QUALITY-ASSURANCE DATA FOR ROUTINE WATER ANALYSIS IN THE LABORATORIES OF THE U.S. GEOLOGICAL SURVEY FOR WATER-YEAR 1983

By Dale B. Peart and Nancy A. Thomas

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QUALITY-ASSURANCE DATA FROM ROUTINE WATER ANALYSIS

IN THE LABORATORIES OF THE

U.S. GEOLOGICAL SURVEY FOR WATER-YEAR 1983

By Dale B. Peart and Nancy A. Thomas

ABSTRACT

The U.S. Geological Survey maintains a quality-assurance program based on the analysis of reference samples for its two water-analysis laboratories located in Atlanta. Georgia and Denver, Colorado. Reference samples containing selected inorganic constituents are prepared at the U.S. Geological Survey's Ocala, Florida, office and disguised as routine samples, and sent daily or weekly, as appropriate, to each laboratory through other U.S. Geological Survey offices. The results are permanently stored in the National Water Data Storage and Retrieval System (WATSTORE), the U.S. Geological Survey's data base for all water data. These data are analyzed statistically for precision, bias, and comparability. The results of these statistical analyses are presented for data collected during the 1983 water year. Nutrient samples, simulated precipitation (low-concentration level) samples and selected pesticide samples were also submitted as samples of unknown concentrations. The results of these determinations were statistically analyzed for comparability and these data are presented. In addition, a summary of recovery and precision data from three different instruments for volatile organics is presented.

INTRODUCTION

The water quality laboratories of the U.S. Geological Survey, located in Atlanta, Georgia and Denver, Colorado, routinely analyze water, suspended sediments, stream— and lake—bed materials for inorganic constituents, many organic substances, including common pesticides, priority pollutants as defined by the U.S. Environmental Protection Agency (Keith and Telliard, 1979), and some physical properties. Results of the quality—assurance program used to monitor the quality of work performed by these two laboratories are presented in this report. Previous reports (Peart and Thomas, 1983a, 1983b) document results from February 1981 through September 1982.

Factors that need to be considered for data interpretation for this period in conjunction with the results presented in this report include the following:

- 1. Nonanalytical errors were not corrected by this project to preserve the data as the laboratory produced it. Thus, if the data reviewer, in the U.S. Geological Survey's office that collected the sample, is familiar with the collection site or the historical data from that site, many errors of this type could be easily corrected. For example, if two samples from different sites are submitted to the laboratory on the same day and happen to get misidentified, so that the analytical data are misreported for these samples, the collecting office very often can detect this situation and correct it, based on historical data from these sites.
- 2. No quality-assurance samples had any constituents redetermined except those requested by the laboratory quality-assurance group. U.S. Geological Survey data reviewers in the offices where the samples were collected are expected to scrutinize incoming new data for discrepancies and make requests for reanalysis; these requests may help detect analytical and nonanalytical errors, so data quality should improve, compared to data quality stated in this report.
- 3. Figures included in this report may be used to determine analytical conditions at any given time. Where they show that an analytical process may have been in control for the majority of the year and out of control for a short period, but long enough so that the statistical tests applied indicated lack of precision or significant bias results for the year, the data from that period when the analytical process was in control can be considered acceptable with respect to precision and bias.

During the 1983 water year, the following constituents were included in this quality-assurance program:

Major inorganic constituents—alkalinity, aluminum, antimony, arsenic, barium, beryllium, boron, cadmium, calcium, chloride, chromium, cobalt, copper, dissolved sollds (residue on evaporation), fluoride, iron, lead, lithium, manganese, magnesium, molybdenum, nickel, potassium, selenium, silica, silver, sodium, strontium, sulfate, and zinc.

<u>Nutrients</u>—ammonia, ammonia plus organic nitrogen, nitrate plus nitrite, nitrite, organic carbon, orthophosphate, and phosphorus.

<u>Precipitation-level</u> <u>samples--specific</u> conductance and low concentration level determinations of: calcium, chloride, fluoride, magnesium, nitrate, phosphorous, potassium, sodium, and sulfate.

<u>Pesticides</u>—organophosphate and organochlorine insecticides and chlorophenoxyacid herbicides.

Physical properties--specific conductance.

<u>Volatile organics</u>—bromoform, chlorobenzene, dichlorobromomethane, ethylbenzene, 1.1.2.2.—tetrachloroethane.

PROGRAM DESCRIPTION

Standard Reference Water Samples (SRWS) (Schroder and others, 1980; Skougstad and Fishman, 1975) are used as the principal component of the reference samples used in this program. The SRWS are diluted with deionized water, mixed in varying proportions with other SRWS, or used undiluted. A large range of concentrations of chemical constituents is achieved thereby, increasing the number of unique samples available for quality-assurance purposes. This increase, in turn, decreases the probability that quality-assurance samples will be recognized in the laboratory due to frequency of analyses or unique sample behavior.

In addition to the SRWS, synthetic samples made from reagent-grade chemicals are used in preparing reference samples. All samples are prepared in the U.S. Geological Survey's Ocala, Florida office, and are made to appear as much like real samples as possible. This effort is coordinated with other Geological Survey offices that will be shipping the samples during any given calendar month. When the samples are prepared and proper forms are completed to assure that appropriate constituents have been requested for the sample, the samples and the forms are shipped to selected Geological Survey offices across the country. These Survey offices then ship the quality-assurance samples to the laboratories daily or weekly, as appropriate, along with their regular samples.

The quality-assurance determinations requested for inorganic constituents, nutrients and specific conductance reflect the frequency of requests for those determinations in the laboratory. The program goal is to have at least one quality-assurance sample analyzed daily for those constituents that are analyzed daily and, similarly, an appropriate number of quality-assurance samples for those constituents determined less frequently. Precipitation-level samples were submitted once each week beginning in June and organic substance samples were submitted once each week during September.

All constituents in the reference materials are in the dissolved phase. Those constituents in this report that are designated as "total recoverable" are from reference samples that have undergone a digestion process (Skougstad and others, 1979) during analysis, rather than from unfiltered or "whole-water" samples.

Quality-assurance samples pass through each laboratory as routine samples; this processing includes the application of laboratory quality-control and quality-assurance procedures. The data then are stored in the U.S. Geological Survey's National Water Data Storage and Retrieval System (WATSTORE). Having passed through the laboratories in this manner, data from these quality-assurance samples should reflect the quality of the analytical data that the laboratories produce for environmental samples. Laboratory errors other than those related to analytical chemistry also will be reflected in these data. These errors include any made in logging the sample into the laboratory, transcription errors by the analyst, and keypunching errors. No effort was

made to correct nonanalytical errors of this type, even when it was quite obvious which corrective measures were appropriate, so that the laboratories' data were preserved as they produced it. Thus, if a data user is capable of detecting errors of this type, he can increase the quality of his data, compared to those data presented in this report.

STATISTICAL EVALUATION

The SRWS initially are analyzed by many laboratories throughout the United States, using several different analytical methods. These results are compiled by calculating the means, standard deviations, and 95-percent confidence limits, and applying a rejection routine (American Society for Testing and Materials, 1980). Resultant means are the values most probably correct or the "most probable values" (MPV). These MPV are used in this quality-assurance program for comparison with laboratory data. For reference samples composed of a mixture of two SRWS or SRWS and deionized water, MPV for each constituent are weight-averaged according to their respective percentage contribution to determine a new set of MPV for the mixture.

Because of an insufficient supply of SRWS for nutrients and pesticides, most of the reference materials used during this period, for these sample categories, were made from reagent chemicals in the Ocala facility. Preparation methods used for these samples are virtually the same as those used for preparing samples for the SRWS Precipitation-level samples were either SRWS prepared at low level concentrations, or were regular SRWS which were diluted to precipitation level However, because of lack of stability data on these samples and no independent analyses of the majority of them, these samples were treated as split samples of unknown concentrations, and statistical tests were applied to determine whether or not significant differences existed between the performances of the two laboratories at the 95% confidence level. A second series of precipitation-level samples was submitted independently and in triplicate to each laboratory. An overall variance was estimated by calculating a pooled variance (Dixon and Massey, 1969) for Those constituents included in this series are the same as each constituent. previously defined except that fluoride and phosphorous were not included.

Initially, the appropriateness of using the mean of two specific-conductance values for an MPV in the case of mixed solution samples was questioned. However, because all SRWS have specific conductances less than 2,100 μ mhos/cm (micromhos per centimeter at 25° Celsius), it was believed that the departure from linearity would not be significant. A comparison of the means of the analyzed specific-conductance values and the MPV for all the mixtures is presented in Peart and Thomas, 1983a. Results of this evaluation indicated that the linearity hypothesis holds true except where the parent samples have widely divergent specific conductances, and no significant bias. We have not used any samples for evaluation purposes where the linearity hypothesis failed to hold true.

Standard deviations were determined by using linear least-squares equations developed by regressing the means of each constituent taken from all the SRWS for which we have data, against the corresponding standard deviations for those constituents. This method allowed an estimation of a most probable standard deviation (MPSD) for each constituent on a sample-by-sample basis to determine whether that determination was in or out of control. For barium, cadmium, cobalt, copper, iron, lead, manganese, molybdenum, and zinc, the means and standard deviations taken from the results of the interlaboratory, multimethod analyses were used. These constituents were being determined by more than one method in the two laboratories.

For all other constituents, the means and standard deviations that are specific to the analytical methods used in the two subject laboratories which are also taken from the same interlaboratory analyses were used. An individual reported value was considered acceptable if it was within two standard deviations of the MPV.

In certain situations, the above criterion was impossible to meet. This was true for cadmium, chromium, copper, lead, molybdenum, silver and zinc. An administrative decision was made to establish a minimum standard deviation for each constituent equal to three-quarters of the value of the reporting level to allow at least one reportable value on each side of the MPV to be accepted. For example, the minimum standard deviation for copper reported to the nearest $10 \mu g/L$ is set to $7.5 \mu g/L$; the minimum standard deviation for silver, reported to the nearest $1 \mu g/L$, is $0.75 \mu g/L$.

The number of standard deviations each constituent deviates from the MPV was calculated by dividing the difference of the reported value and the MPV by the MPSD. This number was used in determining precision and bias. The result for each laboratory and constituent is displayed in figures 1 through 90 in the Supplemental Data section at the back of this report. Three symbols are used on the figures to display results from the lower (+), middle (x), and upper (o) one-thirds of the potential analytical range tested in this program. This range does not necessarily correspond with the analytical capabilities of the laboratory instrumentation or methods, but rather with the analytical range we are capable of testing with the available SRWS or other reference samples used. The three parts of this range are based on the MPV of the quality-assurance samples and not the reporting policy; thus available resources may limit the maximum MPV for chromium to 28 μ g/L (figs. 27 and 28) and still allow a value to be reported to the nearest 10 μ g/L (that is, 30 μ g/L). Not all figures will have all three parts of the analytical range displayed because some flexibility is given to the Ocala, Florida office in sample selection. Points outside the range of the plots are forced to plot at the limit (±6), with the number of standard deviations indicated adjacent to the point.

Precision and bias are determined by applying binomial-distribution equations to the data according to procedures described by Friedman, Bradford, and Peart, 1983; and Peart and Thomas, 1983a. When precision is determined in this manner, it contains an element of bias as well, because MPV, rather than analyzed means, are used as the basis for determining the number of standard deviations each constituent deviates from that value. Thus, in this analysis, precision, or lack of it, is based on whether or not the analytical process was in or out of control. The figures represent control charts.

Calculation of means and relative standard deviations were made for this report. Because standard deviations may vary with concentration in chemical analyses, these calculations were done separately on individual sample mixtures; therefore, they do not give overall appraisals of the analytical processes. Relative standard deviations for major inorganic constituents were calculated and plotted against concentrations in figures 91 through 180 in the Supplemental Data section at the back of this report. These plots allow a data reviewer to estimate the error at any concentration displayed for all constituents.

To determine a measure of comparability between the two laboratories, the raw data were evaluated using a modification of the Wilcoxon Rank-Sum test (Mann-Whitney test) as described by Crawford, Slack and Hirsch, 1983. Each mixture was ranked separately, so that the actual concentration differences between mixtures did not affect

the outcome of the test. By using this method, the undesirable effects of outliers are eliminated, without eliminating the outliers themselves from the data under consideration.

