WATER CHLORINE (RESIDUAL) NO. 2

ANALYTICAL REFERENCE SERVICE REPORT NUMBER 40

ENVIRONMENTAL PROTECTION AGENCY

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Report of a Study Conducted by
ANALYTICAL REFERENCE SERVICE

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ENVIRONMENTAL PROTECTION AGENCY
Office of Water Programs
Cincinnati, Ohio 45213
1971

FOREWORD

The Analytical Reference Service (ARS) is conducted by the Water Hygiene Division of the Environmental Protection Agency to evaluate laboratory methods in the environmental field. Cooperative studies by member organizations, who analyze identical samples and critically review methodology, provide the mechanism for:

> Evaluation of analytical procedures, including precision and accuracy, by comparison of the procedures and results reported by participating laboratories.
>
> Exchange of information regarding method characteristics.
>
> Improvement or replacement of existing methods by development of more accurate procedures, and development of new methodology for determination of new pollution compounds.

Samples are designed to contain measured amounts of selected constituents. Decisions as to qualitative makeup are made by the membership, consultants, and the ARS staff. Notice of each study is sent to the entire membership. To those who desire to participate, a portion of the study sample is sent, along with data forms for reporting numerical values, a critique of the procedures used, comments on modifications, sources of error, difficulties encountered, or other pertinent factors. The results and comments received are compiled, and a report of each study is prepared.

Now primarily directed toward examination of water, in the past studies have included methods for analysis of air, milk, and food. Some studies are periodically repeated for the advantage of new members, the evaluation of new methods, or the reevaluation of existing methods.

The selection of studies is guided by requests from standard methods committees and the responses to questionnaires periodically circulated among the membership, which now includes 299 Federal, state, and municipal agencies; industries; universities; consulting firms; and foreign agencies.

COMPLETED STUDIES

Water-Minerals	Calcium, magnesium, hardness, sulfate, chloride, alkalinity, nitrite, nitrate, sodium, and potassium; study No. 1 completed in 1956, No. 2 in 1958 and No. 3 in 1961.
Water-Metals	Lead, copper, cadmium, aluminum, chromium, iron, manganese, and zinc; study No. 1 completed in 1957 and No. 2 in 1962. These same metals plus silver; study No. 3 completed in 1965. Except for the substitution of magnesium for aluminum, these same metals were analyzed by atomic absorption in 1967; study No. 4. Copper, manganese, and aluminum in the presence and absence of interferences; study No. 5 completed in 1969. Aluminum, beryllium and barium by atomic absorption; study No. 6 completed in 1970.
Water-Fluoride	Fluoride in the presence and absence of interferences, with and without distillation by a specified procedure; study No. 1 completed in 1958 and No. 2 in 1961. Fluoride by ion-exchange and fluoride electrode; study No. 3 completed in 1969.
Water-Radioactivity	Gross beta activity; study No. 1 completed in 1959 and No. 2 in 1961. Gross beta and strontium-90 activity; study No. 3 completed in 1963.
Water-Surfactant	Surfactant in various waters; study No. 1 completed in 1959, No. 2 in 1963 and No. 3 in 1968.
Water-Oxygen Demand	Biochemical oxygen demand and chemical oxygen demand; study No. 1 completed in 1960. Chemical oxygen demand; study No. 2 completed in 1965.
Water-Trace Elements	Arsenic, boron, selenium, and beryllium; study No. 1 completed in 1962. These same metals plus vanadium; study No. 2 completed in 1966.

Freshwater Plankton	Evaluation of the precision and accuracy obtainable by the use of various methods of plankton counting and identification; study No. 1 completed in 1964.
Water-Nutrients	Silicate, phosphate, ammonia nitrogen, organic nitrogen, and nitrate nitrogen; study No. 1 completed in 1966. Ammonia nitrogen, nitrate nitrogen and ortho, poly, and organic phosphate; study No. 2 completed in 1969.
Water-Phenols	Phenol and 2, 4-dichlorophenol in water by two specified methods; study No. 1 completed in 1966.
Water-Cyanides	Potassium cyanide and potassium ferricyanide in water by two specified methods; study No. 1 completed in 1967.
Water-Chlorine	Free and combined chlorine by nine different methods; study No. 1 completed in 1969; study No. 2 completed in 1970.
Air-Inorganics	Chloride, sulfate, fluoride, and nitrate in aqueous solution and on glass-fiber, high-volume filter mats; study No. 1 completed in 1958.
Air-Lead	Filter paper tape impregnated with lead; study No. 1 completed in 1961.
Air-Particulates	Microscopic identification of some common atmospheric particulates; study No. 1 completed in 1964.
Air-Sulfur Dioxide	Sulfur dioxide in air by a specified method; study No. 1 completed in 1963.
Water-Pesticides	Lindane, heptachlor epoxide, DDE, and dieldrin in water; study No. 1 completed in 1965. Lindane, heptachlor, aldrin, heptachlor epoxide, p,p'-DDE, dieldrin, endrin, o,p'-DDT, p,p'-DDT, and methoxychlor in water; study No. 2 completed in 1968. Lindane, heptachlor epoxide, dieldrin, heptachlor, p,p'-DDT and endrin; study No. 3 completed in 1970.

Food-Pesticides	DDT in milk; study No. 1 completed in 1962. Lindane, heptachlor epoxide, DDE, and dieldrin in milk; study No. 2 completed in 1965.
Water-Physics	Total alkalinity, pH, specific conductance and total residue in water; study No. 1 completed in 1970.

Copies of these reports are available from ARS on request as long as the present supply lasts. In most cases reports published prior to 1965 are no longer available. Order by title; namely, Water Metals No. 4, or Water Surfactant No. 3, etc.

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PREFACE

In a previous study nine different methods for the determination of chlorine were studied. As a result of that study it was concluded, among other things, that the precision of all the methods was poorer than anticipated, probably because of the variability introduced by the preparation of samples from dry mixtures.

It has since been observed that a fairly strong chlorine solution sealed in a glass ampoule and stored in the dark will remain stable for at least three months. It seemed advisable, therefore, to repeat the study using the liquid samples to assure more homogeneity of sample aliquots. In addition, the DPD colorimetric procedure was substituted for one of the orthotolidine methods, since the former has been shown by a British study to be one of the best methods and the latter was found to be one of the poorest in the previous ARS study.

ACKNOWLEDGMENTS

Robert T. Williams, Chief, Analytical Applications Laboratory, Waste Identification and Analyses Activities, Cincinnati Water Research Laboratory, Ohio River Basin Region, provided referee results for the samples used in this study.

PARTICIPANTS IN THIS STUDY

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Allentown City Laboratory, Pennsylvania
Arizona State Health Laboratory, Phoenix
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Brown and Caldwell Laboratories, San Francisco, California
Calgon Corporation, Pittsburgh, Pennsylvania
California State Department of Public Health, Los Angeles
California Water Service Company, San Jose, California
Central Water Filtration Plant, Chicago, Illinois
City of Charlotte Water Department, North Carolina
City of Erie, Bureau of Water, Pennsylvania
City of Long Beach, Water Department, California
City of New York, Department of Health, New York
City of Yonkers, Bureau of Water, New York
County of Fresno, Department of Public Health, California
Denver Board of Water Commissioners, Colorado
Department of the Army, APO, New York
Department of Municipal Laboratories, Hamilton, Ontario, Canada
Department of National Health and Welfare, Public Health Engineering Division, Vancouver, B.C., Canada
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First United States Army Medical Laboratory, Fort Sam Houston, Texas
Goodyear Atomic Corporation, Piketon, Ohio
Hackensack Water Company, New Milford, New Jersey
Harris Laboratories, Incorporated, Lincoln, Nebraska
Illinois State Water Survey, Peoria
Illinois State Water Survey, Urbana
Indiana State Board of Health, Indianapolis
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Isotopes - A Teledyne Company, Sandusky, Ohio
Lawrence Experiment Station, Massachusetts
Los Angeles County Flood Control District, California
Los Angeles Department of Public Works, Playa Del Rey, California
Louisiana State Department of Health, New Orleans
Mekoroth Water Company, Tel-Aviv, Israel
Metropolitan Corporation of Greater Winnipeg, Manitoba, Canada
Metropolitan Sanitary District of Greater Chicago, Illinois
Metropolitan Sewer District, Cincinnati, Ohio
Metropolitan Water, Sewerage and Drainage Board, Sydney, Australia
Minneapolis Water Department, Minnesota

Monroe County Health Department, Rochester, New York
National Institute for Water Research, Pretoria, South Africa
New Jersey State Department of Health, Trenton
New York State Department of Health, Albany
North Carolina Department of Water and Air Resources, Raleigh
North Jersey District Water Supply Commission, Wanaque
Ohio State Department of Health, Columbus
Oklahoma State Board of Health, Oklahoma City
Orange County Air Pollution Control District, Anaheim, California
Oregon State Board of Health, Portland
Pacific Gas and Electric Company, Emeryville, California
Pan American World Airways, Patrick AFB, Florida
Philadelphia Suburban Water Company, Bryn Mawr, Pennsylvania
Philadelphia Water Department, Belmont Laboratory, Pennsylvania
Philadelphia Water Department, Torresdale Laboratory, Pennsylvania
Regional Environmental Health Laboratory (SGHK), Kelly AFB, Texas
Sandia Corporation, Albuquerque, New Mexico
San Diego County Department of Public Health, California
Sixth U. S. Army Medical Laboratory, Sausalito, California
Springwells Filtration Plant, Dearborn, Michigan
St. Louis County Water Company, University City, Missouri
Suffolk County Department of Health, Smithtown, New York
United States Pipe and Foundry Company, Birmingham, Alabama
U. S. Army Environmental Hygiene Agency, Edgewood Arsenal, Maryland
USDI, FWQA, AWTR Research Activities, Pomona, California
USDI, FWQA, Chemistry and Physics, Cincinnati, Ohio
Virginia State Department of Health, Bureau of Industrial Hygiene, Richmond
Washington State Department of Health, Seattle
Washington State University, College of Engineering, Research Division, Pullman
Water Commission, Jamaica, West Indies

ABSTRACT

In this study each participant was shipped four sealed glass ampoules of concentrated solution which when diluted according to instructions, provided two samples containing free chlorine and one containing combined chlorine. Each analyst was requested to use two preselected methods from the seven being studied but unfortunately not all complied and although 71 participants submitted results, only seven were submitted for the leuco crystal violet method; whereas sixteen to thirty results were obtained for each of the other methods. Statistical analysis of these results indicated that the best accuracy and precision was obtained by leuco crystal violet and the stabilized neutral orthotolidine (SNORT) procedures, followed by DPD-titrimetric, amperometric titration, DPD-colorimetric and methyl orange. By far the poorest was the orthotolidine-arsenite (OTA) procedure.

WATER CHLORINE (RESIDUAL) NO. 2

DESIGN OF THE STUDY

In order to obtain maximum stability, the samples were prepared as liquid concentrates and shipped in sealed glass ampoules. Samples 1, 2, and 3 were hypochlorite solutions (Zonite) of different concentrations. Ampoule 4 contained an ammonium chloride-borate buffer solution which was to be mixed with sample 3 to produce a combined chlorine solution.

When diluted 10 ml to one liter with chlorine-free, chlorine-demand free water according to instructions, the samples approximated chlorinated water supplies (see Table 1).

Table 1. COMPOSITION OF SAMPLES

	mg/liter in diluted sample		
	Sample 1	Sample 2	Sample 3
Free chlorine	0.44	0.98	(0.00) 0.05[a]
Total chlorine	0.44	0.98	0.66

[a]See section on "Treatment of the Data."

The stock solution was standardized by iodometric titration, and intermediate dilutions were also checked by iodometric titration. The concentrated samples were also diluted according to instructions and checked amperometrically by the Analytical Reference Service staff and by another referee laboratory. The results agreed very closely with the calculated value based on the iodometric titrations of the stock solution.

Instructions for the preparation of chlorine-free, chlorine-demand free water by three different methods were sent with the samples; these were as follows:

Add sufficient chlorine to distilled water to destroy the ammonia. The amount of chlorine required will be about ten times the amount of ammonia nitrogen present; in no case should the initial residual be less than 1.0 mg/l free chlorine but generally this amount will be sufficient. Allow the chlorinated distilled water to stand overnight or longer, then expose to direct sunlight until all residual chlorine is discharged (usually about one day). Since water used for preparation and dilution of samples must also be free of chlorine, this water should be checked for absence of chlorine before use.

The Blak-Ray B-100A long wave ultraviolet lamp (Arthur H. Thomas Company, catalogue number 6323k) will also slowly dechlorinate heavily chlorinated (100 mg/l) distilled water stored in 9 and 18-liter glass bottles. The radiation is directed through the side of the closed bottle with the blue glass fluorescent filter removed from the lamp.

Chlorine-demand free water can also be prepared by the use of an ion-exchange resin. This can be done by mixing 1.6 liters IR-120 and 3.2 liters of IR-400 or using the ready mixed analytical grade Amberlite MB-1 in a 3-foot column of approximately 2.5 to 5 cm diameter. Pass distilled water at a relatively slow rate through the resin bed and collect in a scrupulously clean receiver that will protect the treated water from undue exposure to the atmosphere.

Participants were also instructed to observe the following precautions.

1. Be sure to use chlorine free, and chlorine-demand free water in the preparation of all solutions.

2. Use only scrupulously clean glassware; namely, glassware soaked overnight in acid (potassium dichromate cleaning solution) or in a 1 to 100 dilution of Clorox and then rinsed with chlorine free, and chlorine-demand free water and dried.

3. To protect the chlorine free, chlorine-demand free water, use a sulfuric acid or calcium chloride trap on the air inlet to the stoppered storage bottle. Withdraw the water by a glass siphon arrangement through the same stopper. Unless this is done, the water may very quickly absorb ammonia from the atmosphere. Otherwise, prepare the water fresh daily.

In order to obtain approximately an equal number of data for each method, participants were requested in the announcement letter to indicate on their reply form the two methods they intended to use. As a result of unequally distributed returns, some participants were asked to analyze the samples by a method other than one of the two methods they had indicated. Unfortunately, very few complied.

In the announcement of this study the participants were provided with a copy of the DPD colorimetric procedure, and were told that copies of the methyl orange, leuco crystal violet, DPD titrimetric, and stabilized neutral orthotolidine procedures could be found in the appendices of the previous "Water Chlorine (Residual) No. 1" report, which was sent to those participants who requested it. They were also reminded that the amperometric and orthotolidine-arsenite (OTA)

procedures could be found in the 12th edition of Standard Methods for the Examination of Water and Wastewater.

TREATMENT OF THE DATA

After the results of analysis were received, the data were coded and analyzed by computer for normality of distribution and subsequent rejection of outliers (see Appendix D) that were nonrepresentative because of errors in calculation, dilution, or other indeterminate factors. After rejection of outliers, the data were then statistically analyzed by computer for precision and accuracy (see Appendix C), and finally, their precisions and accuracies were compared for significance of differences (see Appendix E).

If sample 3 was prepared according to instructions, there would be no free chlorine present. However, it is not possible to divide by zero and obtain a numerical value in the calculation of the relative error. The true value for free chlorine in sample 3, therefore, was changed to the overall mean value of 0.05 to permit complete analysis of the data by computer. This value is also more realistic than zero since it is about the minimum amount that can be measured by any of the methods; namely, is equivalent to the variation in the determination of a blank.

For unknown reasons (perhaps, because a different batch of ampoules were used) the chlorine content dropped after shipment in most of the ampoules containing sample 1. The results obtained on the analysis of this sample, therefore, can be used only for comparative purposes and not as a measure of the overall precision or accuracy of the methods.

RESULTS

SAMPLE 1: 0.44 mg/liter free, 0.44 mg/liter total chlorine (Table 2; Figures 1 through 14)

This sample was designed to provide only free chlorine at a concentration likely to be encountered in analysis of treated potable water. Although the sample was analyzed after being sealed in glass ampoules and good agreement with the calculated value was obtained by the two referee analysts, an unexplained slow demand apparently reduced the chlorine concentration about 50%. There is little value, therefore, in considering the accuracy of the determinations except for comparison between methods. The precision data, likewise, is useful only for comparing the methods and should not be used for predicting the degree of precision obtainable by any of the methods.

Table 2. SUMMARY OF DATA ON SAMPLE 1
(0.44 mg/liter free, 0.44 mg/liter total chlorine)

Method	Determination	No. of results	No. of outliers	Mean	Mean error	Standard deviation	Rel. error	Relative std. dev.	95% tol. limits	Total error
Methyl orange	Free	22	0	0.221	-0.219	0.143	49.69	64.68	0.386	114.86
	Total	22	0	0.269	-0.171	0.162	38.84	60.26	0.437	112.59
Leuco crystal violet	Free	7	0	0.190	-0.250	0.085	56.82	44.56	0.339	95.31
	Total	7	0	0.231	-0.209	0.055	47.40	23.85	0.221	72.59
Orthotolidine-arsenite	Free	29	0	0.158	-0.282	0.090	64.03	56.79	0.231	104.95
	Total	28	1	0.187	-0.253	0.098	57.47	52.21	0.252	101.90
SNORT	Free	18	0	0.199	-0.241	0.093	54.67	46.64	0.262	97.04
	Total	17	0	0.242	-0.198	0.092	44.92	38.11	0.264	87.00
DPD-colorimetric	Free	28	0	0.178	-0.263	0.102	59.66	57.51	0.263	106.18
	Total	27	1	0.227	-0.213	0.100	48.32	44.12	0.260	94.00
DPD-titrimetric	Free	17	0	0.181	-0.259	0.110	58.82	60.71	0.314	108.86
	Total	17	0	0.242	-0.198	0.103	44.92	42.45	0.294	91.77
Amperometric titration	Free	23	0	0.199	-0.241	0.106	54.74	53.23	0.283	102.95
	Total	23	0	0.251	-0.189	0.072	42.98	28.64	0.192	75.63
Orthotolidine	Free	1	0	0.170	- - - -	- - -	- - -	- - -	- - -	- - - -
	Total	2	0	0.200	- - - -	- - -	- - -	- - -	- - -	- - - -
DPD-colorimetric (N, N-dimethyl)	Free	--	-	- - -	- - - -	- - -	- - -	- - -	- - -	- - - -
	Total	1	0	0.500	- - - -	- - -	- - -	- - -	- - -	- - - -

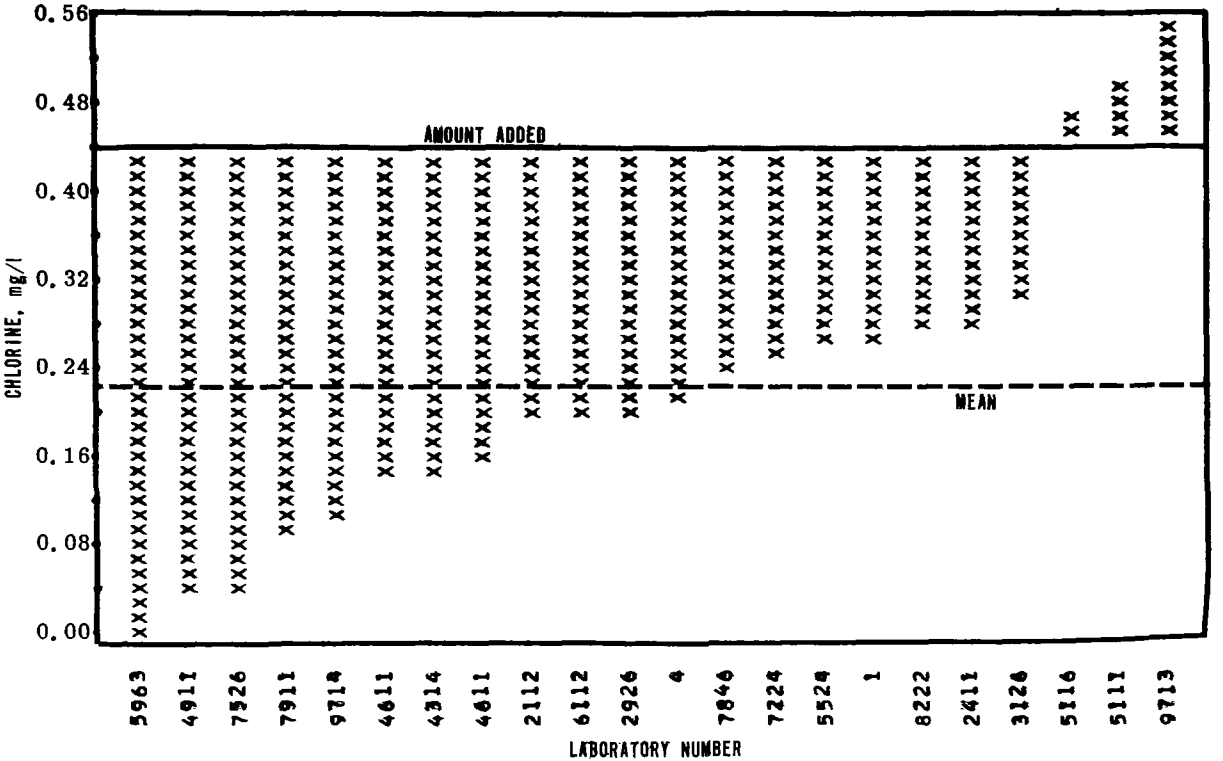

Figure 1. Bar graph for free residual chlorine in sample 1 by methyl orange method.

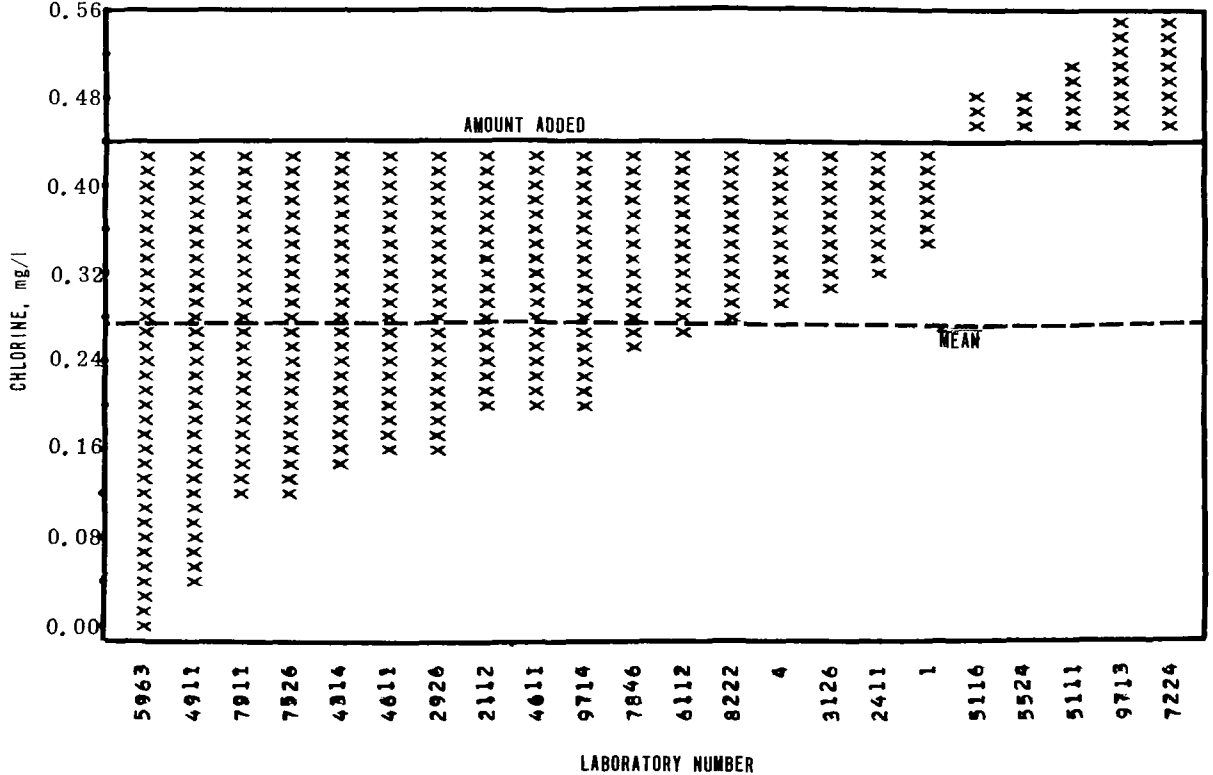

Figure 2. Bar graph for total residual chlorine in sample 1 by methyl orange method.

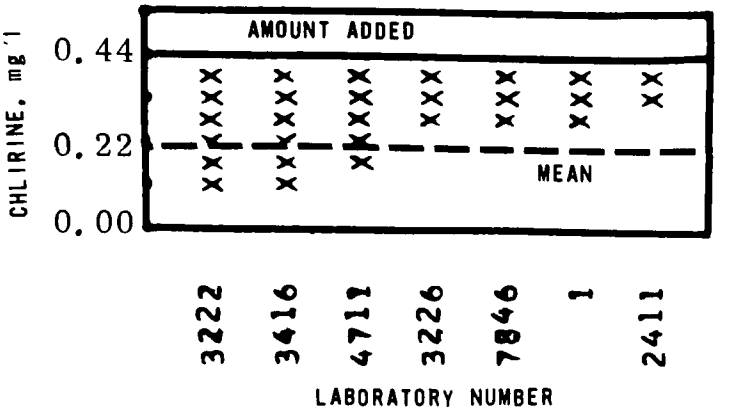

Figure 3. Bar graph for free residual chlorine in sample 1 by leuco crystal violet method.

