M. J. Fishman

REPORT OF
ANALYTICAL EVALUATION PROGRAM
STANDARD WATER SAMPLES NUMBERS 1 and 2

Calcium, Magnesium
Sodium, Potassium
Chloride, Sulfate

U. S. GEOLOGICAL SURVEY
WATER RESOURCES DIVISION
Quality of Water Branch
Denver, Colorado
1962

CONTENTS

4) Each sample in a series will be analyzed for two or more constituents as specified.

5) Sufficient sample will be provided to allow for rinsing of equipment and determination of each constituent in duplicate. Standard forms will be provided for reporting the results of the individual determinations and their average.

6) The analysis of each series should normally be completed and a report submitted within 15 days of receipt of the samples.

7) Each participating laboratory will be identified only by an assigned code number.

The first series of two standard water samples were prepared and distributed in September 1962. This report summarizes and evaluates the data submitted for these two samples identified as Standard Water Samples Nos. 1 and 2. The determinations made on these two samples included calcium, magnesium, sodium, potassium, chloride, and sulfate.

PREPARATION OF THE SAMPLES

Each sample was prepared from accurately weighed amounts of analytical reagent quality chemicals dissolved in an accurately measured volume of distilled water which had been further purified by passage through a mixed-bed exchanger. When necessary to affect solution of the reagent, a slight excess of reagent quality nitric acid was added to the sample.

The following compounds were used for the preparation of the samples:

$CaCO_3$	KCl
$MgSO_4 \cdot 7H_2O$	$NaHCO_3$
NaCl	

Concentrated stock solutions were prepared to contain the following concentrations of the substances indicated:

Stock solution 1A

Calcium (Ca)	1,932 ppm

Stock solution 1B

Magnesium (Mg)	596 ppm
Sodium (Na)	320 ppm
Potassium (K)	320 ppm
Chloride (Cl)	784 ppm
Sulfate (SO_4)	2,352 ppm

Stock solution 2A

Calcium (Ca)	640 ppm

Stock solution 2B

Magnesium (Mg)	120 ppm
Sodium (Na)	860 ppm
Potassium (K)	85 ppm
Chloride (Cl)	328 ppm
Sulfate (SO_4)	472 ppm

Individual 1-liter samples were prepared by taking 25.0 ml each of solutions 1A and 2A and diluting to exactly 1 liter. This comprised Standard Water Sample No. 1. Standard Water Sample No. 2 was prepared in a similar way by diluting 25.0-ml portions of stock solutions Nos. 2A and 2B to exactly 1 liter. The calculated concentrations of the two samples thus prepared were as follows:

	Standard Water Sample No. 1	Standard Water Sample No. 2
Calcium (Ca)	48 ppm	16 ppm
Magnesium (Mg)	15	3.0
Sodium (Na)	8.0	22
Potassium (K)	8.0	2.1
Chloride (Cl)	20	8.2
Sulfate SO_4)	59	12

After preparation, each sample was analyzed in duplicate at 5 different times over a period of about six weeks. The results of these analyses are given in the following table. Neither sample showed any change in the concentration of the substances determined over the period of storage.

Analysis by Preparations Lab[a/]

	Standard Water Sample No. 1	Standard Water Sample No. 2
Calcium (Ca)	49 ppm	16 ppm
Magnesium (Mg)	15	3.4
Sodium (Na)	8.4	22
Potassium (K)	7.1	1.7
Chloride (Cl)	22	9.5
Sulfate (SO_4)	59	13

a/ Each result represents the average of 5 duplicate determinations made over a period of about 6 weeks.

PARTICIPATING LABORATORIES

Alabama, Tuscaloosa

Alaska, Palmer

Arizona, Tucson

Arizona, Yuma

Arkansas, Little Rock

California, Menlo Park

California, Sacramento

Colorado, Denver

District of Columbia

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

REPORTED RESULTS: CALCIUM (ppm)

Code No.	Standard Sample No. 1				Standard Sample No. 2			
	(1)	(2)	(3)	Avge.	(1)	(2)	(3)	Avge.
101	48	48	--	48	16	16	--	16
102	48	48	--	48	16	16	--	16
103	48	48	--	48	16	16	--	16
104	47	48	--	47.5	16	16	--	16
105	48.6	48.4	--	48	16	16	--	16
106	48	48	--	48	16	15	--	15[b/]
107	47	47	--	47	16	16	--	16
108	--	--	--	--	--	--	--	--
109	22	22	--	22[a/]	16	16	--	16
110	48	48	--	48	16	16	--	16
111	47.5	48	--	48	16	16	--	16
112	49	49	--	49	16	16	--	16
113	48	48	--	48	17	16	--	16
114	--	--	--	--	--	--	--	--
115	50	50	48	49	16	16	--	16
116	49	49	--	49	16	16	--	16
117	50	49	--	50	16	16	--	16
118	48	47	--	48	15	15	--	15
119	50	50	--	50	18	17	--	18
120	49	51	--	50	17	17	--	17
121	50	49	--	50	16	16	--	16
122	48	48	--	48	16	16	--	16
123	48	50	--	49	16	18	--	17

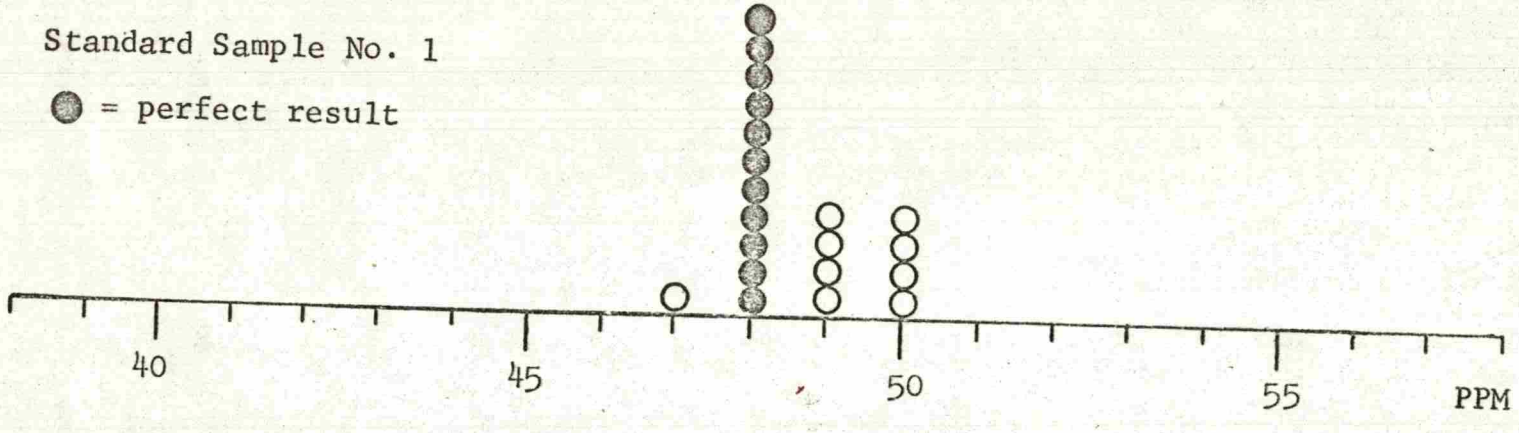
a/ Calculation error; later corrected by participating laboratory to 50 ppm.

b/ Should have been reported as 16 ppm.