RESULTS AND DISCUSSION

Initially, 1983 water-year data were presented statistically in four unpublished reports for the following periods: July 1 - December 31, 1982; January 1 - March 31, 1983; April 1 - June 30, 1983; July 1 - September 31, 1983. From the July through December (1982) unpublished report, only the October through December data will be discussed in this report. The linear least-squares equations used to calculate the MPSD changed for each of the periods because of the addition of data from newly developed SRWS. Data presented in this report were reanalyzed using the latest set of equations to provide uniform criteria throughout the year. Therefore, data presented in this report may not always correspond to data in the unpublished reports. Some tendencies (not statistically significant) toward lack of precision or bias during the quarterly periods may accumulate in the yearly summary to yield a significant indication of lack of precision or bias. Results of binomial-distribution tests for these four periods, as well as overall results for the year are shown in tables 1 through 4.

Precision

The results of statistical testing for lack of precision for each inorganic constituent are presented in tables 1 and 2. For each constituent, these tables indicate significant lack of precision (by LOP) as well as all acceptable results (by a plus).

Aluminum, silver and sodium (ICP) failed the precision criteria three out of four quarters in Atlanta. Copper failed the precision criteria three out of four quarters in Denver. Copper: dissolved solids; and iron, total recoverable failed the precision criteria two out of four quarters in Atlanta. Iron, total recoverable; silver; and zinc, total recoverable failed the precision criteria two out of four quarters in Denver. Iron, total recoverable and sodium (ICP) also had recurring LOP problems in Atlanta in water year 1982 (Peart and Thomas, 1983b). There were no constituents that had recurring LOP problems in Denver for water year 1982 and water year 1983.

For constituents that were determined as both "dissolved" and "total recoverable" on identical samples, the "total recoverable" determinations failed the precision criteria with approximately the same frequency as the dissolved determinations in both Atlanta and Denver. These results indicate significant improvement over the previous water year (Peart and Thomas, 1983b); during that time, the "total recoverable" determinations failed the precision test twice as often as the dissolved determinations in Atlanta, and five times as often as the dissolved determinations in Denver.

Sodium determined by ICP spectrometry in the Atlanta laboratory failed the precision criteria three out of four quarters. This constituent consistently showed lack of precision for water year 1982, (Peart and Thomas, 1983b) also. In general, however, the major ions being determined by ICP in Atlanta show an overall improvement for water year 1983 over the previous year, because calcium and magnesium also showed fairly consistent lack of precision previously (Peart and Thomas, 1983b) and have not done so at any time during this year.

Table 1.--Results of statistical testing for lack of precision in data from the Atlanta Laboratory: inorganic constituents and specific conductance

[LOP, significant lack of precision; ICP, inductively coupled plasma spectrometry; AA, atomic absorption spectrometry; +, acceptable results]

Constituent (dissolved except	OctDec.	lan -Mar	AprJune	July-Sen	Summary OctSep.
as indicated	1982	1983	1983	1983	1982 1983
Alkalinity	+	+	+	+	+
Aluminum	LOP	LOP	LOP	+	LOP
Antimony	+	+	+	+	LOP
Arsenic	LOP	+	+	+	+
Barium	LOP	+	+	+	+
Barium, total recoverable	+	+	+	+	+
Beryllium	+	+	+	+	LOP
Boron	+	+	+	+	+
Cadmium	+	+	+	+	+
Cadmium, total recoverable	+	+	+	+	+
Calcium(ICP)	+	+	+	+	+
Calcium (AA)	+	+	+	+	+
Chloride	LOP	+	+	+	LOP
Chromium	+	+	+	+	+
Chromium, total recoverable	+	+	+	+	+
Cobalt	+	+	+	+	+
Cobalt, total recoverable	+	+	LOP	+	+
Copper	+	LOP	LOP	+	LOP
Copper, total recoverable	+	+	+	+	+
Dissolved solids	+	+	LOP	LOP	LOP
Fluoride	+	+	+	+	LOP
Iron	+	+	+	+	+
Iron, total recoverable	+	LOP	+	LOP	LÓP
Lead	+	+	+	4	+
Lead, total recoverable	+	+	+	+	+
Lithium	+	+	+	+	+
Magnesium (ICP)	+	+	+	+	+
Magnesium (AA)	+	+	+	+	+

Table 1.--Results of statistical testing for lack of precision in data from the Atlanta Laboratory: inorganic constituents and specific conductance--Continued

Constituent (dissolved except as indicated)	OctDec. 1982	JanMar. 1983	Apr. –June 1983	July-Sep. 1983	Summary OctSep. 1982 1983
Manganese	+	+	+	+	+
Manganese, total recoverable	+	+	+	+	+
Molybdenum	+	+	+	+	+
Nickel	+	LOP	+	+	+
Nickel, total recoverable	+	+	+	+	+
Potassium	+	+	+	+	+
Selenium	+	+	+	+	+
Silica	+	+	+	+	+
Silver	LOP	+	LOP	LOP	LOP
Silver, total recoverable	LOP	+	+	+	LOP
Sodium(ICP)	LOP	LOP	LOP	+	LOP
Sodium(AA)	+	+	+	+	+
Specific conductance	+	+	+	+	+
Strontium	+	+	+	+	+
Sulfate	+	+	+	+	+
Zinc	+	+	+	+	+
Zinc, total recoverable	+	+	+	+	+

<u>Bias</u>

Results of the statistical tests for bias are shown in tables 3 and 4. Using the method described previously, it is not possible to determine bias where results from less than eight samples were available. This sitution occurred from July through September for a few constituents in Atlanta as noted in the tables, and for antimony at both laboratories throughout the year.

Potassium has shown a negative bias three out of four quarters, while alkalinity and specific conductance have shown a positive bias three out of four quarters throughout the year in the Atlanta Laboratory. Nickel showed a negative bias for two of four quarters and manganese and sodium(ICP) showed positive bias for two of four quarters in Atlanta. Nickel and potassium both had similar recurring biased results for water year 1982 (Peart and Thomas, 1983b). In Denver, dissolved sollds and potassium have been consistently negatively biased; alkalinity, fluoride, iron, sulfate and zinc have been consistently positively biased.

No predominant patterns appear regarding bias for ICP analyses versus AA analyses or dissolved versus total recoverable analyses. Barium and boron showed a negative bias three out of four quarters and specific conductance showed a positive bias

Table 2.--Results of statistical testing for lack of precision in data from the Denver Laboratory: inorganic constituents and specific conductance

[LOP, significant lack of precision; ICP, inductively coupled plasma spectrometry; AA, atomic absorption spectrometry; +, acceptable results]

Constituent					Summary
(dissolved except as indicated)	OctDec. 1982	JanMar. 1983	AprJun. 1983	July-Sep. 1983	OctSep. 1982 1983
Alkalinity	LOP	+	+	+	+
Aluminum	+	+	+	+	+
Antimony	+	+	+	+	+
Arsenic	+	+	+	+	+
Barium	LOP	+	+	+	LOP
Barium, total recoverable	LOP	+	+	+	LOP
Beryllium	+	+	+	+	+
Boron	+	+	+	+	+
Cadmium	+	+	+	+	+
Cadmium, total recoverable	+	+	+	+	+
Calcium(ICP)	+	+	+	+	+
Calcium(AA)	+	+	+	+	+
Chloride	+	+	+	+	+
Chromium	+	+	+	+	+
Chromium, total recoverable	+	+	+	+	+
Cobalt	+	+	+	+	+
Cobalt, total recoverable	+	+	+	+	+
Copper	LOP	LOP	LOP	+	LOP
Copper, total recoverable	+	LOP	+	+	LOP
Dissolved solids	+	+	+	+	+
Fluoride	+	+	+	+	+
Iron	+	+	+	+	+
iron, total recoverable	LOP	+	LOP	+	LOP
Lead	+	+	+	+	+
Lead, total recoverable	+	+	+	+	+
Lithium	+	+	+	+	+
Magnesium(ICP)	+	+	+	+	+
Magnesium (AA)	+	+	+	+	+

Table 2.--Results of statistical testing for lack of precision in data from the Denver Laboratory: inorganic constituents and specific conductance--Continued

Constituent (dissolved except		JanMar.	•		Summary Oct. –Sep.
as indicated)	1982	1983	1983	1983 	1982 1983
Manganese	+	+	+	+	+
Manganese, total recoverable	+	+	+	+	+
Molybdenum	+	+	+	+	+
Nickel	+	+	+	+	+
Nickel, total recoverable	+	+	+	+	+
Potassium	+	+	+	+	+
Selenium	+	+	+	+	+
Silica	+	+	+	+	+
Silver	LOP	+	LOP	+	+
Silver, total recoverable	+	+	+	+	+
Sodium (ICP)	+	+	+	+	+
Sodium(AA)	+	+	+	+	+
Specific conductance	+	LOP	+	+	LOP
Strontium	+	+	+	+	+
Sulfate	+	+	+	+	+
Zinc	+	+	+	+	+
Zinc, total recoverable	+	+	LOP	LOP	LOP

with the same frequency in Denver. Cobalt, molybdenum and silver were negatively biased two of four quarters and selenium and sodium(ICP) were positively bias for two of four quarters in the Denver laboratory. Barlum, cobalt, dissolved solids, fluoride, molybdenum, selenium, silver, sodium(ICP), specific conductance, sulfate and zinc all also had recurring biased results for water year 1982 in Denver (Peart and Thomas, 1983b).

Because the Denver laboratory has many more constituents with persistent bias than the Atlanta laboratory, it seems unlikely that the problems are related to bias that may be inherent in the methods used for determination of these constituents, except where that bias is persistent in both laboratories. Given the recurrence data presented in the previous paragraph, there are no constituents for which that condition exists; that is, no constituent has failed the bias test consistently even on a recurring basis for the past two years, in both laboratories. This would indicate that the laboratories would do well to begin a standards exchange program or other measures to try to identify their sources of disagreement and improve their comparability.

Table 3.--Results of statistical testing for bias in data from the Atlanta Laboratory: inorganic constituents and specific conductance

[N, negative; P, positive; ICP, inductively coupled plasma spectrometry; AA, atomic absorption spectrometry; +, acceptable results; *, too few analyses to determine]

Constituent (dissolved except	OctDec.	lan -Mar	AprJune	luly-Soo	Summary OctSep.
as indicated)	1982	1983	1983	1983	1982 1983
Alkalinity	Р	Р	+	ρ	Р
Aluminum	+	+	Р	+	P
Antimony	*	*	*	*	+
Arsenic	+	+	P	+	P
Barium	+	+	+	+	+
Barium, total recoverable	+	+	+	*	P
Beryllium	+	+	+	+	+
Boron	N	+	+	+	N
Cadmium	+	+	+	+	+
Cadmium, total recoverable	+	+	+	*	+
Calcium(ICP)	+	+	+	+	+
Calcium(AA)	+	+	+	+	N
Chloride	+	+	+	+	+
Chromium	+	+	+	+	+
Chromium, total recoverable	Р	+	+	*	+
Cobalt	+	+	+	+	+
Cobalt, total recoverable	+	+	+	*	Р
Copper	+	Ρ	+	+	P
Copper, total recoverable	+	+	+	*	+
Dissolved solids	+	+	+	+	+
Fluoride	+	+	+	P	+
Iron	+	+	+	+	+
Iron, total recoverable	+	+	+	*	Р
Lead	+	P	+	+	+
Lead, total recoverable	+	+	+	*	+
Lithium	+	+	+	+	+
Magnesium (ICP)	+	+	+	+	+
Magnesium (AA)	+	+	+	+	+

Table 3.--Results of statistical testing for bias in data from the Atlanta Laboratory: inorganic constituents and specific conductance--Continued

Constituent (dissolved except as indicated)	Oct Dec. 1982	Jan. – Mar. 1983	Apr. –June 1983	July-Sep. 1983	Summary OctSep. 1982 1983
					andre division description of the section of the se
Manganese	+	+	Р	Р	Р
Manganese, total recoverable	+	+	+	*	+ .
Molybdenum	+	+	+	N	N
Nickel	+	+	N	N	N
Nickel, total recoverable	+	+	+	*	+
Potassium	N	+	N	N	N
Selenium	P	+	+	+	P
Silica	+	+	Р	+	+
Silver	+	+	+	+	N
Silver, total recoverable	+	+	+	*	N
Sodium(ICP)	P	P	+	+	Р
Sodium (AA)	+	+	+	+	+
Specific conductance	Р	+	P	P	P
Strontium	+	+	+	+	Р
Sulfate	+	+	+	+	+
Zinc	+	+	+	P	+
Zinc, total recoverable	+	+	Р	*	Р

Several factors may be involved where other constituents show occasional bias, including deterioration of standard calibrating solutions or reagents, improper or inaccurate reagent or standard-solution preparation, undetected problems with analytical instrumentation, undefined matrix effects caused by mixing together two very different SRWS, or undetected contamination. Where bias is statistically significant but precision is good, the bias may have little effect on data interpretation and little practical significance.