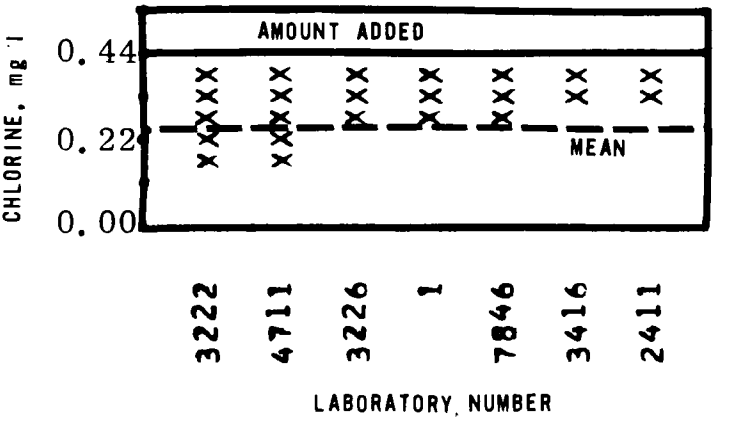

Figure 4. Bar graph for total residual chlorine in sample 1 by leuco crystal violet method.

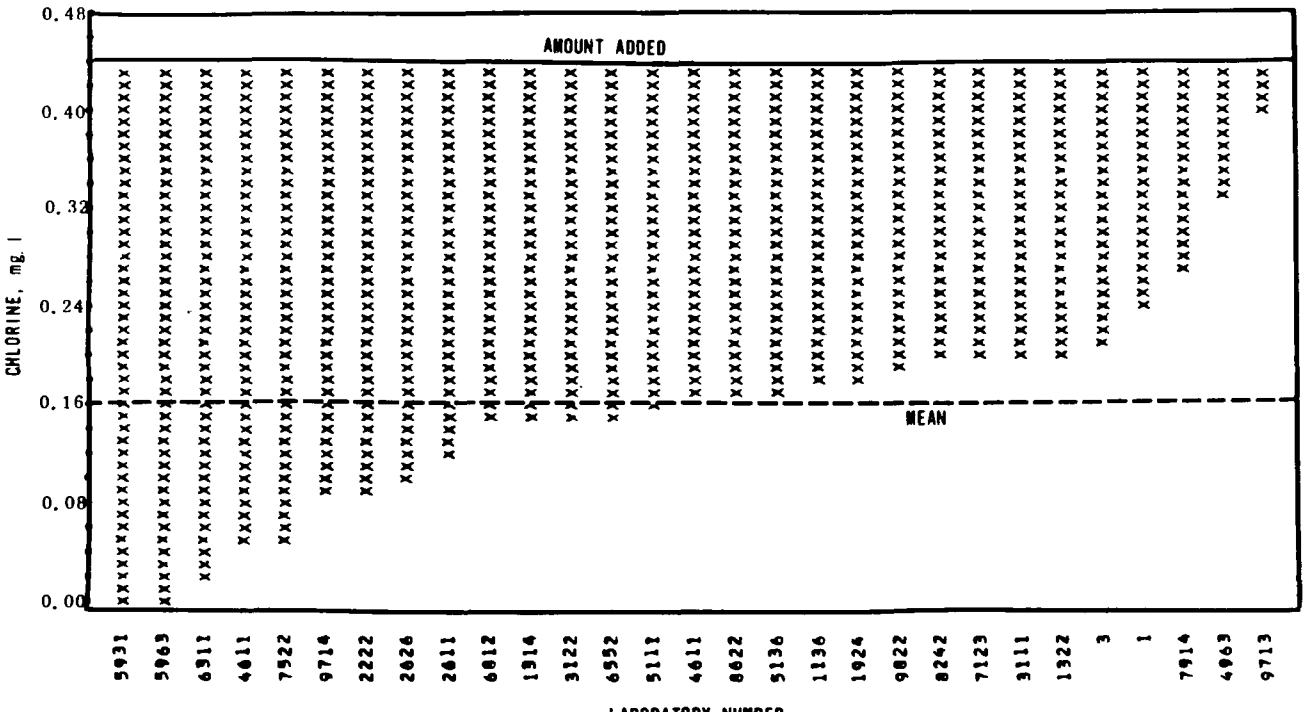

Figure 5. Bar graph for free residual chlorine in sample 1 by orthotolidine-arsenite method.

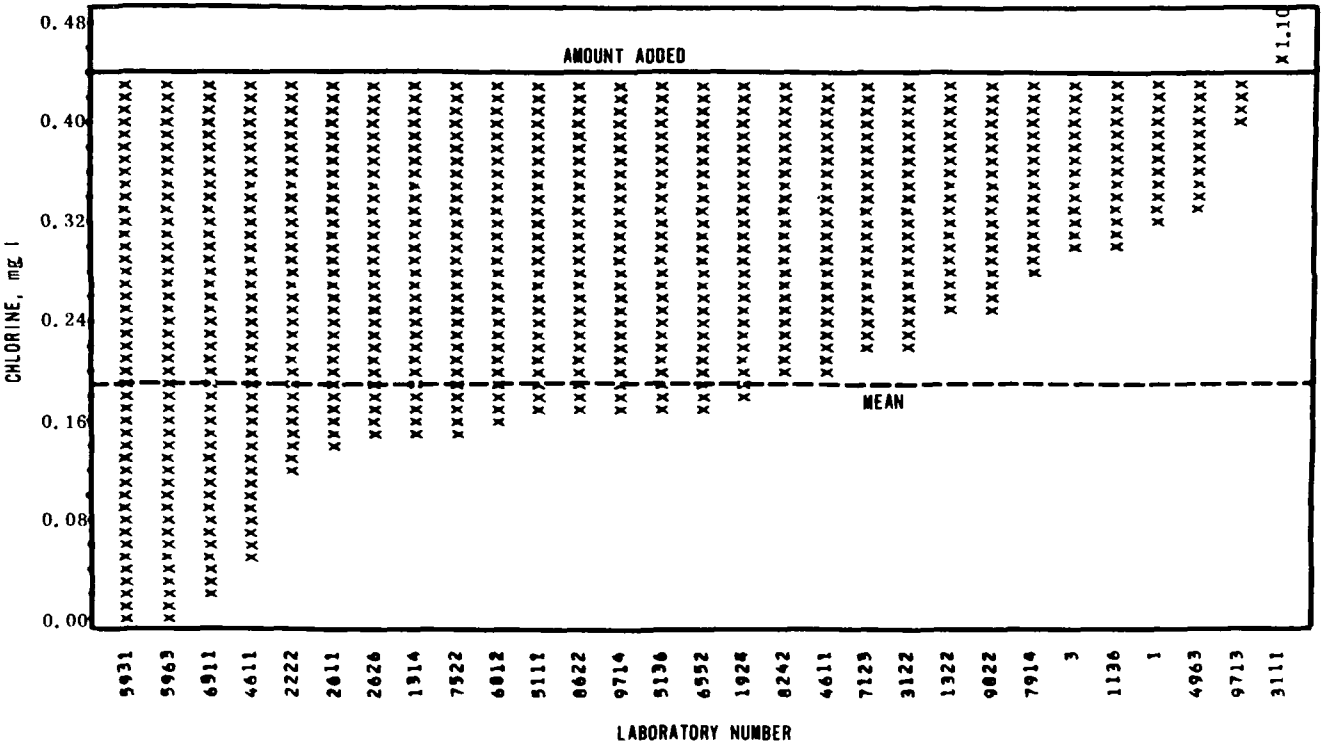

Figure 6. Bar graph for total residual chlorine in sample 1 by orthotolidine-arsenite method.

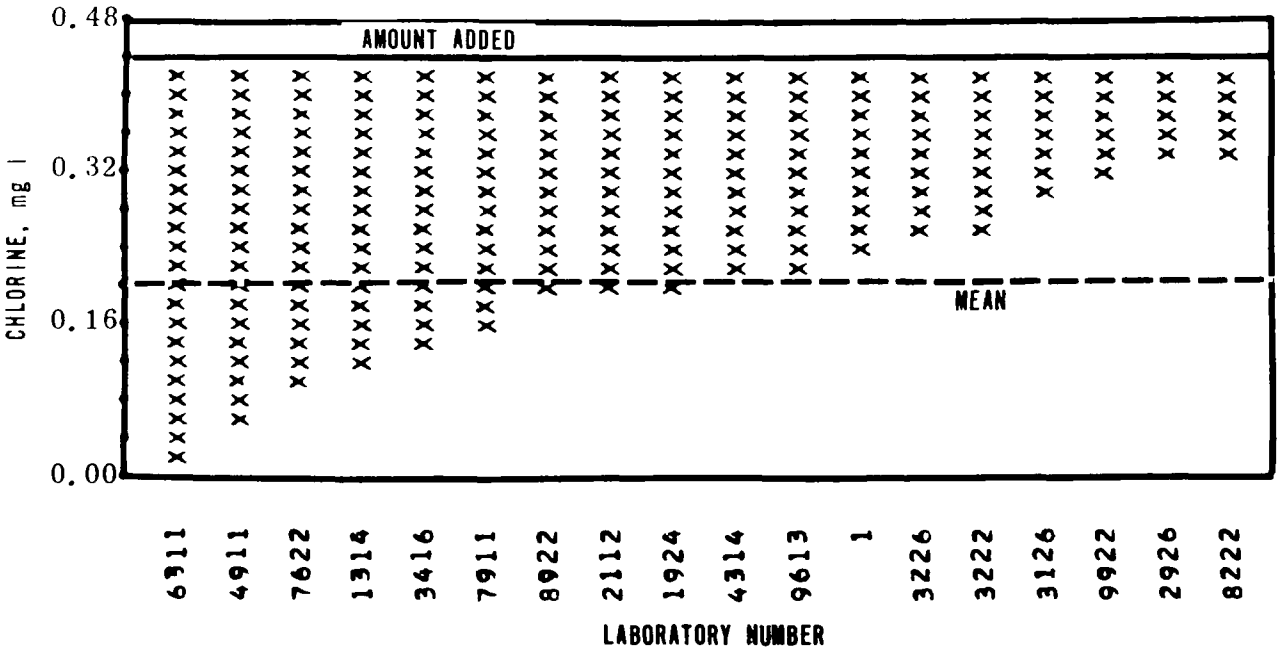

Figure 7. Bar graph for free residual chlorine in sample 1 by stabilized neutral orthotolidine method.

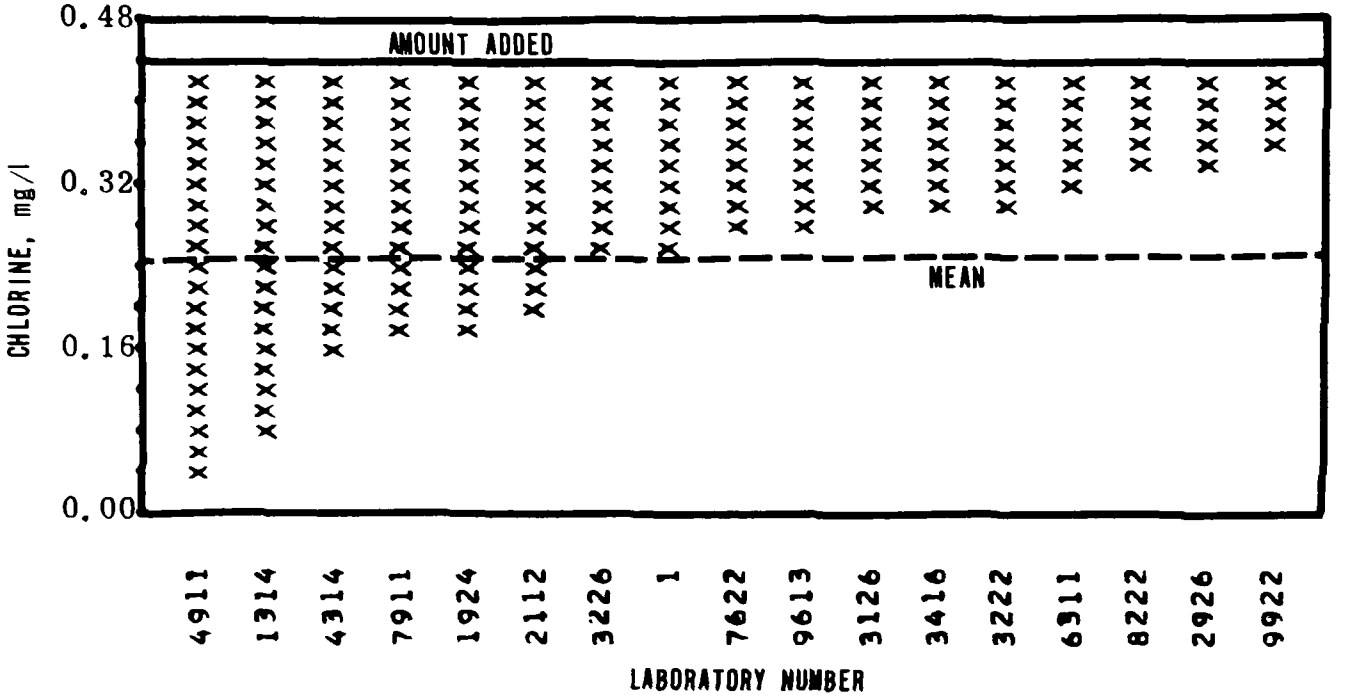

Figure 8. Bar graph for total residual chlorine in sample 1 by stabilized neutral orthotolidine method.

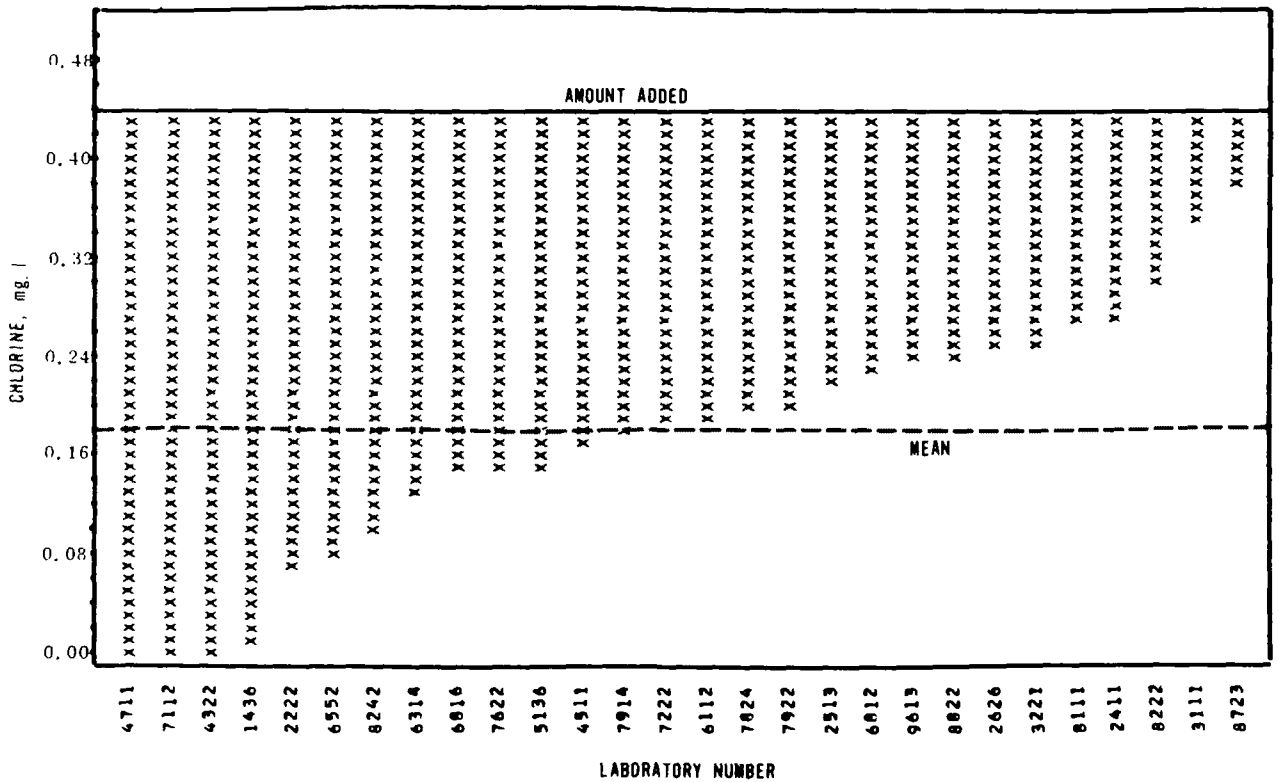

Figure 9. Bar graph for free residual chlorine in sample 1 by DPD-colorimetric method.

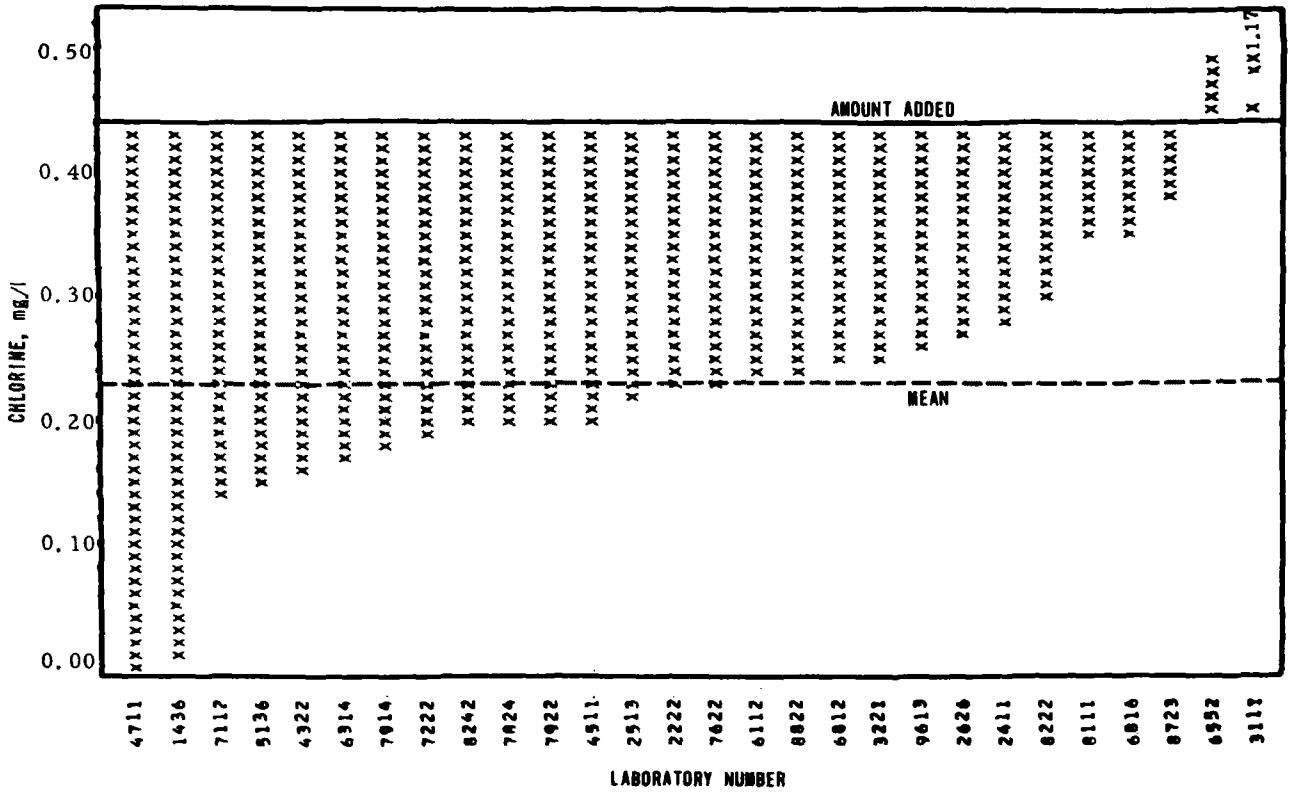

Figure 10. Bar graph for total residual chlorine in sample 1 by DPD-colorimetric method.

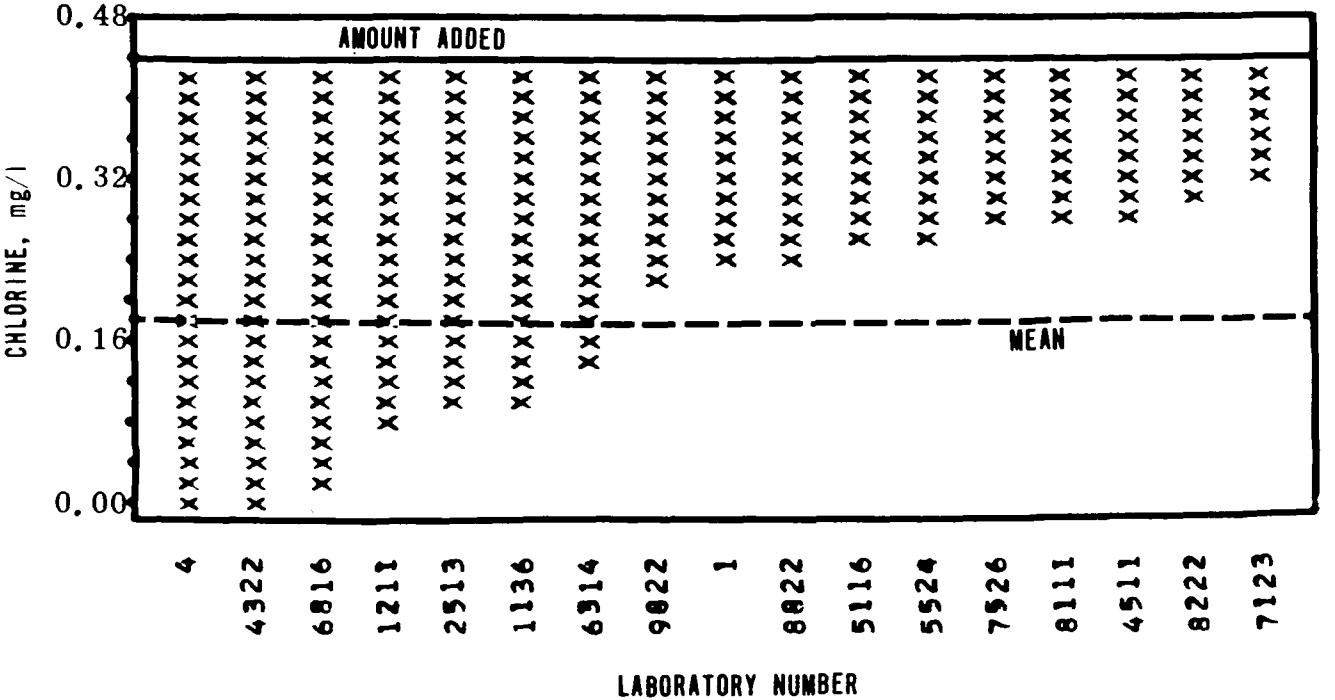

Figure 11. Bar graph for free residual chlorine in sample 1 by DPD-titrimetric method.

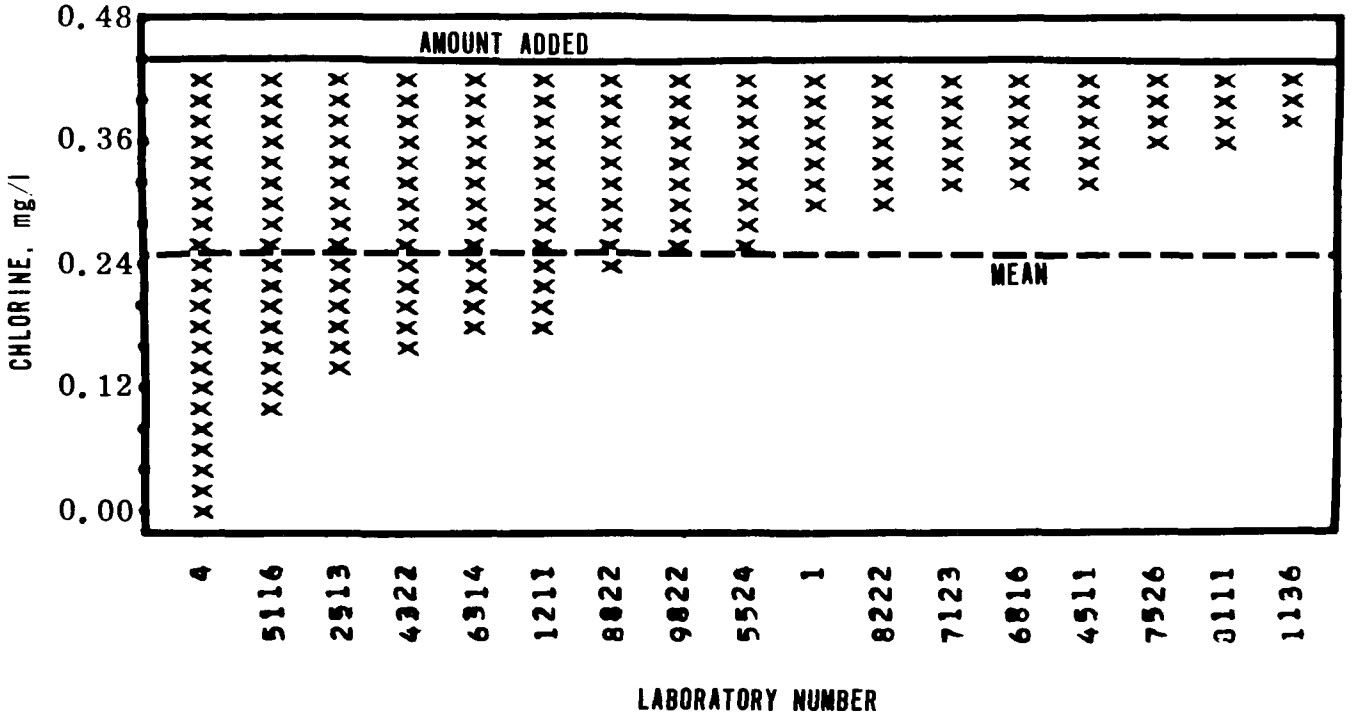

Figure 12. Bar graph for total residual chlorine in sample 1 by DPD-titrimetric method.

