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REPORT OF

ANALYTICAL EVALUATION PROGRAM

STANDARD WATER SAMPLES NUMBERS 5, 6, and 7

Total Alkalinity, Nitrate,

Nitrite, Fluoride, Silica,

Specific Conductance,

pH, Dissolved Solids

U. S. GEOLOGICAL SURVEY

WATER RESOURCES DIVISION

Quality of Water Branch

Denver, Colorado

1963

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PURPOSE AND PLAN

In order to provide a regular, systematic program for the statistical evaluation of the accuracy of analytical data published by all Branch laboratories, Standard Reference Water Samples are prepared and distributed at regular intervals to all Branch laboratories. This report summarizes the analytical data submitted by 23 participating laboratories for Standard Water Samples Nos. 5, 6, and 7, distributed on August 26, 1963.

The following analytical measurements or determinations were made on these samples:

Alkalinity	Silica
Nitrate	Specific conductance
Nitrite	Total dissolved solids
Fluoride	pH

PREPARATION OF THE SAMPLES

Each sample was prepared from accurately weighed amounts of analytical reagent-grade chemicals dissolved in an accurately measured volume of distilled water which had been further purified by passage through a mixed-bed exchanger. The pH of each sample was adjusted with dilute sulfuric acid when necessary to ensure stability of the final solution.

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

$NaHCO_3$	$Na_2SiO_3 \cdot 9H_2O$
KNO_3	$CaCl_2$
KNO_2	$MgSO_4 \cdot 7H_2O$
NaF	

Individual 1-liter standard water samples were prepared from the stock solutions as follows:

Preparation of Standard Water Sample No. 5

Stock Solution	5A	5B	5C
	ppm	ppm	ppm
Alkalinity ($CaCO_3$)	3280	Calcium chloride ($CaCl_2$) 1178	Magnesium sulfate ($MgSO_4 \cdot 7H_2O$) 206
Nitrate (NO_3)	400		
Nitrite (NO_2)	216		
Fluoride (F)	36		
Silica (SiO_2)	1200		
Volume per liter of final solution	25.0 ml	10.0 ml	25.0 ml

	ppm
Alkalinity ($CaCO_3$)	82
Nitrate (NO_3)	10
Nitrite (NO_2)	5.4
Fluoride (F)	0.9
Silica (SiO_2)	30
Calcium chloride ($CaCl_2$)	12
Magnesium sulfate ($MgSO_4 \cdot 7H_2O$)	5.1

Preparation of Standard Water Sample No. 6

Stock Solution	6A	6B	6C
	ppm	ppm	ppm
Alkalinity ($CaCO_3$)	1600	Calcium chloride ($CaCl_2$) 798	Magnesium sulfate ($MgSO_4 \cdot 7H_2O$) 422
Nitrate (NO_3)	80		
Nitrite (NO_2)	92		
Fluoride (F)	32		
Silica (SiO_2)	208		
Volume per liter of final solution	25.0 ml	25.0 ml	25.0 ml

	ppm
Alkalinity ($CaCO_3$)	40
Nitrate (NO_3)	2.0
Nitrite (NO_2)	2.3
Fluoride (F)	0.8
Silica (SiO_2)	5.2
Calcium chloride ($CaCl_2$)	20
Magnesium sulfate ($MgSO_4 \cdot 7H_2O$)	11

Preparation of Standard Water Sample No. 7

Stock solution	7A	7B	7C
	ppm	ppm	ppm
Alkalinity ($CaCO_3$)	6560	Calcium chloride ($CaCl_2$) 3180	Magnesium sulfate ($MgSO_4 \cdot 7H_2O$) 240
Nitrate (NO_3)	400		
Nitrite (NO_2)	0		
Fluoride (F)	12		
Silica (SiO_2)	800		
Volume per liter of final solution	25.0 ml	2.0 ml	25.0 ml

	ppm
Alkalinity ($CaCO_3$)	164
Nitrate (NO_3)	10
Nitrite (NO_2)	0.00
Fluoride (F)	0.3
Silica (SiO_2)	20
Calcium chloride ($CaCl_2$)	6.4
Magnesium sulfate ($MgSO_4 \cdot 7H_2O$)	6.0

After preparation, each sample was analyzed in duplicate, except for specific conductance and dissolved solids (single determinations) at four different times over a period of about six weeks. The results of these analyses are given in the following table. None of the three samples showed any change in the concentration of the substances determined over the 6-week period of storage.

Analysis by Preparations Lab[1/]

	Standard Water Sample		
	No. 5	No. 6	No. 7
	ppm	ppm	ppm
Alkalinity (as $CaCO_3$)	81	42	161
Nitrate (NO_3)(a)	9.7	1.6	9.8
do. (b)	9.9	2.2	9.9
Nitrite (NO_2)(c)	2.52	2.25	0.00
do. (d)	5.50	2.31	0.00
Fluoride (F)	0.8	0.7	0.3
Silica (SiO_2)	26	4.9	17
Conductance	339	164	416
pH	7.7	7.8	8.0
Dissolved solids	218	81	255

1/ Average of 4 duplicate determinations, except for specific conductance and dissolved solids (4 single determinations).

(a) Method D:25b-1, WSP 1454.

(b) Hydrazine reduction-diazotization method, distributed 6/10/63.

(c) Method D:25c-1, WSP 1454.

(d) Diazotization method, distributed 6/10/63.

PARTICIPATING LABORATORIES

Alabama, Tuscaloosa

Alaska, Palmer

Arizona, Yuma

Arkansas, Little Rock

California, Menlo Park

California, Sacramento

Colorado, Denver

District of Columbia, Washington

Florida, Ocala

Kansas, Topeka

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

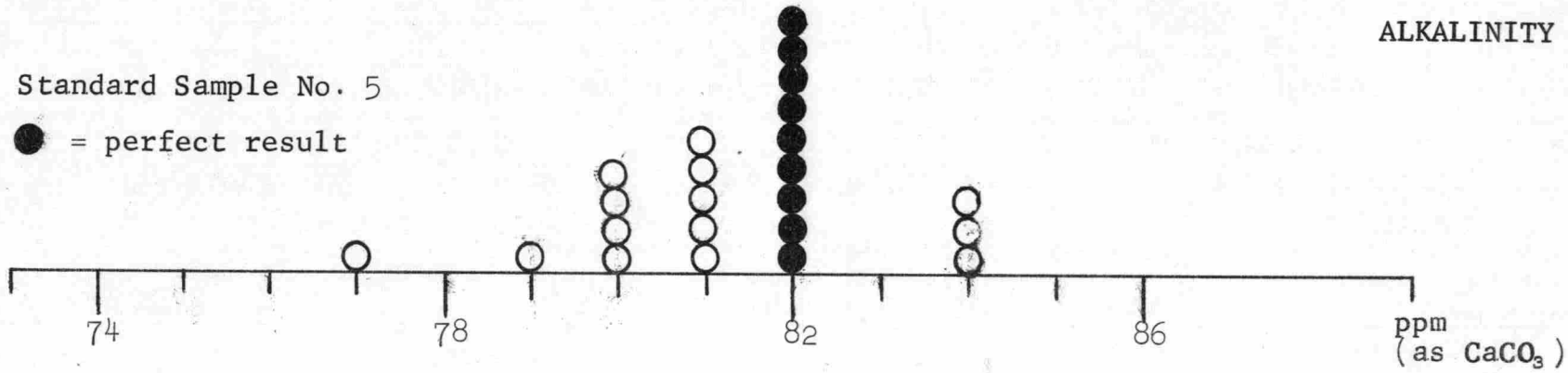
Utah, Salt Lake City

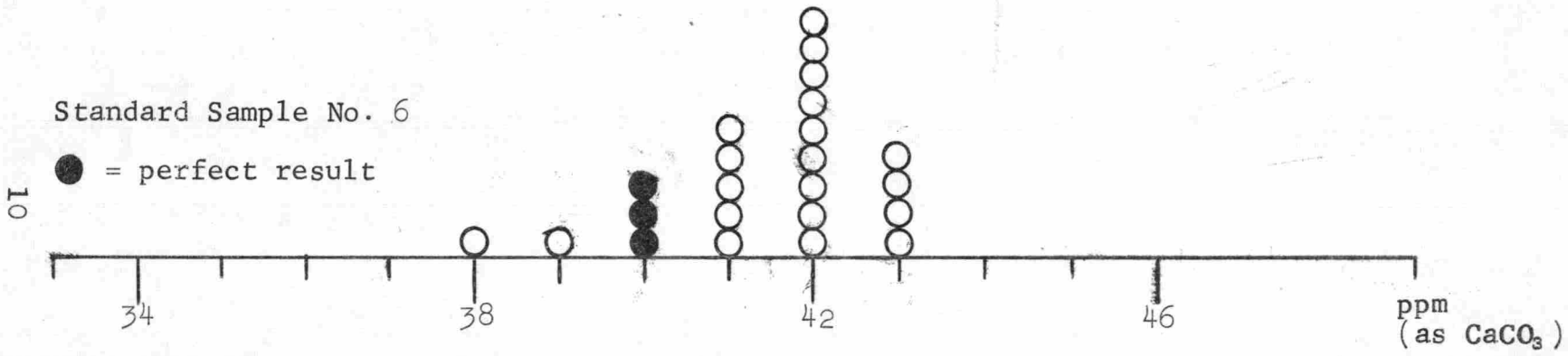
Wyoming, Worland

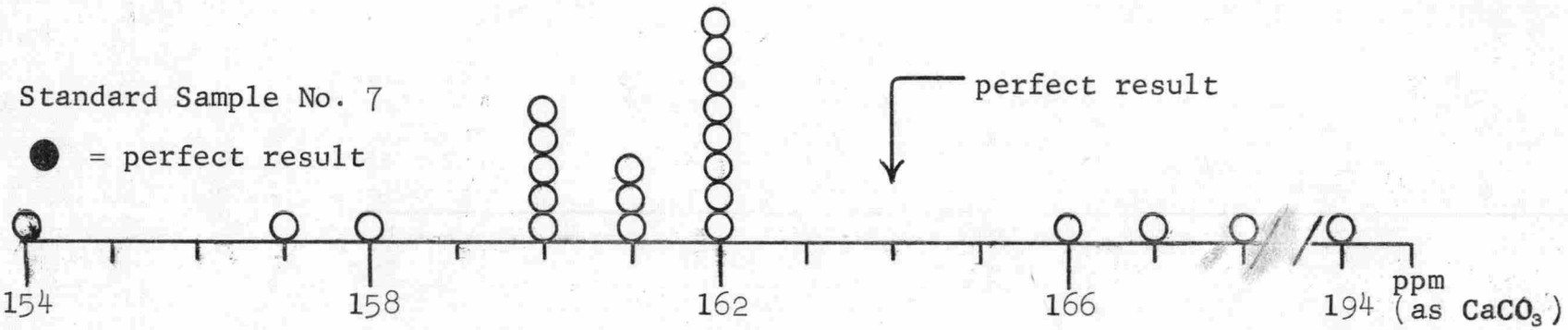
REPORTED RESULTS: ALKALINITY (ppm as $CaCO_3$)