CALCIUM

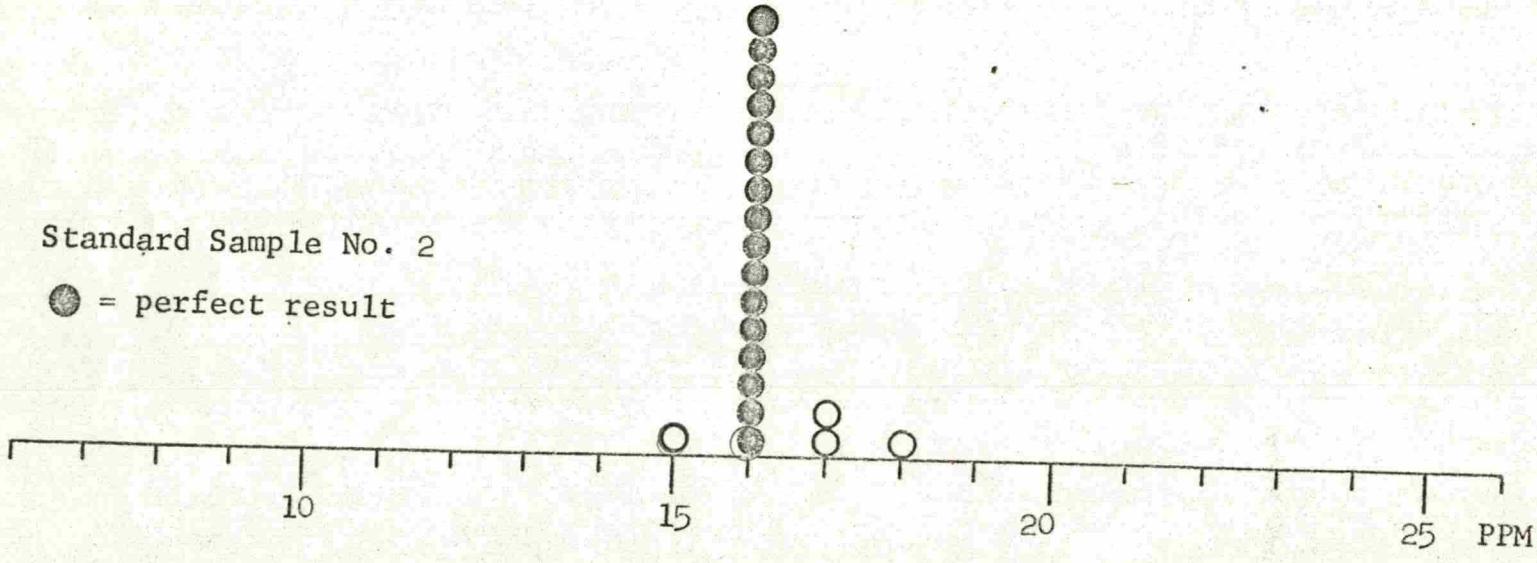
Standard Sample No. 1

● = perfect result



Standard Sample No. 2

● = perfect result



REPORTED RESULTS: MAGNESIUM (ppm)

Code No.	Standard Sample No. 1				Standard Sample No. 2			
	(1)	(2)	(3)	Avge.	(1)	(2)	(3)	Avge.
101	15	15	--	15	3.0	3.0	--	3.0
102	15	15	--	15	3.4	3.5	--	3.4
103	16	16	--	16	3.2	3.4	--	3.3
104	--	--	--	16	--	--	--	2.9
105	16.4	16.4	--	16	3.23	3.28	--	3.2
106	16	16	--	16	3.6	3.5	--	3.5
107	16	16	--	16	3.1	3.1	--	3.1
108	--	--	--	--	--	--	--	--
109	32	32	--	32[a/]	18	18	--	18[b/]
110	15	15	--	15	2.7	2.4	--	2.6
111	16.5	16.9	--	17	3.4	3.4	--	3.4
112	15	15	--	15	3.4	3.4	--	3.4
113	17	17	--	17	3.2	3.8	--	3.5
114	--	--	--	--	--	--	--	--
115	16	16	15	16	3.5	3.3	--	3.4
116	15	15	--	15	2.9	3.2	--	3.0
117	14	15	--	14	3.2	3.2	--	3.2
118	16	15	--	16	3.5	3.5	--	3.5
119	15	15	--	15	2.7	2.9	--	2.8
120	16	14	--	15	3.3	2.8	--	3.0
121	15	15	--	15	2.7	2.8	--	2.8
122	16	16	--	16	3.2	3.2	--	3.2
123	15	15	--	15	2.8	3.2	--	3.0

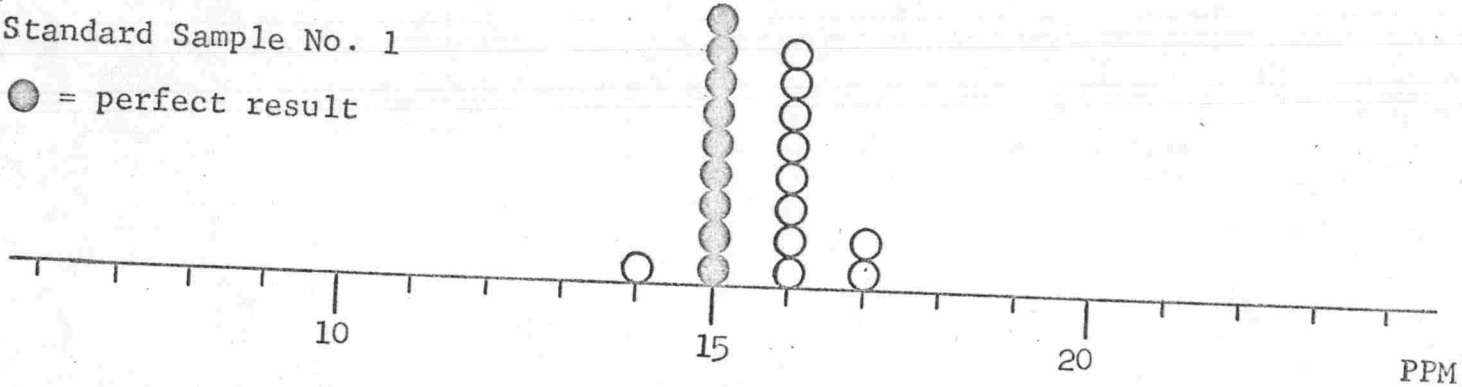
a/ Calculation error; later corrected to 15 ppm.

b/ Calculation error; later corrected to 3.4 ppm.