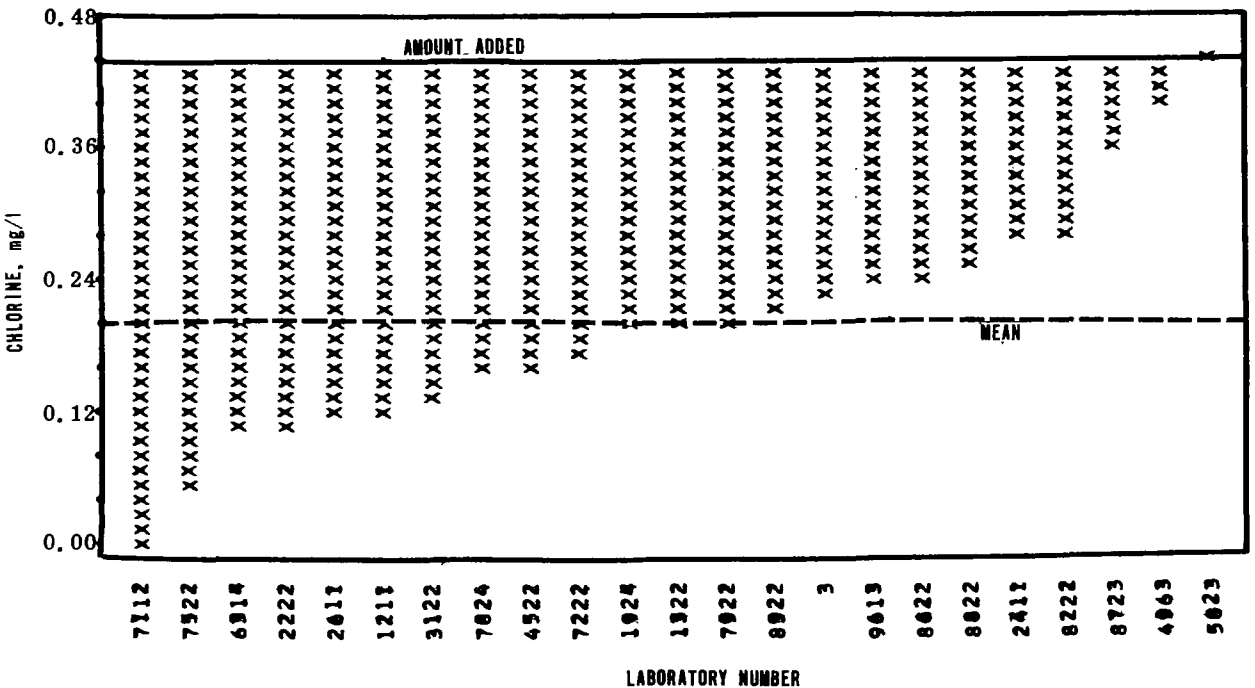

Figure 13. Bar graph for free residual chlorine in sample 1 by amperometric titration method.

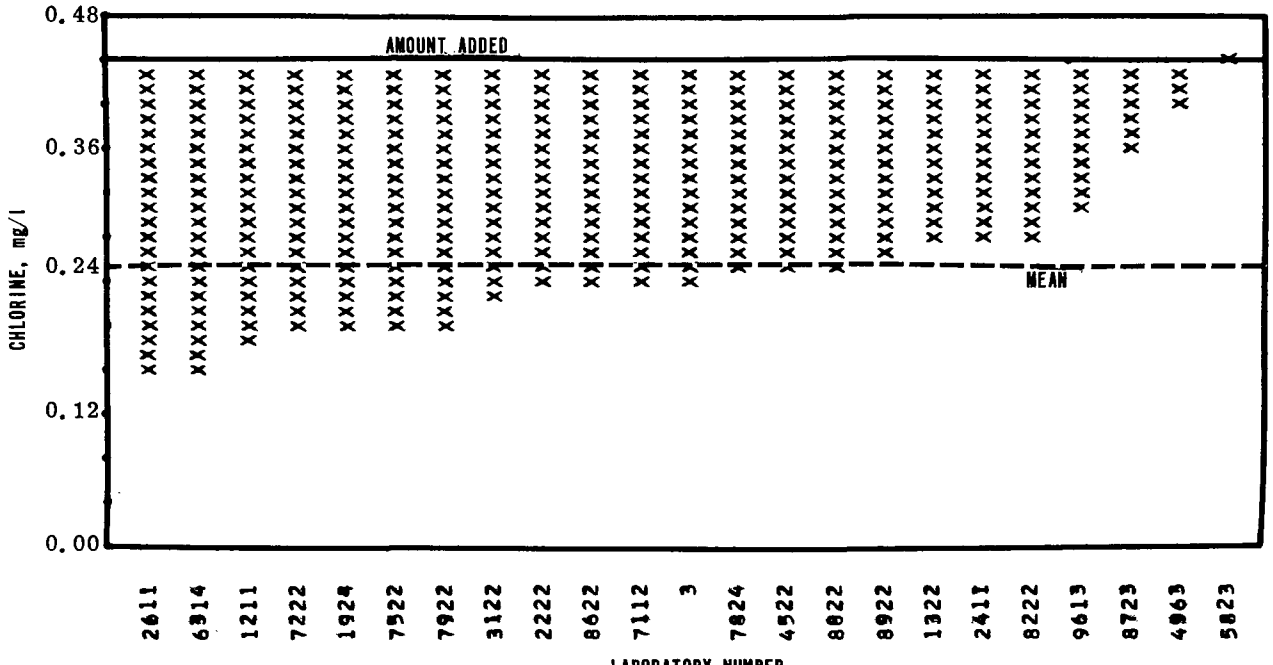

Figure 14. Bar graph for total residual chlorine in sample 1 by amperometric titration method.

All mean values differed significantly from the initially determined true value. The methyl orange results produced the least mean error for both free and total chlorine measurement indicating somewhat better accuracy than the other methods. On the other hand, the methyl orange results were significantly less precise than both OTA and SNORT results in the measurement of total chlorine. There were no other significant differences in precision for either free or total chlorine results. However, the leuco crystal violet results had the least standard deviation for both free and total chlorine, but because of the small number of participants using this method, this observation may not be meaningful.

According to the total error, the leuco crystal violet results were the best and the methyl orange results the poorest for both free and total chlorine. None of the methods, however, can be considered acceptable on the basis of the results obtained on this sample because as previously stated, the sample decomposed during shipment; even if the overall mean were to be considered the true value, the results would still be unacceptable.

SAMPLE 2: 0.98 mg/liter free, 0.98 mg/liter total chlorine (Table 3; Figures 15 through 28)

This sample was designed to provide only free chlorine at about the maximum concentration likely to be encountered in analysis of treated potable water.

For the free chlorine measurement, all method means differed significantly from the true value except for methyl orange.

For total chlorine, all but methyl orange, OTA, and DPD titrimetric differed significantly from the true value.

The precision data is more involved. For free chlorine, leuco crystal violet is significantly more precise than all the rest except for SNORT, which was significantly more precise than methyl orange, OTA, DPD titrimetric and amperometric titration. The DPD colorimetric method was significantly more precise than methyl orange, OTA, and DPD titrimetric. Amperometric titration was significantly more precise than both methyl orange and OTA.

For total chlorine, leuco crystal violet was significantly more precise than all except methyl orange. Amperometric titration was significantly more precise than methyl orange, OTA and DPD titrimetric. Both SNORT and DPD colorimetric were significantly more precise than methyl orange and OTA. DPD titrimetric was significantly more precise than OTA. On examination of the statistical data in Table 3, the large difference in standard deviations for methyl orange and leuco crystal

Table 3. SUMMARY OF DATA ON SAMPLE 2
(0.98 mg/liter free, 0.98 mg/liter total chlorine)

Method	Determination	No. of results	No. of outliers	Mean	Mean error	Standard deviation	Rel. error	Relative std. dev.	95% tol. limits	Total error
Methyl orange	Free	23	0	0.936	-0.044	0.315	4.53	33.70	0.843	68.83
	Total	23	0	0.974	-0.006	0.301	0.62	30.95	0.806	62.12
Leuco crystal violet	Free	4	2	0.895	-0.085	0.042	8.67	4.70	0.268	17.24
	Total	4	2	0.912	-0.070	0.015	7.14	1.64	0.096	10.20
Orthotolidine-arsenite	Free	30	0	0.782	-0.198	0.335	20.20	42.84	0.854	88.57
	Total	30	0	0.878	-0.102	0.325	10.37	37.04	0.829	76.81
SNORT	Free	16	1	0.868	-0.113	0.120	11.48	13.80	0.348	35.95
	Total	15	1	0.873	-0.107	0.142	10.95	16.31	0.420	39.97
DPD-colorimetric	Free	26	3	0.827	-0.153	0.171	15.62	20.72	0.448	50.57
	Total	27	2	0.883	-0.097	0.152	9.94	17.18	0.393	40.83
DPD-titrimetric	Free	17	0	0.788	-0.192	0.298	19.57	37.87	0.853	80.51
	Total	16	1	0.921	-0.059	0.205	6.06	22.29	0.596	47.89
Amperometric titration	Free	23	0	0.750	-0.230	0.206	23.51	27.45	0.550	65.46
	Total	22	1	0.861	-0.119	0.137	12.11	15.96	0.371	40.14
Orthotolidine	Free	1	0	0.100	- - - -	- - -	- -	- - -	- - -	- - -
	Total	2	0	0.700	-0.280	- - -	- -	- - -	- - -	- - -
DPD-colorimetric (N, N-dimethyl)	Free	-	-	- - -	- - - -	- - -	- -	- - -	- - -	- - -
	Total	1	-	1.000	- - - -	- - -	- -	- - -	- - -	- - -

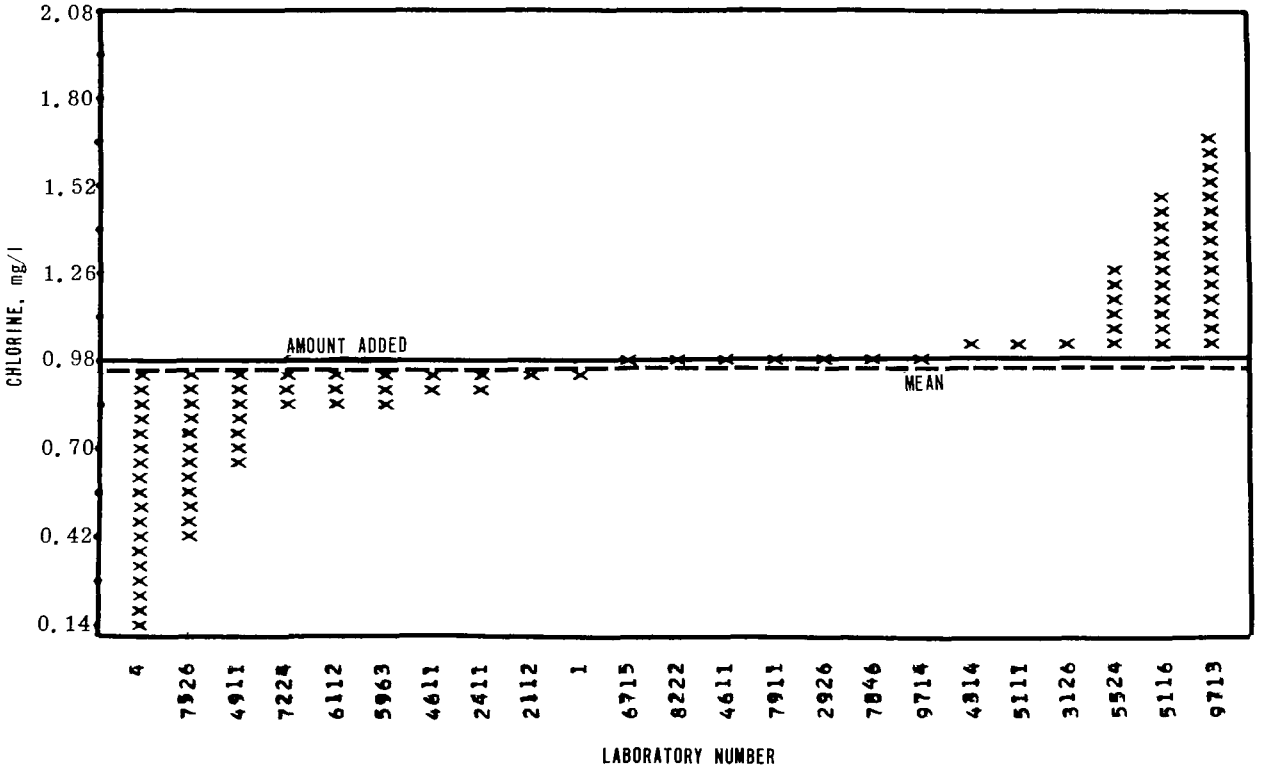

Figure 15. Bar graph for free residual chlorine in sample 2 by methyl orange method.

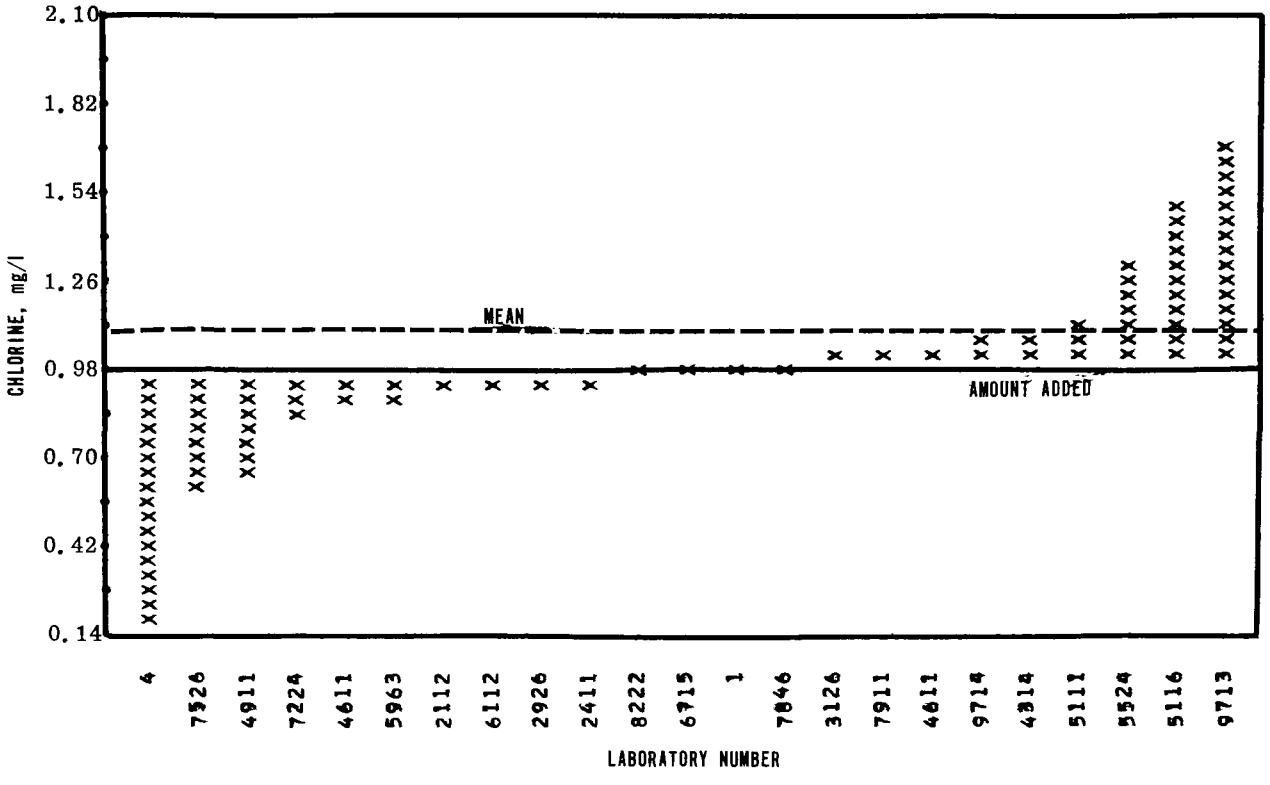

Figure 16. Bar graph for total residual chlorine in sample 2 by methyl orange method.

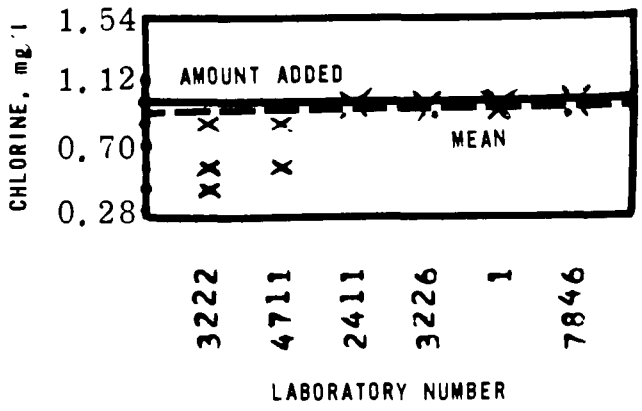

Figure 17. Bar graph for free residual chlorine in sample 2 by leuco crystal violet method.

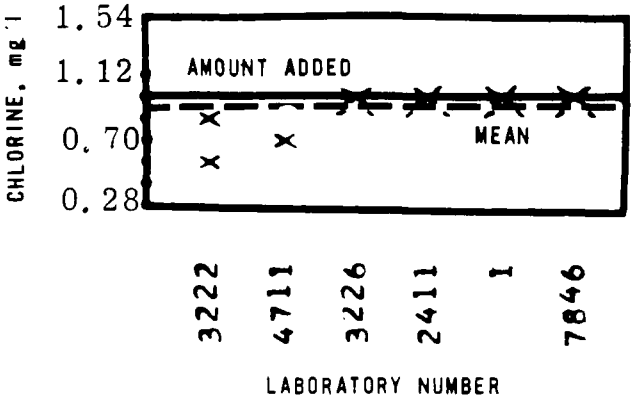

Figure 18. Bar graph for total residual chlorine in sample 2 by leuco crystal violet method.

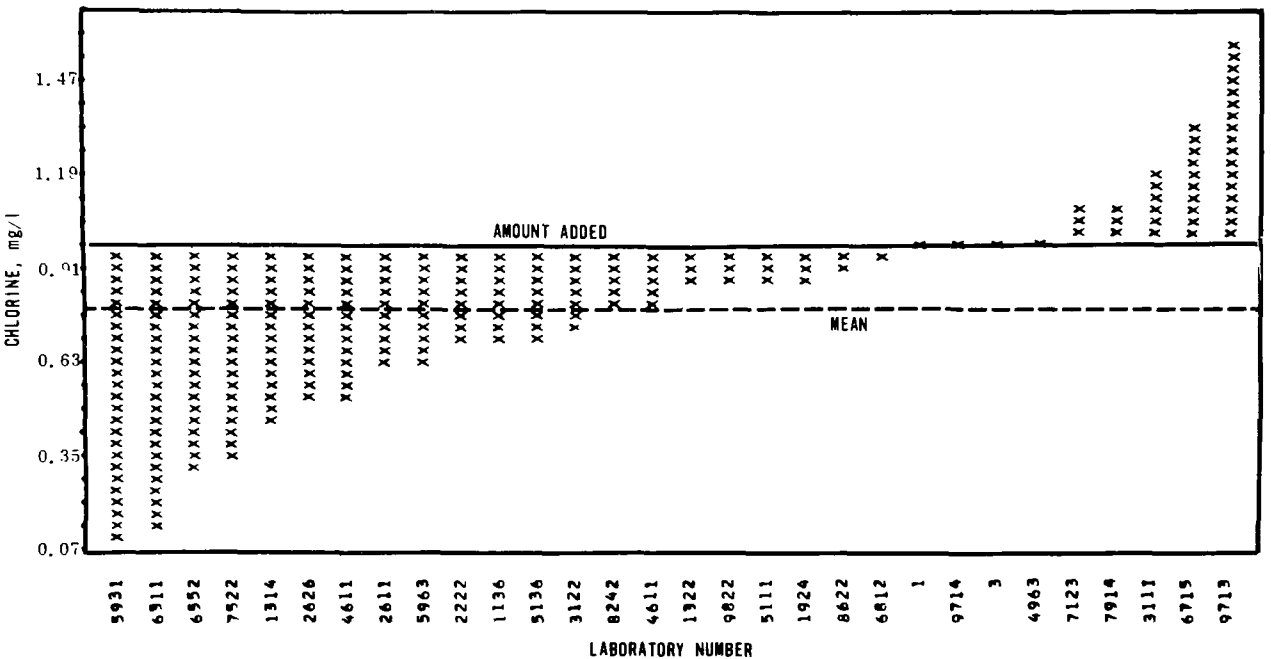

Figure 19. Bar graph for free residual chlorine in sample 2 by orthotolidine-arsenite method.

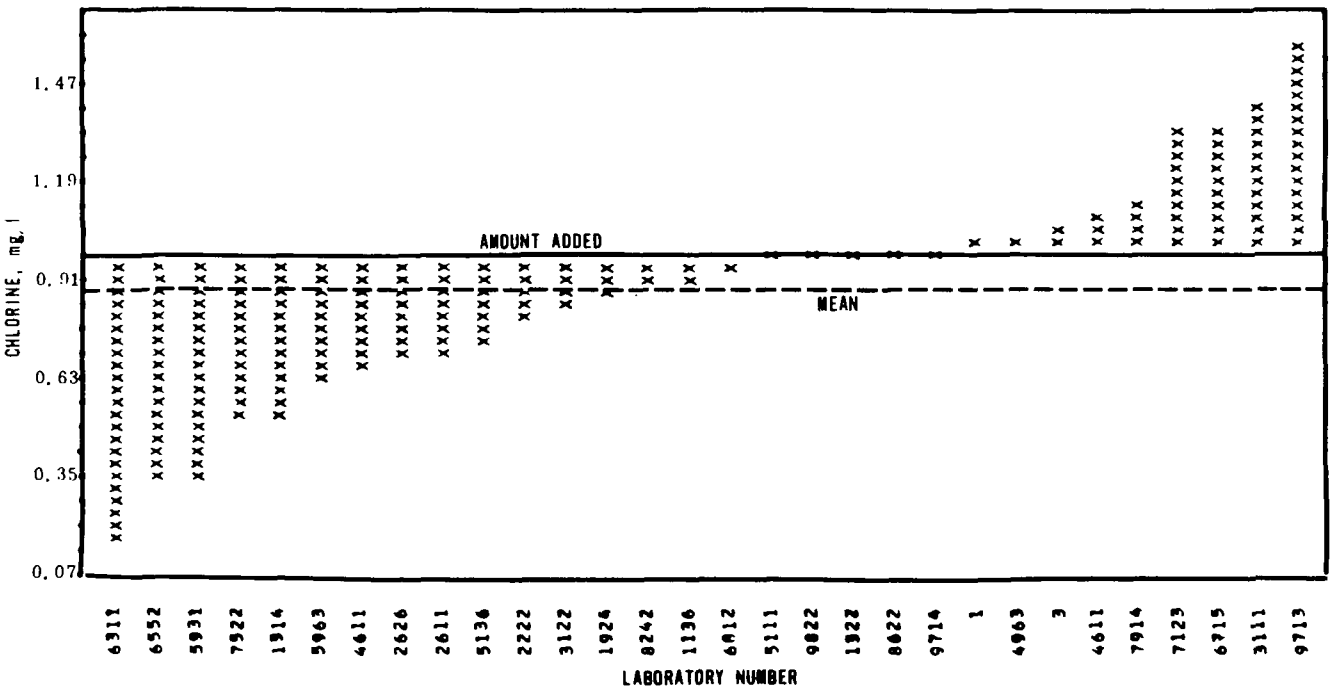

Figure 20. Bar graph for total residual chlorine in sample 2 by orthotolidine-arsenite method.