Code No.	Std. Sample No. 5			Std. Sample No. 6			Std. Sample No. 7		
	(1)	(2)	Avge.	(1)	(2)	Avge.	(1)	(2)	Avge.
101	82	82	82	43	43	43	162	162	162
102	80	80	80	40	40	40	160	160	160
103	82	82	82	43	43	43	162	162	162
104	84	84	84	43	43	43	162	162	162
105	84	84	84	43	43	43	167	167	167
106	81	82	82	42	43	42	161	162	161
107	79	78	79	38	39	39	157	157	157
108	83	82	82	40	41	40	162	162	162
109	80	80	80	41	41	41	157	159	158
110	81	82	82	42	41	42	162	161	162
111	80	80	80	41	41	41	159	160	160
112	81	81	81	41	41	41	159	161	160
113	82	82	82	42	43	42	161	161	161
114	82	82	82	41	42	42	162	161	162
115	81	81	81	41	40	40	195	193	194
116	80	80	80	42	42	42	160	160	160
118	82	82	82	42	43	42	161	163	162
119	76	78	77	38	39	38	154	154	154
120	84	84	84	42	42	42	167	168	168
121	82	83	82	40	43	42	166	165	166
122	81	81	81	41	41	41	159	160	160
123	82	80	81	41	43	42	161	161	161
124	81	81	81	40	42	41	162	162	162

ALKALINITY


Standard Sample No. 5
● = perfect result
74
78
82
86
ppm
(as $CaCO_3$)


Standard Sample No. 6
● = perfect result
10
34
38
42
46
ppm
(as $CaCO_3$)


Standard Sample No. 7
● = perfect result
perfect result
154
158
162
166
194
ppm
(as $CaCO_3$)

Methods used: Alkalinity (as $CaCO_3$)

Lab.	Method	Modifications
101	WSP 1454, D:2a-1	None
102	" "	"
103	(Not designated)	---
104	WSP 1454, D:2a-1	CO_2 free air bubbler used for stirring during titration (to drive off free CO_2 in sample).
105	" "	None
106	" "	"
107	" "	"
108	" "	"
109	" "	"
110	" "	"
111	" "	"
112	" "	"
113	" "	"
114	" "	"
115	" "	"
116	(Not designated)	---
118	WSP 1454, D:2a-1	None
119	Standard Methods, 11th ed., p. 44 (Potentiometric)	"
120	WSP 1454, D:2a-1	"
121	" "	"
122	" "	"
123	" "	"
124	" "	"

ERRORS, ALKALINITY DETERMINATION

Error (absolute)	Number of laboratories reporting	Percentage of 23 laboratories reporting
Standard Water Sample No. 5, 82 ppm ($CaCO_3$)		
0 ppm	9	39 percent
±1 "	14	61 "
±2 "	21	91 "
±3 "	22	96 "
±5 "	23	100 "
Standard Water Sample No. 6, 40 ppm ($CaCO_3$)		
0 ppm	3	13 percent
±1 "	9	39 "
±2 "	19	83 "
±3 "	23	100 "
Standard Water Sample No. 7, 164 ppm ($CaCO_3$)		
0 ppm	0	0 percent
±1 "	0	0 "
±2 "	9	39 "
±3 "	13	57 "
±4 "	19	83 "
±6 "	20	87 "
±7 "	21	91 "
±10 "	22	96 "
±30 "	23	100 "

The alkalinity of a sample is susceptible to change between time of collection and analysis. However, no change in alkalinity occurred for the three standard water samples over the 6-week storage period. The 23 laboratories reported no perfect results for Standard Sample No. 7, and all of the reported results (23 laboratories) except for 4 were lower than the calculated value. Similarly, 11 laboratories reported values lower than the calculated value for Sample No. 5. The opposite occurred for Sample No. 6, where 18 laboratories reported results higher than the calculated value.

From the data, the alkalinity determination is accurate within reasonable limits for routine analysis. More than 80 percent of the laboratories reported values within ±2 ppm of the calculated concentration for Samples Nos. 5 and 6, and within ±4 ppm for Sample No. 7.

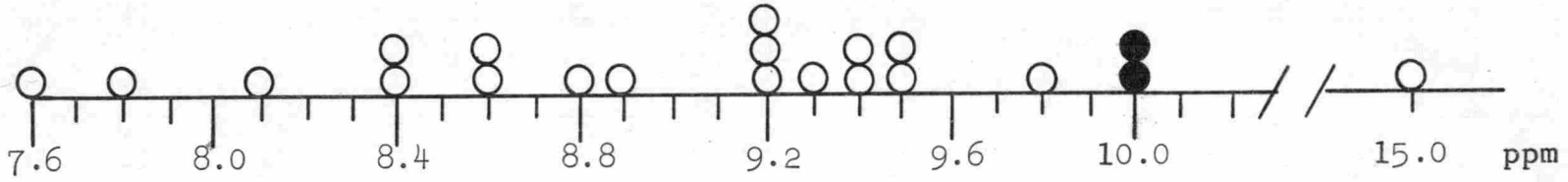
A 194 ppm value was reported for Sample No. 7 by one of the laboratories. It is possible that this is the bicarbonate value since, if multiplied by 0.82, the total alkalinity value is then 159 ppm, which falls in line with the other data.

REPORTED RESULTS: NITRATE (ppm)

Code No.	Std. Sample No. 5			Std. Sample No. 6			Std. Sample No. 7		
	(1)	(2)	Avge.	(1)	(2)	Avge.	(1)	(2)	Avge.
101	8.4	8.4	8.4	1.4	1.4	1.4	8.5	8.7	8.6
102	---	---	---	---	---	---	---	---	---
103	10	9.7	9.8	1.7	1.8	1.8	10	10	10
104	8.1	8.7	8.4	1.6	2.2	1.9	8.2	9.3	8.8
105	8.6	8.9	8.8	1.8	1.7	1.8	8.8	8.8	8.8
106	7.4	7.8	7.6	2.7	2.7	2.7	7.4	7.6	7.5
107	9.3	9.2	9.2	1.4	1.6	1.5	10	10	10
108	15	15	15	4.1	4.0	4.0	9.1	9.0	9.0
109	7.8	7.7	7.75	1.2	1.4	1.3	7.6	7.8	7.7
110	9.4	9.5	9.4	1.7	1.9	1.8	9.7	10	9.8
111	9.5	9.5	9.5	1.7	1.7	1.7	9.8	9.8	9.8
112	9.2	9.3	9.2	1.9	1.8	1.8	9.4	9.7	9.6
113	9.0	8.9	8.9	1.5	1.5	1.5	8.9	9.0	9.0
114	9.2	9.1	9.2	1.7	1.5	1.6	9.7	9.4	9.6
115	8.6	8.7	8.6	1.5	1.5	1.5	9.2	9.2	9.2
116	---	---	---	---	---	---	---	---	---
118	9.3	9.4	9.3	1.1	1.2	1.1	9.2	9.4	9.3
119	10	9.9	10	1.8	1.6	1.7	8.8	8.7	8.8
120	10	10	10	2.0	2.0	2.0	10	10	10
121	9.3	9.6	9.4	1.7	1.7	1.7	9.1	9.7	9.4
122	8.0	8.2	8.1	1.6	1.5	1.6	8.8	8.5	8.6
123	9.5	9.5	9.5	1.8	1.9	1.8	9.8	9.8	9.8
124	8.7	8.5	8.6	1.5	1.5	1.5	9.2	9.3	9.25

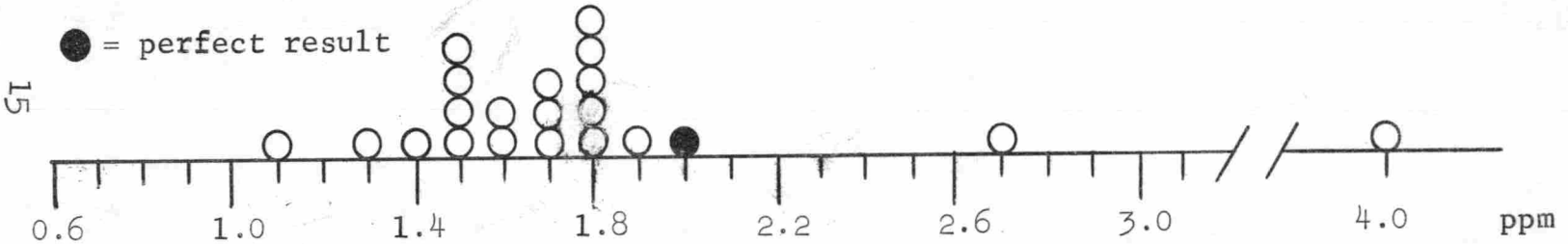
Standard Sample No. 5

● = perfect result



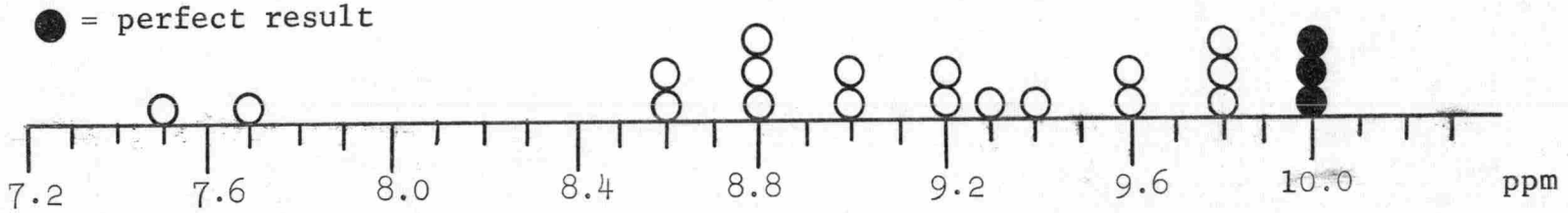
Standard Sample No. 6

● = perfect result



Standard Sample No. 7

● = perfect result



Methods used: Nitrate (NO_3)