MAGNESIUM

Standard Sample No. 1

● = perfect result



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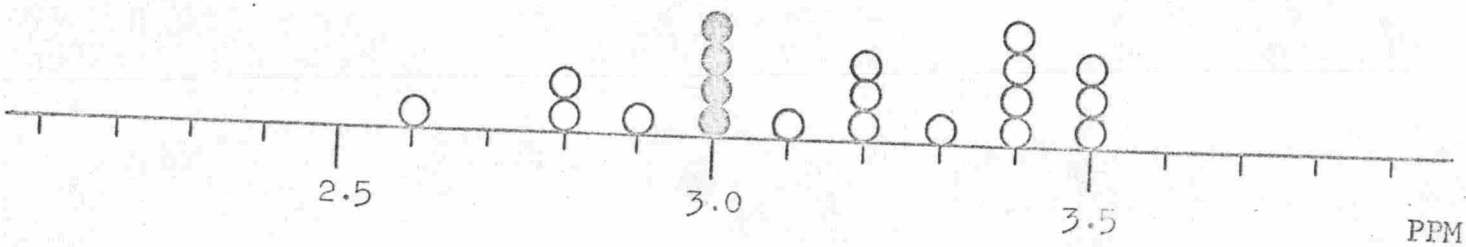
Standard Sample No. 2

● = perfect result



Methods used: Calcium (Ca) and Magnesium (Mg)

Lab.	Calcium (Ca)	Modifications	Magnesium (Mg)	Modifications
101	D:8a-1	None	D:17a-1; D:23a-1	None
102	"	"	Titan yellow	"
103	"	Na_2 EDTA: 1 ml≈1.0 mg $CaCO_3$	D:17a-1; D:23a-1	"
104	"	None	" "	"
105	(not designated)	--	(not designated)	--
106	D:8a-1	None	~~D:17a-1;~~ D:23a-3 D:17a-1; D:23a-1	None
107	"	Na_2 EDTA: 1 ml≈1.00 mg $CaCO_3$ ≈ 0.40 mg Ca		Eriochrome Black T dry mixture; Na_2 EDTA, 1.00 ml≈1.00 mg $CaCO_3$ ≈ 0.243 mg Mg
108	(not analyzed)	--	(not analyzed)	--
109	D:8a-1	None	D:17a-1; D:23a-1	None
110	"	"	" "	"
111	"	"	" "	"
112	"	No NaCN added. Na_2 EDTA: 1.00 ml≈ 0.40 mg Ca	" "	Porcelain dish used. 1 ml conc. NH_4OH 1 ml 3% $NH_2OH \cdot HCl$ 1 ml Eriochrome Black T per 50 ml sample Na_2 EDTA: 1.00 ml≈ 1 mg $CaCO_3$
113	D:8a-2	Samples hand-stirred; reaction viewed through illumination through the beaker.	" "	None
114	(not analyzed)	--	(not analyzed)	--
115	(not designated)	--	(not designated)	--
116	D:8a-1	None	D:17a-1; D:23a-1	None

Methods used: Calcium (Ca) and Magnesium (Mg) (continued)

Lab.	Calcium (Ca)	Modifications	Magnesium (Mg)	Modifications
117	D:8a-1	Porcelain evap. dish; 50-ml buret; $NH_2OH \cdot HCl$, NaOH, NaCN added in order (1.5 ml ea.) with dropping pipet; murexide added with 0.2 g cup; no blank correction.	D:17a-1; D:23a-1	$NH_2OH \cdot HCl$, NH_4OH, NaC added in order (1.5 m ea.) with dropping pipet; 10-ml buret us for hardness titratio
118	"	Porcelain dish used; hand stirring; no blank correction.	" "	None
119	"	Hach Calver II indicator (contains NaCN) added after 1.0 ml of 85% KOH sol'n; $NH_2OH \cdot HCl$ is not added; Na_2EDTA: 1.0 ml≈1.0 mg $CaCO_3$ (0.400 mg Ca).	" "	Hach Univer.I indicator; $NH_2OH \cdot HCl$, NaCN, $K_4Fe(CN)_6$ are not use
120	"	No blank correction.	" "	None
121	"	None	" "	"
122	"	NH_2OH and NaCN used only when significant concentrations of heavy metals present.	" "	"
123	WSP 54 (?)	--	WSP 54 (?)	--

ERRORS, CALCIUM DETERMINATION

Standard Water Sample No. 1, 48 ppm

Error (absolute)	Number of laboratories reporting	Percentage of 20 laboratories reporting[a]
0 ppm	11	55 percent
±1 "	16	80 "
±2 "	20	100 "

a/ One laboratory reported 22 ppm, later corrected to 50 ppm; this result not included.

Standard Water Sample No. 2, 16 ppm

Error (absolute)	Number of laboratories reporting	Percentage of 20 laboratories reporting
0 ppm	16	76 percent
±1 "	20	95 "
±2 "	21	100 "

The data show that the most probable value for the concentration of calcium in Sample No. 1 is 48 ppm, and in Sample No. 2, 16 ppm. The errors in this determination are positive, that is, higher than true values are reported. Two of the four laboratories which reported the highest (+2 ppm) deviation for the 48 ppm sample also reported higher than the true value for Sample No. 2. Three laboratories indicated that no blank correction is made; of these, two reported high values for calcium in No. 1 and one a high value for Sample No. 2. Perhaps other laboratories do not apply a blank correction but neglected to indicate this on the report. The blank correction, however, would be less significant at calcium concentrations of the order of 48 ppm, where, in fact, the greater deviations occurred.

The calcium determination is accurate within reasonable limits of routine analyses.

ERRORS, MAGNESIUM DETERMINATION

Standard Water Sample No. 1, 15 ppm

Error (absolute)	Number of laboratories reporting	Percentage of 20 laboratories reporting
0 ppm	9	45 percent
±1 "	18	90 "
±2 "	20[a]	100 "

a/ One laboratory reported 32 ppm, later changed to 15 ppm after correcting for a calculation error. This result was not included in the evaluation.

Standard Water Sample No. 2, 3.0 ppm

Error (absolute)	Number of laboratories reporting	Percentage of 20 laboratories reporting
0.0 ppm	4	20 percent
±0.1 "	6	30 "
±0.2 "	11	55 "
±0.3 "	12	60 "
±0.4 "	17	85 "
±0.5 "	20	100 "

The reported results for magnesium are generally somewhat less satisfactory than those for calcium. This is to be expected in view of the fact that magnesium is determined by difference, except for one laboratory which determines magnesium by a direct photometric method.

Evaluation of the data shows that the methods used are accurate to within ±1 ppm at the 15 ppm concentration level and that there is no justification for reporting results to the nearest 0.1 ppm at concentration levels below 10 ppm. If results for magnesium concentrations below 10 ppm are to be reported to the nearest 0.1 ppm either (a) the technique must be improved to demonstrate this accuracy, or (b) the results so reported must be clearly stated as having an accuracy of ±0.5 ppm.

The data also indicate the possibility of a bias in favor of reporting even-numbered values for the analytical data. Thus, for calcium the calculated values quite by chance turned out to be even-numbered values. This appears to have been a fortunate choice since most of the values reported by the participating laboratories coincide with the calculated value. However, the number of laboratories reporting 50 ppm appears to be unrealistically large in comparison with the number of 49 ppm values reported. The tendency to report even-numbered values biases the analysis in favor of these values.

This is even more apparent in the case of the reported values for magnesium. For Sample No. 1, the calculated value happened to be an odd-numbered value (15 ppm). However, almost as many laboratories reported 16 ppm, again a possible indication of prejudice in favor of an even-numbered value. Seventy percent of all values reported for magnesium in Sample No. 2 were even-numbered values.