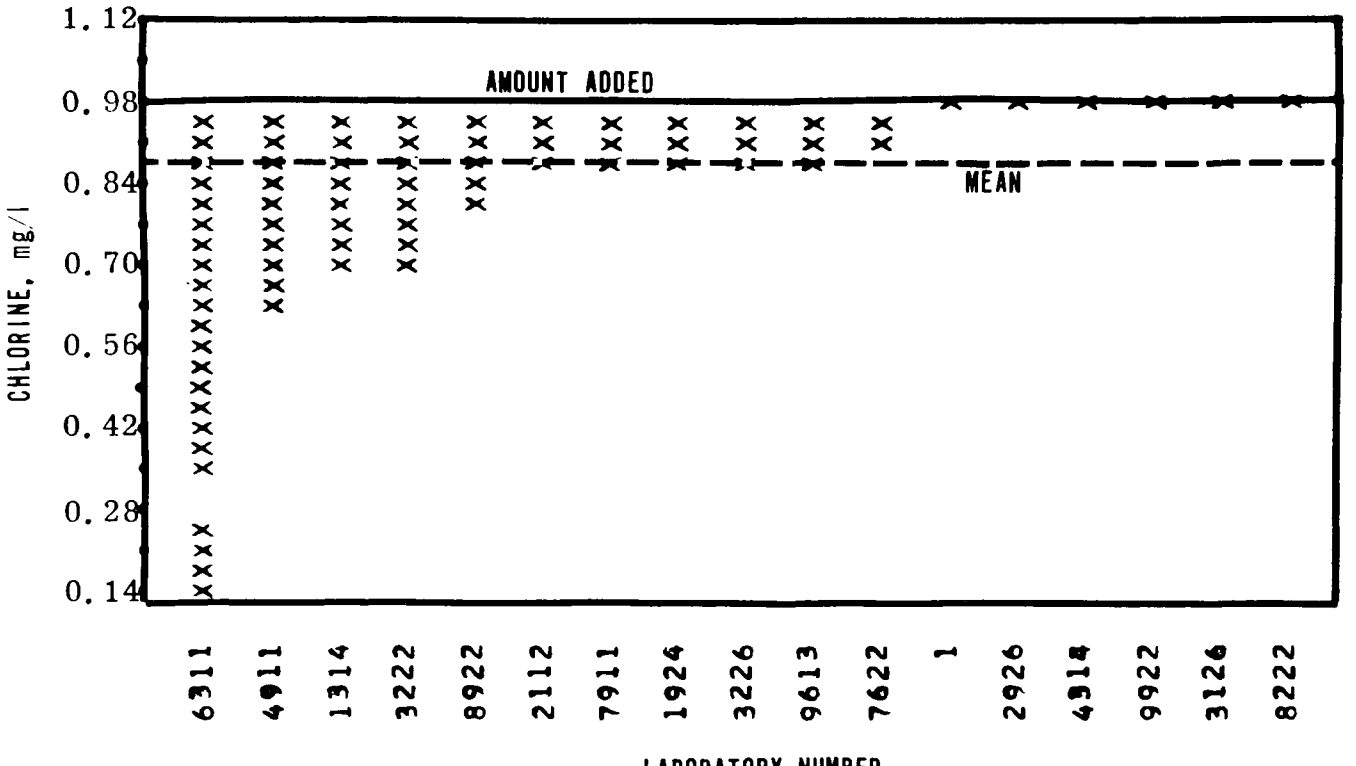

Figure 21. Bar graph for free residual chlorine in sample 2 by stabilized neutral orthotolidine method.

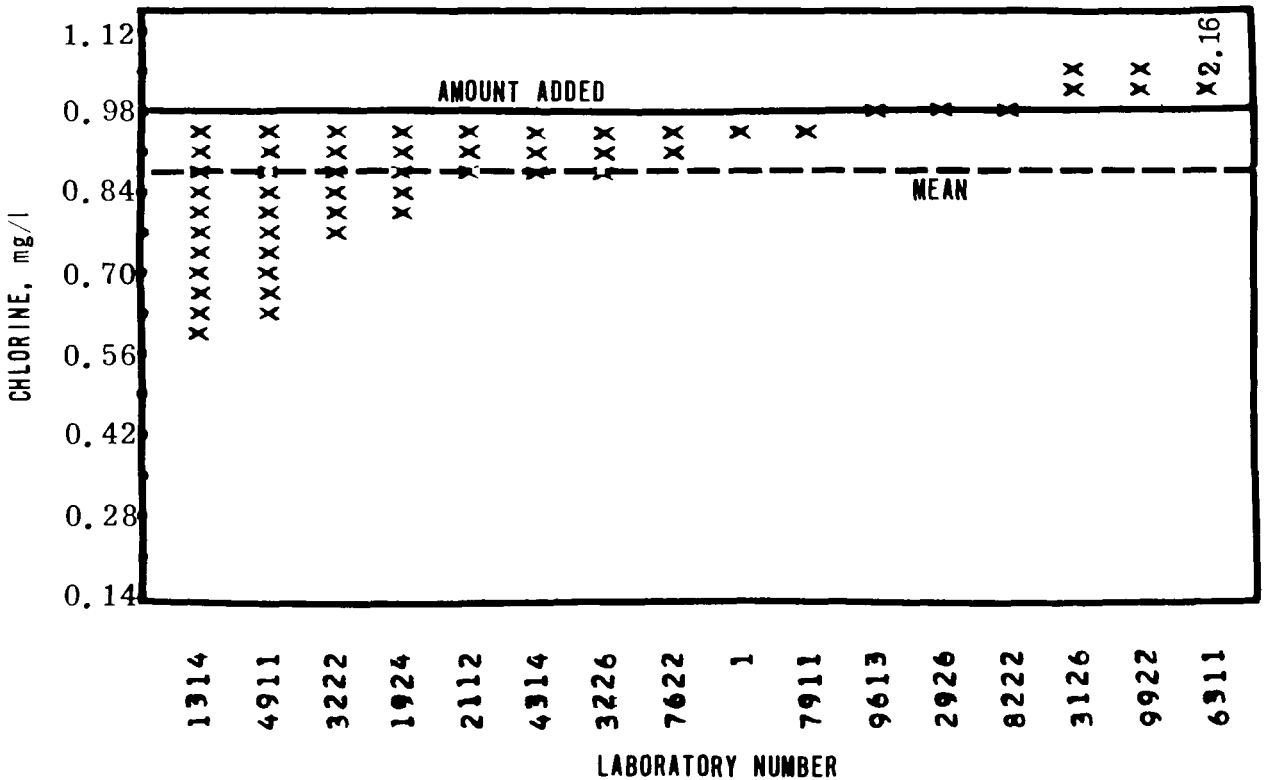

Figure 22. Bar graph for total residual chlorine in sample 2 by stabilized neutral orthotolidine method.

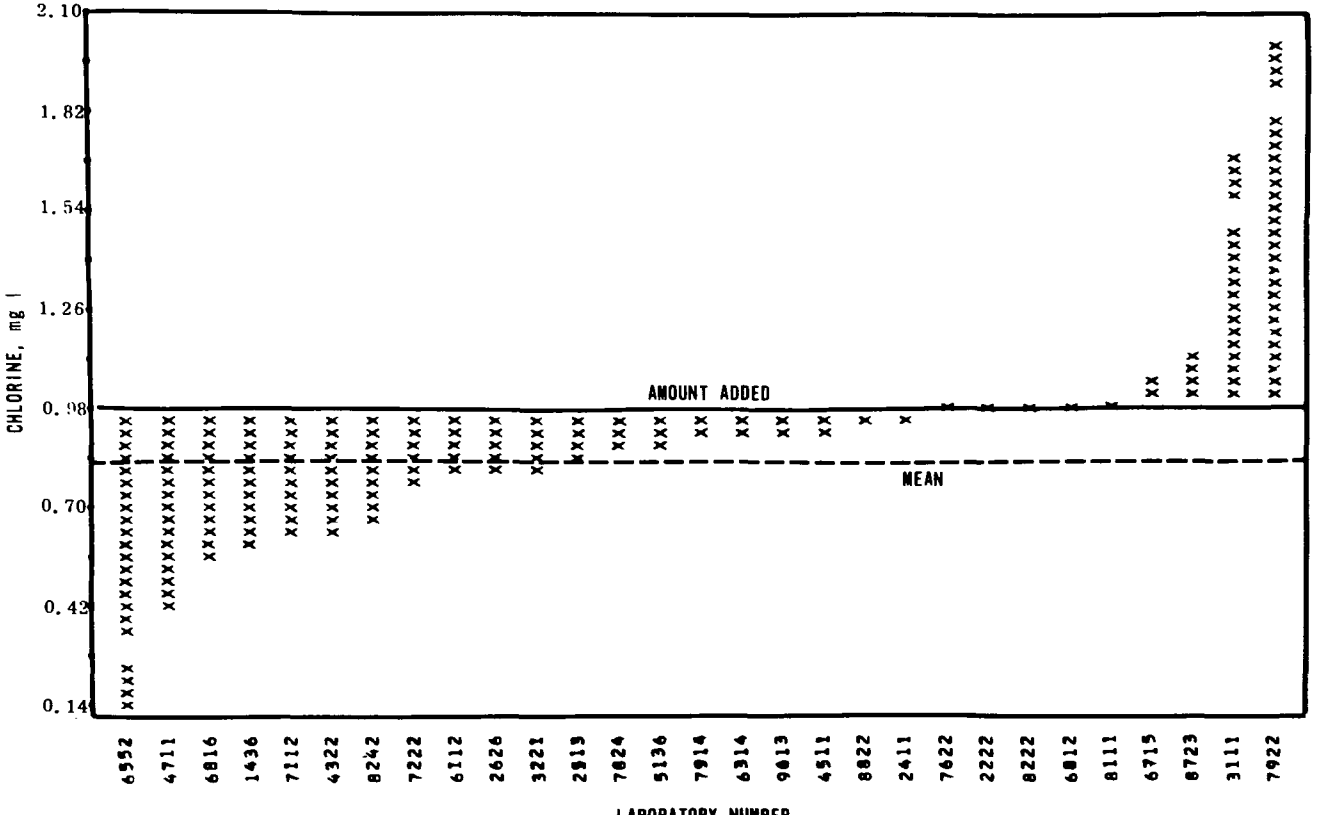

Figure 23. Bar graph for free residual chlorine in sample 2 by DPD-colorimetric method.

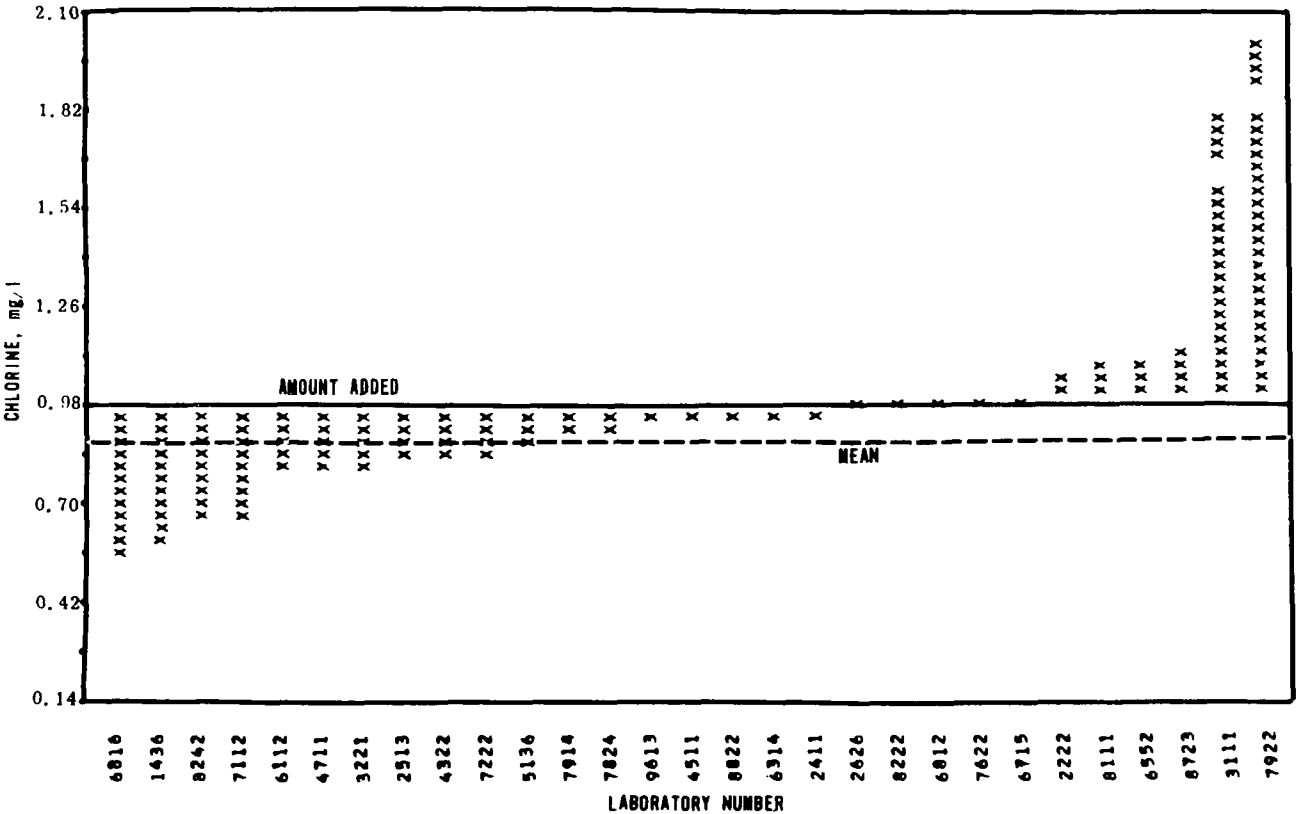

Figure 24. Bar graph for total residual chlorine in sample 2 by DPD-colorimetric method.

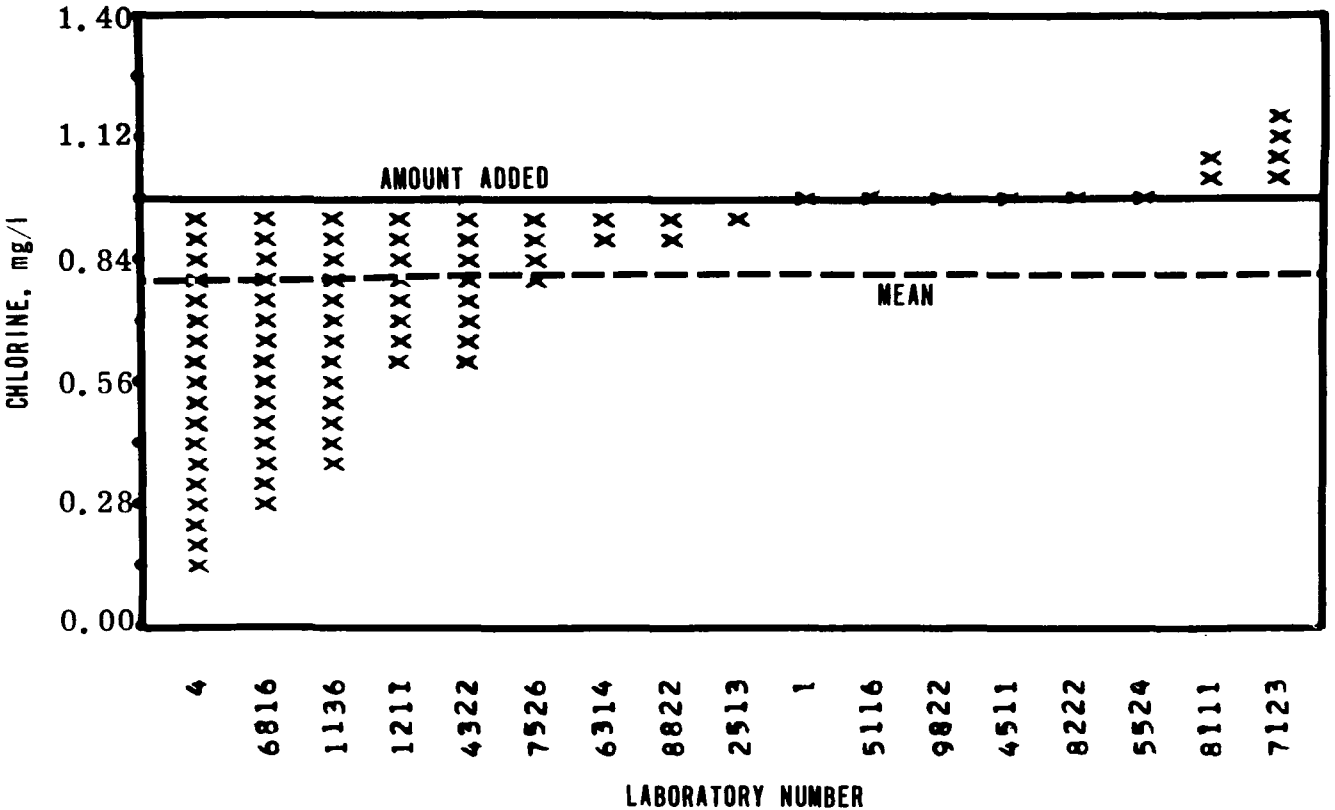

Figure 25. Bar graph for free residual chlorine in sample 2 by DPD-titrimetric method.

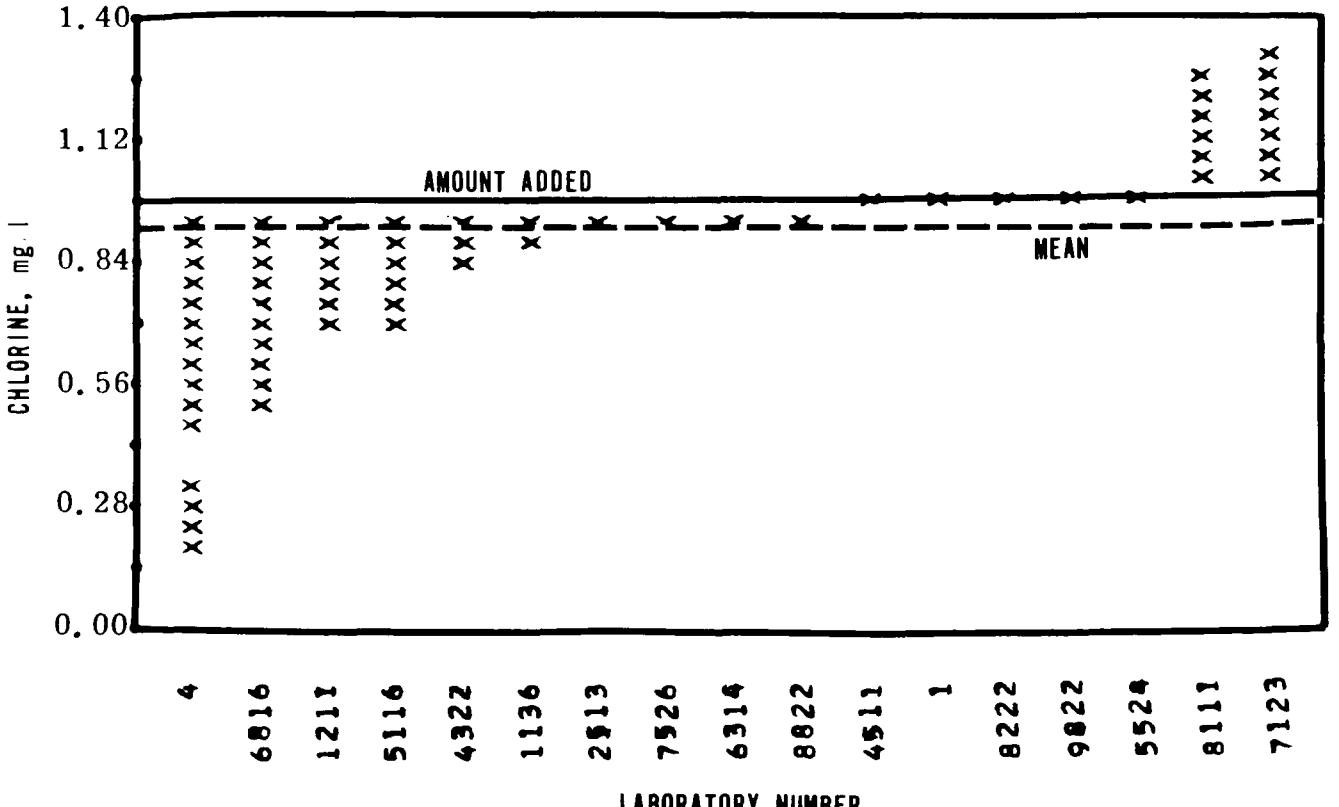

Figure 26. Bar graph for total residual chlorine in sample 2 by DPD-titrimetric method.

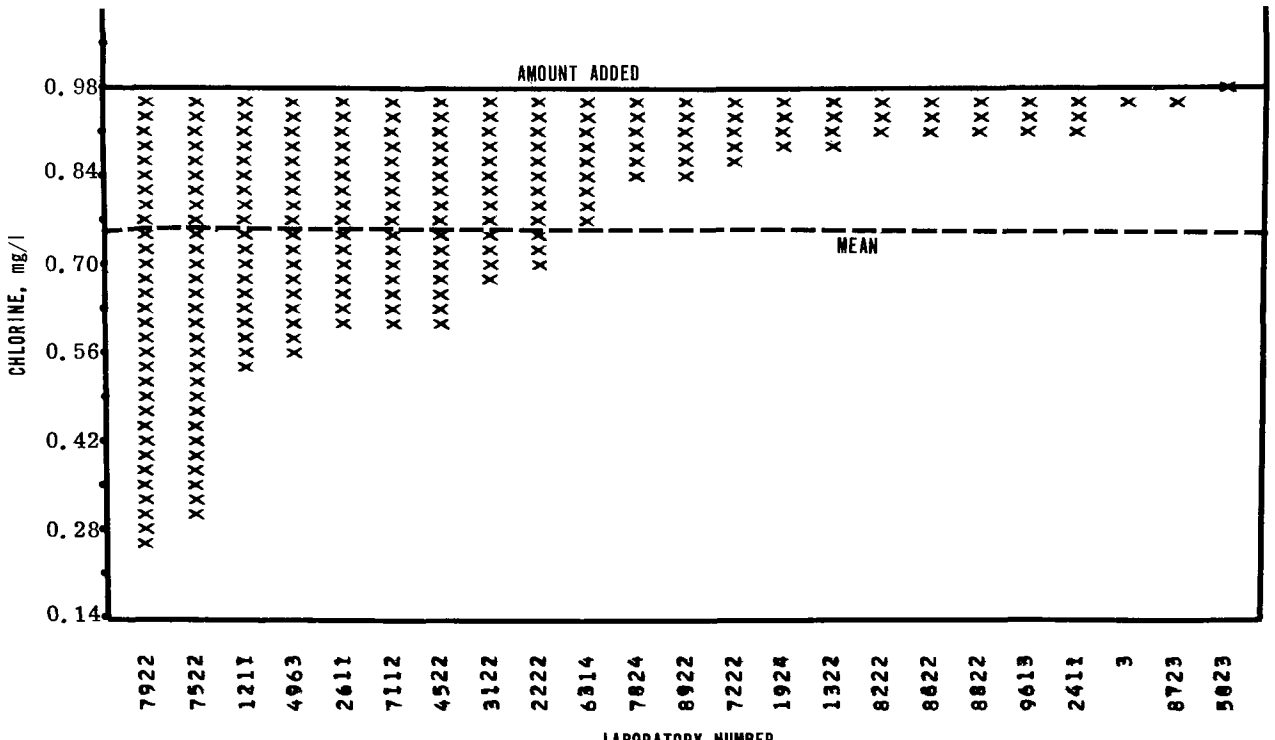

Figure 27. Bar graph for free residual chlorine in sample 2 by amperometric titration method.