Lab.	Method	Modifications
101	WSP 1454, D:25b-1	None
102	(Not determined)	--
103	(Not designated)	--
104	WSP 1454, D:25b-1	Fisher Electrophotometer used with fixed filter and wavelength, B 425 23 mm cells used.
105	" "	None
106	Proposed hydrazine reduction-diazotization method.	"
107	WSP 1454, D:25b-1	"
108	" "	To each sample and standard, added 2 drops of 2N NaOH and 1 ml of 1.5 % H_2O_2 before evaporating.
109	" "	None
110	" "	"
111	" "	"
112	" "	"
113	" "	Air bath.
114	" "	Wavelength of 415 mμ used.
115	" "	None
116	(Not determined)	--
118	WSP 1454, D:24b-1	None
119	Phenoldisulfonic acid, Standard Methods, 11th ed.,p.175	"
120	WSP 1454, D:25b-1	"
121	" "	"
122	" "	"
123	" "	"
124	" "	"

ERRORS, NITRATE DETERMINATION

Error (absolute)	Number of laboratories reporting	Percentage of 21 laboratories reporting
Standard Water Sample No. 5, 10 ppm (NO_3)		
0.0 ppm	2	10 percent
±0.1 "	2	10 "
±0.2 "	3	14 "
±0.5 "	5	24 "
±0.6 "	7	33 "
±0.7 "	8	38 "
±0.8 "	11	52 "
±1.1 "	12	57 "
±1.2 "	13	62 "
±1.4 "	15	71 "
±1.6 "	17	81 "
±1.9 "	18	86 "
±2.2 "	19	90 "
±2.4 "	20	95 "
±5.0 "	21	100 "
Standard Water Sample No. 6, 2.0 ppm (NO_3)		
0.0 ppm	1	5 percent
±0.1 "	2	10 "
±0.2 "	7	33 "
±0.3 "	10	48 "
±0.4 "	12	57 "
±0.5 "	16	76 "
±0.6 "	17	81 "
±0.7 "	19	90 "
±0.9 "	20	95 "
±2.0 "	21	100 "

(continued)

ERRORS, NITRATE DETERMINATION
(continued)

Error (absolute)	Number of laboratories reporting	Percentage of 21 laboratories reporting
Standard Water Sample No. 7, 10 ppm (NO_3)		
0.0 ppm	3	14 percent
±0.2 "	6	29 "
±0.4 "	8	38 "
±0.6 "	9	43 "
±0.7 "	10	48 "
±0.8 "	12	57 "
±1.0 "	14	67 "
±1.2 "	17	81 "
±1.4 "	19	90 "
±2.3 "	20	95 "
±2.5 "	21	100 "

The reported results for nitrate were much lower than the calculated values. For Samples Nos. 5 and 7, where the calculated concentrations were 10 ppm, results as low as 7.5 ppm were reported. Only 2 laboratories reported perfect results for Sample No. 5, and 3 laboratories for Sample No. 7. The same is true for Sample No. 6 (2.0 ppm) where 18 of 21 laboratories reported values lower than the calculated one. All but one laboratory determined nitrate by the phenoldisulfonic acid method, and it was expected that low results would occur since chloride interferes. The chloride in these samples was less than 15 ppm.

Almost 50 percent of the laboratories reported results with a difference greater than 1 ppm of the calculated value for Samples Nos. 5 and 7, and 25 percent with a difference greater than 0.5 ppm for Sample No. 6.

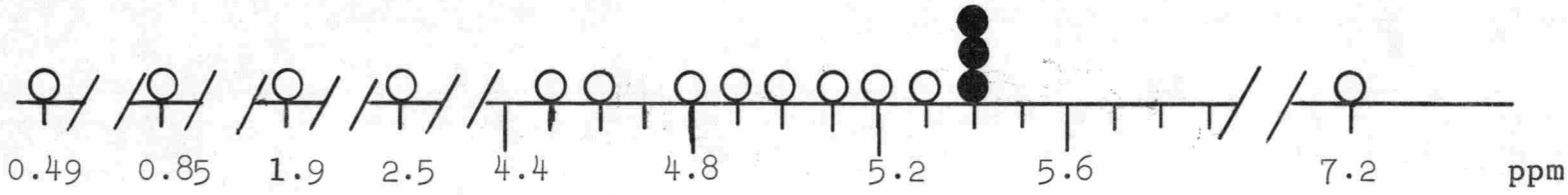
No evaluation can be made at this time for the hydrazine method since only one laboratory reported results using this new procedure.

REPORTED RESULTS: NITRITE (ppm)

Code	Std. Sample No. 5			Std. Sample No. 6			Std. Sample No. 7		
No.	(1)	(2)	Avge.	(1)	(2)	Avge.	(1)	(2)	Avge.
101	2.5	2.5	2.5	1.2	1.2	1.2	0.02	0.02	0.02
102	---	---	---	---	---	---	---	---	---
103	1.9	1.9	1.9	0.88	0.87	0.88	0.00	0.00	0.00
104	0.84	0.86	0.85	0.35	0.39	0.37	0.00	0.01	0.00
105	4.6	---	4.6	3.9	---	3.9	0.0	0.0	0.0
106	---	---	---	---	---	---	---	---	---
107	7.1	7.2	7.2	2.9	3.0	3.0	0.05	0.04	0.04
108	5.5	5.3	5.4	2.3	2.2	2.2	0.01	0.02	0.02
109	5.0	4.8	4.9	2.3	2.1	2.2	0.05	0.00	0.025
110	5.5	5.3	5.4	2.2	2.2	2.2	0.00	0.01	0.00
111	5.4	5.4	5.4	2.2	2.3	2.2	.02	.01	.02
112	5.0	5.2	5.1	2.2	2.3	2.2	0.01	0.00	0.00
113	---	---	---	---	---	---	---	---	---
114	5.3	5.2	5.3	2.2	2.2	2.2	0.01	0.01	0.01
115	---	---	---	---	---	---	---	---	---
116	---	---	---	---	---	---	---	---	---
118	---	---	---	---	---	---	---	---	---
119	4.8	4.8	4.8	2.0	2.0	2.0	0.01	0.01	0.01
120	5.0	5.0	5.0	2.2	2.2	2.2	0.05	0.05	0.05
121	0.52	0.46	0.49	0.21	0.20	0.20	0.00	0.00	0.00
122	5.2	5.2	5.2	2.1	2.2	2.2	.01	.01	.01
123	4.8	4.2	4.5	2.0	2.0	2.0	0.00	0.02	0.01
124	---	---	---	---	---	---	---	---	---

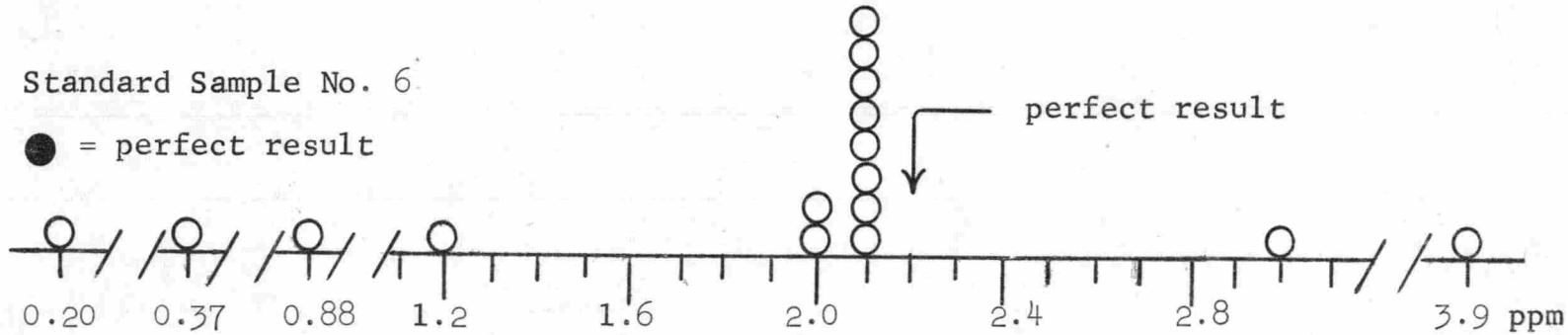
Standard Sample No. 5

● = perfect result



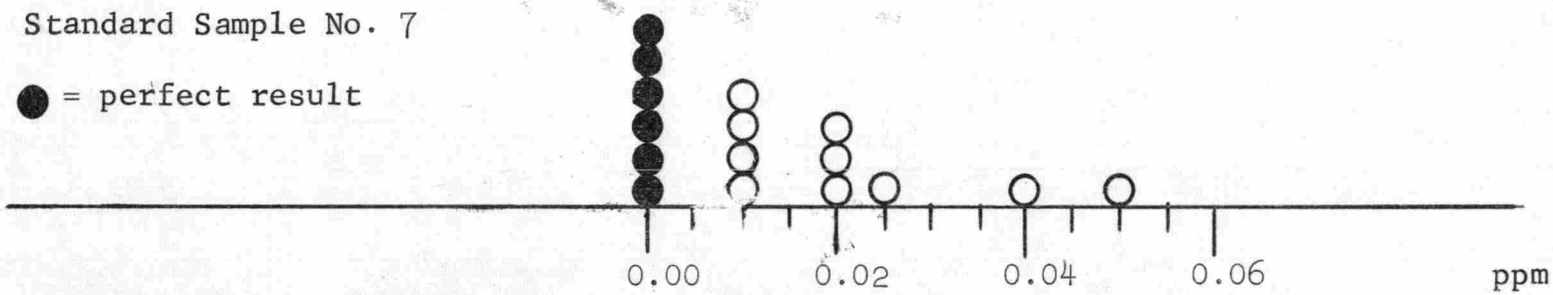
Standard Sample No. 6

● = perfect result



Standard Sample No. 7

● = perfect result



Methods used: Nitrite (NO_2)