COMPARABILITY BETWEEN LABORATORIES

The following constituents showed statistically significant differences at the 5 percent level with respect to the results of the modified Wilcoxon Rank-Sum test (Mann-Whitney test):

Alkalinity; aluminum; barlum; barlum, total recoverable; beryllium; cadmium, total recoverable; chloride; chromium, total recoverable; cobalt; cobalt, total recoverable; dissolved solids; iron; lead, total recoverable; magnesium(ICP); manganese; nickel; potassium; strontium; sulfate; and zinc.

Table 4.--Results of statistical testing for bias in data from the Denver Laboratory: inorganic constituents and specific conductance

[N, negative; P, positive; ICP, inductively coupled plasma spectrometry; AA, atomic absorption spectrometry; +, acceptable results; *, too few analyses to determine]

Constituent (dissolved except as indicated)	Oct Dec. 1982	Jan. – Mar. 1983	Apr. –June 1983	July-Sep. 1983	Summary OctSep. 1982 1983
Alkalinity	Р	P	P	Р	P
Aluminum	P	+	+	N	+
Antimony	+	*	*	*	+
Arsenic	+	+	+	+	+
Barium	N	N	N	+	N
Barium, total recoverable	N	+	+	+	+
Beryllium	+	+	+	+	+
Boron	N	N	+	N	N
Cadmium	+	+	+	+	+
Cadmium, total recoverable	+	+	+	+	+
Calcium(ICP)	+	+	+	+	+
Calcium(AA)	+	+	+	+	+
Chloride	+	+	+	P	P
Chromium	P	+	+	+	+
Chromium, total recoverable	+	+	+	+	+
Cobalt	N	+	+	N	N
Cobalt, total recoverable	+	+	N	+	N
Copper	P	+	+	+	P
Copper, total recoverable	P	+	+	+	+
Dissolved solids	N	N	N	N	N
Fluoride	P	P	P	P	P
Iron	P	P	P	P	P
Iron, total recoverable	+	+	Р	+	Р
Lead	+	P	+	+	+
Lead, total recoverable	+	+	Р	+	P
Lithium	+	+	+	N	+
Magnesium (ICP)	+	+	+	+	P
Magnesium (AA)	+	P	+	+	P

Table 4.--Results of statistical testing for bias in data from the Denver Laboratory: inorganic constituents and specific conductance--Continued

Constituent (dissolved except	OctDec	Jan -Mar	AprJune	July-Sep.	Summary OctSep.
as indicated)	1982	1983	1983	1983	1982 1983
Manganese	+	+	+	N	+
Manganese, total recoverable	Р	+	+	+	+
Molybdenum	+	N	+	N	N
Nickel	+	+	+	+	N
Nickel, total recoverable	+	+	+	+	+
Potassium	N	N	N	N	N
Selenium	Р	+	Р	+	Р
Silica	+	+	+	N	+
Silver	N	+	N	+	N
Silver, total recoverable	+	+	+	+	N
Sodium(ICP)	+	Р	+	P	Р
Sodium (AA)	+	+	+	+	+
Specific conductance	P	Р	Р	+	Р
Strontium	+	+	+	+	+
Sulfate	Р	Р	P	P	Р
Zinc	P	Р	Р	P	Р
Zinc, total recoverable	+	+	+	Р	Р

This constitutes 43 percent of the major inorganic constituents (as defined in the introduction) determined in both laboratories with measurable differences such that the data cannot be considered comparable.

As explained previously, the nutrients were treated as split samples of unknown concentrations. The yearly summaries in tables 5 and 6 show that both laboratories are performing similarly on all nutrient constituents except ammonia plus organic nitrogen, in which the means and the standard deviations are significantly different.

Data for precipitation level samples are summarized in table 7 and 8. There is no significant difference in the mean values produced by the two laboratories for any constituents in this category except phosphorus where a significant difference in the means is shown in table 7. The pooled variances in table 8 indicate that calcium, potassium and nitrate have comparable variances while the remaining constituents differ by an approximate factor of two. By combining the data in tables 7 and 8, one can conclude that the laboratories are performing similarly on calcium, potassium, nitrate and perhaps fluoride, but because fluoride was not included in the determinations for

Table 5.—Results of statistical evaluation for comparison of means on nutrient samples.

[A, no significant difference; B, significant difference]

Constituent					Summary
	OctDec. 1982	JanMar. 1983	AprJune 1983	July-Sep. 1983	OctSep. 1982-1983
Ammonia	A	Α	Α	Α	Α
Ammonia plus organic nitrogen	В	В	В	Α	В
Carbon, organic	Α	Α	Α	Α	Α
Nitrite plus nitrate	Α	Α	Α	Α	Α
Nitrite	Α	Α	Α	Α	Α
Phosphorus	Α	Α	Α	Α	Α
Phosphorus, ortho	Α	Α	Α	Α	Α

Table 6. -- Results of statistical evaluation for comparison of standard deviations on nutrient samples.

[A, no significant difference; B, significant difference]

Constituent					Summary
	OctDec. 1982	Jan. – Mar. 1983	AprJun. 1983	July-Sep. 1983	OctSep. 1982-1983
Ammonia	Α	В	В	Α	Α
Ammonia plus organic nitrogen	В	Α	В	Α	В
Carbon, organic	Α	В	Α	Α	Α
Nitrite plus nitrate	В	Α	Α	В	Α
Nitrite	Α	Α	Α	В	Α
Phosphorus	Α	Α	Α	Α	Α
Phosphorus, ortho	Α	Α	Α	Α	Α

Table 7.--Results of statistical evaluation for precipitation level analyses for June through September 1983
[A, no significant difference; B, significant difference]

Constituent	Comparison of means
 Calcium	Α
Chloride	Α
Fluoride	Α
Magnesium	Α
Nitrate,	Α
Phosphorus	В
Potassium	Α
Sodium	Α
Specific conductance	Α
Sulfate	Α

Table 8.—Pooled variances for replicate precipitation level samples analyzed between November 1982 and September 1983.
[One replicate set is three individual analyses]

	Atla	<u>inta</u>	De	nver
Constituent (Dissolved)	No. of replicate sets	Pooled variance (mg/L)	No. of replicate sets	Pooled variance (mg/L)
Calcium	20	0. 087	23	0.075
Magnesium	22	0.027	23	0.054
Potassium	22	0.051	24	0.053
Specific Conductance	21	2.15	19	1.03
Sodium	22	0.045	25	0.098
Chloride	22	0.049	23	0.089
Sulfate	23	0.132	22	0.58
Nitrate-nitrogen	11	0.028	12	0.033

pooled variance, it cannot be stated explicitly that fluoride is, in fact, comparable. The pesticide data in table 9 shows that all constituents compare well between the laboratories.

A study comparing the results from two instruments used in Atlanta and one used in Denver for the determination of volatile organic compounds was conducted during June. The laboratories performed the analyses simultaneously on samples that were prepared in Denver shortly before the study began. A summary of recovery and precision data is presented in table 10. This data shows that the Finnigan 4023 in Denver and the Hewlett Packard 5922 in Atlanta produce similar results but the Finnigan 3200 in Atlanta produced results that were significantly different. In this study, it was not possible to distinguish between instrumental differences and single operator errors because each instrument was operated by a different individual.

Table 9.--Results of statistical evaluation for pesticide samples for September 1983
[A, no significant difference]

constituent	Comparison of means
2, 4-D	Α
2, 4-DP	Α
2, 4 5-T	Α
Aldrin	Α
DDD	Α
DDE	Α
DDT	Α
Diazinon	Α
Dieldrin	Α
Endrin	Α
Ethion	Α
Heptachlor epoxide	A
Heptachlor	Α
Lindane	Α
Malathion	Α
Methoxychlor	Α
Methylpharathion	Α
Mirex	Α
Parathion	Α
Silvex	Α

SUMMARY AND CONCLUSIONS

Reference samples with known MPV are disguised as regular samples and submitted with real samples by selected offices of the U.S. Geological Survey to the two water-quality laboratories operated by the Survey and located in Atlanta, Georgia and Denver, Colorado. The data generated are stored in the U.S. Geological Survey's National Water Data Storage and Retrieval System (WATSTORE). These data are then statistically analyzed for precision and bias, using a binomial-probability-distribution equation, and for comparability using a modified Wilcoxon Rank-Sum test (Mann-Whitney test).

Recurring problems during the year with lack of precision existed in Atlanta for aluminum; copper; dissolved solids; iron, total recoverable; silver; and sodium(ICP); and in Denver for copper; iron, total recoverable; silver; and zinc, total recoverable. Iron, total recoverable and sodium(ICP) have also exhibited recurring problems with lack of precision for water year 1982 in Atlanta. There were no constituents in the Denver laboratory that had recurring problems in this area for both water years 1982 and 1983.

An overall evaluation of the data for the year, shows a lack of precision in Atlanta for aluminum; antimony; beryllium; chloride; copper; dissolved solids; fluoride; iron, total recoverable; silver; silver, total recoverable; and sodium(ICP); and in Denver for

Table 10. Summary of recovery and precision data from three different instruments for volatile organics. [\mu g/L, micrograms per liter]

		Þ	Average recovery (percent)	overy	Relativ	Relative standard (deviation
Compound	Amount added (µg/L)	(Denver) Finnigan 4023	(Atlanta) Finnigan 3200	(Atlanta) Hewlett Packard 5992	(Denver) Finnigan 4023	(Atlanta) Finnigan 3200	(Atlanta) Hewlett Packard 5992
Bromoform	12	58	<15	90	თ	1	
•	ග ්	47	<17	123	4		1 6
	16	69	51	85	0	10	1
Chlorobenzene	œ	79	66	89	7	တ	10
	16	92	68	77	œ	12	თ
Dichlorobromomethane	10	83	31	85	ဖ	62	23
	6	65	< 28	88	ω		26
	10	99	72	92	N	14	!
Ethylbenzene	4	48	42	\$ 80	တ	1	1
	20	92	68	78	ဒ	15	5.
	14	95	63	79	4	18	
1, 1, 2, 2-Tetrachloroethane	01	76	42	93	7	36	01
	40	92	90	78	N	33	10,
	20	84	60	77	ω	œ	! !

¹ Relative standard deviation not calculated because reported values included "less than" figures

or because only two results were reported.

¹⁸

barium; barium, total recoverable; copper; copper, total recoverable; iron, total recoverable; specific conductance; and zinc, total recoverable.

Significant bias recurred during the year in Atlanta for alkalinity, manganese, nickel, potassium, sodium(ICP), and specific conductance; and in Denver for alkalinity, barium, boron, cobalt, dissolved solids, fluoride, iron, molybdenum, potassium, selenium, silver, sodium(ICP), specific conductance, sulfate, and zinc. Nickel and potassium both also had similar recurring bias for water year 1982 in the Atlanta laboratory. Barium, cobalt, dissolved solids, fluoride, molybdenum, selenium, silver, sodium(ICP), specific conductance, and zinc also had recurring bias for water year 1982 in Denver. There were no constituents for which recurring bias existed for the past two water years in both laboratories. This would indicate that the bias problems are laboratory dependent rather than method dependent.

An overall evaluation of the data for the year shows a significant bias in Atlanta for alkalinity; aluminum; arsenic; barium, total recoverable; boron; calcium(AA); cobalt, total recoverable; copper; iron, total recoverable; manganese; molybdenum; nickel; potassium; selenium; silver; silver, total recoverable; sodium(ICP); specific conductance; strontium; and zinc, total recoverable. The yearly evaluation of Denver data shows a significant bias for alkalinity; barium; boron; chloride; cobalt; cobalt, total recoverable; lead, total recoverable; magnesium(ICP); magnesium(AA); molybdenum; nickel; potassium; selenium; silver; silver, total recoverable; sodium(ICP); specific conductance; sulfate; zinc; and zinc, total recoverable.

A modified Wilcoxon Rank-Sum test (Mann-Whitney test) was applied to the inorganic constituent data to test for comparability between the two laboratories. Forty-three percent of the constituents determined in both laboratories showed measurable differences such that the data cannot be considered comparable.

Both laboratories are performing similarly on all nutrient constituents except ammonia plus organic nitrogen, in which the means and the standard deviations are significantly different.

Both laboratories are performing comparably on precipitation-level analyses except for phosphorus, where a significant difference in the means is shown, and chloride, magnesium, specific conductance, sodium and sulfate, where a significant difference in the variance is shown.

Both laboratories performed comparably on organic substances during September which was the only month when comparisons were done for this period.