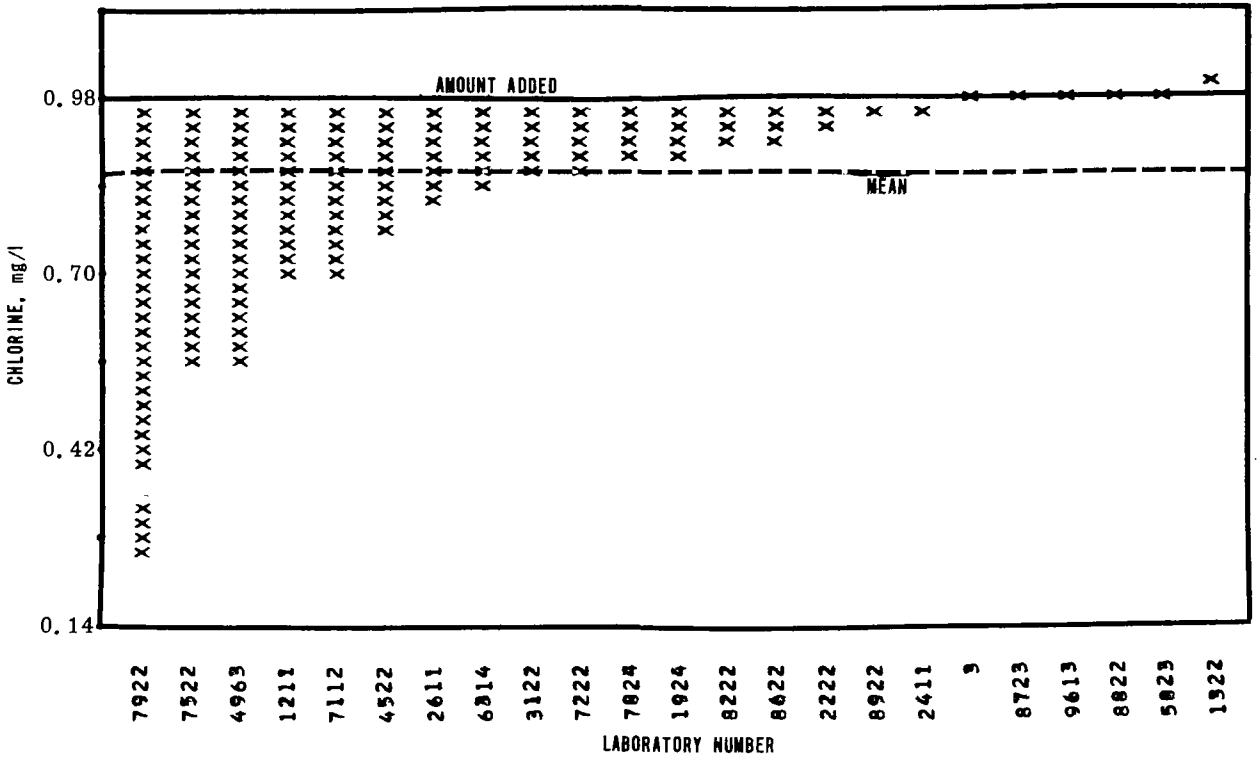

Figure 28. Bar graph for total residual chlorine in sample 2 by *amperometric titration method.*

violet would appear significant. However, the F-test employed to determine significance of differences in precision takes into account the number of values for each method. The very small number of results (4) for the leuco crystal violet method compared to 23 values for methyl orange prevents the difference in precision from being statistically significant. In addition, two outliers were rejected from the total of 6 results submitted for leuco crystal violet, while the methyl orange results were statistically normal and no values were rejected.

According to the total error, leuco crystal violet would be considered excellent for both free and total chlorine measurement, SNORT would be acceptable for both free and total, and DPD titrimetric, DPD colorimetric, and amperometric titration would be acceptable only for total chlorine measurement. Again, the OTA method was the poorest.

It is interesting to note the large discrepancy between free and total chlorine results for the two titration procedures. Apparently, the DPD titrimetric and amperometric titration methods have greater difficulty with free chlorine measurement than the other methods.

SAMPLE 3: 0.05 mg/liter free, 0.66 mg/liter total chlorine (Table 4; Figures 29 through 42)

This sample was designed to provide only combined chlorine to simulate an insufficiently chlorinated water having no free chlorine residual. However, as explained under "Treatment of the Data," the value of 0.05 mg/liter free chlorine has been selected as the "true" value to facilitate computation, and as a more realistic estimate of the measurable amount present.

It is evident that the OTA method is outstandingly inaccurate, and significantly less precise than all the other methods for free chlorine measurement. Leuco crystal violet was significantly more precise than all the other methods; SNORT was significantly more precise than all the methods except leuco crystal violet; and DPD titrimetric was significantly more precise than all except leuco crystal violet and SNORT.

In the measurement of total chlorine (combined chlorine), the mean values for OTA, DPD colorimetric, and amperometric titration differ significantly from the true value. OTA and DPD colorimetric were also significantly less precise than methyl orange, leuco crystal violet, SNORT, and DPD titrimetric. SNORT, in addition, was also more precise than amperometric titration.

According to the total error, methyl orange, leuco crystal violet, SNORT, and DPD titrimetric would be considered acceptable for total chlorine measurement.

Table 4. SUMMARY OF DATA ON SAMPLE 3
(0.05 mg/liter free, 0.66 mg/liter total chlorine)

Method	Determination	No. of results	No. of outliers	Mean	Mean error	Standard deviation	Rel. error	Relative std. dev.	95% tol. limits	Total error
Methyl orange	Free	18	4	0.049	-0.006	0.055	12.01	111.31	0.155	232.00
	Total	22	0	0.689	0.029	0.143	4.34	20.79	0.386	47.75
Leuco crystal violet	Free	4	2	0.000	-0.050	0.000	100.00	0.00	0.000	100.00
	Total	6	1	0.653	-0.007	0.089	1.01	13.64	0.394	28.06
Orthotolidine-arsenite	Free	27	1	0.164	0.114	0.195	228.20	118.78	0.506	1007.80
	Total	29	0	0.568	-0.092	0.218	14.00	38.37	0.559	79.93
SNORT	Free	15	2	0.002	-0.048	0.004	96.00	207.02	0.012	112.40
	Total	15	2	0.628	-0.032	0.110	4.85	17.51	0.325	38.15
DPD-colorimetric	Free	26	2	0.036	-0.014	0.057	27.60	158.23	0.149	256.40
	Total	25	3	0.763	0.103	0.210	15.58	27.58	0.553	79.33
DPD-titrimetric	Free	13	4	0.012	-0.038	0.019	77.00	165.37	0.059	153.40
	Total	15	2	0.629	-0.031	0.121	4.75	19.24	0.357	41.33
Amperometric titration	Free	19	3	0.038	-0.012	0.040	23.20	103.84	0.111	182.80
	Total	23	0	0.552	-0.108	0.171	16.34	30.99	0.457	68.21
Orthotolidine	Free	1	0	0.100	- - - -	- - -	- - -	- - - -	- - -	- - - -
	Total	2	0	0.700	0.040	- - -	- - -	- - - -	- - -	- - - -
DPD-colorimetric (N, N-dimethyl)	Free	-	-	- - -	- - - -	- - -	- - -	- - - -	- - -	- - - -
	Total	1	-	2.000	- - - -	- - -	- - -	- - - -	- - -	- - - -

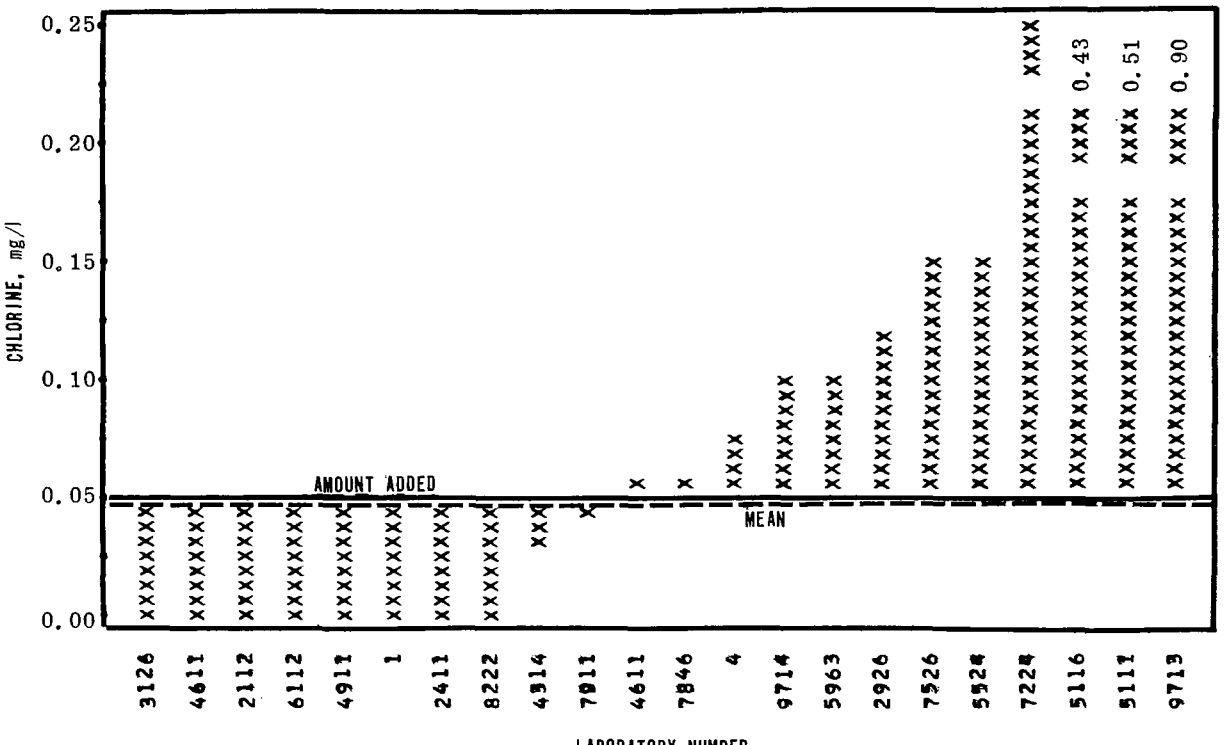

Figure 29. Bar graph for free residual chlorine in sample 3 by methyl orange method.

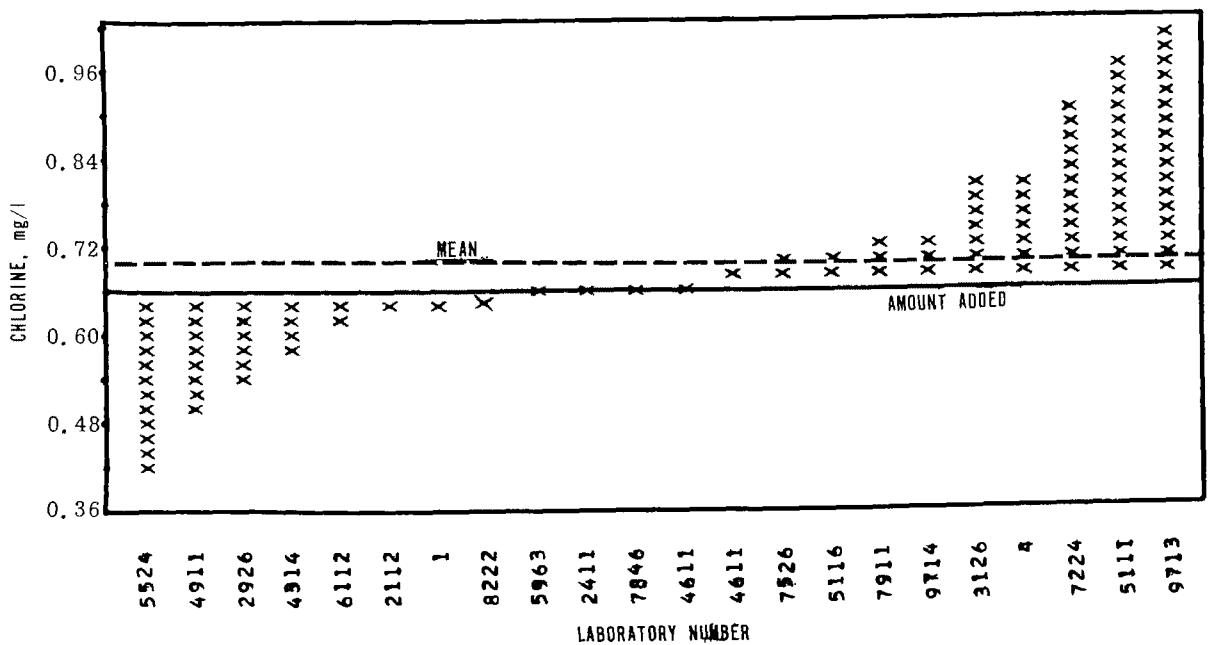

Figure 30. Bar graph for total residual chlorine in sample 3 by methyl orange method.

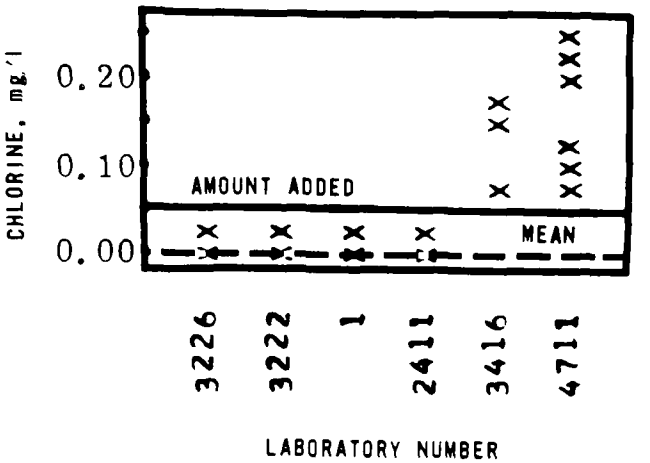

Figure 31. Bar graph for free residual chlorine in sample 3 by leuco crystal violet method.

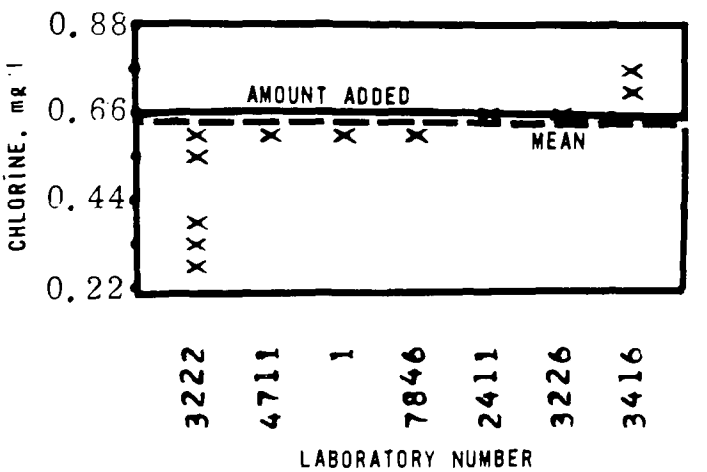

Figure 32. Bar graph for total residual chlorine in sample 3 by leuco crystal violet method.

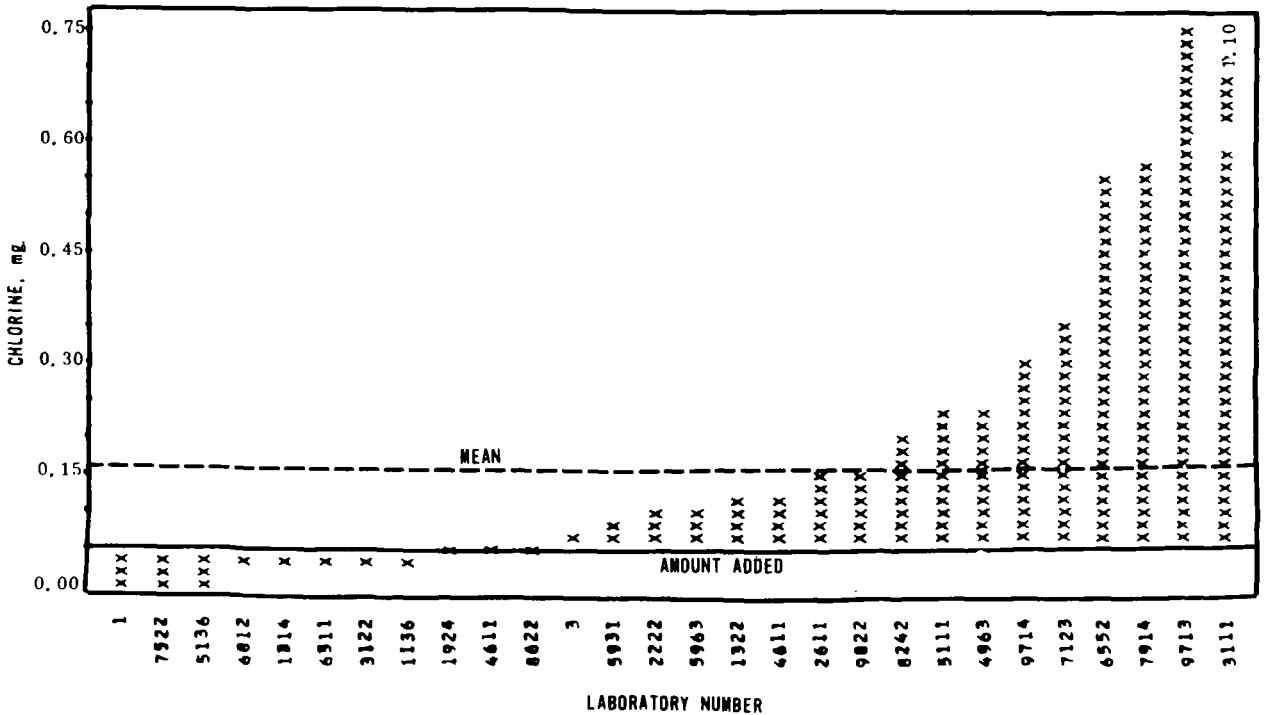

Figure 33. Bar graph for free residual chlorine in sample 3 by orthotolidine-arsenite method.

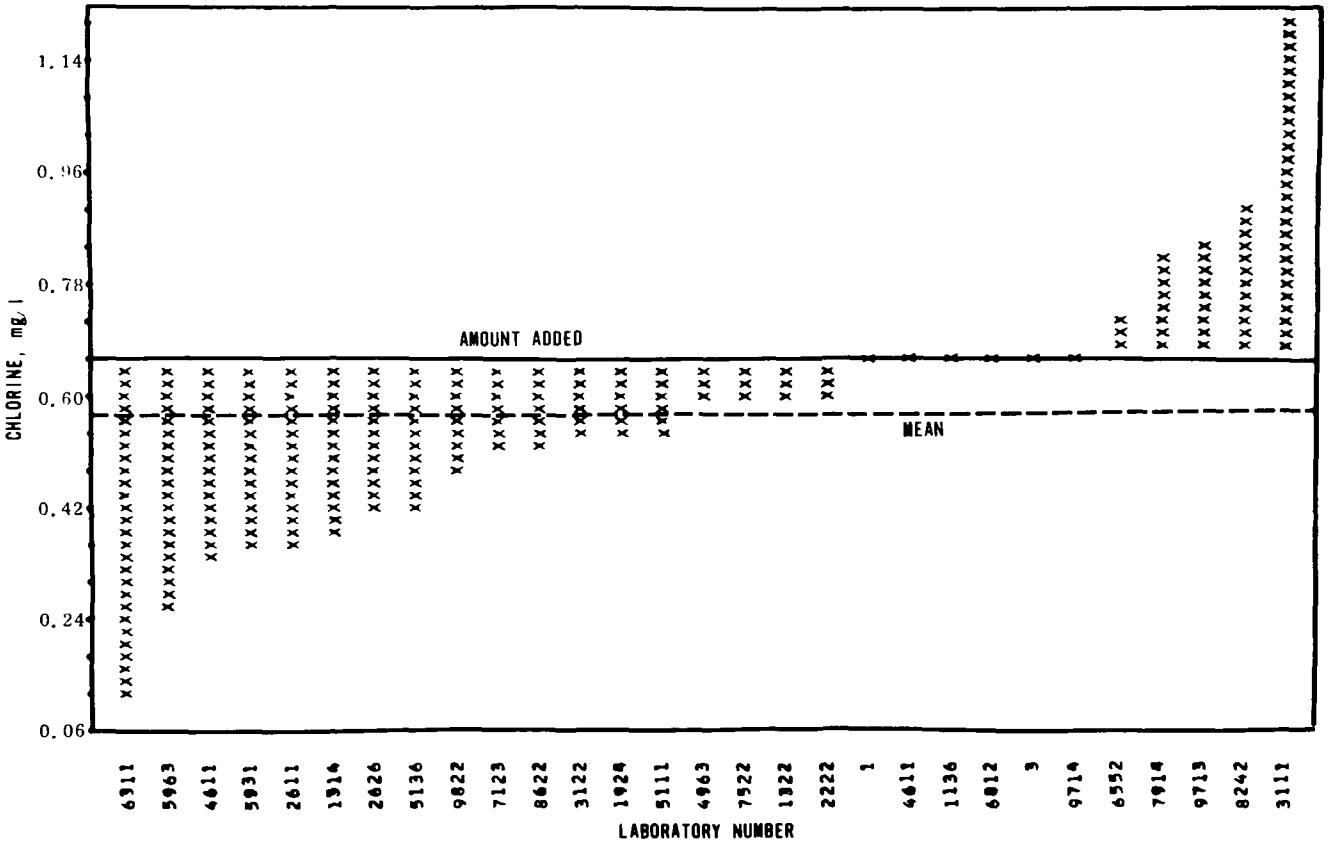

Figure 34. Bar graph for total residual chlorine in sample 3 by orthotolidine-arsenite method.

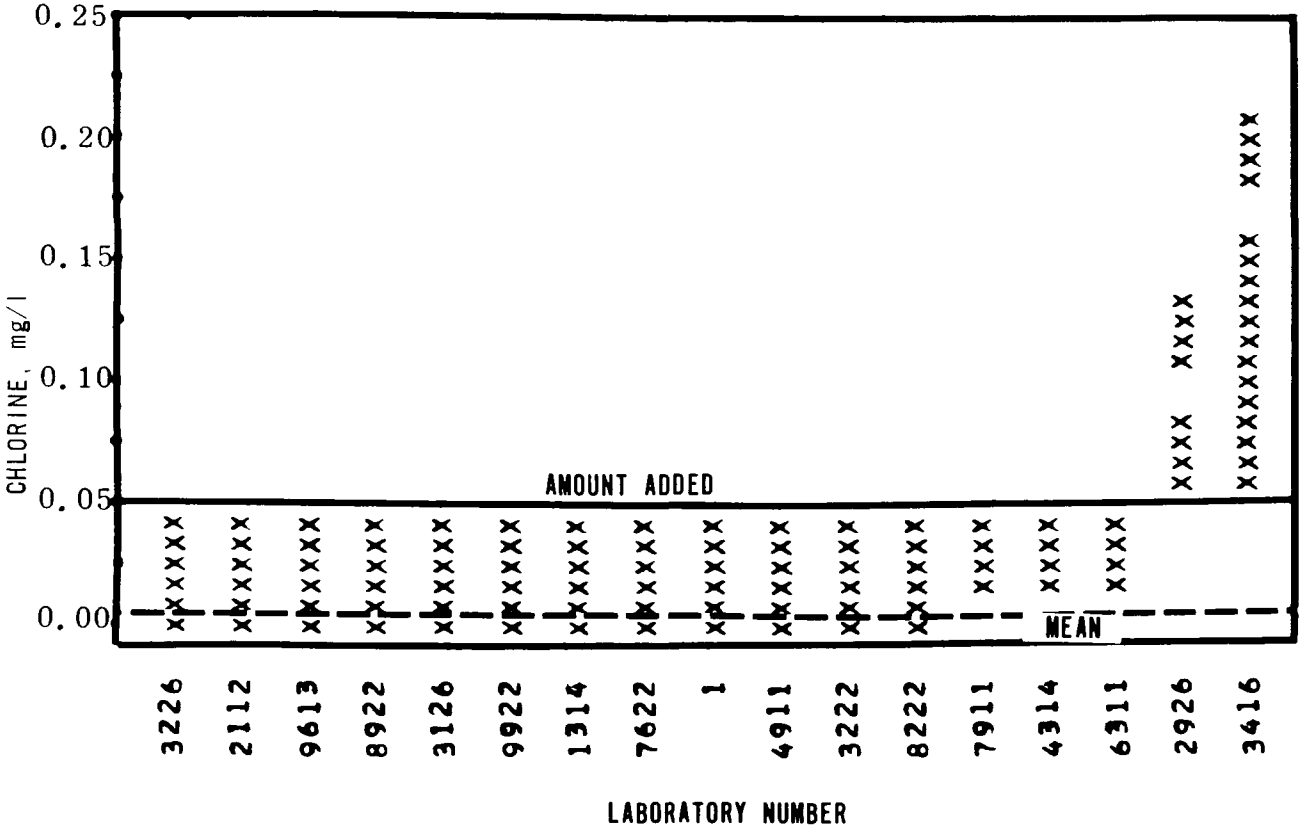

Figure 35. Bar graph for free residual chlorine in sample 3 by stabilized neutral orthotolidine method.