REPORTED RESULTS: SODIUM (ppm)

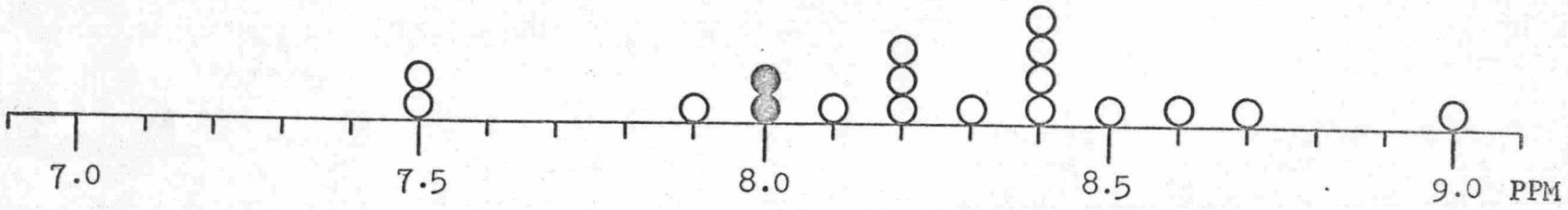
Code No.	Standard Sample No. 1				Standard Sample No. 2			
	(1)	(2)	(3)	Avge.	(1)	(2)	(3)	Avge.
101	8.5	8.3	--	8.4	22	21	--	22
102	8.1	8.1	--	8.1	21	21	--	21
103	8.9	9.1	--	9.0	22	22	--	22
104	--	--	--	--	--	--	--	--
105	7.5	7.5	--	7.5	19	19	--	19
106	8.2	8.4	--	8.3	21	21	--	21
107	8.0	7.9	--	8.0	21	21	--	21
108	--	--	--	--	--	--	--	--
109	--	--	--	--	--	--	--	--
110	8.7	8.7	--	8.7	22	22	--	22
111	8.4	8.4	--	8.4	22	22	--	22
112	8.2	8.2	--	8.2	22	22	--	22
113	7.5	7.5	--	7.5	21	21	--	21
114	--	--	--	--	--	--	--	--
115	7.8	7.9	7.9	7.9	20	21	20	20
116	--	--	--	--	--	--	--	--
117	8.4	8.4	--	8.4	22	22	--	22
118	8.7	8.6	--	8.6	22	22	--	22
119	8.3	8.6	--	8.4	22	22	--	22
120	8.0	8.0	--	8.0	22	22	--	22
121	8.5	8.5	--	8.5	21	21	--	21
122	8.2	8.3	--	8.2	21	21	--	21
123	8.2	8.2	--	8.2	22	22	--	22

Median = 8.25

SODIUM

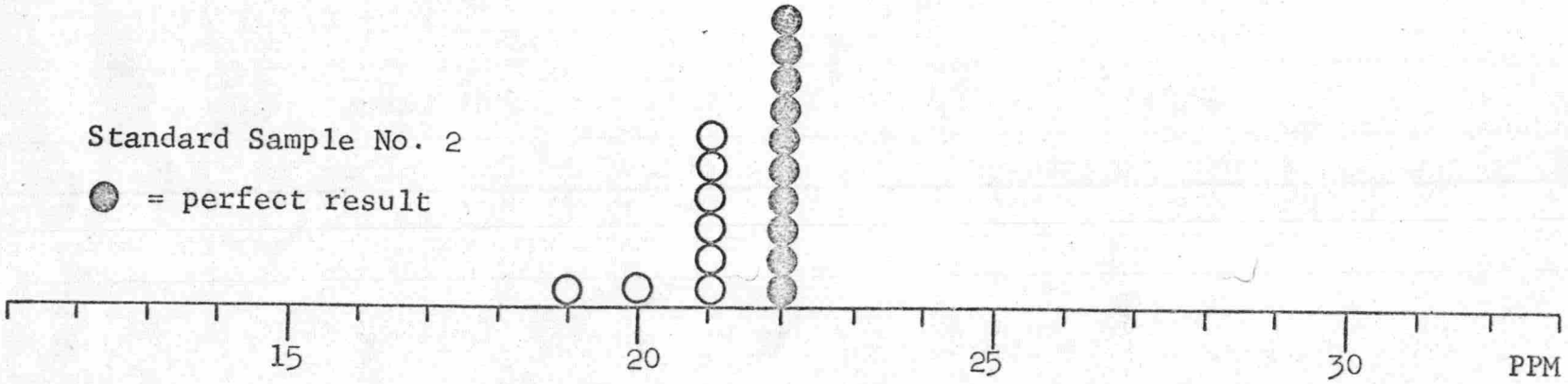
Standard Sample No. 1

● = perfect result



Standard Sample No. 2

● = perfect result



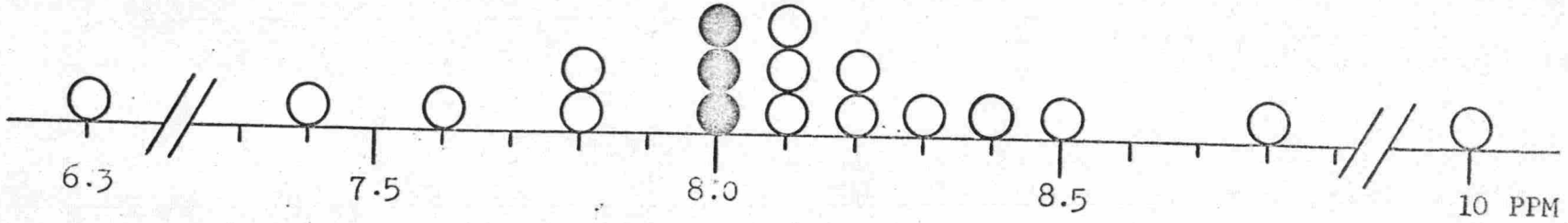
REPORTED RESULTS: POTASSIUM (ppm)

Code No.	Standard Sample No. 1				Standard Sample No. 2			
	(1)	(2)	(3)	Avge.	(1)	(2)	(3)	Avge.
101	6.3	6.3	--	6.3	1.8	1.8	--	1.8
102	7.9	8.0	--	8.0	2.3	2.3	--	2.3
103	8.2	8.4	--	8.3	2.0	2.1	--	2.0
104	--	--	--	--	--	--	--	--
105	8.4	8.4	--	8.4	2.6	2.6	--	2.6
106	7.8	7.5	--	7.6	2.0	2.2	--	2.1
107	7.8	7.9	--	7.8	2.2	2.2	--	2.2
108	--	--	--	--	--	--	--	--
109	--	--	--	--	--	--	--	--
110	8.0	8.0	--	8.0	2.1	2.1	--	2.1
111	10	10	--	10	3.0	3.0	--	3.0
112	8.8	8.8	--	8.8	2.4	2.4	--	2.4
113	8.1	8.1	--	8.1	2.2	2.2	--	2.2
114	--	--	--	--	--	--	--	--
115	8.1	8.1	8.1	8.1	2.2	1.8	2.0	2.0
116	--	--	--	--	--	--	--	--
117	8.2	8.3	--	8.2	2.3	2.4	--	2.4
118	8.2	8.0	--	8.1	2.4	2.2	--	2.3
119	7.4	7.5	--	7.4	1.9	1.9	--	1.9
120	7.9	7.8	--	7.8	2.4	2.2	--	2.3
121	8.0	8.0	--	8.0	2.0	2.0	--	2.0
122	8.2	8.2	--	8.2	2.0	2.0	--	2.0
123	8.5	8.5	--	8.5	2.3	2.3	--	2.3