Lab.	Method	Modifications
101	WSP 1454, D:25c-1	None
102	(Not determined)	---
103	(Not designated)	---
104	WSP 1454, D:25c-1	Volumes doubled, 23 mm cells used.
105	" "	None
106	(Not determined)	---
107	Proposed diazotization method.	None
108	do.	"
109	WSP 1454, D:25c-1	"
110	" "	"
111	" "	"
112	" "	"
113	(Not determined)	---
114	WSP 1454, D:25c-1	None
115	(Not determined)	---
116	do.	---
118	do.	---
119	Diazotization method, Standard Methods, 11th ed.,p.180.	None
120	WSP 1454, D:25c-1	"
121	" "	"
122	" "	"
123	" "	"
124	(Not determined)	---

ERRORS, NITRITE DETERMINATION

Error (absolute)	Number of laboratories reporting	Percentage of 16 laboratories reporting
Standard Water Sample No. 5, 5.4 ppm (NO_2)		
0.0 ppm	3	19 percent
±0.1 "	4	25 "
±0.2 "	5	31 "
±0.3 "	6	37 "
±0.4 "	7	44 "
±0.5 "	8	50 "
±0.6 "	9	56 "
±0.8 "	10	62 "
±0.9 "	11	69 "
>±1.0 and <±4.9 ppm	16	100 "
Standard Water Sample No. 6, 2.3 ppm (NO_2)		
0.0 ppm	0	0 percent
±0.1 "	8	50 "
±0.3 "	10	62 "
±0.8 "	11	69 "
±1.0 "	12	75 "
>±1.0 and <±2.0 ppm	16	100 "
Standard Water Sample No. 7, 0.00 ppm (NO_2)		
0.00 ppm	6	37 percent
±0.01 "	10	62 "
±0.02 "	13	81 "
±0.025 "	14	87 "
±0.04 "	15	94 "
±0.05 "	16	100 "

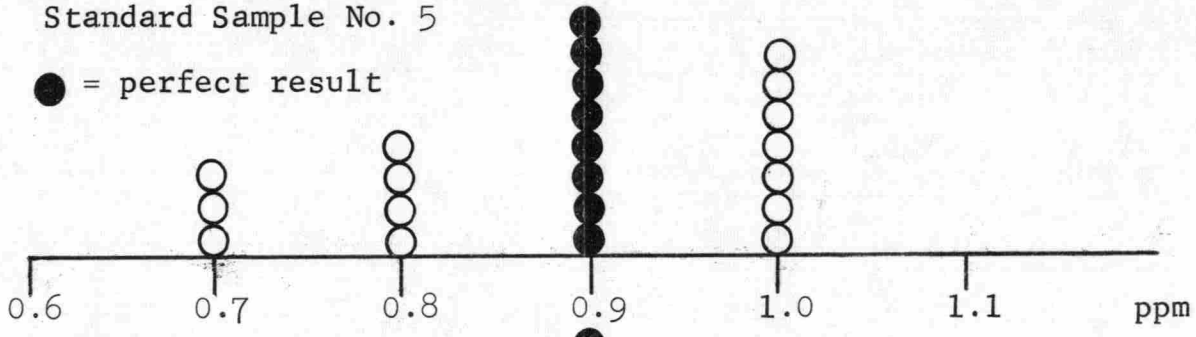
The range of results for nitrite in Samples 5 and 6 was from 0.49 to 7.2 and 0.20 to 3.9 ppm, respectively. The reported values for all but one were lower than the calculated concentration (5.4 ppm, Sample No. 5; 2.3 ppm, Sample No. 6) by using the present diazotization method. Three perfect results were found for Sample No. 5 and 50 percent of the results were within ±0.5 ppm. No perfect results were reported for Sample No. 6, however 50 percent of the results were within ±0.1 ppm. Sample No. 7 contained no nitrite and 62 percent of the laboratories reported either 0.00 or 0.01 ppm.

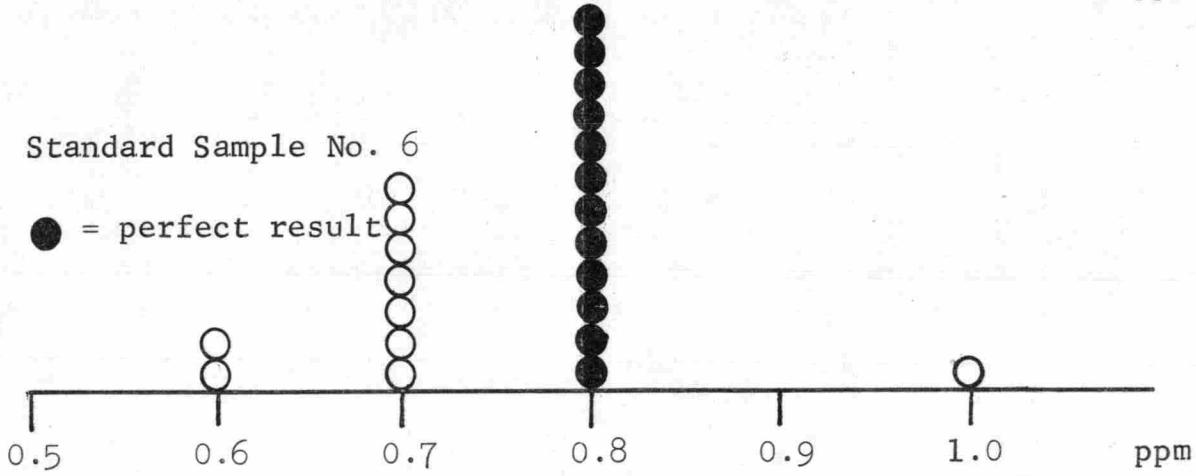
Two laboratories reported results using the proposed diazotization method. One laboratory was within the limit of the method, 0.1 ppm for Samples Nos. 5 and 6, while the other laboratory had high results; for Sample No. 5, 1.8 ppm higher, and 0.8 ppm higher for Sample No. 6.

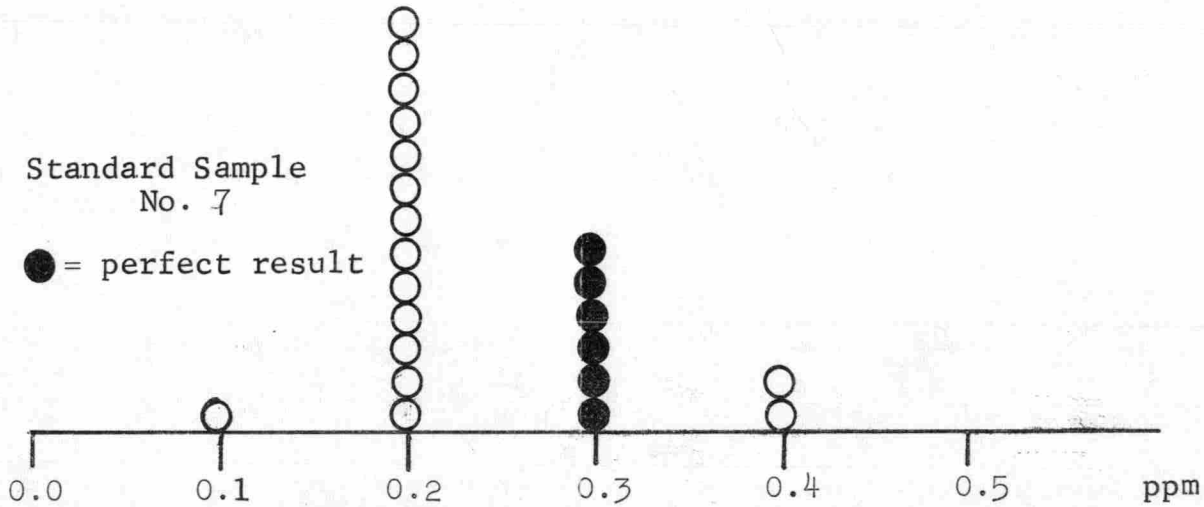
REPORTED RESULTS: FLUORIDE (ppm)

Code	Std. Sample No. 5			Std. Sample No. 6			Std. Sample No. 7		
No.	(1)	(2)	Avge.	(1)	(2)	Avge.	(1)	(2)	Avge.
101	1.0	1.0	1.0	0.8	0.8	0.8	0.3	0.3	0.3
102	0.70	0.76	0.73	0.86	0.83	0.84	0.19	0.20	0.20
103	0.8	0.8	0.8	0.7	0.7	0.7	0.2	0.1	0.2
104	0.9	1.0	1.0	0.8	0.8	0.8	0.2	0.3	0.2
105	0.9	0.9	0.9	0.7	0.7	0.7	0.2	0.3	0.2
106	0.81	0.92	0.9	0.83	0.75	0.8	0.29	0.24	0.3
107	0.9	0.9	0.9	0.8	0.8	0.8	0.3	0.3	0.3
108	0.8	0.8	0.8	0.7	0.7	0.7	0.2	0.2	0.2
109	0.9	1.0	0.95	0.8	0.8	0.8	0.3	0.2	0.25
110	0.8	0.8	0.8	0.6	0.6	0.6	0.2	0.2	0.2
111	1.0	1.0	1.0	0.8	0.8	0.8	0.3	0.3	0.3
112	0.9	0.8	0.8	0.7	0.8	0.8	0.2	0.2	0.2
113	0.7	0.8	0.7	0.8	0.7	0.7	0.1	0.2	0.1
114	1.0	1.0	1.0	0.8	0.8	0.8	0.3	0.4	0.4
115	0.7	0.7	0.7	0.6	0.6	0.6	0.2	0.2	0.2
116	---	---	---	---	---	---	---	---	---
118	0.8	1.0	0.9	0.9	1.0	1.0	0.1	0.2	0.2
119	0.9	0.9	0.9	0.7	0.7	0.7	0.2	0.2	0.2
120	0.9	0.9	0.9	0.7	0.7	0.7	0.3	0.3	0.3
121[a/]	0.85	0.87	0.86	0.68	0.68	0.68	0.23	0.24	0.24
122	0.9	0.9	0.9	0.8	0.8	0.8	0.3	0.3	0.3
123	0.9	1.2	1.0	0.8	0.8	0.8	0.4	0.3	0.4
124	1.0	1.0	1.0	0.8	0.7	0.75	0.2	0.2	0.2

a/ Fluorimetric method values determined were: No. 5, 0.900 and 0.800 ppm; No. 6, 0.800 and 0.700 ppm; and No. 7, 0.156 and 0.140 ppm.