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SUPPLEMENTAL DATA

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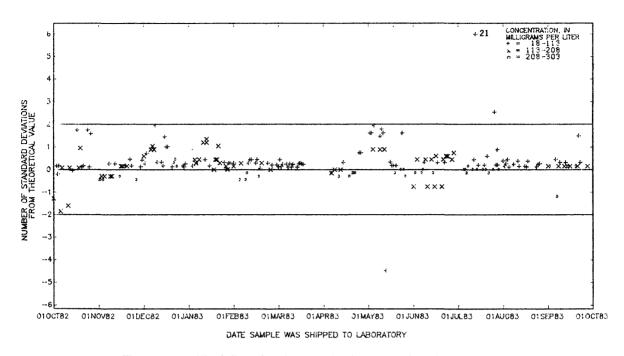


Figure 1. -- Alkalinity, dissolved, data from the Atlanta laboratory.

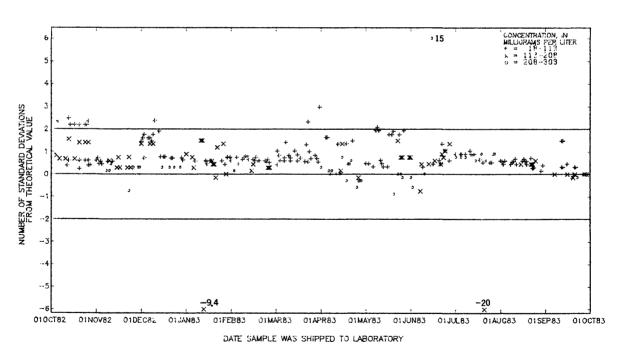


Figure 2. -- Alkalinity, dissolved, data from the Denver laboratory.

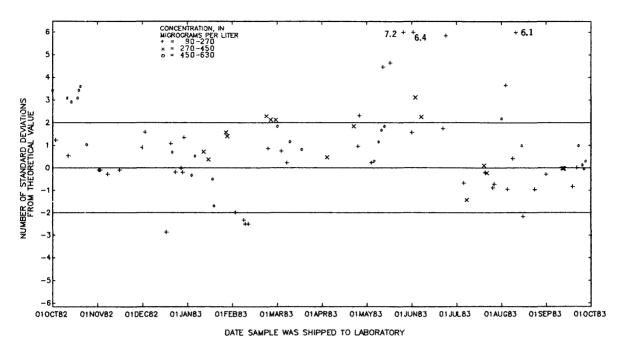


Figure 3.—Aluminum, dissolved, data from the Atlanta laboratory.

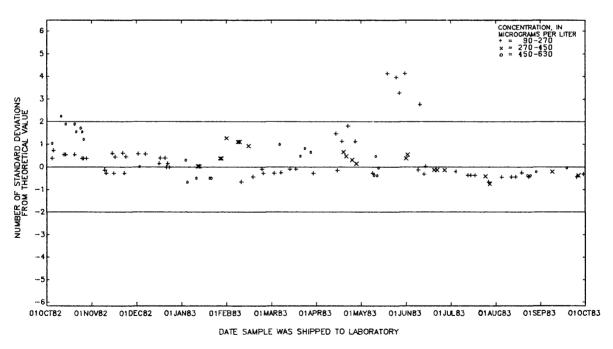


Figure 4.—Aluminum, dissolved, data from the Denver laboratory.

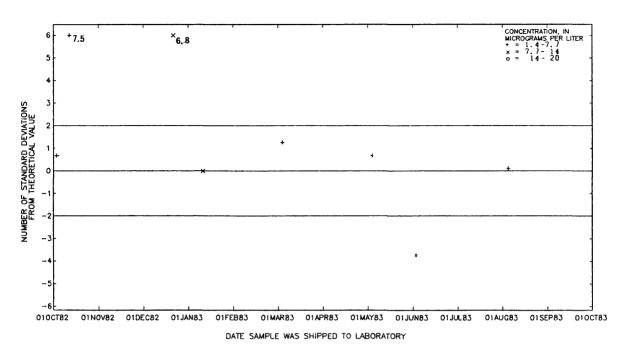


Figure 5. -- Antimony, dissolved, data from the Atlanta laboratory.

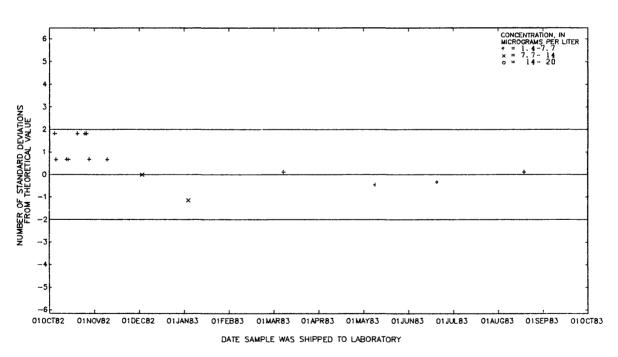


Figure 6.—Antimony, dissolved, data from the Denver laboratory.

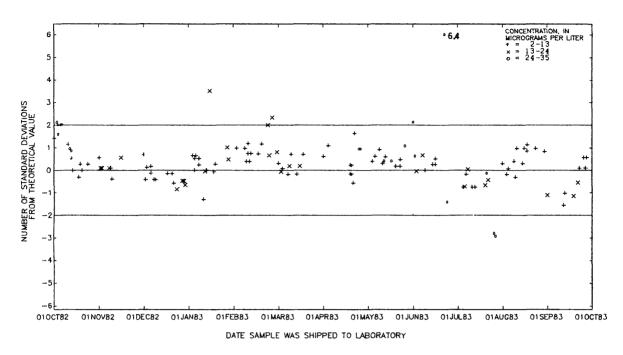


Figure 7.—Arsenic, dissolved, data from the Atlanta laboratory.

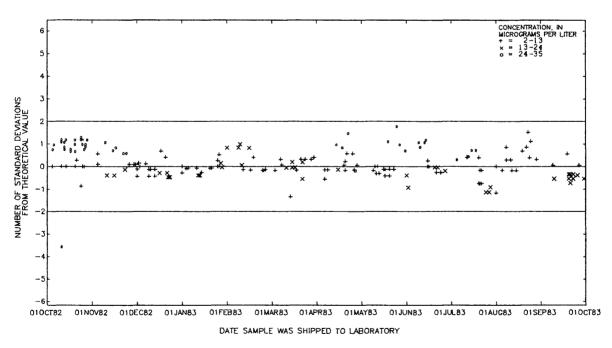


Figure 8.——Arsenic, dissolved, data from the Denver laboratory.

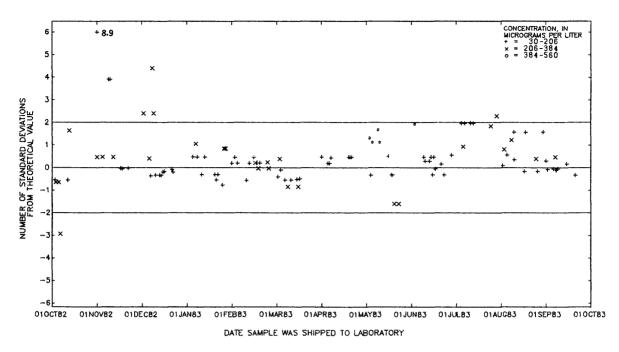


Figure 9.—Barium, dissolved, data from the Atlanta laboratory.

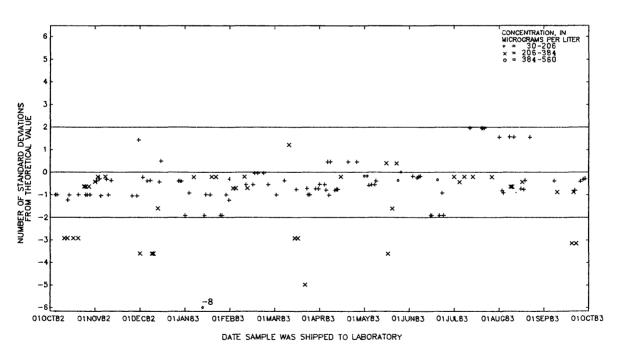


Figure 10.—Barium, dissolved, data from the Denver laboratory.

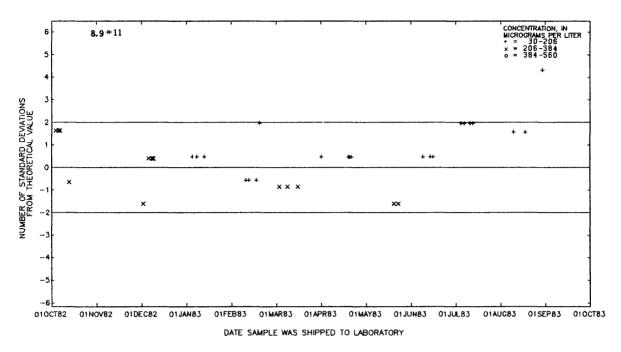


Figure 11.—Barium, total recoverable, data from the Atlanta laboratory.

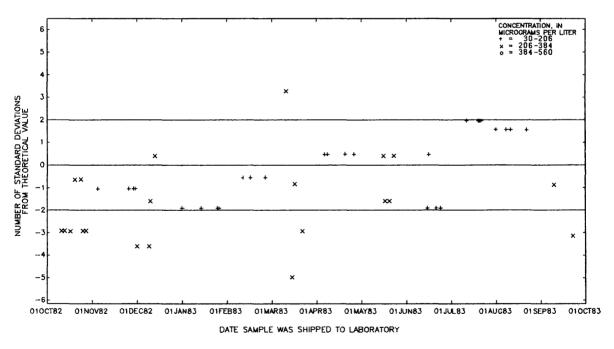


Figure 12.—Barium, total recoverable, data from the Denver laboratory.

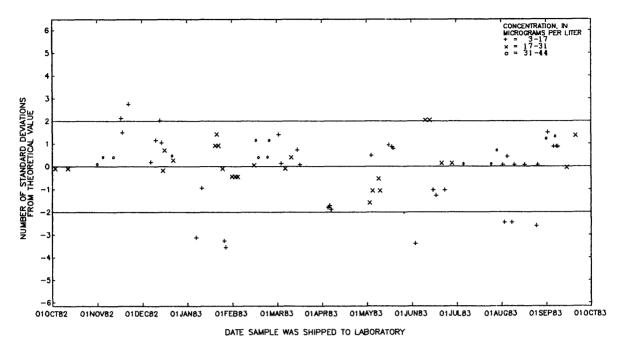


Figure 13.——Beryllium, dissolved, data from the Atlanta laboratory.

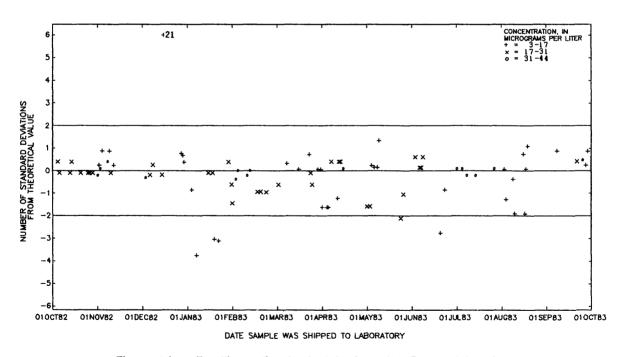


Figure 14.—Beryllium, dissolved, data from the Denver laboratory.

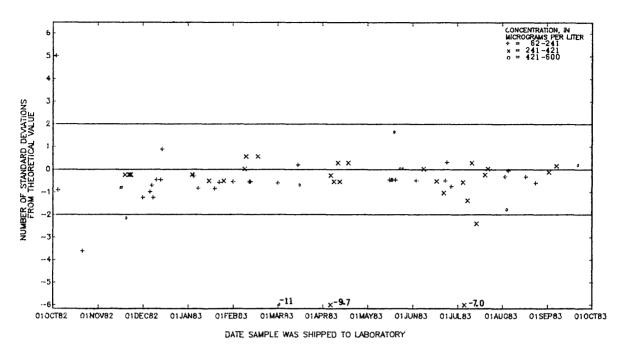


Figure 15.—Boron, dissolved, data from the Atlanta laboratory.

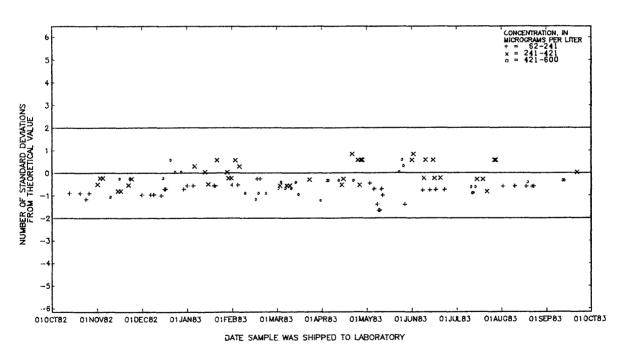


Figure 16. --Boron, dissolved, data from the Denver laboratory.