POTASSIUM

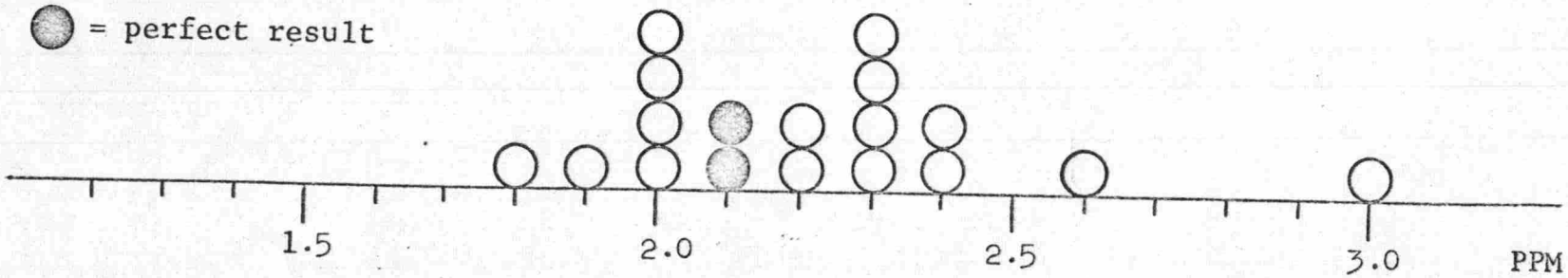
Standard Sample No. 1

● = perfect result



Standard Sample No. 2

● = perfect result



Methods used: Sodium (Na) and Potassium (K)

Lab.	Sodium (Na)	Modifications	Potassium (K)	Modifications
101	Flame photometer	Beckman Model 41; calibrated with std. solutions of Na + K; m.e. read directly.	Flame photometer	Beckman Model 41; calibrated with std. solutions of Na + K; m.e. read directly.
102	Flame photometer; WSP 1454, 35a-1	Perkin-Elmer Model 52-C.	Flame photometer; WSP 1454, 32a-1	Perkin-Elmer Model 52-C.
103	Flame photometer	Beckman Model DU with flame attachment; table prep'd from std. curves: 0-25 ppm Na and 25-100 ppm.	Flame photometer	Beckman Model DU with flame attachment; table prep'd from series of standard curves to correct for sodium.
104	--	--	--	--
105	--	--	--	--
106	Flame photometer: WSP 1454, D:35a-1	--	Flame photometer; WSP 1454, D:32a-1	--
107	Flame photometer	Beckman Model DU with photomultiplier and flame attachments; oxygen-hydrogen flame; two ranges: 0-10 ppm and 10-50 ppm; bracketing between standards; % T- readings converted to antilogs for computations; 589 mμ.	Flame photometer	Beckman DU with photomultiplier and flame attachments; oxygen-hydrogen flame; 768 mμ.
108	Not determined	--	Not determined	--
109	" "	--	" "	--
110	Flame photometer	Beckman 4100 direct reading flame photometer.	Flame photometer	Beckman 4100 direct reading flame photometer.
111	Flame photometer; WSP 1454, D:35a-1	--	Flame photometer; WSP 1454, D:32a-1	--

Methods used: Sodium (Na) and Potassium (K) (continued)

Lab.	Sodium (Na)	Modifications	Potassium (K)	Modifications
112	Flame photometer	Beckman DU; 589 mμ; std. curve prep'd from NaCl solutions containing 2, 4, and 6 ppm.	Flame photometer	Beckman DU; sample diluted 1:1 with 1,000 ppm sodium; 768 mμ.
113	Flame photometer	Beckman DU; photomultiplier and flame attachments; oxygen-hydrogen flame.	Flame photometer	Beckman DU (see Na method).
114	Not determined	--	Not determined	--
115	--	--	--	--
116	Not determined	--	Not determined	--
117	Flame photometer	Beckman Model B; oxygen-acetylene flame; standard curves for 0-10 ppm, 10-25 ppm, and 25-50 ppm.	Flame photometer	5 ml of 2,000 ppm Na std. added to each sample (25 ml) aliquot.
118	Flame photometer; WSP 1454, D:35a-1	--	Flame photometer; WSP 1454, D:32a-1	--
119	Flame photometer; WSP 1454	Beckman Model DU flame spectrophotometer; bracketing system; oxygen-acetylene flame	Flame photometer; WSP 1454	Beckman DU flame spectrophotometer; each sample brought to 1,000 ppm Na by adding NaCl solution (1 ml=25 mg Na); bracketing system.
120	Flame photometer	Perkin-Elmer Model 52-C, propane flame; internal standard method using Li_2SO_4 solution.	Flame photometer	(See sodium determination)
121	Flame photometer; WSP 1454, D:35a-1	--	Flame photometer; WSP 1454, D:32a-1	--
122	Flame photometer; WSP 1454, D:35a-1	Beckman Model B; oxygen-acetylene flame; bracketing system.	Flame photometer; WSP 1454, D:32a-1	Na content of all sampl adjusted to 500 ppm wit NaCl soln;bracketing sy
123	WSP 54 (?)	--	WSP 54 (?)	--

ERRORS, SODIUM DETERMINATION

Standard Water Sample No. 1, 8.0 ppm

Error (absolute)	Number of laboratories reporting	Percentage of 18 laboratories reporting
0.0 ppm	2	11 percent
±0.1 "	4	22 "
±0.2 "	7	39 "
±0.3 "	8	44 "
±0.4 "	12	67 "
±0.5 "	15	83 "
±0.6 "	16	89 "
±0.7 "	17	94 "
±1.0 "	18	100 "

Standard Water Sample No. 2, 22 ppm

Error (absolute)	Number of laboratories reporting	Percentage of 18 laboratories reporting
0 ppm	10	56 percent
±1 "	16	89 "
±2 "	17	94 "
±3 "	18	100 "

The sodium determination does not justify reporting values of concentrations of less than 10 ppm to the nearest 0.1 ppm. Values reported for Sample No. 1 which contained 8.0 ppm ranged from 7.5 to 9.0 ppm; the median of all values reported was between 8.2 and 8.3 ppm. Twenty-two percent of the laboratories reported the calculated value ±0.1 ppm. Fifty-six percent of the laboratories reported higher values and only 17 percent reported values less than the calculated value ±0.1 ppm. Sodium values at concentration levels of 10 ppm tend to be high. The method used should be examined carefully to make certain that accuracy is maintained at the lower concentration ranges.

The flame photometric method is satisfactory within ±1 ppm at sodium concentration levels of 22 ppm. Eighty-nine percent of all laboratories reported within 1 ppm of the correct value.