Standard Sample No. 5
● = perfect result
0.6
0.7
0.8
0.9
1.0
1.1
ppm


Standard Sample No. 6
● = perfect result
0.5
0.6
0.7
0.8
0.9
1.0
ppm


Standard Sample
No. 7
● = perfect result
0.0
0.1
0.2
0.3
0.4
0.5
ppm

Methods used: Fluoride (F)

Lab.	Method	Modifications
101	WSP 1454, D:16a-1	None
102	(Not designated)	---
103	" "	---
104	WSP 1454, D:16a-2	SO_4 and Cl determined for correcting F.
105	" "	None
106	" D:16a-1	25-ml aliquots used, $BaSO_4$ ppt centrifuged, blank set at an absorbance of 0.60.
107	" "	None
108	" "	"
109	WSP 1454 ---	"
110	" D:16a-1	"
111	" "	"
112	" "	"
113	" ---	"
114	" D:16a-1	"
115	" "	"
116	(Not determined)	---
118	WSP 1454, D:16a-1	None
119	Scott-Sanchis method, Standard Methods, 11th ed., p. 127.	"
120	WSP 1454 ---	"
121a	" D:16a-2	"
121b	Fluorescence extinction method.	---
122	WSP 1454, D:16a-3 (distillation).	None
123	WSP 1454, D:16a-1	No distillation.
124	" "	none

ERRORS, FLUORIDE DETERMINATION

Error (absolute)	Number of laboratories reporting	Percentage of 22 laboratories reporting
Standard Water Sample No. 5, 0.9 ppm		
0.0 ppm	8	36 percent
±0.1 "	19	86 "
±0.2 "	22	100 "
Standard Water Sample No. 6, 0.8 ppm		
0.0 ppm	12	55 percent
±0.1 "	19	86 "
±0.2 "	22	100 "
Standard Water Sample No. 7, 0.3 ppm		
0.0 ppm	6	27 percent
±0.1 "	21	95 "
±0.2 "	22	100 "

Eighteen laboratories used the zirconium-eriochrome cyanine R method for fluoride, and 3 laboratories used the zirconium-alizarin method. For the three samples, 86, 86, and 95 percent of the laboratories, respectively, reported results within ±0.1 ppm of the calculated concentrations. There appear to be no problems with either method for the range of fluoride concentrations encountered here.

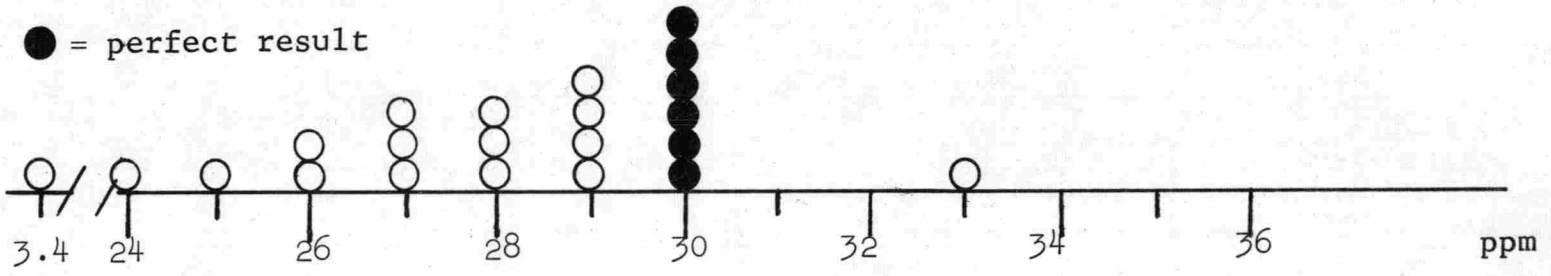
REPORTED RESULTS: SILICA (ppm)

Code	Std. Sample No. 5			Std. Sample No. 6			Std. Sample No. 7		
No.	(1)	(2)	Avge.	(1)	(2)	Avge.	(1)	(2)	Avge.
101	24	24	24	4.9	5.0	5.0	16	16	16
102	27	27	27	4	4	4	18	18	18
103	28	27	28	5.0	5.0	5.0	19	19	19
104	28	29	28	5.1	5.0	5.0	19	19	19
105	27	27	27	4.4	5.1	4.8	19	19	19
106	27	27	27	5	5	5	19	19	19
107	29	30	30	5.1	5.3	5.2	19	20	20
108	30	30	30	5.4	5.3	5.4	20	21	20
109	28	30	29	6.6	7.5	7.0	21	20	20.5
110	30	31	30	5.7	5.8	5.8	20	21	20
111	29	29	29	5.6	5.7	5.6	20	20	20
112	31	30	31	5.7	5.8	5.8	20	21	20
113	29	30	30	5.1	5.0	5.0	19	19	19
114	29	29	29	5.4	5.4	5.4	20	20	20
115	26	26	26	4.8	4.8	4.8	18	18	18
116	---	---	---	---	---	---	--	--	--
118	28	28	28	5.1	5.1	5.1	19	19	19
119	25	25	25	4.0	4.0	4.0	16	16	16
120	30	30	30	5.0	5.0	5.0	20	20	20
121	3.5	3.4	3.4	5.2	5.0	5.1	21	21	21
122	33	33	33	5.9	5.9	5.9	22	22	22
123	29	29	29	5.5	5.5	5.5	20	20	20
124	27	26	26.5	3.5	3.5	3.5	18	17	17.5

SILICA

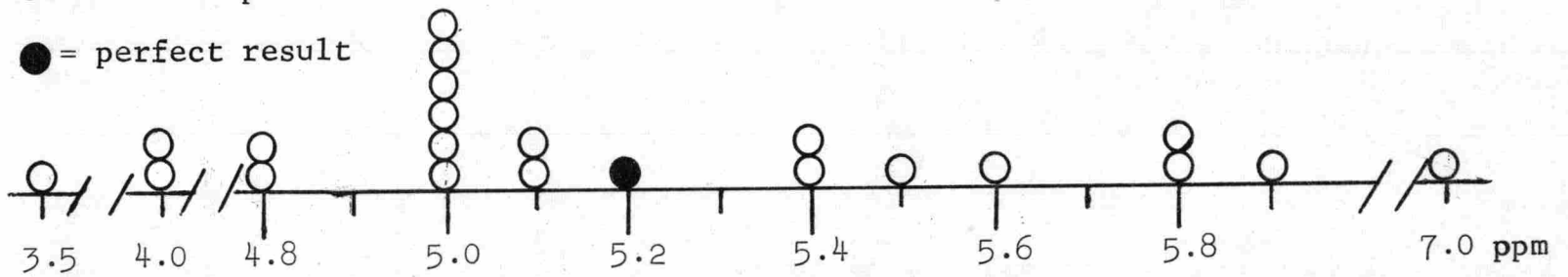
Standard Sample No. 5

● = perfect result



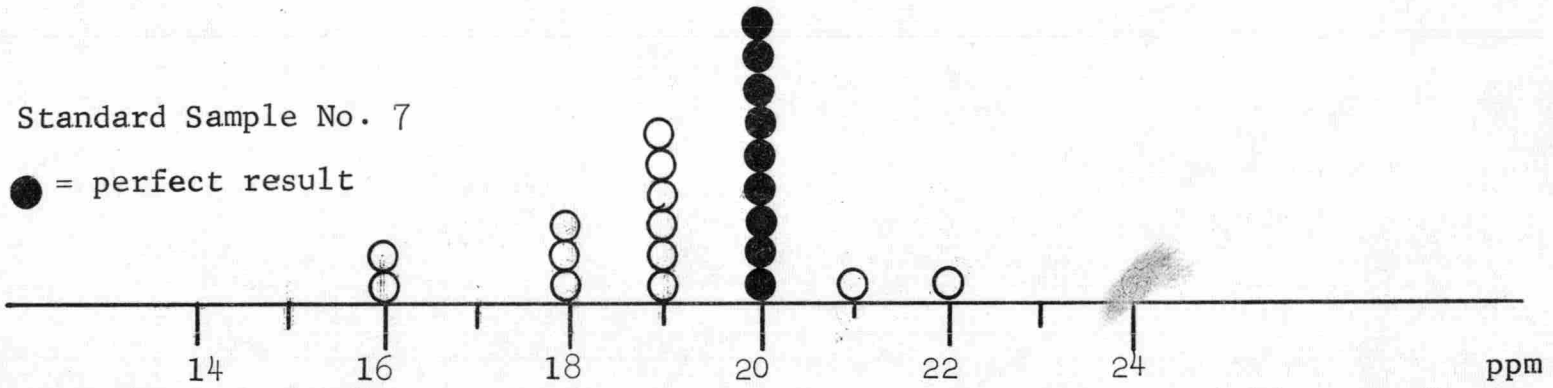
Standard Sample No. 6

● = perfect result



Standard Sample No. 7

● = perfect result



Methods used: Silica (SiO_2)