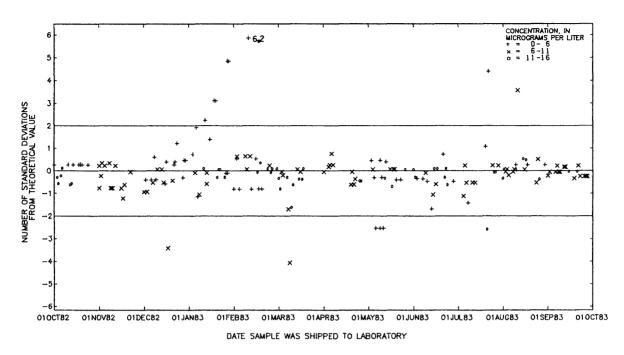


Figure 17.—Cadmium, dissolved, data from the Atlanta laboratory.

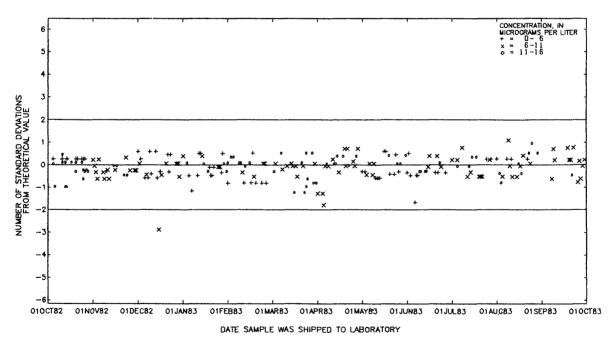


Figure 18.——Cadmium, dissolved, data from the Denver laboratory.

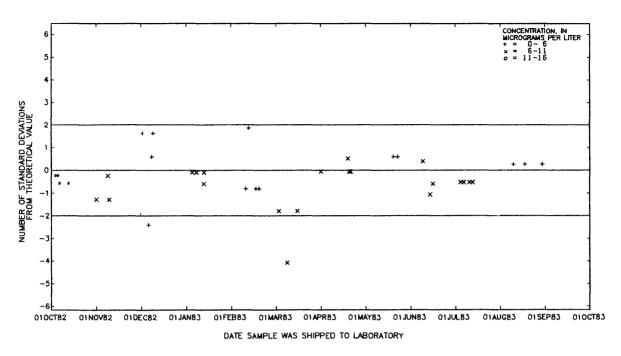


Figure 19.——Cadmium, total recoverable, data from the Atlanta laboratory.

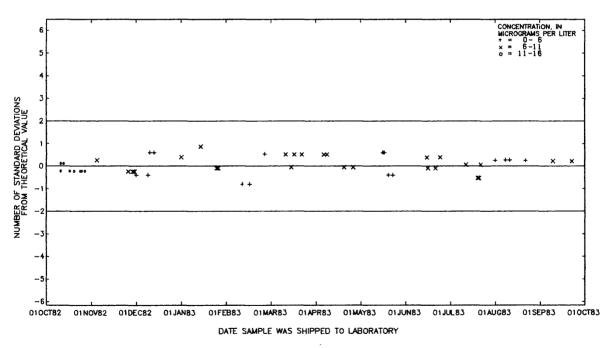


Figure 20.—Cadmium, total recoverable, data from the Denver laboratory.

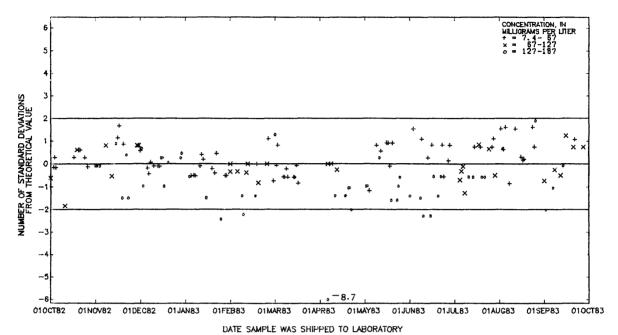
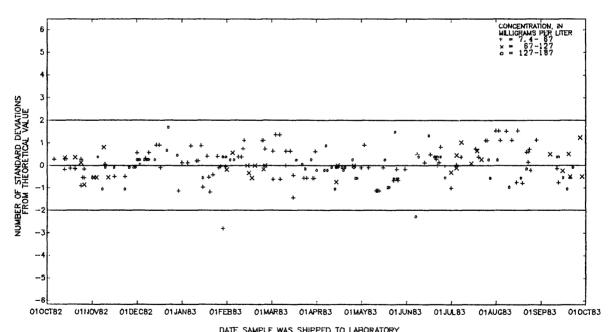


Figure 21.—Calcium, dissolved (inductively coupled plasma emission spectrometry), data from the Atlanta laboratory.



DATE SAMPLE WAS SHIPPED TO LABORATORY
Figure 22.—Calcium, dissolved (inductively coupled plasma emission spectrometry), data from the Denver laboratory.

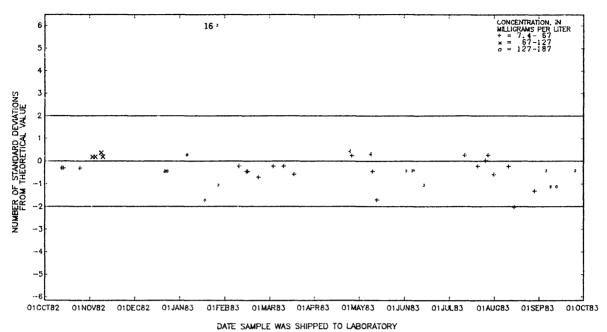


Figure 23.—Calcium, dissolved (atomic absorption spectrometry), aata from the Atlanta laboratory.

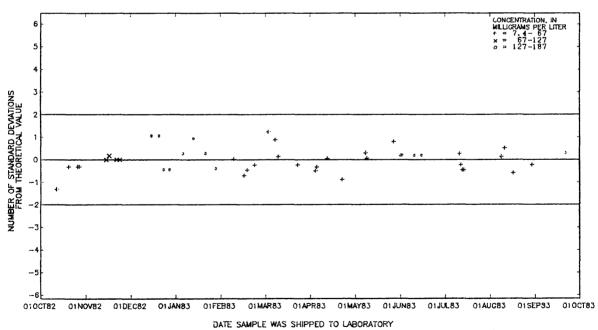


Figure 24.—Calcium, dissolved (atomic absorption spectrometry), data from the Denver laboratory.

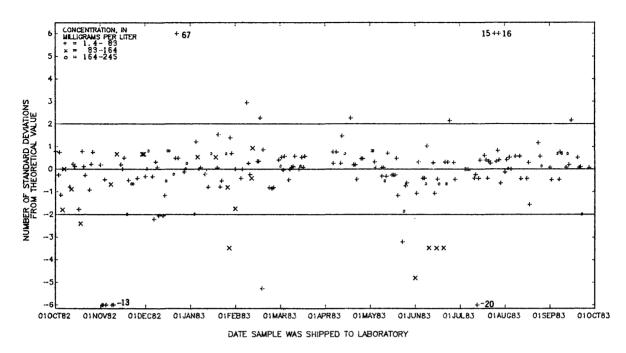


Figure 25.——Chloride, dissolved, data from the Atlanta laboratory.

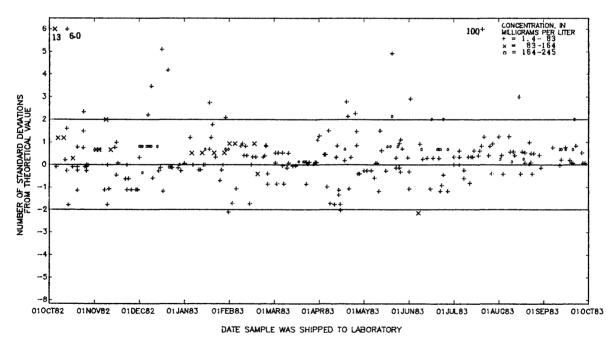


Figure 26.——Chloride, dissolved, data from the Denver laboratory.

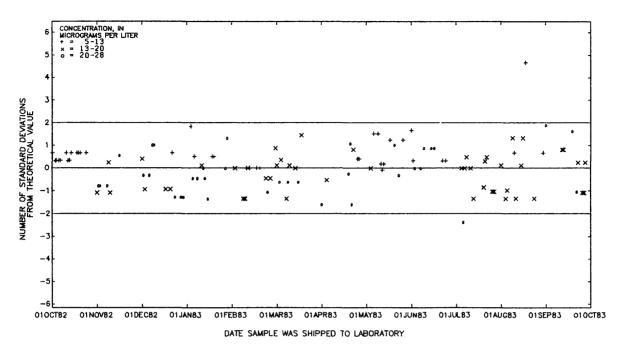


Figure 27.—Chromium, dissolved, data from the Atlanta laboratory.

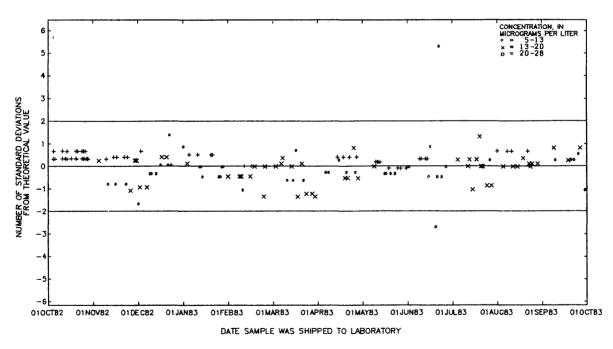


Figure 28.——Chromium, dissolved, data from the Denver laboratory.

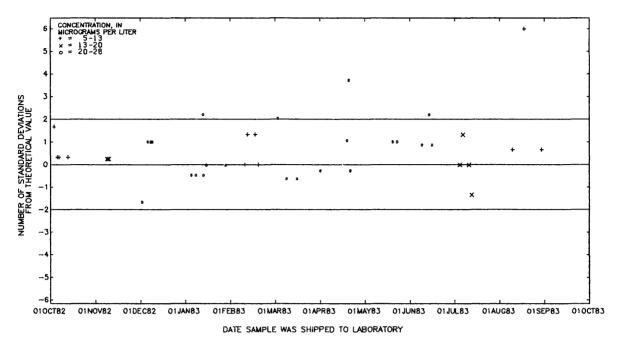


Figure 29.—Chromium, total recoverable, data from the Atlanta laboratory.

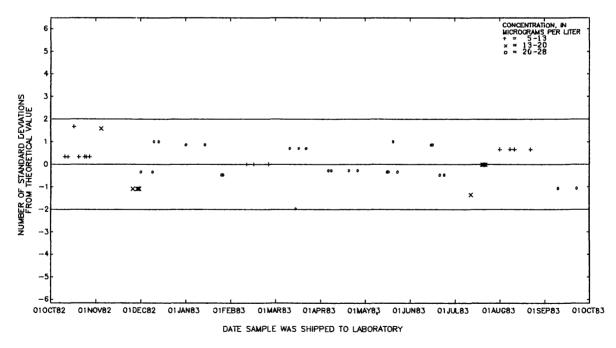


Figure 30.——Chromium, total recoverable, data from the Denver laboratory.

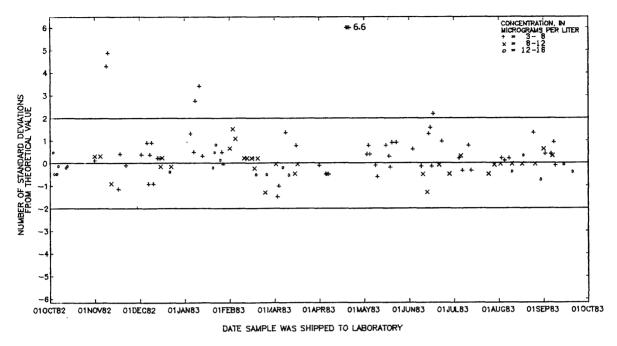


Figure 31.—Cobalt, dissolved, data from the Atlanta laboratory.

