	17	94	94
SO_4	22	9	20	65	100
Cl	23	0	48	70	100
F	22	4	33	33	100
NO_3	21	10	--	--	--
PO_4	20	15	--	--	--
Specific Conductance	23	30	50	75	100
pH	23	13	40	65	100

STANDARD SAMPLE NUMBER 17

Determination	Number of labs reporting	Percentage of values rejected	Percentage of unrejected values lying within:		
			90% CI	$\bar{X} \pm s$	$\bar{X} \pm 2s$
SiO_2	21	28	20	67	100
Al	16	0	--	--	--
Fe	22	4	--	--	--
Mn	17	12	--	--	--
Ca	22	4	38	38	100
Mg	22	14	5	58	100
Na	20	25	13	80	93
K	19	5	44	72	100
HCO_3	23	22	39	39	100
SO_4	22	23	53	59	100
Cl	23	17	--	--	--
F	22	0	41	73	96
NO_3	21	10	--	--	--
PO_4	20	15	--	--	--
Specific Conductance	23	30	25	87	100
pH	23	17	47	68	100