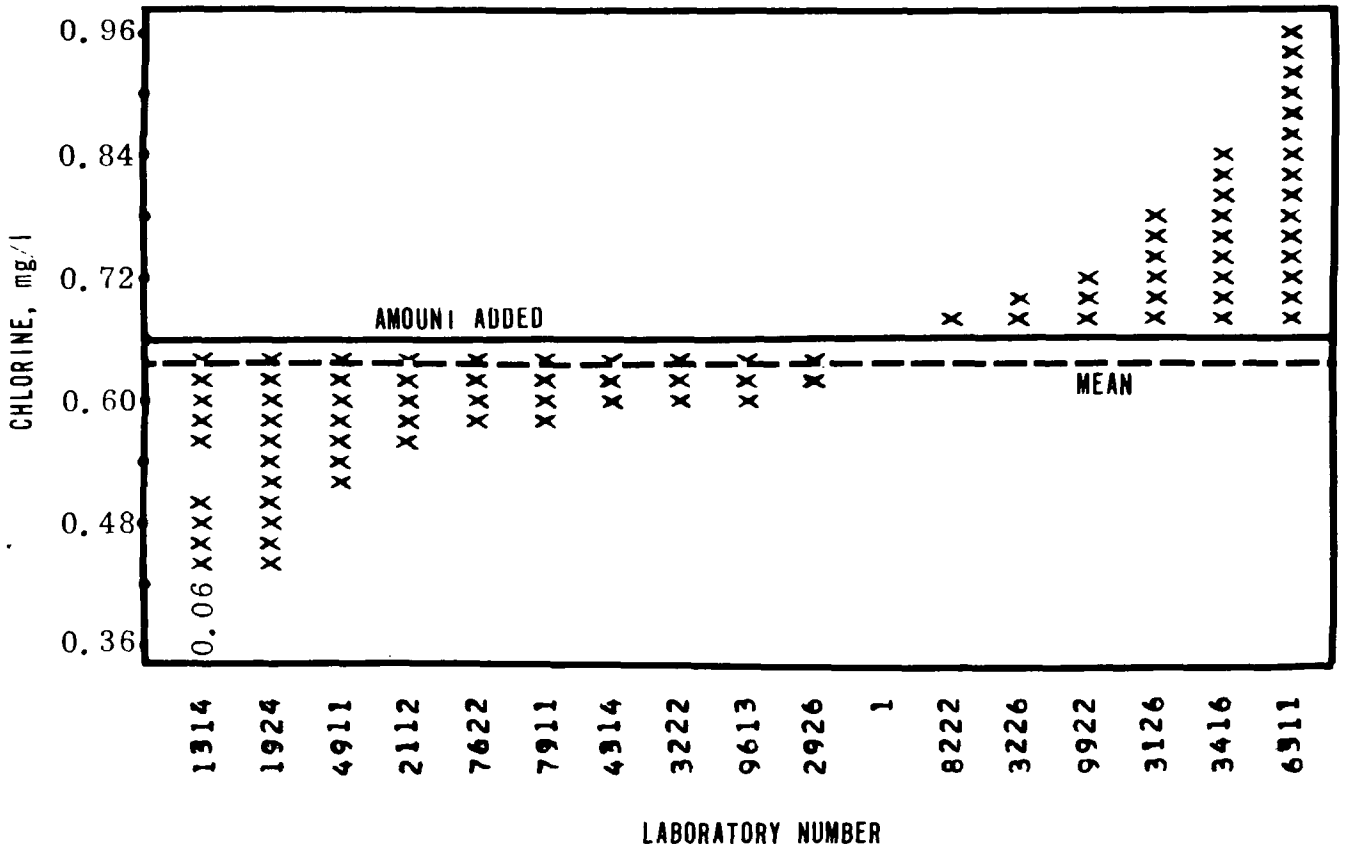

Figure 36. Bar graph for total residual chlorine in sample 3 by stabilized neutral orthotolidine method.

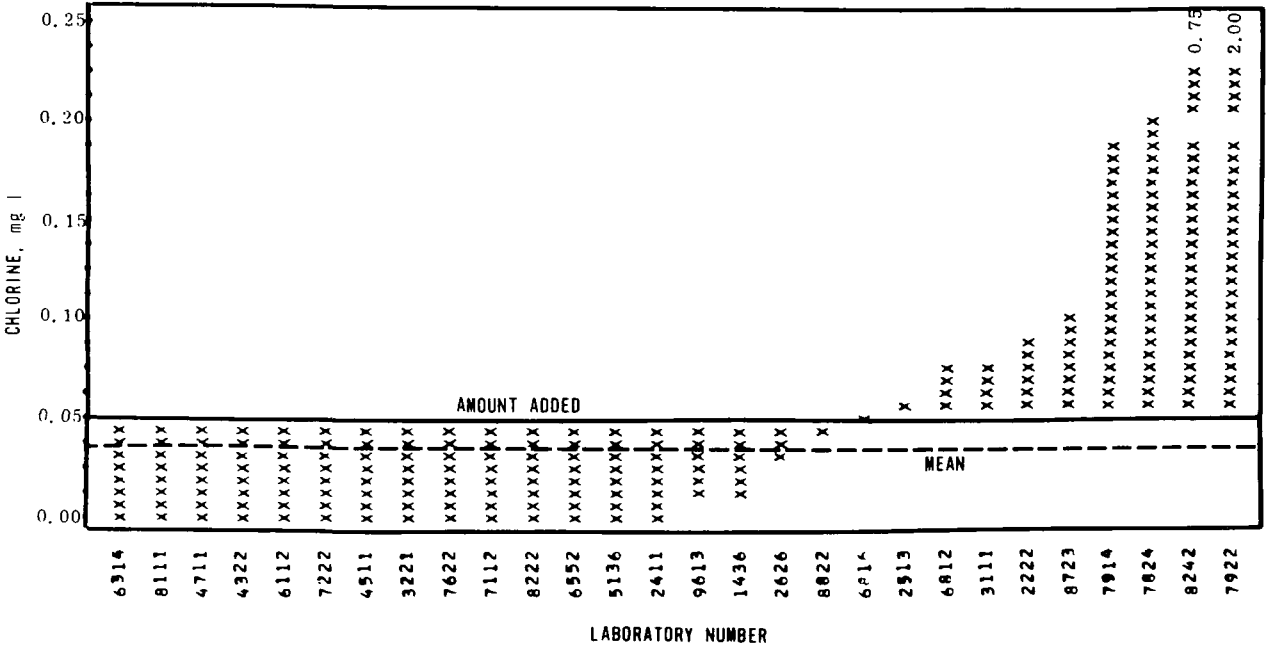

Figure 37. Bar graph for free residual chlorine in sample 3 by DPD-colorimetric method.

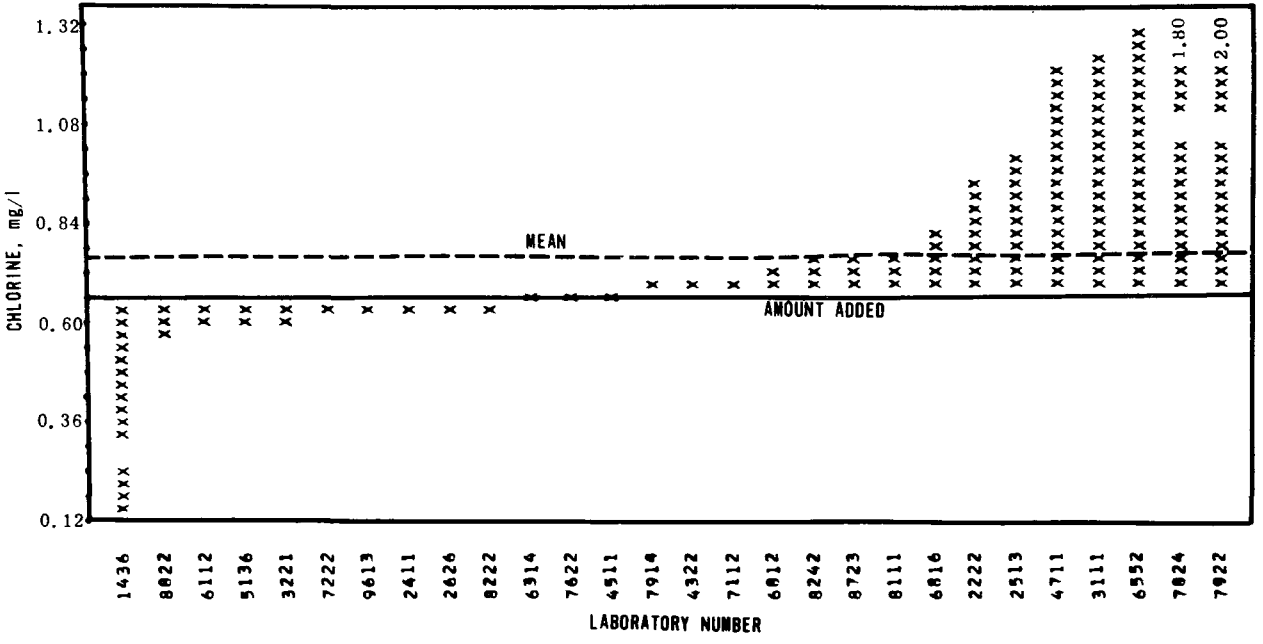

Figure 38. Bar graph for total residual chlorine in sample 3 by DPD-colorimetric method.

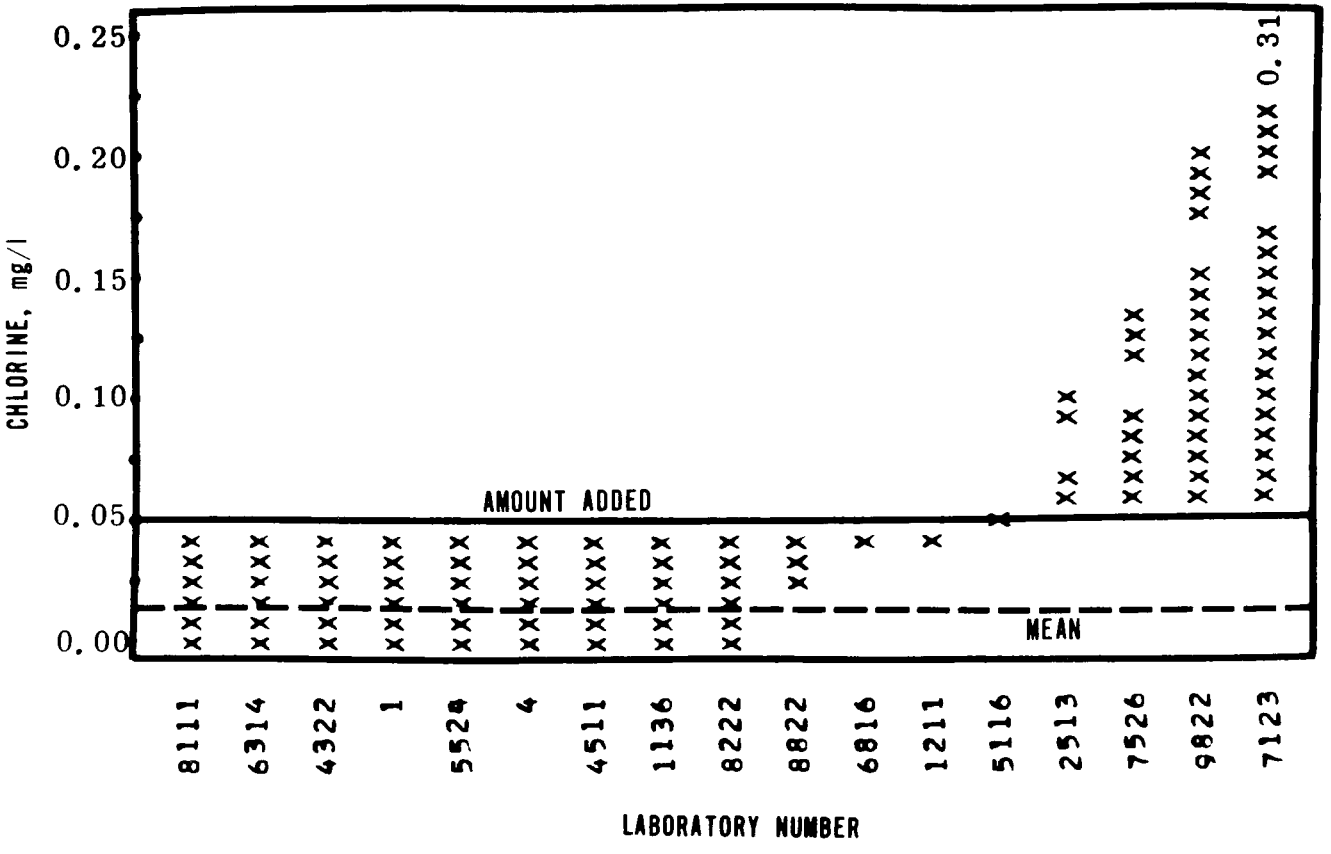

Figure 39. Bar graph for free residual chlorine in sample 3 by DPD-titrimetric method.

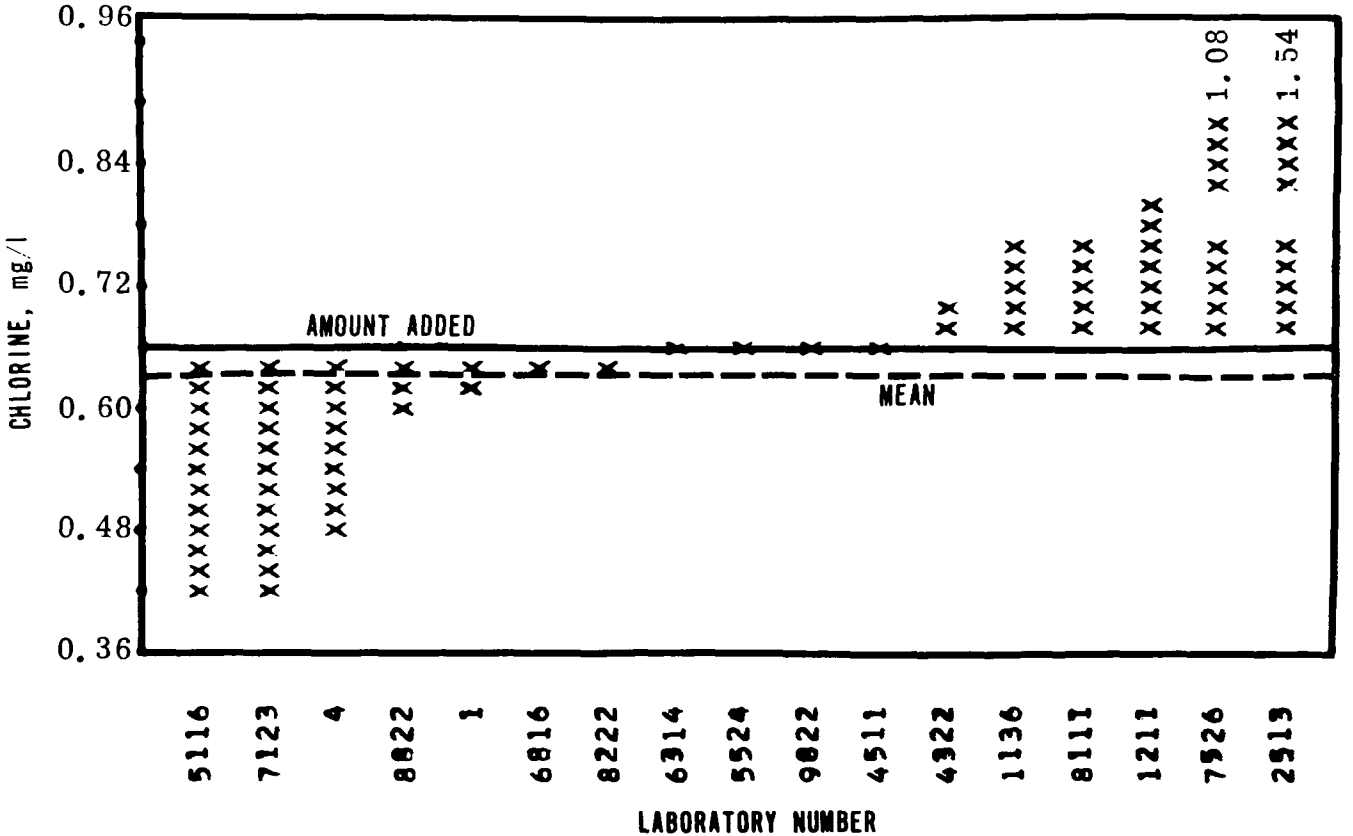

Figure 40. Bar graph for total residual chlorine in sample 3 by DPD-titrimetric method.

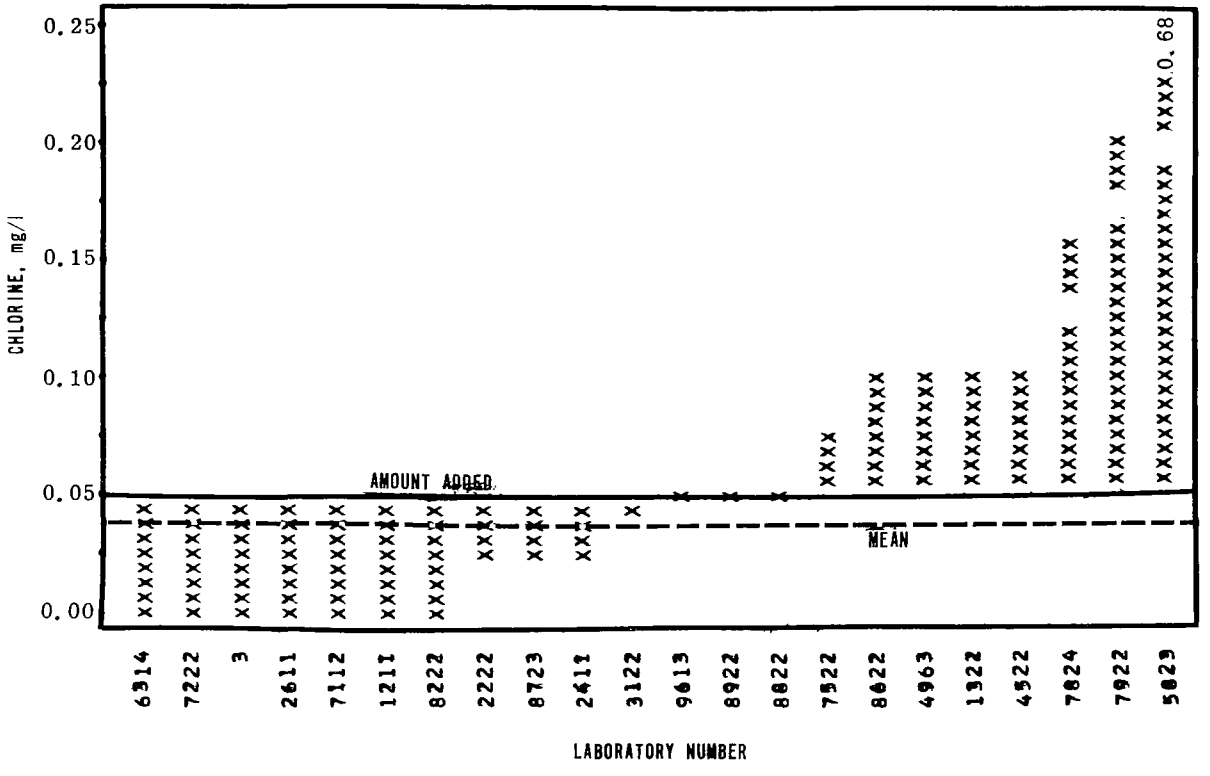

Figure 41. Bar graph for free residual chlorine in sample 3 by amperometric titration method.

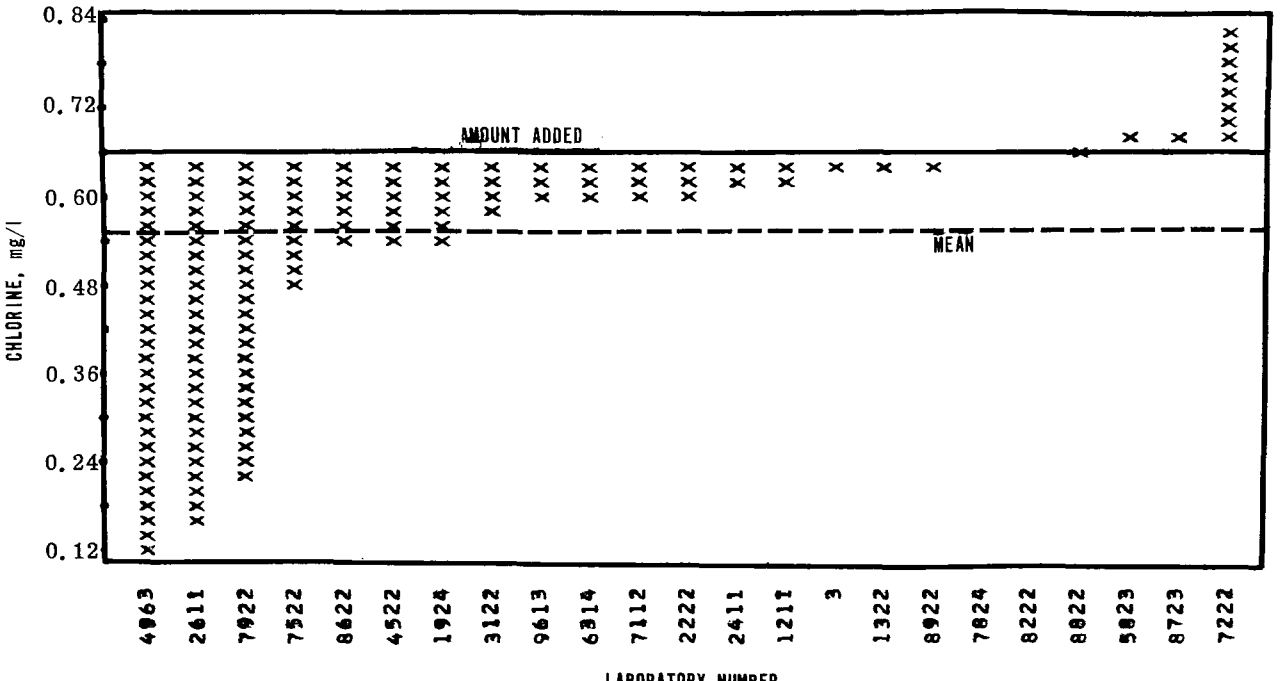

Figure 42. Bar graph for total residual chlorine in sample 3 by amperometric titration method.

COMMENTS OF THE PARTICIPANTS

Methyl Orange Method

1. We were unable to obtain reproducible standard curves for either the SNORT or Methyl Orange methods by following the instructions accompanying the samples. Our basic approach was:

   a. "Clorox" was standardized iodometrically.

   b. Suitable dilutions of "Clorox" were prepared as standards.

   c. The freshly prepared standard samples were run following the recommended procedure.

   The results obtained were consistently unreproducible. Fading of the methyl orange color required about 10 minutes for a stable absorbance, yet the method indicates 2 - 2.5 minutes for free Cl_2. "Clorox" should not contain any combined Cl_2. (ed. note: The method indicates 1 1.5 min. for free Cl_2, and 10 min. for combined Cl_2).

   The results obtained were completely erratic and random. Values much too high as well as too low were obtained. This is presumably caused by absorption and/or volatilization and/or reaction of the Cl_2 with water impurities. Pretreatment of glass surfaces with diluted "Clorox" (16 ppm Cl_2), as recommended, did not improve the situation. Volatilization was minimized by keeping the solution stoppered and by minimizing elapsed time. The pH was checked and found to be within the indicated range for both methods. Satisfactory reproducible standard curves were then obtained for both methods by "in situ" dilution and reaction of the Cl_2 standards using a diluted "Clorox" solution containing 164 ppm Cl_2, rather than the indicated 0 2 ppm Cl_2. (ed. note: The method indicates a suitable range of 0 - 2 ppm Cl_2, but does not specify the strength of stock chlorine standard solution to be used).

2. The SNORT method would appear to be superior to the Methyl Orange method because:

   a. The standard curve data are more consistent.

   b. The color is stable.

   c. Color comparisons are compared directly with a blank rather than involving sample and blank comparisons against a third sample, water in this case.

3. We analyzed the samples using hydrochloric acid and chloroacetic acid to adjust the test pH. Results were identical.

4. Absorbance decreased drastically after 1.0 minute with sample 3 (combined chlorine). Two standard curves are required. One for 0 1 ppm (low range), and one for 0 - 2 ppm (high range).

5. Some difficulty in reproducing standard curve.

Leuco-Crystal Violet Method

1. Our leuco crystal violet curve for free chlorine is linear only to 0.7 mg/l. In the range of 0.5 0.7 mg/l for total chlorine, the developed color was not stable and began to fade within 1 minute after indicator addition. Therefore, it was necessary to prepare a 1 + 1 dilution of test sample 3 prior to the total chlorine determination.

   In both "Water Chlorine (Residual) Studies 1 and 2" and in our own independent evaluation of the leuco crystal violet method for chlorine we have consistently had difficulty with reproducibility of colors with free chlorine concentrations greater than 0.7 mg/l. In this study, we finally worked out our own technique in order to obtain better reproducibility. We used 250 ml beakers instead of 100 ml volumetric flasks. The tip of the pipet was placed just under the spout of the beaker and the indicator was allowed to flow down the inside glass surface to the sample with a minimum of initial agitation of the sample. We also learned that for samples containing a free chlorine concentration greater than 0.7 mg/l, the rate of addition of 1 ml of indicator solution is quite critical to color development. We used a standard 15 second addition time.

2. Color development for free chlorine was slow. About 5 minutes were required for development.

3. No correlation was apparent with DPD. Too tedious for routine, rapid analyses by central labs.

4. Obtained no color development with leuco crystal violet in sample or standards.

Orthotolidine-Arsenite Method

1. Used Taylor slide comparator as standard. Results at best are good to ± 0.1 mg/l. We found that it takes too long to add sample and arsenite to the sample to get lowest possible free Cl_2 result unless temperature is near 0°C.