Lab.	Method	Modifications
101	WSP 1454, D:34a-1	None
102	Hach high range procedure.	Hach colorimeter and Hach reagents.
103	(Not designated)	---
104	WSP 1454, D:34a-1	None
105	" "	"
106	" "	"
107	" "	"
108	" "	2-ml sample, let stand 15 minutes before reading absorbance, 23-ml cells.
109	" "	None
110	" "	"
111	" "	"
112	" "	"
113	" "	"
114	" "	Wavelength used for measuring was 695 mμ.
115	" "	None
116	(Not determined)	---
118	WSP 1454, D:34a-1	None
119	Molybdosilicate method, Standard Methods, 11th ed., p. 225.	Conversion step omitted.
120	WSP 1454, D:34a-1	None
121	" "	"
122	" "	"
123	" "	"
124	" "	"

ERRORS, SILICA DETERMINATION

Error (absolute)	Number of laboratories reporting	Percentage of 22 laboratories reporting
Standard Water Sample No. 5, 30 ppm (SiO_2)		
0 ppm	6	27 percent
±1 "	10	45 "
±2 "	13	59 "
±3 "	17	77 "
±4 "	19	86 "
±5 "	20	91 "
±6 "	21	95 "
⋮	⋮	⋮
±26.6 "	22	100 "
Standard Water Sample No. 6, 5.2 ppm (SiO_2)		
0.0 ppm	1	5 percent
±0.1 "	3	14 "
±0.2 "	11	50 "
±0.3 "	12	55 "
±0.4 "	15	68 "
⋮	⋮	⋮
±0.6 "	17	77 "
±0.7 "	18	82 "
⋮	⋮	⋮
±1.2 "	20	91 "
⋮	⋮	⋮
±1.7 "	21	95 "
±1.8 "	22	100 "
Standard Water Sample No. 7, 20 ppm (SiO_2)		
0 ppm	9	41 percent
±1 "	16	73 "
±2 "	20	91 "
⋮	⋮	⋮
±4 "	22	100 "

The trend again, as occurred in some of the other methods, is reporting lower than calculated values. This may be due in the preparation of the water samples since sodium silicate picks up water rapidly. Even with the lower reported results, 27 percent of the laboratories for Sample No. 5 and 41 percent for Sample No. 7 reported perfect results. However, only one laboratory reported a perfect result for Sample No. 6. The latter sample contained only 5.2 ppm where samples Nos. 5 and 7 contained 30 and 20 ppm. Between 60 and 70 percent of the laboratories reported results within ±1 ppm for Samples Nos. 5 and 7. The results for Sample No. 6 ranged from 3.5 to 7.0 ppm. Only 14 percent of the laboratories reported results to ±0.1 ppm of the calculated value (5.2 ppm). Approximately 90 percent of the laboratories were within ±1 ppm of the calculated value.

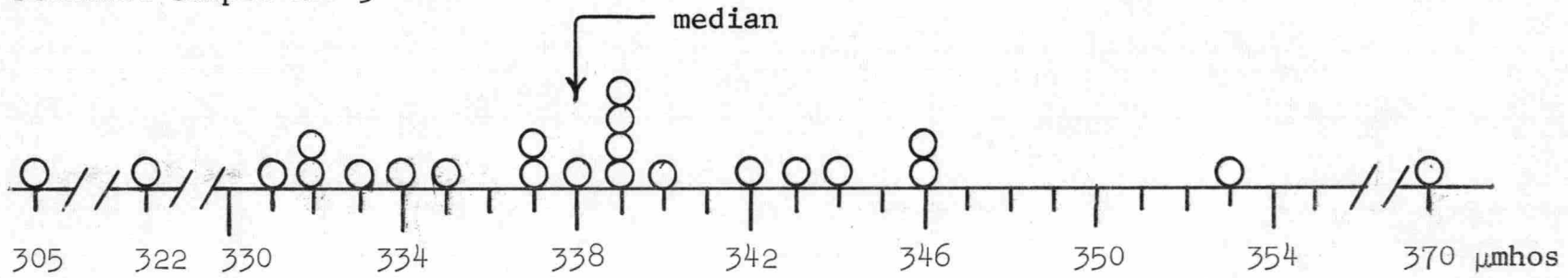
REPORTED RESULTS: CONDUCTANCE (μmhos)

Code No.	Std. Sample No. 5	Std. Sample No. 6	Std. Sample No. 7
101	340	165	417
102	353	166	430
103	322	158	400
104	344	165	417
105	339	164	419
106	332	161	414
107	346	174	423
108	339	164	414
109	305[a/]	148[a/]	375[a/]
110	339	164	417
111	334	161	408
112	339	165	416
113	346	166	423
114	338	164	413
115	332	162	410
116	370	184	448
118	335	162	413
119	343	167	421
120	333	162	411
121	342	167	422
122	337	163	412
123	331	160	406
124	337	165	418

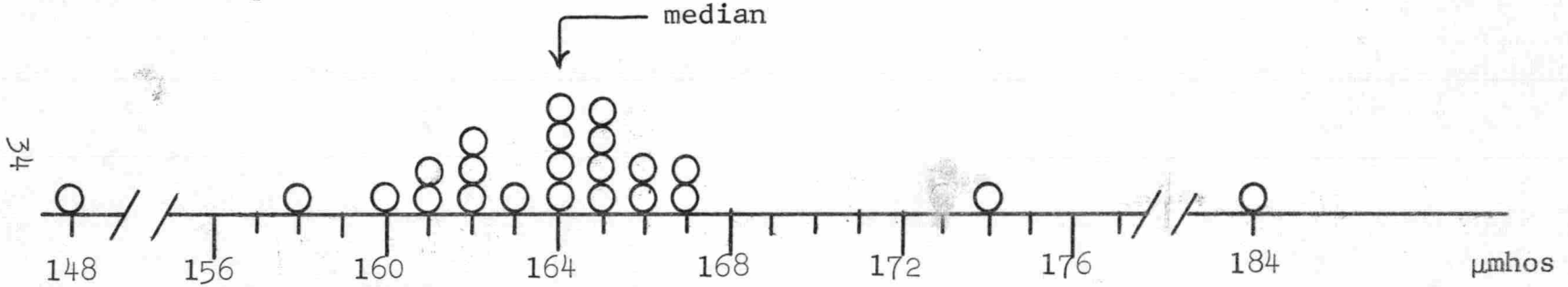
a/ Used wrong potassium chloride solution; later corrected by participating laboratory to 342, 166, and 421, respectively.

CONDUCTANCE

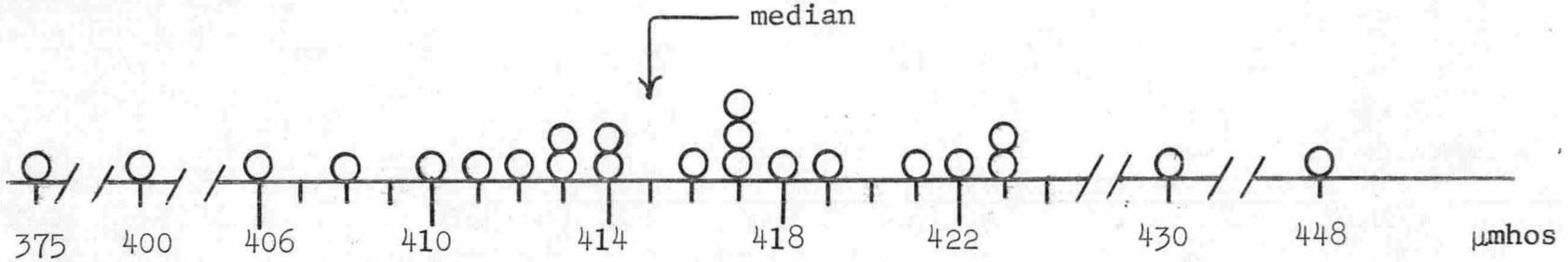
Standard Sample No. 5



Standard Sample No. 6



Standard Sample No. 7



Methods used: Specific Conductance

Lab.	Method	Modifications
101	WSP 1454, D:37a-1	None
102	Conductivity bridge	Industrial Instrument Model RC-16 B2 lab. cond. bridge. Conductance computed from tables, USDA Handbook 60, Table 15, p. 90.
103	WSP 1454, D:37a-1	None
104	" "	"
105	" "	"
106	" "	"
107	" "	"
108	" "	"
109	" "	"
110	" "	"
111	" "	"
112	" "	"
113	" "	"
114	" "	"
115	" "	"
116	Leads and Northrup conductivity meter.	---
118	WSP 1454, D:37a-1	None
119	Conductivity bridge, Standard Methods, 11th ed., p. 114.	"
120	WSP 1454, D:37a-1	"
121	" "	"
122	Leads and Northrup conductivity meter.	Pipette-type cell; cell constant approx. 0.3 reciprocal cm.
123	WSP 1454, D:37a-1	Instrument, Serfass Direct-Reading Conductivity Bridge, Model RCM 15B1, temp. compensated.
124	" "	None

ERRORS, CONDUCTANCE DETERMINATION

Error (median)	Number of laboratories reporting	Percentage of 23 laboratories reporting
Standard Water Sample No. 5, Median: 338 µmhos		
0 µmhos	1	4 percent
±1 "	7	30 "
±2 "	8	35 "
±3 "	9	39 "
±4 "	11	48 "
±5 "	13	57 "
±6 "	16	70 "
±7 "	17	74 "
±8 "	19	83 "
⋮	⋮	⋮
±15 "	20	87 "
±16 "	21	91 "
⋮	⋮	⋮
±32 "	22	96 "
±33 "	23	100 "
Standard Water Sample No. 6, Median: 164 µmhos		
0 µmhos	4	17 percent
±1 "	9	39 "
±2 "	14	61 "
±3 "	18	78 "
±4 "	19	83 "
⋮	⋮	⋮
±6 "	20	87 "
⋮	⋮	⋮
±10 "	21	91 "
⋮	⋮	⋮
±16 "	22	96 "
⋮	⋮	⋮
±20 "	23	100 "