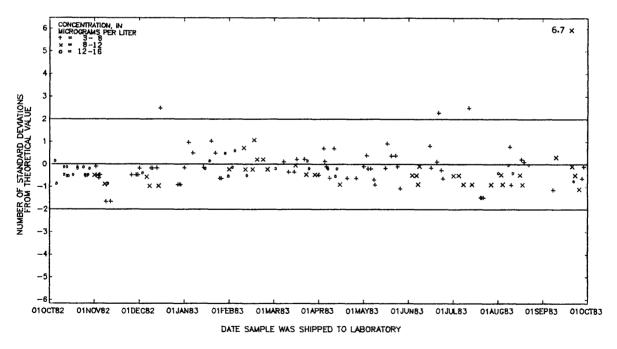


Figure 32.—Cobalt, dissolved, data from the Denver laboratory.

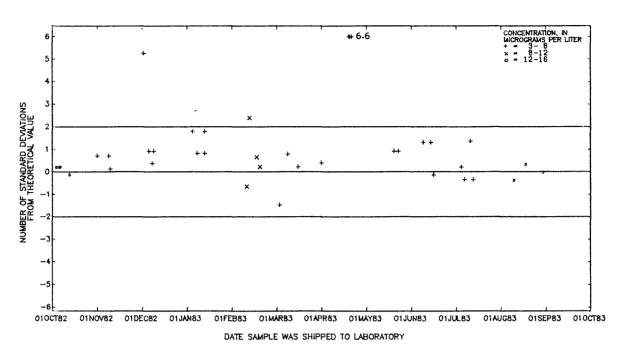


Figure 33.——Cobalt, total recoverable, data from the Atlanta laboratory.

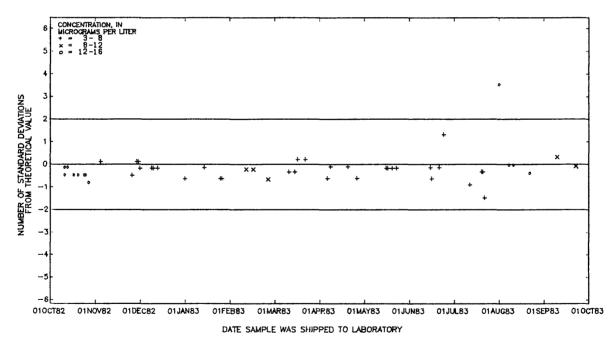


Figure 34.—Cobalt, total recoverable, data from the Denver laboratory.

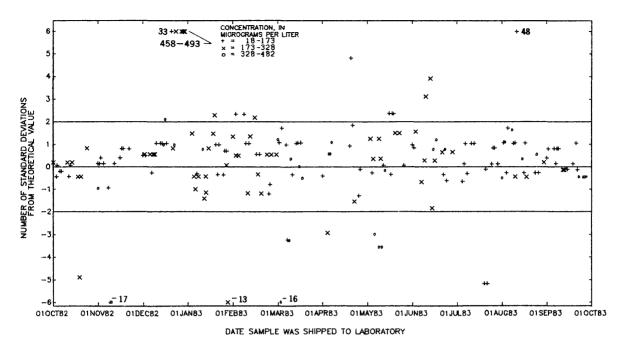


Figure 35.—Copper, dissolved, data from the Atlanta laboratory.

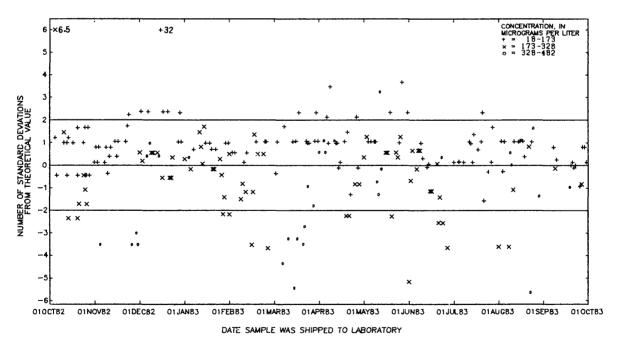


Figure 36.—Copper, dissolved, data from the Denver laboratory.

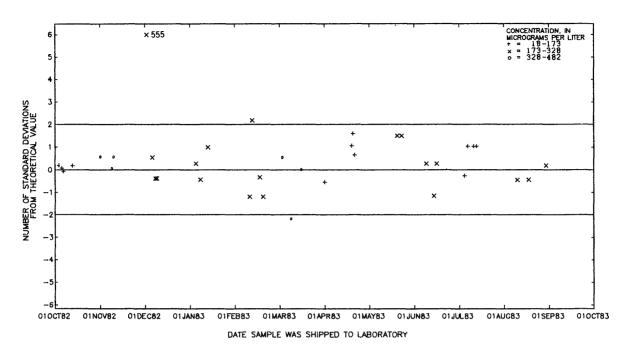


Figure 37.—Copper, total recoverable, data from the Atlanta laboratory.

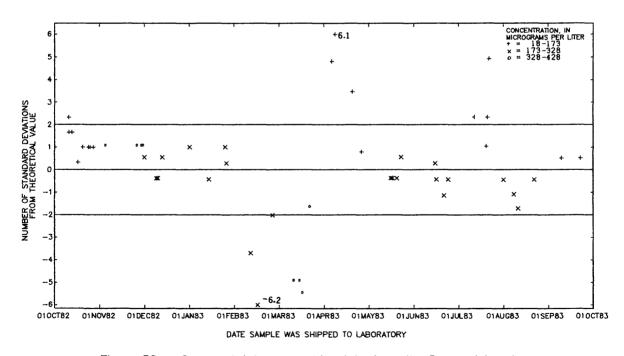


Figure 38.——Copper, total recoverable, data from the Denver laboratory.

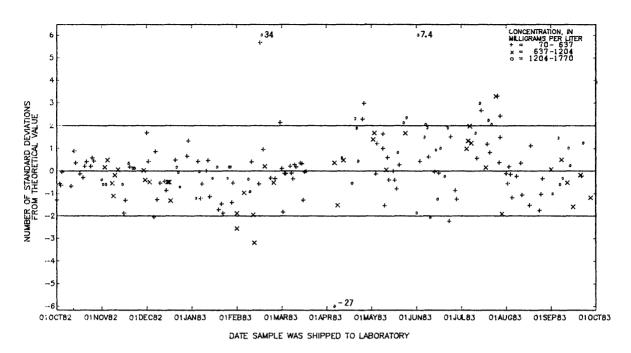


Figure 39.—Dissolved Solids, data from the Atlanta laboratory.

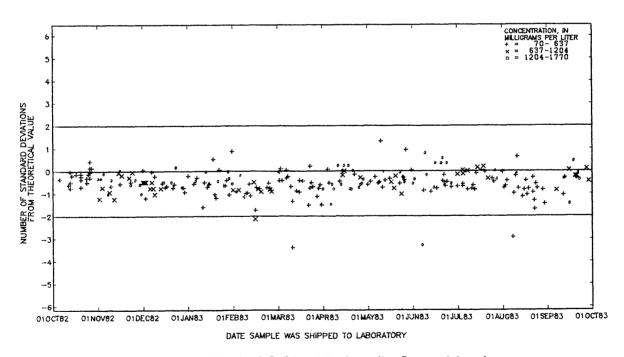


Figure 40.——Dissolved Solids, data from the Denver laboratory.

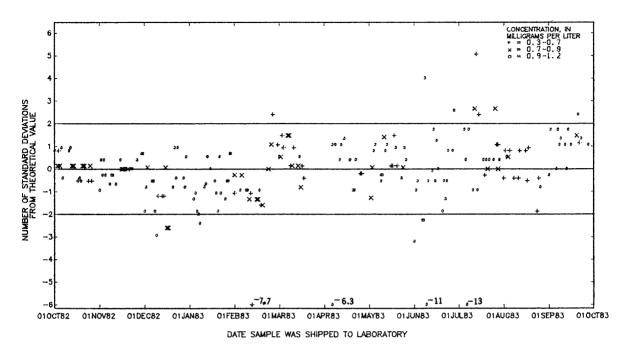


Figure 41.—Fluoride, dissolved, data from the Atlanta laboratory.

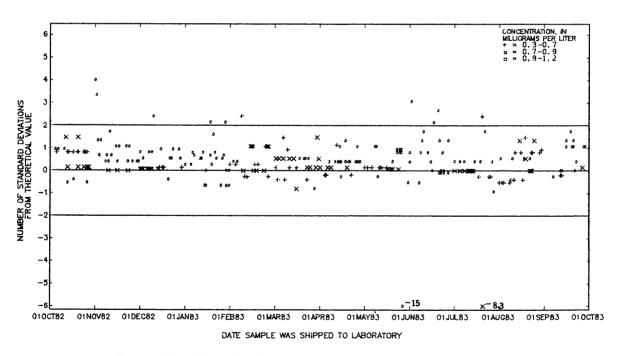


Figure 42.—Fluoride, dissolved, data from the Denver laboratory.

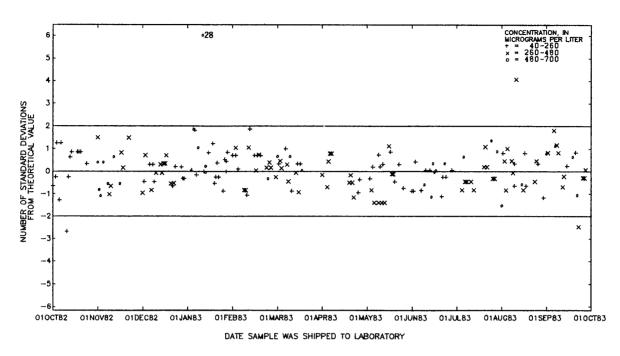


Figure 43.——Iron, dissolved, data from the Atlanta laboratory.

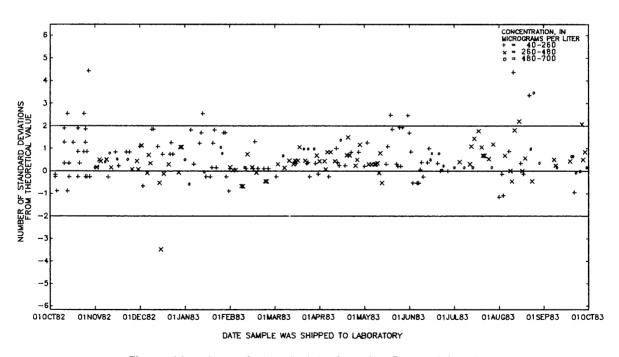


Figure 44.——Iron, dissolved, data from the Denver laboratory.

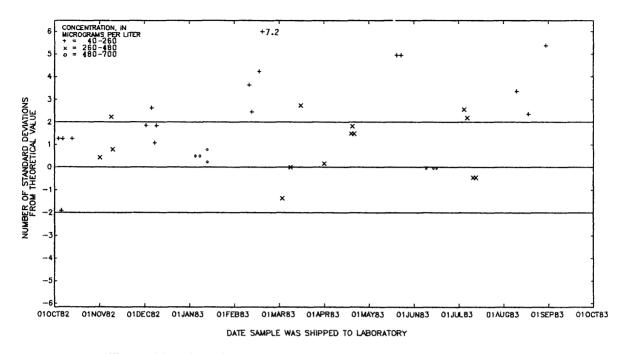


Figure 45.—Iron, total recoverable, data from the Atlanta laboratory.

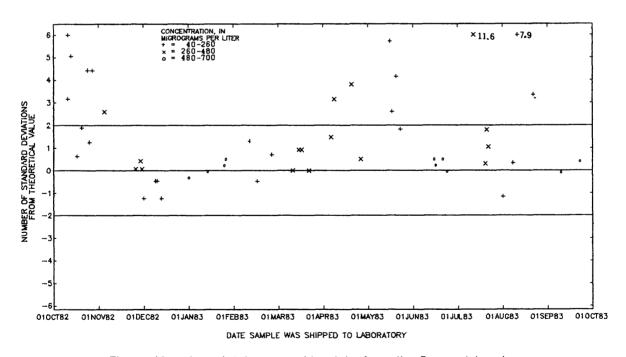


Figure 46.——Iron, total recoverable, data from the Denver laboratory.

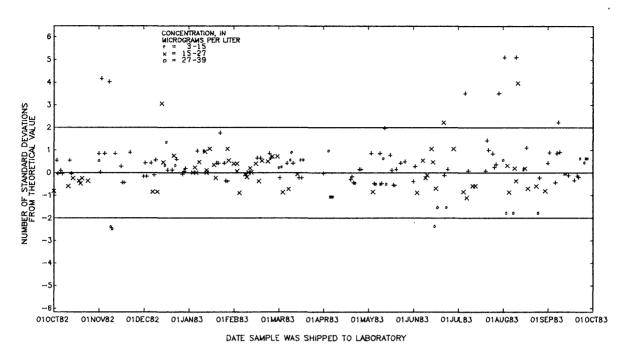


Figure 47.—Lead, dissolved, data from the Atlanta laboratory.