ERRORS, POTASSIUM DETERMINATION

Standard Water Sample No. 1, 8.0 ppm

Error (absolute)	Number of laboratories reporting	Percentage of 18 laboratories reporting
0.0 ppm	3	17 percent
±0.1 "	6	33 "
±0.2 "	10	56 "
±0.3 "	11	61 "
±0.4 "	13	72 "
±0.5 "	14	78 "
±0.6 "	15	83 "
±0.8 "	16	89 "
±2.0 "	18	100 "

Standard Water Sample No. 2, 2.1 ppm

Error (absolute)	Number laboratories reporting	Percentage of 18 laboratories reporting
0.0 ppm	2	11 percent
±0.1 "	8	44 "
±0.2 "	13	72 "
±0.3 "	16	89 "
±0.5 "	17	94 "
±0.9 "	18	100 "

The range of reported values for potassium in Sample No. 1 was excessive, although, in general, the reported values were satisfactory if not within the ±0.1 ppm accuracy indicated by the method and the reported value. If the accuracy is ±0.5 ppm for potassium concentrations below 10 ppm, then 78 percent of all labs would have reported acceptable values for potassium in Sample No. 1, and 89 percent acceptable values for Sample No. 2.

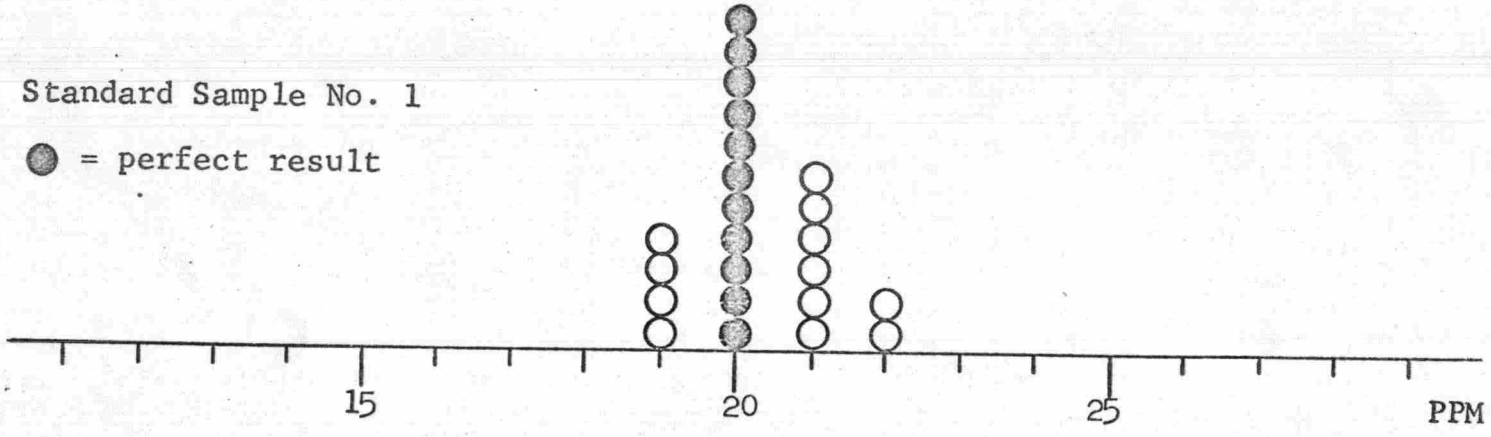
REPORTED RESULTS: CHLORIDE (ppm)

Code No.	Standard Sample No. 1				Standard Sample No. 2			
	(1)	(2)	(3)	Avge.	(1)	(2)	(3)	Avge.
101	19	19	--	19	8.0	8.2	--	8.1
102	20	20	--	20	8.9	9.2	--	9.0
103	21	21	--	21	9.2	9.2	--	9.2
104	22	22	--	22	11	12	--	11.5
105	19	19.5	--	19	9.5	10	--	9.8
106	20	18	--	19	8.1	8.0	--	8.0
107	20	20	--	20	9.0	9.2	--	9.1
108	21	21	--	21	10	10	--	10
109	20	20	--	20	9.0	9.0	--	9.0
110	21	20	--	20	10	10	--	10
111	19	19	--	19	7.8	7.8	--	7.8
112	21	21	--	21	9.2	9.0	--	9.1
113	21	21	--	21	9.5	9.5	--	9.5
114	20	20	--	20	9.0	9.0	--	9.0
115	20	20	20	20	10	10	9.5	10
116	21	21	--	21	9.5	9.6	--	9.6
117	22	22	--	22	7.8	8.0	--	7.9
118	20	20	--	20	8.5	8.2	--	8.4
119	20	21	--	20	10	9.5	--	9.8
120	22	20	--	21	9.4	8.8	--	9.1
121	20	20	--	20	10	9.0	--	9.5
122	21	20	--	20	8.4	8.2	--	8.3
123	20	21	--	20	10	10	--	10

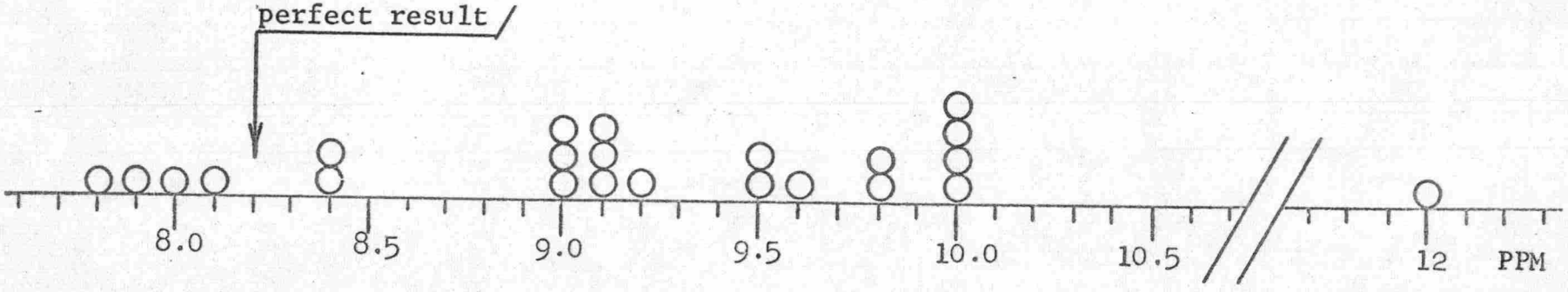
CHLORIDE

Standard Sample No. 1

● = perfect result



Standard Sample No. 2



Methods Used: Chloride

Lab.	Method	Modifications
101	Mohr; WSP 1454, D:10a-1	None
102	" " "	"
103	" " "	"
104	" " "	Yellow light not used; 0.15 ml blank
105	(Method not submitted)	--
106	Mohr; WSP 1454, D:10a-1	None
107	" " "	"
108	" " "	"
109	" " "	"
110	" " "	"
111	" " "	"
112	" " "	Blank correction of 0.10 ml
113	Gravimetric; WSP 1454, D:10a-2	None
114	Mohr; WSP 1454, D:10a-1	"
115	(Method not submitted)	--
116	Mohr; WSP 1454, D:10a-1	None
117	" " "	6 to 7 drops of K_2CrO_4 indicator used
118	" " "	None
119	" " "	None of significance
120	" " "	3 drops of indicator used; a blank correction us
121	" " "	None
122	" " "	"
123	WSP 54 (?)	--