2. Test was carried out using an ice bath at 1.6°C. The temperature of the sample caused the cuvettes to fog up in seconds making accurate and timed readings nearly impossible. As this test doesn't guarantee accurate results over 1°C during the addition of the reagents, I don't find this test very practical or convenient.

Stabilized Neutral Orthotolidine Method

1. Approximate range of free and total chlorine in the samples would be very valuable in knowing what range of standards to use in constructing the curves. Rapidity in analysis is essential.

2. The total chlorine results were found to be less than the sum of free chlorine + monochloramine, even after repeated tests with new sets of reagents. In the determination of free chlorine in sample 3 there was a gradual increase in color development after one minute.

3. Calibration curve must be run several times to get reproducible points. Mixing step is critical.

4. Absorbance began to increase after 2 minutes development with sample 3.

5. This is our preferred colorimetric method.

DPD-Colorimetric

1. We found that the wavelength of maximum absorbance for DPD oxalate is 552 mμ. An equally well-defined peak does occur at 515 mμ but this peak is 0.023 ± .001 absorbance units lower. We found no apparent differences in the chlorine residuals determined at each wavelength if a calibration curve is prepared for each wavelength.

2. A second reading of standards read about five minutes after initial readings indicated fading of color.

3. Readings fade too fast for DU Spectrophotometer.

4. Sample 3 was very unstable increased absorbance with time.

5. Very unstable color changed markedly between 15 and 30 minutes after development, which is almost instantaneous.

6. Timing is a very critical factor in this test. Slight deviation from precise timing will inevitably give erroneous results.

- Reaction times specified for mono, di, and trichloramines are difficult to follow with large samples.

- Red color fades on addition of KI crystals when testing for dichloramine.

)PD-Titrimetric Method

- It appears that this method is not applicable to chlorine analysis in this range because of the low volume of titrant required.

- This method is preferred above the methyl orange method.

- Timing of readings appears to be critical. Permanganate standards are better than chlorine standards. More reliable and easier to work with.

- The directions for the calculations could be more explicit.

mperometric Method

- In sample 3 the free chlorine endpoint was difficult to detect. With the first addition of phenyl arsenoxide, there is a definite movement of the microammeter pointer to the left (down). We did not experience this with the free chlorine titration of distilled water to the endpoint prior to each sample processing.

SUMMARY AND CONCLUSIONS

Sample 1 showed an unexplained loss of approximately 50% of ts total chlorine, making the absolute accuracy and precision data neaningless. Nevertheless, the data is useful for comparison of the nethods. Samples 2 and 3 were stable and maintained their initial ralues throughout the study. As explained previously, the free chlorine :ontent of sample 3 is an artifact, and actually is zero. This data, also, s useful only for comparison.

As shown in Table 5, the best overall accuracy was obtained vith the methyl orange procedure, as indicated by the low average mean :rror. This apparently good performance unfortunately is nullified by he poor precision (Table 6) as indicated by the consistently high standard leviation. Methyl orange performed acceptably only for total chlorine n sample 3. Examination of the bar graphs, figures 15, 16, 30, how-:ver, indicates in the case of the free and total chlorine measurement n sample 2 and the total chlorine measurement in sample 3, that the arge standard deviation is due mainly to three divergent results at each

Table 5. SUMMARY OF OVERALL ACCURACY
(Average Mean Error)

Method	Sample 1		Sample 2		Sample 3		Overall	Omitting all data on Sample 1 and Free on Sample 3
	Free	Total	Free	Total	Free	Total	Average	
Methyl Orange	-0.219	-0.171	-0.044	-0.006	-0.006	+0.029	0.079	0.026
Leuco Crystal Violet	-0.250	-0.209	-0.085	-0.070	-0.050	-0.007	0.112	0.054
SNORT	-0.241	-0.198	-0.113	-0.107	-0.048	-0.032	0.123	0.084
DPD-Titrimetric	-0.259	-0.198	-0.192	-0.059	-0.038	-0.031	0.130	0.094
DPD-Colorimetric	-0.263	-0.213	-0.153	-0.097	-0.014	+0.103	0.140	0.117
Amperometric	-0.241	-0.189	-0.230	-0.119	-0.012	-0.108	0.150	0.152
OTA	-0.282	-0.253	-0.198	-0.102	+0.114	-0.092	0.174	0.130

Table 6. SUMMARY OF OVERALL PRECISION

(Average Standard Deviation)

Method	Sample 1		Sample 2		Sample 3		Overall Average	Omitting all data on Sample 1 and Free on Sample 3
	Free	Total	Free	Total	Free	Total		
Leuco Crystal Violet	0.085	0.055	0.042	0.015	0.000	0.089	0.048	0.049
SNORT	0.093	0.092	0.120	0.142	0.004	0.110	0.094	0.124
Amperometric	0.106	0.072	0.206	0.137	0.040	0.171	0.122	0.171
DPD-Colorimetric	0.102	0.100	0.171	0.152	0.057	0.210	0.132	0.177
DPD-Titrimetric	0.110	0.103	0.298	0.205	0.019	0.121	0.143	0.208
Methyl Orange	0.143	0.162	0.315	0.301	0.055	0.143	0.187	0.253
OTA	0.090	0.098	0.335	0.325	0.195	0.218	0.210	0.293

end of the array. The symmetry of their distribution prevents their rejection by statistical tests, but it is evident that the other 17 results are very accurate and precise. The logical conclusion, therefore, is that the method is capable of excellent accuracy and precision in spite of difficulties encountered by a few analysts.

The apparently excellent performance of leuco crystal violet is somewhat inconclusive because of the very small amount of data for this method. Beyond all doubt, the SNORT procedure performed well and produced acceptable results for the three most meaningful determinations; namely, free and total chlorine in sample 2, and total chlorine in sample 3. This data is summarized in the last column of Table 5. According to the overall average of the most meaningful data, the two DPD procedures, colorimetric and titrimetric were nearly equal in overall performance. Better accuracy was obtained with the DPD titration (Table 5), while the DPD colorimetric showed better precision (Table 6). The DPD colorimetric data shows better precision than the DPD titrimetric results for samples 1 and 2, possibly indicating difficulty mainly with measurement of combined chlorine as in sample 3. The overall performance of the amperometric titration ranked below the DPD methods, and an acceptable performance was obtained only for the total chlorine measurement in sample 2.

The poorest results were obtained with the orthotolidine-arsenite (OTA) procedure. The data shows the method to be the least in precision and next to last in accuracy and is unacceptable for all determinations. The average total error (Table 7) for OTA is one third more than the next poorest method; methyl orange.

In samples 1 and 2, containing only free chlorine, the rather similar differences between means for free and for total chlorine suggests that, regardless of method used, a common source of error may be ammonia in the distilled water, on the glassware, or in the laboratory atmosphere. The generally better precision for total than for free chlorine measurement, likewise seems to indicate contamination of the samples by the participants.

Table 7. SUMMARY OF OVERALL (AVERAGE) TOTAL ERROR

Method	Sample 1		Sample 2		Sample 3		Overall	Omitting all data on Sample 1 and Free on Sample 3
	Free	Total	Free	Total	Free	Total	Average	
Leuco Crystal Violet	95.31	72.59	17.24	10.20	100.00	28.06	53.90	18.52
SNORT	97.04	87.00	35.95	39.97	112.40	38.15	68.42	38.02
DPD-Titrimetric	108.86	91.77	80.51	47.89	153.40	41.33	87.29	56.64
Amperometric	102.95	75.63	65.46	40.14	182.80	68.21	89.20	57.94
DPD-Colorimetric	106.18	94.00	50.57	40.83	256.40	79.33	104.55	56.90
Methyl Orange	114.86	112.59	68.83	62.12	232.00	47.75	106.36	59.56
OTA	104.95	101.90	88.57	76.81	1007.80	79.93	243.33	81.77

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    a. New Methods for the Colorimetric Determination of Halogen Residuals. Part I. Iodine, Iodide, and Iodate. Black, A. P. and G. P. Whittle. J.A.W.W.A. 59:471, April, 1967.

    b. New Methods for the Colorimetric Determination of Halogen Residuals. Part II. Free and Total Chlorine. Black, A. P. and G. P. Whittle. J.A.W.W.A. 59:607, May, 1967.

3. Orthotolidine-Arsenite (OTA) Method; Standard Methods for the Examination of Water and Wastewater, pp 101-102, 12th edition. APHA, AWWA, WPCF. New York, 1965.

4. Stabilized Neutral Orthotolidine (SNORT) Method for Residual Chlorine and Iodine; Analytical Reference Service report "Water Chlorine (Residual) No. 1." Public Health Service Publication No. 1988, Cincinnati, Ohio, 1969.

5. DPD-Colorimetric Method for Free Chlorine, Monochloramine, Dichloramine, and Nitrogen Trichloride. Appendix A.

6. DPD-Titrimetric Method; Ferrous Method for Free Available Chlorine, Monochloramine, Dichloramine, and Nitrogen Trichloride. Analytical Reference Service report "Water Chlorine (Residual) No. 1." Public Health Service Publication No. 1988, Cincinnati, Ohio, 1969.

7. Amperometric Titration Method; Standard Methods for the Examination of Water and Wastewater, pp. 103-108. 12th edition. APHA, AWWA, WPCF. New York, 1965.

8. Orthotolidine Method. Ibid. pp. 93-100.

9. Same as method 5 except N, N-dimethyl-p-phenylenediamine was substituted for N, N-diethyl-p-phenylenediamine.

APPENDICES

APPENDIX A

DPD COLORIMETRIC METHOD FOR FREE CHLORINE, MONOCHLORAMINE, DICHLORAMINE, AND NITROGEN TRICHLORIDE

1. GENERAL DISCUSSION

1.1. Principle: This is a colorimetric version of the Palin DPD method and is based upon the same principles. Instead of titrating with standard ferrous ammonium sulfate (FAS) solution as in the Ferrous Method the colors are evaluated by means of a colorimetric procedure.

2. APPARATUS

Colorimetric Equipment One of the following is required

2.1. Spectrophotometer, for use at a wavelength of 515 mμ and providing a light path of 1 cm or longer.

2.2. Filter Photometer, equipped with a filter having maximum transmission in the wavelength range of 490 to 530 mμ and providing a light path of 1 cm or longer.

3. REAGENTS

3.1. Phosphate buffer solution: Dissolve 24 g anhydrous disodium hydrogen phosphate, Na_2HPO_4, and 46 g anhydrous potassium dihydrogen phosphate KH_2PO_4, in distilled water. Combine this solution with 100 ml distilled water in which 0.8 g disodium ethylenediamine tetraacetate dihydrate, also called (ethylenedinitrilo) tetraacetic acid sodium salt, has been dissolved. Dilute to 1 liter with distilled water and add 20 mg mercuric chloride to prevent mold growth. (The presence of the mercuric chloride also prevents interference in the free chlorine test that might otherwise be caused by trace amounts of iodide in the reagents).

3.2. N, N-Diethyl-p-phenylenediamine (DPD) indicator reagent: Dissolve 1 g DPD Oxalate (Eastman Chemical No. 7102) or 1.5 g p-amino-N:N-diethyl-aniline sulphate (British Drug Houses chemical available from Gallard-Schlesinger Chemical Mfg. Corp., 584 Mineola Ave., Carle Place, Long Island, N. Y. 11514) in chlorine-free distilled water containing 8 ml 1 + 3 sulfuric acid and 200 mg disodium ethylenediamine tetraacetate dihydrate, also called (ethylenedinitrilo) tetraacetic acid sodium salt. Make up to 1 liter, store in a brown glass stoppered bottle and discard when discolored.

3.3. Potassium iodide crystals.

4. PROCEDURE

4.1. Calibration of photometer or colorimeter: Calibrate the available instrument with chlorine (a) or potassium permanganate (b) solutions.

a. Chlorine solutions: Prepare chlorine standards in the range of 0.05 to 4 mg/l from chlorine water and chlorine demand-free distilled water. Develop the color by first placing 5 ml phosphate buffer solution and 5 ml DPD indicator reagent in a flask and then adding 100 ml chlorine standard with thorough mixing as described in Sec. 4.2 - 4.3. Fill the photometer or colorimeter cell from the flask and read the color at 515 mμ. Return the contents of the cell to the flask and titrate the solution with standard ferrous ammonium sulfate (FAS) titrant as a check on the chlorine concentration.

b. Potassium permanganate solutions: Prepare a stock solution containing 891 mg $KMnO_4$ per 1,000 ml. Dilute 10.00 ml stock solution to 100 ml with distilled water in a volumetric flask. When 1 ml of this solution is made up to 100 ml with distilled water a chlorine equivalent of 1.00 mg/l will be produced during the DPD reaction. Prepare a series of permanganate standards encompassing the chlorine equivalent range of 0.05 to 4 mg/l. Develop the color by first placing 5 ml phosphate buffer and 5 ml DPD indicator reagent in a flask and then adding 100 ml standard with thorough mixing as described in Sec. 4.2 - 4.3. Fill the photometer or colorimeter cell from the flask and read the color at 515 mμ. Return the contents of the cell to the flask and titrate the solution with standard ferrous ammonium sulfate (FAS) titrant as a check on any absorption of permanganate by the distilled water.

4.2. Volume of sample: Use a sample volume appropriate to the particular photometer or colorimeter available. Since the following procedure is based on the use of 10-ml volumes, adjust the quantities of reagents proportionately for alternate sample volumes.

Dilute the sample when the total available chlorine exceeds 4 mg/l.

4.3. Free chlorine: Place 0.5 ml each of buffer reagent and DPD indicator reagent in a test tube or photometer cell. Add 10-ml of sample and mix. Read the color immediately (reading A).

4.4. Monochloramine: Continue by adding one very small crystal of potassium iodide and mix. If the dichloramine concentration is expected to be high, instead of the small crystal, preferably add 0.1 ml (two drops) of freshly prepared potassium iodide solution (0.1 g/100 ml). Read the color immediately (reading B).

4.5. Dichloramine: Continue by adding a few crystals of potassium iodide (about 0.1 g) and mix to dissolve. Allow to stand for about 2 min before reading the color (reading C).

4.6. Nitrogen trichloride: Absence of color in step 4.3 (free chlorine) indicates the absence of nitrogen trichloride. Otherwise proceed as follows:

Place a very small crystal of potassium iodide in a clean test tube or photometer cell. Add 10-ml of sample and mix. Then add 0.5 ml each of buffer and indicator reagents and mix. Read the color immediately (reading D).

5. CALCULATION

Reading	NCl_3 Absent	NCl_3 Present
A	free Cl	free Cl
B A	NH_2Cl	NH_2Cl
C B	$NHCl_2$	$NHCl_2 + \frac{1}{2}NCl_3$
D	--	free Cl + $\frac{1}{2}NCl_3$
2(D A)	--	NCl_3
C D	--	$NHCl_2$

Should monochloramine be present with nitrogen trichloride, which is unlikely, include in reading D, in which case NCl_3 is obtained from 2(D - B).

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APPENDIX B.

TABULATION OF RESULTS

Table B-1. Sample 1, Free Chlorine (0.44 mg/l)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
1	0.26	1	2222	0.10	7
1	0.25	2	2222	0.09	3
1	0.24	3	2222	0.07	5
1	0.23	4	2411	0.28	1
1	0.24	6	2411	0.27	5
3	0.21	3	2411	0.27	7
3	0.22	7	2411	0.29	2
4	0.21	1	2513	0.10	6
4	0.00	6	2513	0.22	5
4	0.17	8	2611	0.12	3
1136	0.10	6	2611	0.12	7
1136	0.18	3	2626	0.10	3
1211	0.08	6	2626	0.25	5
1211	0.12	7	2926	0.20	1
1314	0.15	3	2926	0.33	4
1314	0.12	4	3111	0.35	5
1322	0.20	3	3111	0.20	3
1322	0.20	7	3122	0.13	7
1436	0.01	5	3122	0.15	3
1924	0.20	4	3126	0.30	4
1924	0.18	3	3126	0.30	1
1924	0.20	7	3221	0.25	5
2112	0.19	1	3222	0.25	4
2112	0.20	4	3222	0.07	2

(Table B-1 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
3226	0.23	2	5116	0.25	6
3226	0.25	4	5136	0.15	5
3416	0.09	2	5136	0.17	3
3416	0.13	4	5524	0.26	1
4314	0.14	1	5524	0.26	6
4314	0.21	4	5823	0.45	7
4322	0.00	6	5931	0.00	3
4322	0.00	5	5963	0.00	3
4511	0.28	6	5963	0.00	1
4511	0.17	5	6112	0.20	1
4522	0.15	7	6112	0.19	5
4611	0.14	1	6311	0.02	3
4611	0.17	3	6311	0.01	4
4611	0.05	3	6314	0.13	5
4611	0.15	1	6314	0.14	6
4711	0.16	2	6314	0.10	7
4711	0.00	5	6552	0.15	3
4911	0.05	4	6552	0.08	5
4911	0.04	1	6812	0.23	5
4963	0.40	7	6812	0.15	3
4963	0.33	3	6816	0.02	6
5111	0.16	3	6816	0.15	5
5111	0.50	1	7112	0.00	7
5116	0.47	1	7112	0.00	5

(Table B-1 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
7123	0.20	3	8222	0.30	5
7123	0.31	6	8222	0.27	1
7222	0.17	7	8222	0.33	4
7222	0.19	5	8242	0.20	3
7224	0.25	1	8242	0.10	5
7522	0.05	3	8622	0.23	7
7522	0.05	7	8622	0.17	3
7526	0.04	1	8723	0.35	7
7526	0.27	6	8723	0.38	5
7622	0.15	5	8822	0.24	5
7622	0.10	4	8822	0.24	6
7824	0.15	7	8822	0.25	7
7824	0.20	5	8922	0.21	7
7846	0.23	1	8922	0.19	4
7846	0.24	2	9613	0.23	7
7911	0.09	1	9613	0.24	5
7911	0.15	4	9613	0.22	4
7914	0.18	5	9713	0.40	3
7914	0.27	3	9713	0.55	1
7922	0.20	7	9714	0.09	3
7922	0.20	5	9714	0.10	1
8111	0.27	5	9822	0.21	6
8111	0.28	6	9822	0.19	3
8222	0.28	7	9922	0.32	4
8222	0.30	6			

Table B-2. Sample 2, Free Chlorine (0.98 mg/l)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
1	0.92	1	2222	0.70	3
1	0.92	2	2222	0.70	7
1	0.95	3	2222	0.96	5
1	0.95	4	2411	0.92	5
1	0.94	6	2411	0.91	7
3	0.99	3	2411	0.85	2
3	0.94	7	2411	0.88	1
4	0.11	1	2513	0.82	5
4	0.12	6	2513	0.90	6
4	0.10	8	2611	0.60	3
1136	0.36	6	2611	0.60	7
1136	0.70	3	2626	0.50	3
1211	0.58	6	2626	0.78	5
1211	0.53	7	2926	0.98	1
1314	0.43	3	2926	0.96	4
1314	0.68	4	3111	1.70	5
1322	0.85	3	3111	1.20	3
1322	0.88	7	3122	0.73	3
1436	0.57	5	3122	0.66	7
1924	0.86	4	3126	1.05	1
1924	0.87	3	3126	1.01	4
1924	0.87	7	3221	0.80	5
2112	0.89	1	3222	0.35	2
2112	0.85	4	3222	0.70	4

(Table B-2 continued)

LAB. NC.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
3226	0.87	2	5136	0.70	3
3226	0.87	4	5524	1.01	6
4314	1.04	1	5524	1.26	1
4314	0.98	4	5823	1.00	7
4322	0.60	6	5931	0.09	3
4322	0.63	5	5963	0.82	1
4511	0.95	6	5963	0.60	3
4511	0.90	5	6112	0.78	5
4522	0.60	7	6112	0.81	1
4611	0.85	1	6311	0.02	4
4611	0.50	3	6311	0.14	3
4611	0.96	1	6314	0.87	6
4611	0.80	3	6314	0.89	5
4711	0.50	2	6314	0.77	7
4711	0.40	5	6552	0.31	3
4911	0.62	1	6552	0.02	5
4911	0.62	4	6715	0.95	1
4963	0.55	7	6715	1.35	3
4963	1.00	3	6715	1.07	5
5111	0.86	3	6812	0.97	5
5111	1.05	1	6812	0.93	3
5116	1.50	1	6816	0.55	5
5116	0.95	6	6816	0.28	6
5136	0.85	5	7112	0.62	5

(Table B-2 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
7112	0.60	7	8222	0.96	5
7123	1.10	3	8222	1.01	4
7123	1.17	6	8222	0.98	6
7222	0.76	5	8222	0.95	1
7222	0.86	7	8242	0.65	5
7224	0.80	1	8242	0.80	3
7522	0.30	7	8622	0.90	3
7522	0.35	3	8622	0.90	7
7526	0.76	6	8723	1.13	5
7526	0.40	1	8723	0.95	7
7622	0.95	5	8822	0.90	7
7622	0.90	4	8822	0.92	5
7824	0.83	7	8822	0.88	6
7824	0.85	5	8922	0.84	7
7846	0.94	2	8922	0.78	4
7846	0.99	1	9613	0.91	7
7911	0.97	1	9613	0.87	4
7911	0.86	4	9613	0.89	5
7914	1.11	3	9713	1.60	3
7914	0.88	5	9713	1.70	1
7922	0.25	7	9714	1.02	1
7922	2.00	5	9714	0.95	3
8111	1.10	6	9822	0.95	6
8111	1.00	5	9822	0.85	3
8222	0.89	7	9922	0.98	4

Table B-3. Sample 3, Free Chlorine (0.005 mg/l)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
1	0.000	1	2222	0.090	5
1	0.000	2	2411	0.000	5
1	0.000	3	2411	0.020	7
1	0.000	4	2411	0.000	1
1	0.000	6	2411	0.000	2
3	0.080	3	2513	0.060	5
3	0.000	7	2513	0.100	6
4	0.000	6	2611	0.000	7
4	0.080	1	2611	0.150	3
4	0.100	8	2626	0.030	5
1136	0.030	3	2926	0.140	4
1136	0.000	6	2926	0.120	1
1211	0.000	7	3111	0.080	5
1211	0.040	6	3111	1.100	3
1314	0.020	3	3122	0.030	3
1314	0.000	4	3122	0.040	7
1322	0.100	7	3126	0.000	1
1322	0.120	3	3126	0.000	4
1436	0.010	5	3221	0.000	5
1924	0.040	3	3222	0.000	4
2112	0.000	4	3222	0.000	2
2112	0.000	1	3226	0.000	2
2222	0.020	7	3226	0.000	4
2222	0.100	3	3416	0.190	2

(Table B-3 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
3416	0.210	4	5524	0.150	1
4314	0.030	1	5524	0.000	6
4314	0.010	4	5823	0.680	7
4322	0.000	6	5931	0.090	3
4322	0.000	5	5963	0.100	3
4511	0.000	6	5963	0.100	1
4511	0.000	5	6112	0.000	5
4522	0.100	7	6112	0.000	1
4611	0.000	1	6311	0.030	3
4611	0.060	1	6311	0.010	4
4611	0.050	3	6314	0.000	7
4611	0.130	3	6314	0.000	6
4711	0.000	5	6314	0.000	5
4711	0.250	2	6552	0.000	5
4911	0.000	1	6552	0.560	3
4911	0.000	4	6812	0.020	3
4963	0.100	7	6812	0.080	5
4963	0.240	3	6816	0.040	6
5111	0.240	3	6816	0.050	5
5111	0.510	1	7112	0.000	7
5116	0.050	6	7112	0.000	5
5116	0.430	1	7123	0.310	6
5136	0.000	3	7123	0.360	3
5136	0.000	5	7222	0.000	5

(Table B-3 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
7222	0.000	7	8242	0.200	3
7224	0.250	1	8242	0.750	5
7522	0.080	7	8622	0.100	7
7522	0.000	3	8622	0.050	3
7526	0.150	1	8723	0.020	7
7526	0.140	6	8723	0.100	5
7622	0.000	5	8822	0.020	6
7622	0.000	4	8822	0.040	5
7824	0.200	5	8822	0.050	7
7824	0.160	7	8922	0.000	4
7846	0.060	1	8922	0.050	7
7911	0.010	4	9613	0.050	7
7911	0.040	1	9613	0.000	4
7914	0.580	3	9613	0.010	5
7914	0.190	5	9713	0.900	1
7922	2.000	5	9713	0.750	3
7922	0.200	7	9714	0.100	1
8111	0.000	5	9714	0.310	3
8111	0.000	6	9822	0.150	3
8222	0.000	1	9822	0.200	6
8222	0.000	5	9922	0.000	4
8222	0.000	6			
8222	0.000	7			
8222	0.000	4			