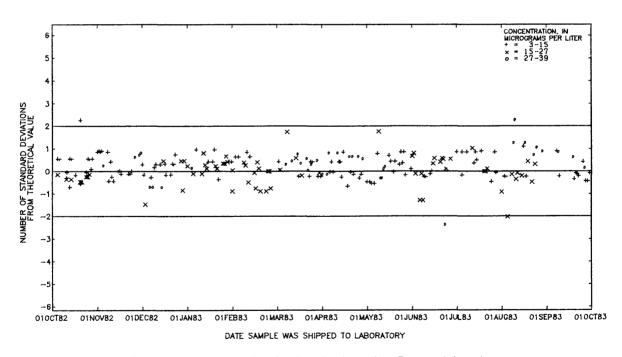


Figure 48.—Lead, dissolved, data from the Denver laboratory.

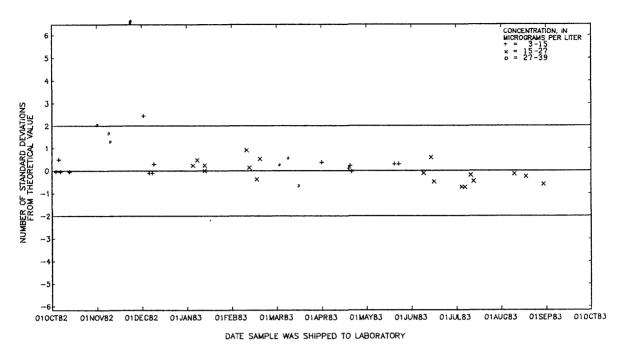


Figure 49.—Lead, total recoverable, data from the Atlanta laboratory.

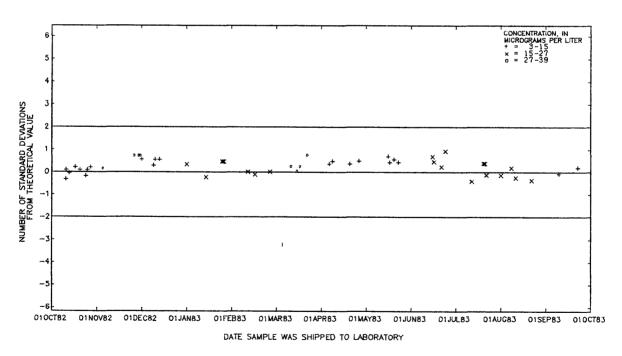


Figure 50.—Lead, total recoverable, data from the Denver laboratory.

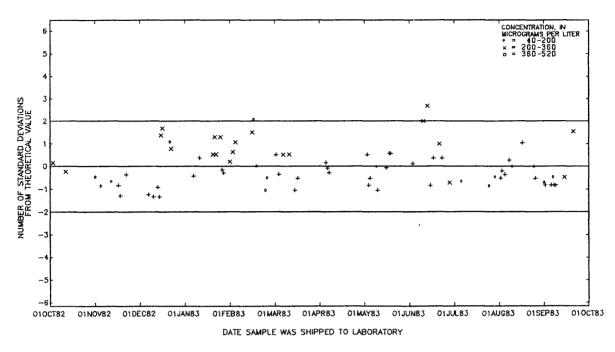


Figure 51.——Lithium, dissolved, data from the Atlanta laboratory.

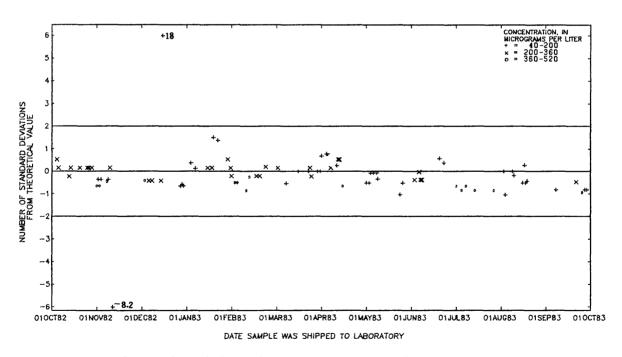


Figure 52.——Lithium, dissolved, data from the Denver laboratory.

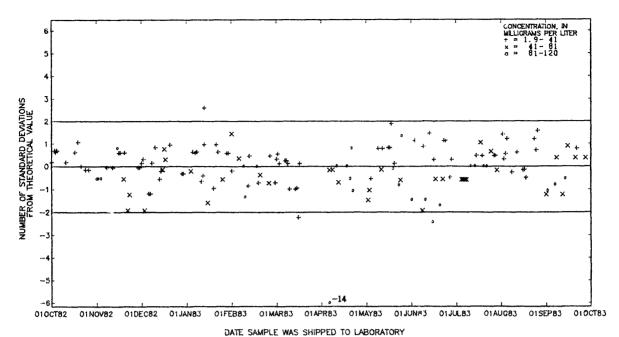


Figure 53.—Magnesium, dissolved (inductively coupled plasma emission spectrometry), data from the Atlanta laboratory.

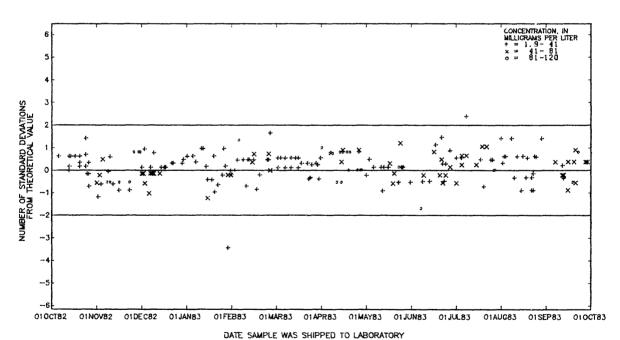


Figure 54.—Magnesium, dissolved (inductively coupled plasma emission spectrometry), data from the Denver laboratory.

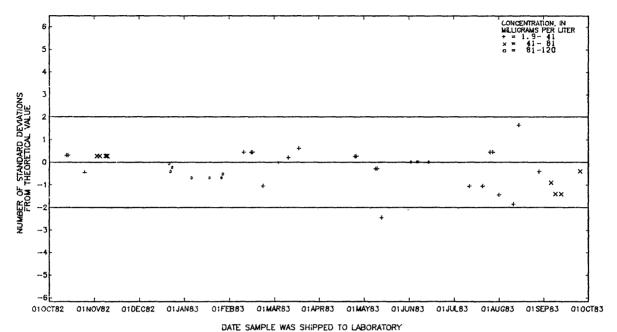


Figure 55. —Magnesium, dissolved (atomic absorption spectrometry), data from the Atlanta laboratory.

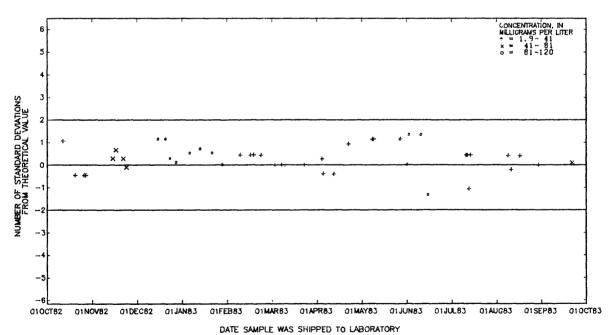


Figure 56.—Magnesium, dissolved (atomic absorption spectrometry), data from the Denver laboratory.

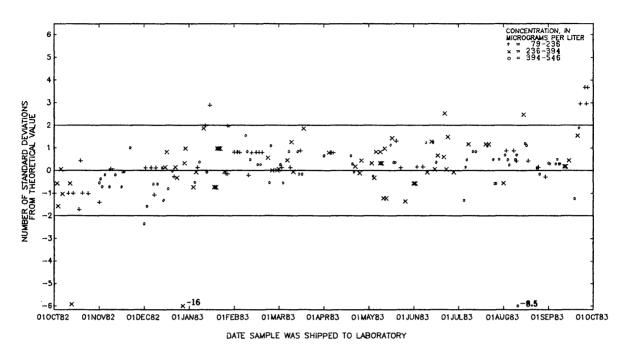


Figure 57.—Manganese, dissolved, data from the Atlanta laboratory.

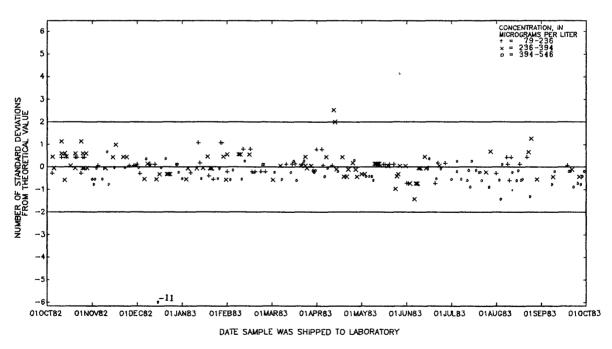


Figure 58.——Manganese, dissolved, data from the Denver laboratory.

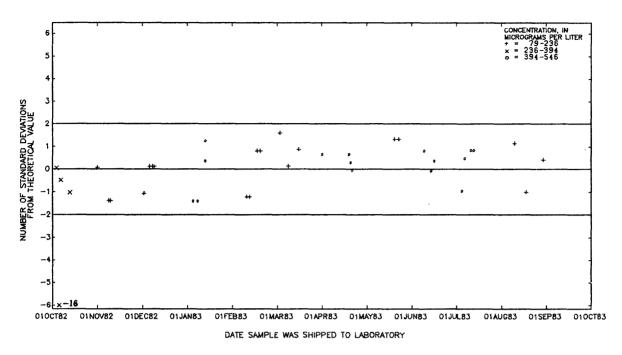


Figure 59.—Manganese, total recoverable, data from the Atlanta laboratory.

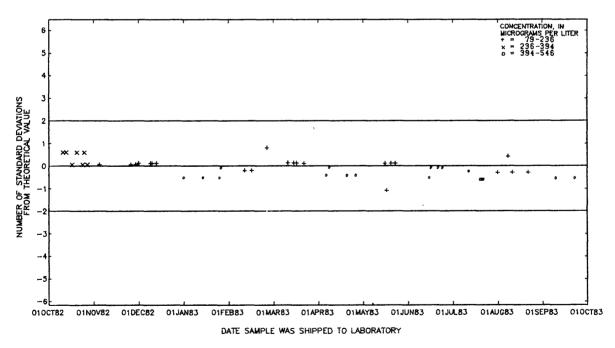


Figure 60.—Manganese, total recoverable, data from the Denver laboratory.

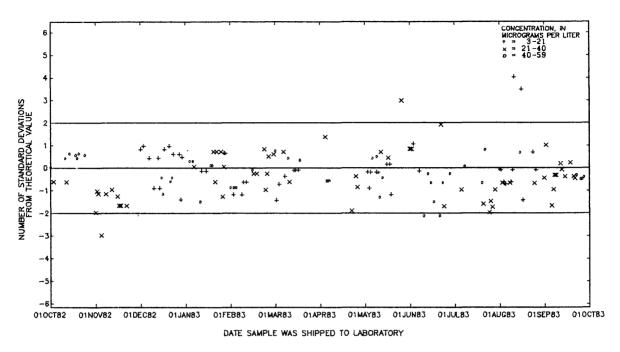


Figure 61.—Molybdenum, dissolved, data from the Atlanta laboratory.

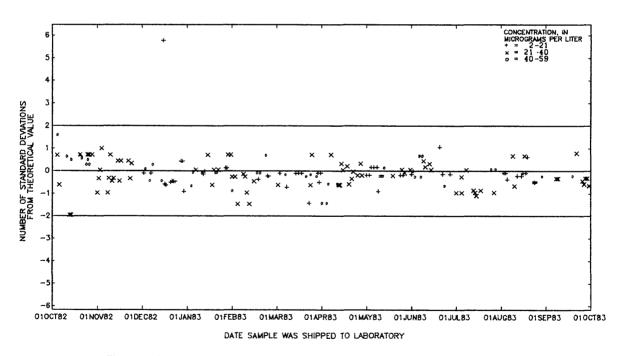


Figure 62.—Molybdenum, dissolved, data from the Denver laboratory.