ERRORS, CHLORIDE DETERMINATION

Standard Water Sample No. 1, 20 ppm

Error (absolute)	Number of laboratories reporting	Percentage of 23 laboratories reporting
0 ppm	11	48 percent
±1 "	21	96 "
±2 "	23	100 "

Standard Water Sample No. 2, 8.2 ppm

Error (absolute)	Number of laboratories reporting	Percentage of 23 laboratories reporting
0.0 ppm	0	0 percent
±0.1 "	1	4 "
±0.2 "	4	17 "
±0.3 "	5	22 "
±0.4 "	6	26 "
±0.8 "	9	39 "
±0.9 "	12	52 "
±1.0 "	13	57 "
±1.3 "	15	65 "
±1.6 "	18	78 "
±1.8 "	22	96 "

The values reported for chloride at a concentration level of 20 ppm were nearly all in agreement with the calculated value ±1 ppm. Less than 10 percent of all results reported exceeded the calculated value by more than 1 ppm and the maximum error was only 2 ppm.

The determination of chloride at a concentration level of 8.2 ppm, however, is quite different. The 23 values reported ranged from 7.8 to 12 ppm. Eighty-three percent of the reported values exceeded the calculated value by 0.2 ppm or more. Because of the wide spread in the results submitted for chloride in this sample, it is evident that with the method used, chloride should not be reported to the nearest 0.1 ppm, even at concentrations of less than 1.0 ppm. The statement is made in WSP 1454, p. 142, that the accuracy that may be expected for this determination when using a titrant of such concentration that 1.0 ml ≙ 0.50 mg of chloride, is ±0.05 mg. Thus, using a maximum sample aliquot of 50 ml, the accuracy corresponds to ±1 ppm. Even for concentrations of 10 ppm or less the results should not be reported to one decimal place.

REPORTED RESULTS: SULFATE (ppm)

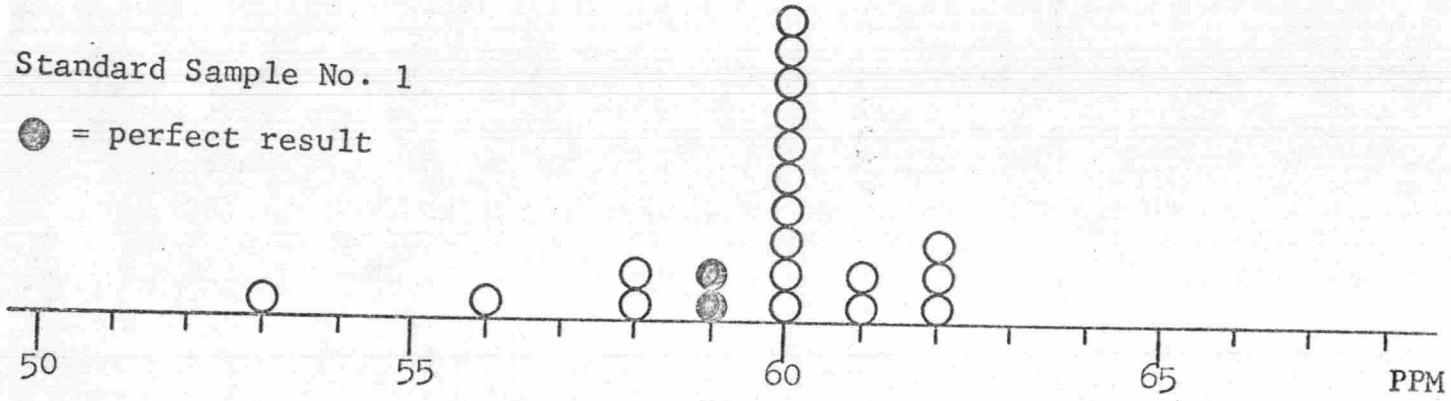
Code No.	Standard Sample No. 1				Standard Sample No. 2			
	(1)	(2)	(3)	Avge.	(1)	(2)	(3)	Avge.
101	61	61	--	61	13	13	--	13
102	58	58	--	58	12	12	--	12
103	58	60	--	59	12	11	--	12
104	62	62	--	62	12	18[a/]	--	12
105	60	60	--	60	12.2	12.6	--	12
106	60	60	--	60	11	11	--	11
107	60	60	--	60	13	13	--	13
108	--	--	--	--	--	--	--	--
109	62	62	--	62	13	13	--	13
110	59	59	--	59	12	12	--	12
111	60.3	60.9	--	61	12	12	--	12
112	53	53	--	53	13	13	--	13
113	60	60	--	60	12	12	--	12
114	--	--	--	--	--	--	--	--
115	60	60	60	60	12	12	12	12
116	59	58	--	58	12	13	--	12
117	60	60	--	60	13	14	--	14
118	56	55	--	56	11	11	--	11
119	60	64	--	62	12	13	--	12
120	60	60	--	60	12	12	--	12
121	60	60	--	60	13	12	--	12
122	60	59	--	60	11	11	--	11
123	59	61	--	60	12	12	--	12

a/ Not included in calculating average.