Table B-4. Sample 1, Total Chlorine (0.44 mg/l)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
1	0.34	1	2222	0.12	3
1	0.25	2	2222	0.23	5
1	0.32	3	2222	0.23	7
1	0.26	4	2411	0.31	1
1	0.29	6	2411	0.28	5
3	0.30	3	2411	0.28	7
3	0.24	7	2411	0.29	2
4	0.29	1	2513	0.22	5
4	0.00	6	2513	0.14	6
4	0.20	8	2611	0.15	7
1136	0.30	3	2611	0.14	3
1136	0.37	6	2626	0.15	3
1211	0.18	6	2626	0.27	5
1211	0.18	7	2926	0.15	1
1314	0.15	3	2926	0.33	4
1314	0.07	4	3111	1.17	5
1322	0.27	7	3111	1.10	3
1322	0.25	3	3122	0.22	7
1436	0.01	5	3122	0.22	3
1924	0.18	4	3126	0.30	4
1924	0.18	3	3126	0.30	1
1924	0.20	7	3221	0.25	5
2112	0.20	4	3222	0.15	2
2112	0.19	1	3222	0.30	4

(Table B-4 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
3226	0.25	4	5111	0.17	3
3226	0.24	2	5116	0.10	6
3322	0.20	8	5116	0.49	1
3322	0.50	9	5136	0.15	5
3416	0.30	4	5136	0.17	3
3416	0.28	2	5524	0.49	1
4314	0.15	4	5524	0.26	6
4314	0.14	1	5823	0.45	7
4322	0.16	5	5931	0.00	3
4322	0.15	6	5963	0.00	3
4511	0.20	5	5963	0.00	1
4511	0.32	6	6112	0.24	5
4522	0.25	7	6112	0.26	1
4611	0.05	3	6311	0.02	3
4611	0.20	1	6311	0.32	4
4611	0.15	1	6314	0.18	6
4611	0.20	3	6314	0.16	7
4711	0.16	2	6314	0.17	5
4711	0.00	5	6552	0.17	3
4911	0.04	4	6552	0.49	5
4911	0.04	1	6812	0.16	3
4963	0.40	7	6812	0.25	5
4963	0.33	3	6816	0.32	6
5111	0.51	1	6816	0.35	5

(Table B-4 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
7112	0.23	7	8222	0.33	4
7112	0.14	5	8222	0.30	5
7123	0.32	6	8222	0.30	6
7123	0.22	3	8222	0.27	1
7222	0.19	7	8222	0.28	7
7222	0.19	5	8242	0.20	3
7224	0.55	1	8242	0.20	5
7522	0.15	3	8622	0.17	3
7522	0.20	7	8622	0.23	7
7526	0.35	6	8723	0.35	7
7526	0.12	1	8723	0.38	5
7622	0.23	5	8822	0.24	6
7622	0.27	4	8822	0.24	5
7824	0.20	5	8822	0.25	7
7824	0.25	7	8922	0.26	7
7846	0.25	1	9613	0.26	5
7846	0.25	2	9613	0.28	4
7911	0.12	1	9613	0.30	7
7911	0.18	4	9713	0.40	3
7914	0.28	3	9713	0.55	1
7914	0.18	5	9714	0.17	3
7922	0.20	7	9714	0.20	1
7922	0.20	5	9822	0.25	6
8111	0.35	6	9822	0.25	3
8111	0.35	5	9922	0.36	4

Table B-5. Sample 2, Total Chlorine (0.98 mg/l)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
1	0.98	1	2222	0.80	3
1	0.92	2	2222	1.08	5
1	1.02	3	2222	0.93	7
1	0.92	4	2411	0.95	7
1	0.98	6	2411	0.94	5
3	1.07	3	2411	0.90	2
3	0.98	7	2411	0.92	1
4	0.17	1	2513	0.82	5
4	0.17	6	2513	0.90	6
4	1.00	8	2611	0.70	3
1136	0.88	6	2611	0.80	7
1136	0.90	3	2626	0.70	3
1211	0.69	6	2626	0.95	5
1211	0.69	7	2926	0.92	1
1314	0.52	3	2926	0.96	4
1314	0.59	4	3111	1.81	5
1322	1.02	7	3111	1.40	3
1322	0.95	3	3122	0.84	3
1436	0.57	5	3122	0.85	7
1924	0.79	4	3126	1.05	1
1924	0.87	3	3126	1.05	4
1924	0.87	7	3221	0.80	5
2112	0.85	4	3222	0.45	2
2112	0.89	1	3222	0.75	4

(Table B-5 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
3226	0.90	2	5116	0.70	6
3226	0.87	4	5136	0.71	3
3322	0.40	8	5136	0.85	5
3322	1.00	9	5524	1.01	6
4314	0.85	4	5524	1.31	1
4314	1.10	1	5823	1.00	7
4322	0.83	5	5931	0.35	3
4322	0.80	6	5963	0.60	3
4511	0.92	5	5963	0.86	1
4511	0.95	6	6112	0.78	5
4522	0.77	7	6112	0.89	1
4611	0.65	3	6311	2.16	4
4611	1.10	3	6311	0.16	3
4611	0.85	1	6314	0.94	5
4611	1.06	1	6314	0.84	7
4711	0.80	5	6314	0.92	6
4711	0.64	2	6552	0.33	3
4911	0.60	4	6552	1.10	5
4911	0.63	1	6715	0.96	1
4963	1.02	3	6715	1.00	5
4963	0.55	7	6715	1.35	3
5111	1.13	1	6812	0.97	5
5111	0.95	3	6812	0.93	3
5116	1.50	1	6816	0.55	5

(Table B-5 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
6816	0.48	6	8111	1.10	5
7112	0.70	7	8111	1.28	6
7112	0.65	5	8222	0.95	1
7123	1.35	3	8222	0.89	7
7123	1.33	6	8222	0.98	6
7222	0.86	7	8222	1.01	4
7222	0.84	5	8222	0.96	5
7224	0.80	1	8242	0.65	5
7522	0.55	7	8242	0.90	3
7522	0.50	3	8622	1.00	3
7526	0.91	6	8622	0.90	7
7526	0.57	1	8723	0.99	7
7622	0.98	5	8723	1.13	5
7622	0.90	4	8822	1.00	7
7824	0.87	7	8822	0.92	5
7824	0.90	5	8822	0.92	6
7846	0.93	2	8922	0.94	7
7846	1.02	1	9613	0.95	4
7911	1.05	1	9613	0.92	5
7911	0.94	4	9613	1.00	7
7914	0.88	5	9713	1.70	1
7914	1.12	3	9713	1.60	3
7922	0.25	7	9714	1.01	3
7922	2.00	5	9714	1.09	1

(Table B-5 continued)

LAB. NO.	RESULTS	METHOD	
9822	1.00	6	
9822	0.95	3	
9922	1.06	4	

Table B-6. Sample 3, Total Chlorine (0.66 mg/l)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
1	0.62	1	2222	0.60	3
1	0.60	2	2222	0.60	7
1	0.65	3	2222	0.93	5
1	0.64	4	2411	0.64	2
1	0.61	6	2411	0.62	5
3	0.67	3	2411	0.65	1
3	0.62	7	2411	0.61	7
4	0.81	1	2513	1.54	6
4	0.48	6	2513	0.99	5
4	0.60	8	2611	0.15	7
1136	0.65	3	2611	0.35	3
1136	0.76	6	2626	0.63	5
1211	0.81	6	2626	0.40	3
1211	0.61	7	2926	0.61	4
1314	0.37	3	2926	0.54	1
1314	0.06	4	3111	1.25	5
1322	0.63	7	3111	1.20	3
1322	0.60	3	3122	0.53	3
1436	0.13	5	3122	0.57	7
1924	0.43	4	3126	0.80	1
1924	0.54	7	3126	0.79	4
1924	0.53	3	3221	0.60	5
2112	0.55	4	3222	0.25	2
2112	0.62	1	3222	0.60	4

(Table B-6 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
3226	0.68	2	5111	0.96	1
3226	0.71	4	5116	0.71	1
3322	0.80	8	5116	0.40	6
3322	2.00	9	5136	0.40	3
3416	0.85	4	5136	0.60	5
3416	0.82	2	5524	0.40	1
4314	0.58	4	5524	0.66	6
4314	0.56	1	5823	0.68	7
4322	0.70	5	5931	0.34	3
4322	0.70	6	5963	0.65	1
4511	0.67	6	5963	0.25	3
4511	0.68	5	6112	0.60	5
4522	0.53	7	6112	0.61	1
4611	0.69	1	6311	1.55	4
4611	0.67	1	6311	0.10	3
4611	0.65	3	6314	0.66	6
4611	0.33	3	6314	0.66	5
4711	0.58	2	6314	0.59	7
4711	1.20	5	6552	1.30	5
4911	0.50	4	6552	0.73	3
4911	0.49	1	6812	0.67	3
4963	0.59	3	6812	0.74	5
4963	0.12	7	6816	0.82	5
5111	0.54	3	6816	0.62	6

(Table B-6 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
7112	0.60	7	8222	0.69	4
7112	0.70	5	8222	0.64	1
7123	0.50	3	8222	0.63	5
7123	0.41	6	8222	0.62	6
7222	0.82	7	8222	0.64	7
7222	0.61	5	8242	0.75	5
7224	0.90	1	8242	0.90	3
7524	0.47	7	8622	0.52	7
7522	0.60	3	8622	0.50	3
7526	1.08	6	8723	0.76	5
7526	0.71	1	8723	0.69	7
7622	0.66	5	8822	0.59	6
7622	0.57	4	8822	0.56	5
7824	0.64	7	8822	0.65	7
7824	1.80	5	8922	0.63	7
7846	0.60	2	9613	0.59	7
7846	0.66	1	9613	0.62	5
7911	0.73	1	9613	0.60	4
7911	0.57	4	9713	1.00	1
7914	0.82	3	9713	0.85	3
7914	0.69	5	9714	0.67	3
7922	0.20	7	9714	0.73	1
7922	2.00	5	9822	0.67	6
8111	0.77	6	9822	0.47	3
8111	0.77	5	9922	0.73	4

APPENDIX C

GLOSSARY OF STATISTICAL TERMS

A glossary of statistical terms defined as they are used in this report is presented to ensure uniformity of understanding.[1]

Arithmetic mean — The sum of the sample results divided by the number of results in the sample. Let X_i ($i = 1, 2, \ldots, n$) denote the i^{th} results in a sample of n results. The arithmetic mean denoted $\overline{X}$ is given by $\overline{X} = \sum_{i=1}^{n} \frac{X_i}{n}$.

Median — Halfway point in the results when they have been arranged in order of magnitude (the middle result of an odd number of results, or the average of the middle two for an even number).

Accuracy — The correctness of a measurement, or the degree of correspondence between the results and the true value (actual amount added).

Measures of accuracy — Measures that relate to the difference between the mean of the results and the true value when the latter is known or assumed. The following measures apply:

Mean error — The average difference with regard to sign between the results and the true value. Equivalently, the difference between the mean of the results and the true value (T. V.).

$$\text{Mean error} = \overline{X} \quad \text{T. V.}$$

Relative error — The absolute value of the mean error expressed as a percentage of the true value.

$$\text{Relative error} = \frac{\left| \overline{X} \quad \text{T. V.} \right|}{\text{T. V.}} \times 100$$

Precision — The reproducibility of sample results or the degree of agreement among the results.

Measures of precision

Measures of the variation among the sample results themselves, i.e., the spread or dispersion of the results without regard to the true value. The following measures apply.

Sample variance — Sum of squared deviations of the sample results from their mean divided by one less than the number of results in the sample. The sample variance denoted s^2 is given by

$$s^2 = \frac{\sum_{i=1}^{n} (X_i - \overline{X})^2}{n - 1}$$

where n is the number of results.

Sample standard deviation — Square root of the sample variance.

$$s = \sqrt{\frac{\sum_{i=1}^{n} (X_i - \overline{X})^2}{n - 1}}$$

Relative standard deviation (coefficient of variation) — Sample standard deviation expressed as a percentage of the mean.

$$\text{Rel. Std. Dev.} = \frac{s}{\overline{X}} \times 100$$

Range — The difference between the largest and smallest results in the sample.

Confidence limits — Limits within which the true mean, μ, of the population (the theoretically infinite number of possible replications of the analysis) will lie with probability equal to $1 - \alpha$, where α is the probability that the limits do not contain the true mean. The upper and lower $1 - \alpha$ confidence limits are given by

$$\text{Confidence limits} = \overline{X} \pm t_{\alpha/2} s/\sqrt{n}$$

where $\overline{X}$ and s are the sample mean and standard deviation, $t_{\alpha/2}$ is the upper $\alpha/2$ point of "Student's" t-distribution, and n is the number of results in the sample used to compute $\overline{X}$.

Tolerance limits — Limits within which one can state with probability γ that at least a proportion P of the entire population will lie. The upper and lower tolerance limits are given by

$$\text{Tolerance limits} = \overline{X} \pm Ks,$$

where K is the factor for two-sided tolerance limits for normal populations.[2] The value of K depends upon the chosen values of γ and **P**.

Total error

A criterion for judging acceptability of analytical methods. The total error is given by[3]

$$\frac{\text{Absolute value of mean error} + 2(\text{Std. Dev.})}{\text{True Value}} \times 100$$

On the basis of this total error, methods can be divided into three categories: excellent (total error 25% or less), acceptable (total error 50% or less), and unacceptable (total error greater than 50%).

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2. Natrella, M. G. Experimental Statistics. National Bureau of Standards. 1963. p. T-10.

3. McFarren, E. F., R. J. Lishka, and J. H. Parker. Criterion for Judging Acceptability of Analytical Methods. Anal. Chem. 42:358, 1970.

APPENDIX D

TESTS FOR NORMALITY AND REJECTION OF OUTLIERS

Test for normality

The Kolmogorov-Smirnov goodness-of-fit test was used to determine whether the observations reported could reasonably be thought to have come from a normal distribution. [1]

Briefly, the test involves computing the observed cumulative frequency distribution (the percent of values less than or equal to each value in the distribution) and comparing it with the theoretical normal cumulative frequency distribution. The point at which the two distributions, theoretical and observed, show greatest divergence is determined. Reference of the value of the divergence to a table of critical values for the Kolmogorov-Smirnov goodness-of-fit test indicates whether such a large divergence is likely on the basis of chance. If such a large divergence is not likely, the distribution is designated as nonnormal; otherwise the distribution is designated as normal.

Tests for rejection of outliers

1. If the distribution is designated as nonnormal, the suspected outlier (the farthest value from the mean) is rejected only if the distance between it and the mean is greater than three standard deviations; otherwise the suspected outlier is accepted.

2. If the distribution is designated as normal and the sample size is less than or equal to 30, the suspected outlier, the farthest value from the mean, is tested for rejection by a method developed by Dixon. [2] Briefly, this test involves computing a ratio that compares the distance of the suspected value being tested from its neighbors with the range of all, or most all, of the observations (depending on the total number of suspected values in the sample). Reference of the ratio to a table of critical values for test ratios for gross errors indicates whether such a large ratio is likely on the basis of chance. If the ratio is greater than or equal to the critical value, the probability that the suspected outlier is from the sample distribution is small; hence, the outlier is rejected. If the ratio is less than the critical value, the suspected outlier probably came from the sample distribution; hence, the suspected outlier is accepted

3. If the distribution is designated as normal, and the sample size is greater than 30, the suspected outlier is tested for rejection by a method developed by Santner. [3] This method employs the statistic, $\frac{\overline{X} - X_o}{s}$, where $\overline{X}$ is the sample mean, X_o is the suspected outlier (the

farthest value from the mean) and s is the sample standard deviation. This statistic is compared with a table of critical values to determine whether its value is larger than would be expected on the basis of chance. If the statistic is greater than or equal to the critical value, the suspected outlier is rejected; otherwise, the suspected outlier is accepted.

Application of tests for normality and for rejection of outliers to ARS studies

The test for normality and the subsequent test for rejection of outliers are applied to the observed data in two ways: first, to each method for a given substance at a given concentration; then to a given substance at a given concentration regardless of method. In either case, it is first necessary to determine whether the original distribution is normal or nonnormal. If the original distribution is designated as nonnormal, method 1 is used to test for rejection of the suspected outlier farthest from the mean. If the suspected outlier is not rejected, no further tests for normality or rejection of outliers are made, and the distribution is designated as nonnormal. On the other hand, if the suspected outlier is rejected, the new distribution, which excludes the rejected observation, is then tested for normality. If the new distribution is nonnormal, the next suspected outlier is tested for rejection by method 1. This cycle of testing for normality and testing for rejection of outliers continues until a suspected value is not rejected or the test for normality designates the distribution as normal. If the distribution is designated as normal, subsequent tests for rejection of outliers made by method 2 or 3 are the same as if the original distribution had been normal. This case is discussed next.

If the original distribution is designated as normal or a new distribution that was originally nonnormal is designated as normal after the rejection of one or more outliers, and if the number of observations is not greater than 30, then method 2 is used to test for rejection the suspected outlier farthest from the mean. If the suspected outlier is not rejected, no further tests are made, and the distribution is designated as normal. If the suspected outlier is rejected, then the suspected outlier farthest from the mean of the new distribution is tested for rejection, and so on until the suspected value of a new distribution is not rejected; when this occurs, no further tests are made, and the final distribution is designated as normal. On the other hand, if the number of observations in the original distribution is greater than 30, method 3 is used to test the suspected outlier for rejection. If the suspected outlier is not rejected, no further tests are made, and the distribution is designated as normal. If the suspected outlier is rejected, than the suspected outlier farthest from the mean of the new distribution, which excludes the rejected value, is tested for rejection. Testing for outliers continues by this method until a suspected outlier is not rejected or the number of

observations is no longer greater than 30, in which case, method 2 is used for testing for rejection of any remaining suspected outliers.

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APPENDIX E

COMPARISON OF METHODS FOR STATISTICALLY SIGNIFICANT DIFFERENCES IN PRECISION AND ACCURACY

The methods are compared in two ways with respect to precision and accuracy. In the first case, two methods are compared at a given concentration with respect to precision and to accuracy. The unknown variances, σ_1^2 and σ_2^2 (estimated by the sample variances, s_1^2 and s_2^2), of the two methods are first compared by the F-test[1] to determine whether there is a significant difference in the precision of the two methods. The unknown means, μ_1 and μ_2 (estimated by the sample means, $\overline{X}_1$ and $\overline{X}_2$), of the two methods are then compared by the t-test[2] to determine whether there is a significant difference in the accuracy of the two methods. The t-test employed is based on the result of the F-test. These two tests of hypotheses will produce one of the following results.

Outcome 1: $\sigma_1^2 \quad \sigma_2^2, \ \mu_1 = \mu_2$

Outcome 2: $\sigma_1^2 = \sigma_2^2, \ \mu_1 \neq \mu_2$

Outcome 3: $\sigma_1^2 \neq \sigma_2^2, \ \mu_1 \quad \mu_2$

Outcome 4: $\sigma_1^2 \neq \sigma_2^2, \ \mu_1 \neq \mu_2$

In outcome 1, we conclude that the sample results do not indicate that a significant difference in either precision or accuracy exists between the two methods.

In outcome 2, we conclude that there is no indication of a significant difference in precision between the two methods, but there is a significant difference in the accuracy of the two methods; specifically, the method whose sample mean is closer to the true value is deemed the more accurate. In outcome 3, we conclude that there is no indication of a significant difference in the accuracy of the two methods, but the method with the smaller sample variance is the more precise.

In outcome 4, we conclude that there is a significant difference in the precision and in the accuracy of the two methods. The method with the smaller sample variance is the more precise, and the method whose sample mean is closer to the true value is the more accurate.

In the second case, more than two methods are compared at a given level of concentration with respect to precision and accuracy. Bartlett's

Test[3] is used first to test the hypothesis of equality of the unknown variances, σ_i^2, of the methods in order to compare the precision of the methods. If we conclude that the precision is the same, the Analysis of Variance[4] is then used to test whether a significant difference exists among the means, μ_i, in order to compare the accuracy of the methods. If there is a significant difference among the means. Duncan's Multiple Range Test[5,6] is used to determine which method means differ significantly. If the precision is not the same, then the Kruskal-Wallis One-way Analysis of Variance by Ranks[7] is used to determine whether a significant difference exists among the means in order to compare the accuracy of the methods.

Once again, there are basically four possible outcomes for the above tests of hypotheses.

Outcome 1: all σ_i^2 are equal, all μ_i are equal

Outcome 2: all σ_i^2 are equal, not all μ_i are equal

Outcome 3: not all σ_i^2 are equal, all μ_i are equal

Outcome 4: not all σ_i^2 are equal, not all μ_i are equal

In outcome 1, we conclude that the sample results do not indicate a significant difference in either the precision or the accuracy of the methods.

In outcome 2, we conclude that there is no indication of a significant difference in the precision of the methods; however, at least one method does differ significantly from the rest with respect to accuracy, and Duncan's Multiple Range Test indicates which methods differ. For example, in comparing four methods, we might conclude $\mu_1 \quad \mu_2$ and $\mu_3 \quad \mu_4$, but μ_1 and μ_2 differ significantly from μ_3 and μ_4; or we might conclude that $\mu_1 \quad \mu_2 = \mu_3$, but μ_4 differs significantly from μ_1, μ_2, and μ_3.

In outcome 3, we conclude that there is no indication of a significant difference in the accuracy of the methods, but at least one method differs significantly from the rest with respect to precision.

In outcome 4, we conclude that the methods differ significantly with respect to both precision and accuracy.

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3. Ibid., pp. 136-38.

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5. Ibid., pp. 31-33.

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APPENDIX F

ANALYTICAL REFERENCE SERVICE MEMBERSHIP

STATE AGENCIES

Alabama State Department of Public Health, Montgomery
Alabama Water Improvement Commission, Montgomery
Arizona State Department of Health, Phoenix
Arkansas Pollution Control Commission, Little Rock
Arkansas State Department of Health, Little Rock
California Department of Water Resources, Sacramento
California State Department of Public Health, Los Angeles
California State Department of Public Health, Air and Industrial Hygiene Laboratory, Berkeley
California State Department of Public Health, Sanitation and Radiation Laboratory, Berkeley
Colorado Department of Public Health, Denver
Connecticut State Department of Health, Hartford
Delaware Water and Air Resources Commission, Dover
District of Columbia Department of Public Health, Washington, D. C.
Florida Department of Agriculture, Tallahassee
Florida State Board of Health, Jacksonville
Florida State Board of Health, Pensacola
Florida State Board of Health, Winter Haven
Hawaii State Department of Health, Laboratories Branch, Honolulu
Hawaii State Department of Health, Occupational and Radiological Health Section, Honolulu
Idaho Department of Health, Boise
Illinois Department of Public Health, Springfield
Illinois State Water Survey, Champaign
Illinois State Water Survey, Peoria
Indiana State Board of Health, Indianapolis
Iowa State Hygienic Laboratory, Des Moines
Iowa State Hygienic Laboratory, Iowa City
Kentucky State Department of Health, Division of Laboratory Services, Frankfort
Kentucky State Department of Health, Radiological Health Program, Frankfort
Lawrence Experiment Station, Massachusetts
Louisiana State Department of Health, New Orleans
Los Angeles County Flood Control District, California
Maryland State Department of Health, Bureau of Environmental Chemistry, Baltimore
Maryland State Department of Health, Bureau of Laboratories, Baltimore
Maryland State Department of Water Resources, Annapolis

Massachusetts Department of Public Health, Amherst
Massachusetts Department of Public Health, Boston
Michigan Department of Conservation, Lansing
Michigan Department of Public Health, Lansing
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Minnesota Department of Health, Minneapolis
Missouri Department of Health, Jefferson City
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Montana Health Department, Helena
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Nevada State Department of Health, Reno
Nevada State Department of Health and Welfare, Las Vegas
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New Hampshire Water Supply and Pollution Control Commission, Concord
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New York State Department of Health, Division of Laboratories and Research, Albany
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New York State Department of Labor, New York City
North Carolina Department of Water and Air Resources, Raleigh
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North Jersey District Water Supply Commission, Wanaque
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Oklahoma State Health Department, Oklahoma City
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Pennsylvania Department of Agriculture, Harrisburg
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Pennsylvania Department of Health, Water Quality Section, Harrisburg
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Rhode Island State Department of Health, Providence
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Texas State Department of Health, Austin
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Vermont State Department of Health, Barre
Vermont State Department of Health, Burlington

Virginia State Department of Health, Bureau of Industrial Hygiene, Richmond
Virginia State Department of Health, Bureau of Laboratories, Richmond
Virginia State Water Control Board, Richmond
Washington State Department of Health, Seattle
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West Virginia Department of Natural Resources, Charleston
Wisconsin Department of Agriculture, Madison

MUNICIPAL AGENCIES

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Albuquerque Department of Environmental Health, Food and Institutional Division, New Mexico
Baltimore City Health Department, Maryland
Bay Area Air Pollution Control District, San Francisco, California
Beaumont Health Department, Texas
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City of Amarillo, Water Reclamation Department, Texas
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City of Cincinnati, Division of Water Pollution Control, Ohio
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City of Miami, Alexander Orr, Jr. Water Treatment Plant, Florida
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Department of Public Works and Utilities, Flint, Michigan
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Louisville Water Company, Kentucky
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Metropolitan Sanitary District of Greater Chicago, Illinois
Metropolitan Utilities District, Omaha, Nebraska
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Minneapolis Water Department, Minnesota
Monroe County Health Department, Rochester, New York
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New York City Department of Air Pollution Control, New York
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