(continued)

ERRORS, CONDUCTANCE DETERMINATION
(continued)

Error (median)	Number of laboratories reporting	Percentage of 23 laboratories reporting
Standard Water Sample No. 7, Median: 415 µmhos		
0 µmhos	0	0 percent
±1 "	3	13 "
±2 "	8	35 "
±3 "	10	43 "
±4 "	12	52 "
±5 "	13	57 "
±6 "	14	61 "
±7 "	16	70 "
±8 "	18	78 "
±9 "	19	83 "
±15 "	21	91 "
±33 "	22	96 "
±40 "	23	100 "

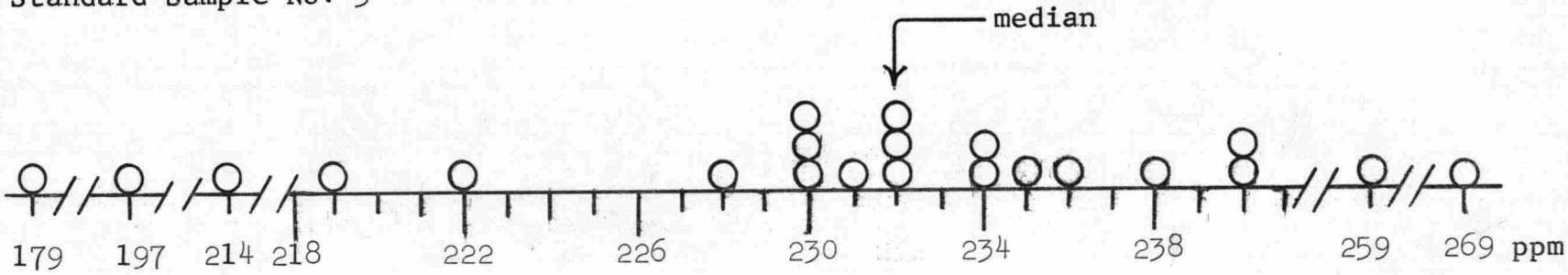
There was no calculated value for specific conductance. The data were evaluated by determining the median of all reported results. The median specific conductances were 338, 164, and 415 µmhos for Standard Samples Nos. 5, 6, and 7, respectively. Almost 90 percent of the participating laboratories reported results within ±10 µmhos of the average.

REPORTED RESULTS: TOTAL DISSOLVED SOLIDS (ppm)

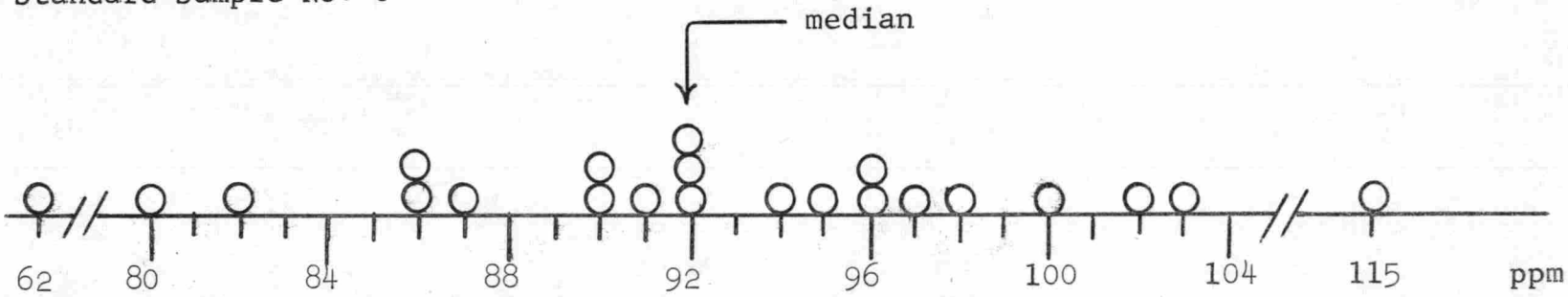
Code No.	Std. Sample No. 5	Std. Sample No. 6	Std. Sample No. 7
101	234	94	272
102	259	90	258
103	232	96	270
104	235	97	276
105	238	102	276
106	230	80	260
107	231	96	272
108	230	91	270
109	234	100	266
110	219	82	256
111	230	92	267
112	228	90	268
113	214	62	254
114	236	95	274
115	232	92	276
116	---	---	---
118	240	98	274
119	179	87	287
120	197	86	250
121	240	103	278
122	232	92	271
123	269	115	303
124	222	86	258

TOTAL DISSOLVED SOLIDS

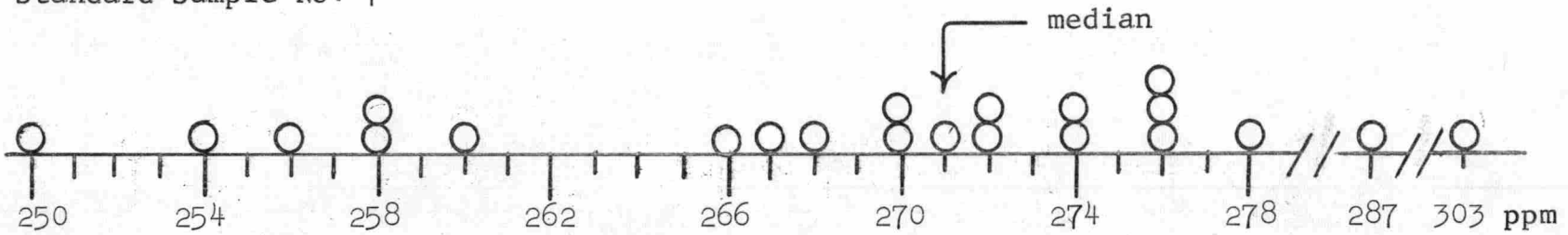
Standard Sample No. 5



Standard Sample No. 6



Standard Sample No. 7



Methods used: Total Dissolved Solids

Lab.	Method	Modifications
101	WSP 1454, D:36a-1	None
102	" D:36a-2	Nitrate not determined, not included in sum.
103	(Not designated)	---
104	WSP 1454, D:36a-1	None
105	" "	"
106	" "	"
107	" "	"
108	" "	"
109	" "	"
110	" "	"
111	" "	"
112	" "	"
113	" "	Air bath
114	" "	None
115	" "	"
116	(Not determined)	---
118	WSP 1454, D:36a-1	None
119	Evaporation 180° C.	---
120	WSP 1454, D:36a-1	None
121	" "	"
122	" "	"
123	" "	"
124	" "	"

ERRORS, TOTAL DISSOLVED SOLIDS DETERMINATION

Error (median)	Number of laboratories reporting	Percentage of 22 laboratories reporting
Standard Water Sample No. 5, Median: 232 ppm		
0 ppm	3	14 percent
±1 "	4	18 "
±2 "	9	41 "
±3 "	10	45 "
±4 "	12	55 "
±6 "	13	59 "
±8 "	15	68 "
±10 "	16	73 "
±13 "	17	77 "
±18 "	18	82 "
±27 "	19	86 "
±35 "	20	91 "
±37 "	21	95 "
±53 "	22	100 "
Standard Water Sample No. 6, Median: 92 ppm		
0 ppm	3	14 percent
±1 "	4	18 "
±2 "	7	32 "
±3 "	8	36 "
±4 "	10	45 "
±5 "	12	55 "
±6 "	15	68 "
±8 "	16	73 "
±10 "	18	82 "
±11 "	19	86 "
±12 "	20	91 "
±23 "	21	95 "
±30 "	22	100 "

(continued)

ERRORS, TOTAL DISSOLVED SOLIDS DETERMINATION
(continued)

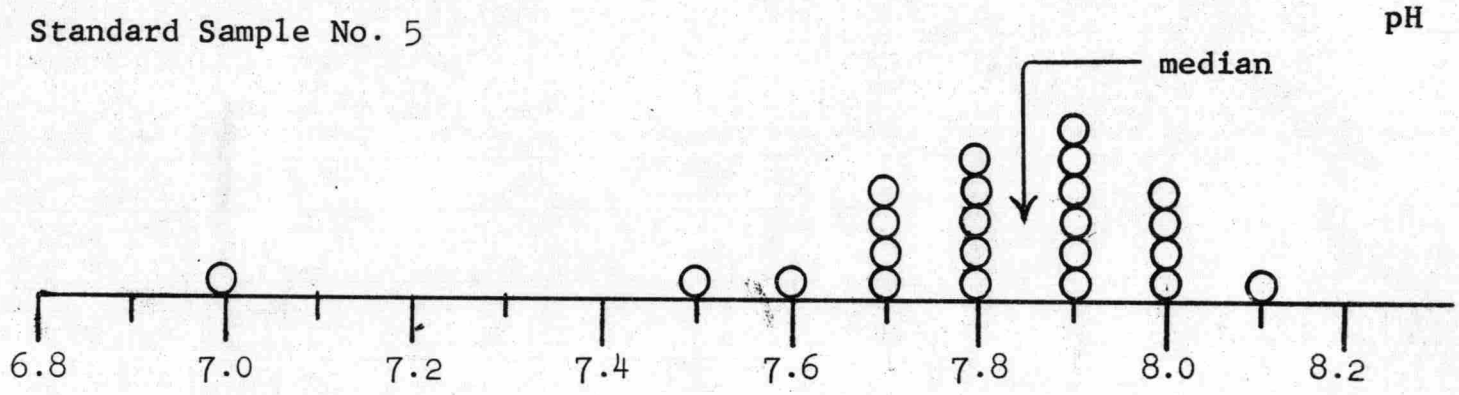
Error (median)	Number of laboratories reporting	Percentage of 22 laboratories reporting
Standard Water Sample No. 7, Median: 271 ppm		
0 ppm	2	9 percent
±1 "	3	14 "
±2 "	6	27 "
±3 "	7	32 "
±4 "	10	45 "
±6 "	13	59 "
±8 "	14	64 "
±10 "	15	68 "
±12 "	17	77 "
±14 "	18	82 "
±16 "	19	86 "
±17 "	20	91 "
±20 "	21	95 "
±33 "	22	100 "

The median value obtained from the results submitted by the participating laboratories was used for evaluating the total dissolved solids determination. Approximately, 75 percent of the laboratories reported results which were within ±10 ppm of the median. Excellent agreement is obtained between the median total solids concetration and the calculated median total solids concentration obtained from multiplying the median specific conductance by 0.65. The latter values were 220, 107, and 270 ppm, while the median reported from the total solids results were 232, 92, and 271 ppm, respectively.