SULFATE

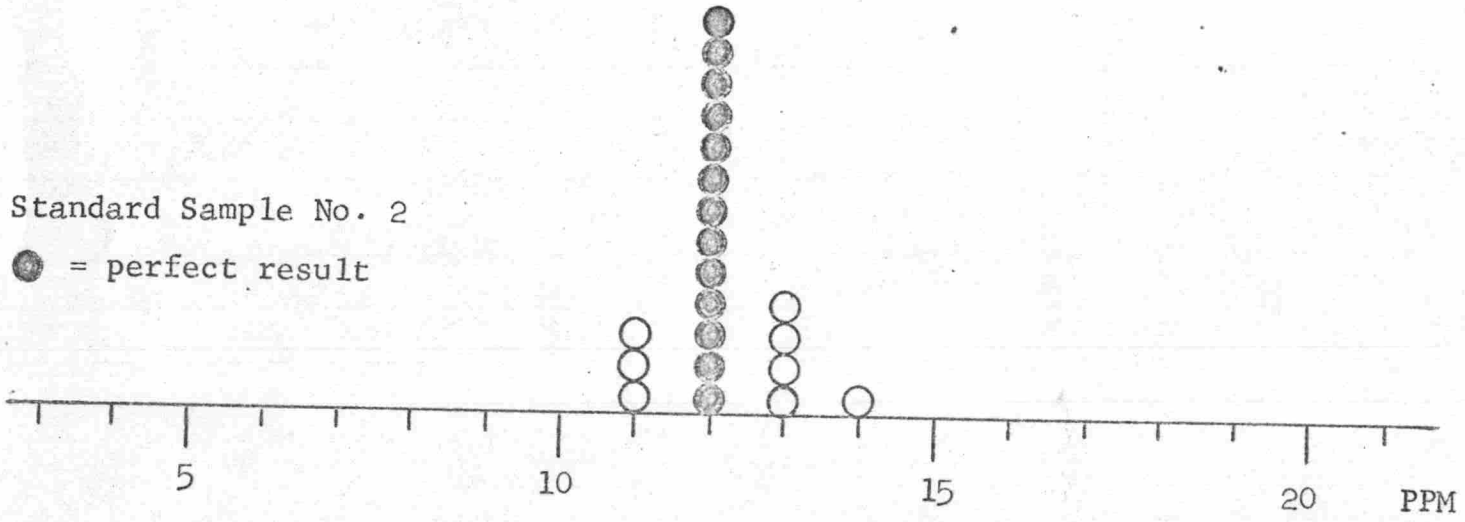
Standard Sample No. 1

● = perfect result



Standard Sample No. 2

● = perfect result



Method used: Sulfate

Lab.	Method	Modifications
101	Spectrophotometric thorin; WSP 1454, D:38a-2	None
102	do.	do.
103	do.	do.
104	Turbidimetric; Hach colorimeter, sulfaver reagent.	None
105	(None submitted)	--
106	Spectrophotometric thorin; WSP 1454, D:38a-2	50 ml of solvent-indicator solution used.
107	do.	None
108	(Not determined)	--
109	Spectrophotometric thorin; WSP 1454, D:38a-2	Lumetron colorimeter used; λ=450 mμ; Use sufficient sample to obtain 25 ml of effluent from the exchanger; sample aliquot (25 ml max.) containing 3 mg SO_4 and 25 mg dissolved solids transferred to absorption cell; 125 ml solvent-indicator added; titrate to absorbance of 0.19; blank = 0.60 ml.
110	Visual thorin	Modification of WSP 1454, D:38a-1
111	Spectrophotometric thorin; WSP 1454, D:38a-2	None
112	do.	Titration from absorbance of 0.100 to 0.300; 100-ml. beakers used instead of 50-mm cells.
113	do.	None
114	(Not determined)	--
115	(Method not submitted)	--
116	Visual thorin; WSP 1454, D:38a-1	ETOH used instead of dioxane; for SO_4 concentrations of <100 ppm, $BaCl_2$ solution (1 ml = 0.20 mg SO_4) used instead of $BaCl_2$ solution (1 ml = 0.50 mg SO_4).

Method used: Sulfate
(continued)

Lab.	Method	Modifications
117	Visual thorin; WSP 1454, D: 38a-1	ETOH used for thorin reagent is denatured with acetone; exchange columns are 18"x1"-diameter tubes containing 10"-column of Amberlite resin; flow rate of sample is approx. 20 ml/min.
118	do	Lumetron colorimeter; λ= 490 mμ; E.P. at 0.19 absorbance.
119	Gravimetric; WSP 1454, D:38a-3	SiO_2 not removed; steps 2-4, 6-8, and 10 (WSP 1454, p.284).
120	Spectrophotometric thorin; WSP 454, D:38a-2	Solvent-indicator solution unstable, therefore separate solutions of indicator and solvent are prepared; indicator: 1g thorin + 20 g NaOAc per liter (1 ml HCHO added as preservative); solvent: 12 ml HOAc per 1000ml 95% ETOH; 1 ml of indicator + 40 ml solvent added to each sample.
121	Visual thorin; WSP 1454, D:38a-1	40 ml of alc. sol'n of thorin indicator is used in place of steps 5 and 6; indicator solution: 1.3 ml of 0.2% aq. thorin added to 1,000 ml ETOH.
122	Spectrophotometric thorin; WSP 1454, D:38a-2	pH adjusted with 1N NaOH and 20% HOAc using bromocresol green; buffer solution not used; 0.5 ml of thorin indicator solution (1 mg/ml) and 50 ml of 95% ETOH added to each sample.
123	WSP 54	--

ERRORS, SULFATE DETERMINATION

Standard Water Sample No. 1, 59 ppm

Error (absolute)	Number of laboratories reporting	Percentage of 21 laboratories reporting
0 ppm	2	10 percent
±1 "	14	66 "
±2 "	19	90 "
±4 "	20	95 "
±6 "	21	100 "

Standard Water Sample No. 2, 12 ppm

Error (absolute)	Number of laboratories reporting	Percentage of 21 laboratories reporting
0 ppm	13	62 percent
±1 "	20	95 "
±2 "	21	100 "

The reported values for sulfate were good. At the 12 ppm concentration level, 95 percent of the 21 laboratories reported a value which fell within 1 ppm of the calculated value. At the 60 ppm concentration level (Standard Sample No. 1), only 63 percent of the laboratories reported values within 1 ppm of the calculated values. However, 91 percent were within 2 ppm, which, at this concentration level, represents an accuracy of ±3.4 percent of the amount present.

There is no serious problem with the sulfate determination and there is no significant difference among the several methods used in the analysis of these samples. About one-half of the participating laboratories used the spectrophotometric thorin method, one-fourth the visual thorin method, one a turbidimetric method, and one a gravimetric method. Three laboratories did not indicate the method used.

The results for the determination of sulfate may again indicate a bias in favor of reporting an even-numbered value for the determination.

CONCLUSIONS AND RECOMMENDATIONS

CALCIUM

1. Calcium concentrations over the range of from 16 to 48 ppm can be determined to within 1 ppm.

2. No changes are proposed in methods used or in method of reporting results.

MAGNESIUM

1. Magnesium concentrations greater than 10 ppm can be determined to within 1 ppm.

2. Magnesium concentrations less than 10 ppm cannot be determined to within 0.1 ppm by the present method, and, therefore, should not be reported to the nearest 0.1 ppm.

3. The reliability of the present method for determining magnesium is ±0.5 ppm, and results should be reported with this notation.

SODIUM

1. Sodium concentrations of the order of 20 ppm can be determined with an accuracy of ±1 ppm.

2. Sodium concentrations of less than 10 ppm cannot be determined to within 0.1 ppm by the present flame photometric methods, and, therefore should not be reported to the nearest 0.1 ppm.

3. The accuracy of the sodium determination at concentration levels of less than 10 ppm is not better than ±0.5 ppm, and results should be reported with this notation.

POTASSIUM

1. The accuracy of the present methods for determining potassium is at best ±0.5 ppm for concentrations less than 10 ppm, and results should be reported with this notation.

CHLORIDE

1. Chloride concentrations of the order of 20 ppm can be determined to within 1 ppm.

2. Chloride concentrations of less than 10 ppm cannot, by the Mohr method, be determined to within 0.1 ppm.

3. The Mohr method should not be used for samples containing less than 10 ppm of chloride because of the great uncertainty of the result obtained.

4. A mercurimetric (mercuric nitrate) method is being investigated as a superior method for chloride at all concentration levels except extremely low (<1 ppm) concentrations. This procedure will be distributed to all laboratories as soon as its evaluation has been completed.

SULFATE

1. Sulfate concentrations of the order of 12 ppm can be determined to within 1 ppm.

2. The accuracy of the sulfate method at concentration levels of the order of 60 ppm is probably within 2 ppm. However, the precentage error in terms of the amount present is only about 3 percent, which is a reasonable amount.