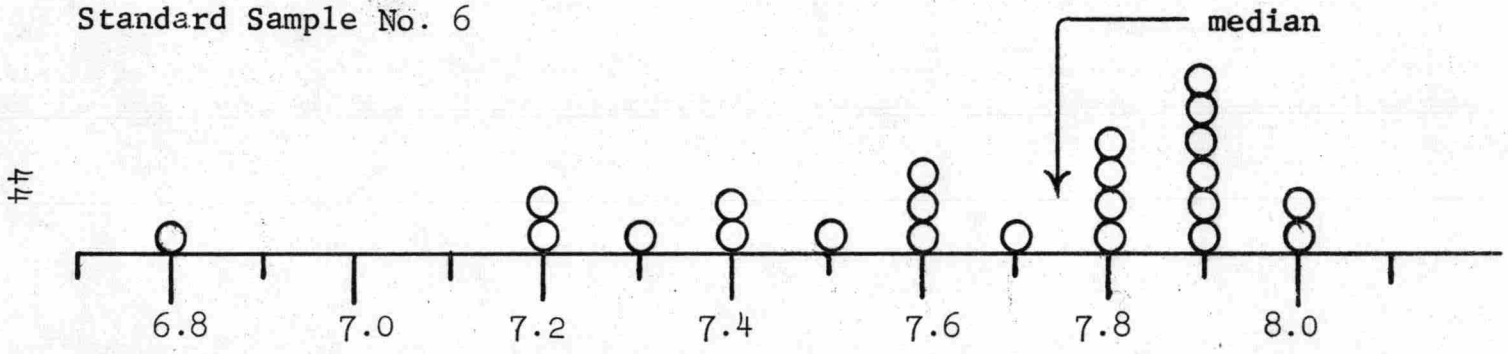
REPORTED RESULTS: pH

Code No.	Std. Sample No. 5			Std. Sample No. 6			Std. Sample No. 7		
	(1)	(2)	Avge.	(1)	(2)	Avge.	(1)	(2)	Avge.
101	7.7	7.7	7.7	7.3	7.3	7.3	7.8	7.8	7.8
102	7.55	7.50	7.52	7.50	7.50	7.50	7.75	7.75	7.75
103	7.9	7.9	7.9	7.9	7.9	7.9	8.2	8.2	8.2
104	7.8	7.6	7.7	7.4	7.4	7.4	7.7	7.8	7.8
105	7.8	7.8	7.8	7.8	7.8	7.8	8.1	8.1	8.1
106	7.8	7.9	7.8	7.9	7.8	7.8	8.1	8.1	8.1
107	7.0	6.9	7.0	6.8	6.9	6.8	7.3	7.3	7.3
108	7.8	7.9	7.8	7.8	7.8	7.8	8.1	8.0	8.0
109	7.9	7.9	7.9	7.8	7.9	7.85	8.1	8.1	8.1
110	7.9	7.8	7.8	7.2	7.2	7.2	8.0	8.0	8.0
111	7.9	7.9	7.9	7.7	7.7	7.7	8.1	8.1	8.1
112	8.1	8.15	8.1	7.85	7.9	7.9	8.3	8.3	8.3
113	8.0	8.0	8.0	8.0	8.0	8.0	8.2	8.1	8.2
114	7.9	7.9	7.9	8.0	7.9	8.0	8.2	8.2	8.2
115	7.7	7.7	7.7	7.4	7.4	7.4	7.8	7.9	7.8
116	8.0	8.0	8.0	7.9	7.9	7.9	8.3	8.3	8.3
118	7.7	7.8	7.7	7.6	7.7	7.6	8.0	8.1	8.0
119	7.9	7.9	7.9	7.9	7.9	7.9	8.1	8.1	8.1
120	8.0	8.0	8.0	7.9	7.9	7.9	8.2	8.2	8.2
121	8.05	8.00	8.02	7.90	7.85	7.88	8.30	8.30	8.30
122	7.8	7.8	7.8	7.6	7.6	7.6	8.1	8.1	8.1
123	7.7	7.6	7.6	7.1	7.2	7.2	7.9	8.0	8.0
124	7.9	7.9	7.9	7.6	7.6	7.6	8.1	8.1	8.1

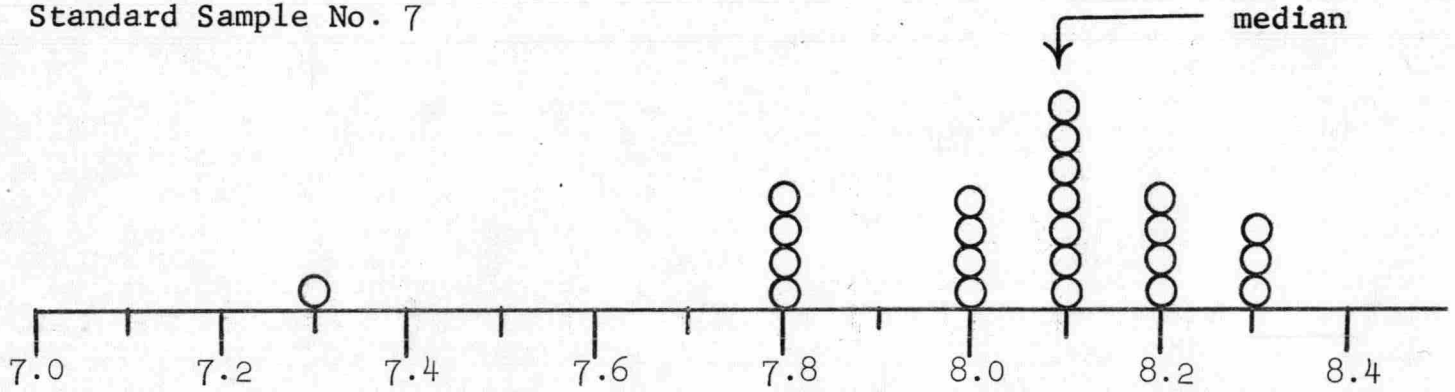
Standard Sample No. 5



Standard Sample No. 6



Standard Sample No. 7



Methods used: pH

Lab.	Method	Modifications
101	WSP 1454, D:29a-1	None
102	" "	"
103	" "	"
104	" "	"
105	" "	"
106	" "	"
107	" "	"
108	" "	"
109	" "	"
110	" "	"
111	" "	"
112	" "	"
113	" "	"
114	" "	"
115	" "	"
116	" "	"
118	" "	"
119	Instrument method.	"
120	WSP 1454, D:29a-1	"
121	" "	"
122	" "	"
123	" "	"
124	" "	"

ERRORS, pH DETERMINATION

Error (median)	Number of laboratories reporting	Percentage of 23 laboratories reporting
Standard Water Sample No. 5, Median: 7.85		
0.0	11	48 percent
±0.1	19	83 "
±0.2	21	91 "
±0.3	22	96 "
!	!	!
±0.8	23	100 "
Standard Water Sample No. 6, Median: 7.6		
0.0	5	12 percent
±0.1	14	61 "
±0.2	17	74 "
±0.3	19	83 "
±0.4	20	87 "
±0.5	22	96 "
!	!	!
±0.8	23	100 "
Standard Water Sample No. 7, Median: 8.1		
0.0	7	30 percent
±0.1	15	65 "
±0.2	18	78 "
±0.3	22	96 "
!	!	!
±0.8	23	100 "

The acidity of the standard samples was adjusted to a pH between 7.5 and 8.0 with sulfuric acid. The pH was checked on each of the samples over a period of several weeks. Even with occasional opening of the bottles over this period, very little change in pH occurred.

The average pH from the reported results of participating laboratories was used in summarizing the data. Approximately 70 percent of the laboratories reported results to within ±0.1 pH unit of the median. In almost all instances where a low pH was reported, the alkalinity value reported was also low.

CONCLUSIONS AND RECOMMENDATIONS

Total alkalinity

1. No changes are proposed in the method used or in the method of reporting results, except to emphasize the importance of determining alkalinity as soon as the bottle is opened.

Nitrate

1. Nitrate concentration of the order of 10 ppm cannot be determined to within 0.1 ppm by the phenoldisulfonic acid method. It should be reported to the nearest ppm.

2. The accuracy of the above method at 2.0 ppm nitrate is, at best, ±0.5 ppm.

3. It is recommended that a series of standard samples be sent to each laboratory, checking the proposed hydrazine method.

Nitrite

1. Nitrite concentration below 5.4 ppm cannot be determined accurately to 0.1 ppm.

2. There is need for improvement in the diazotization method, and it is recommended that a series of standard samples be sent to each laboratory, checking the proposed diazotization method.

Fluoride

1. The present methods are satisfactory, and no changes are proposed in the method used, or in the method of reporting results.

Silica

1. It is probably justifiable to report results to the nearest ppm for silica above 10 ppm.

2. The results indicate that silica at 5.2 ppm cannot be determined to 0.1 ppm.

Specific conductance

1. The accuracy of the specific conductance determination at concentration levels below 500 μmhos is not better than ±10 μmhos, and results should be reported to two significant figures.

Total dissolved solids

1. The accuracy of the total dissolved solids determination at concentration levels below 300 ppm is not better than ±10 ppm, and results should be reported to two significant figures.

pH

1. It is probably justifiable to report pH to 0.1 of a unit if the pH meter used is checked carefully with a good quality pH buffer.