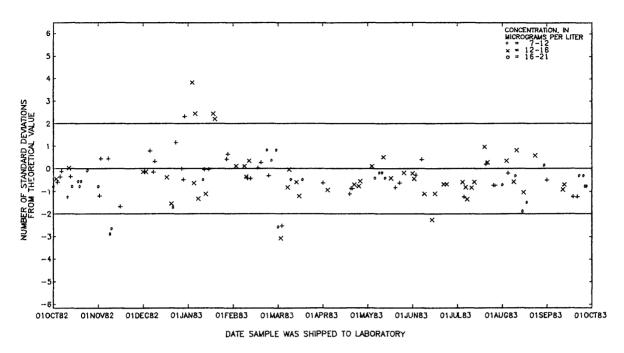


Figure 63. -- Nickel, dissolved, data from the Atlanta laboratory.

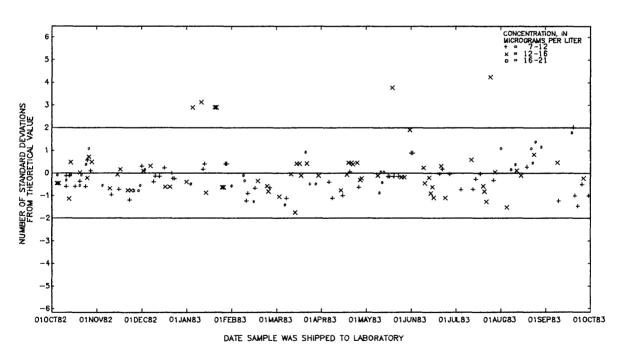


Figure 64.—Nickel, dissolved, data from the Denver laboratory.

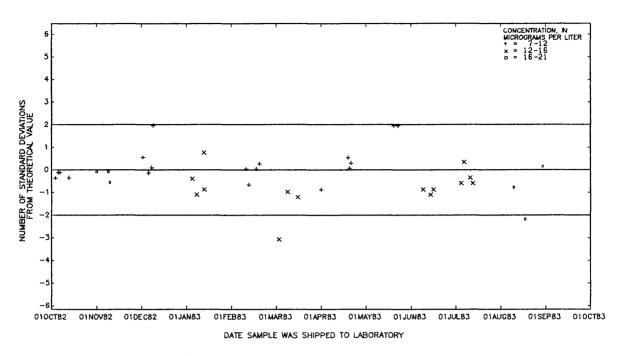


Figure 65.—Nickel, total recoverable, data from the Atlanta laboratory.

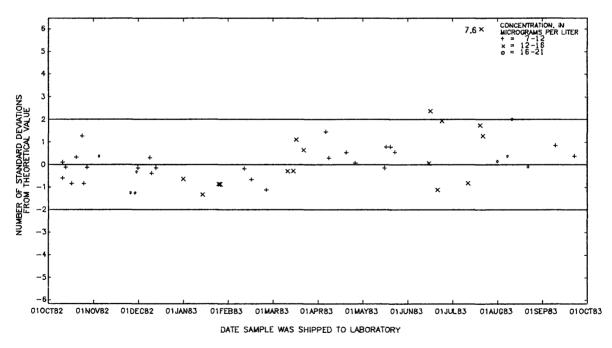


Figure 66.—Nickel, total recoverable, data from the Denver laboratory.

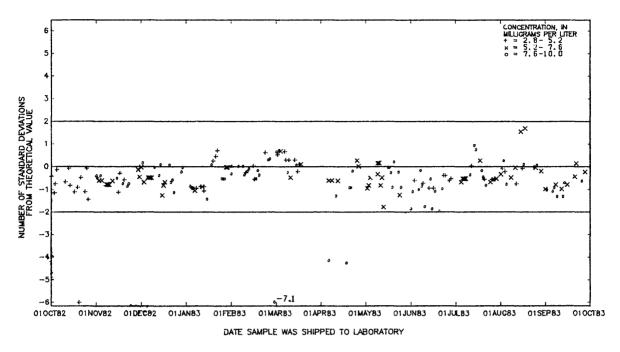


Figure 67.—Potassium, dissolved, data from the Atlanta laboratory.

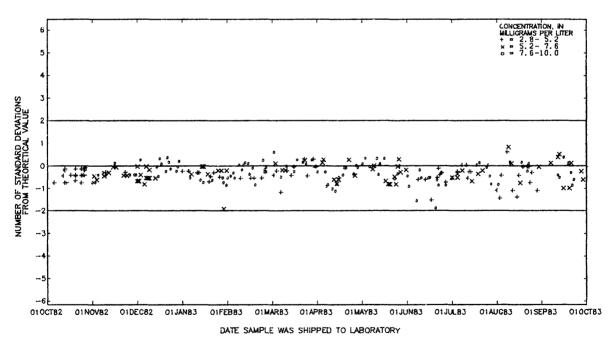


Figure 68.—Potassium, dissolved, data from the Denver laboratory.

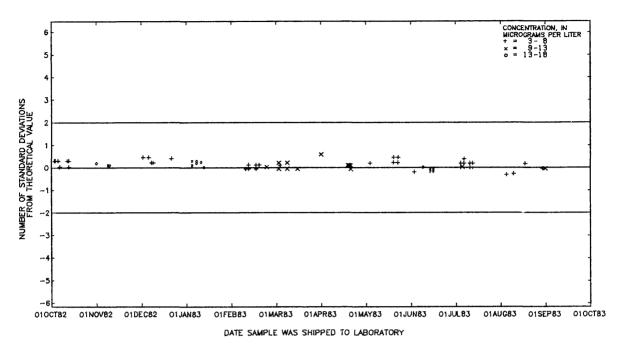


Figure 69.——Selenium, dissolved, data from the Atlanta laboratory.

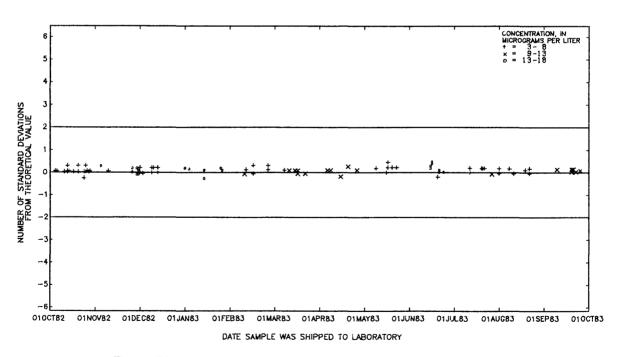


Figure 70.——Selenium, dissolved, data from the Denver laboratory.

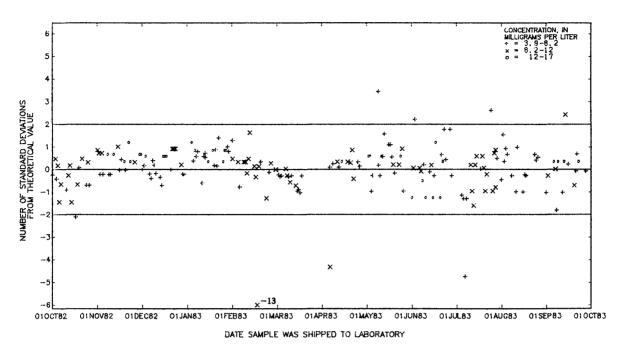


Figure 71.——Silica, dissolved, data from the Atlanta laboratory.

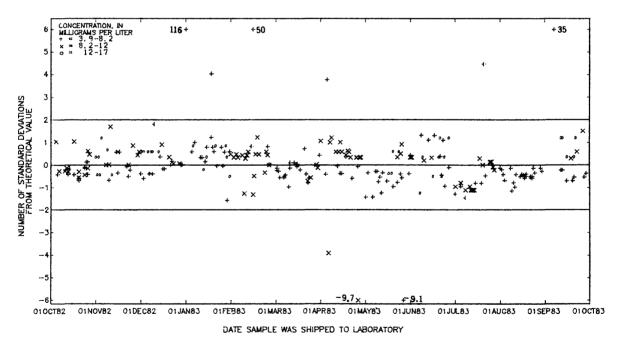


Figure 72.—Silica, dissolved, data from the Denver laboratory.

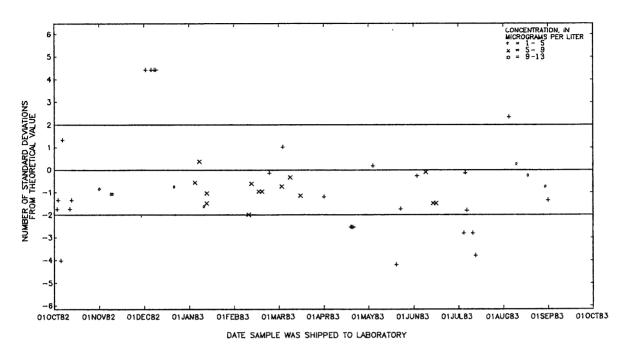


Figure 73.—Silver, dissolved, data from the Atlanta laboratory.

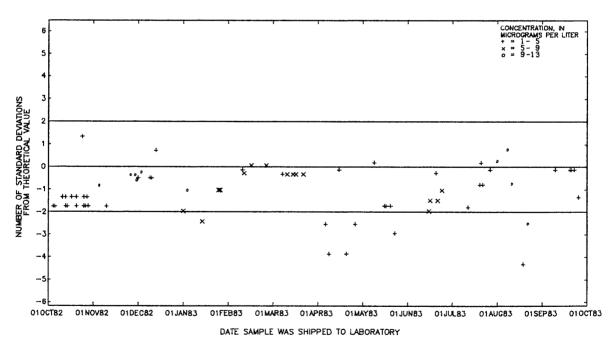


Figure 74.—Silver, dissolved, data from the Denver laboratory.

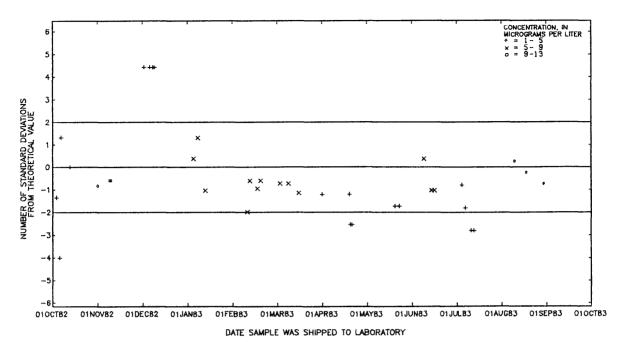


Figure 75.—Silver, total recoverable, data from the Atlanta laboratory.

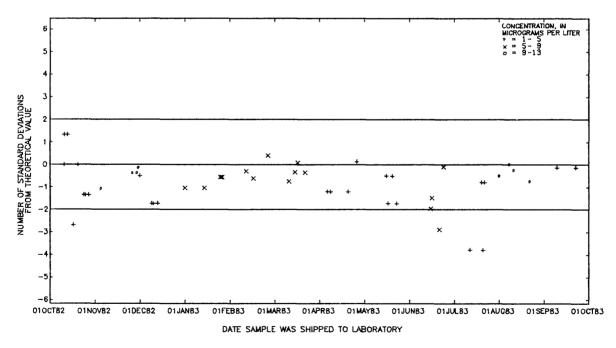


Figure 76.——Silver, total recoverable, data from the Denver laboratory.

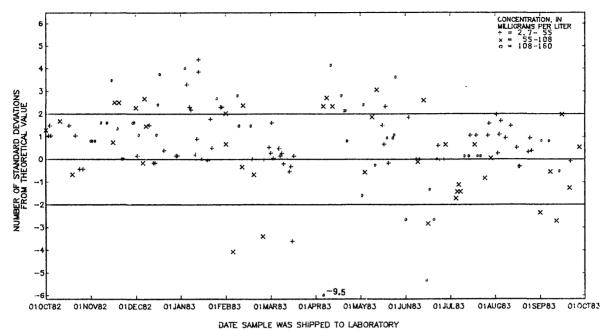


Figure 77.—Sodium, dissolved (inductively coupled plasma emission spectometry), data from the Atlanta laboratory.

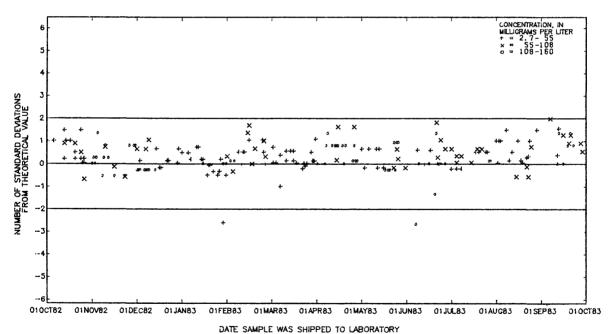


Figure 78.—Sodium, dissolved (inductively coupled plasma emission spectrometry), data from the Denver laboratory.

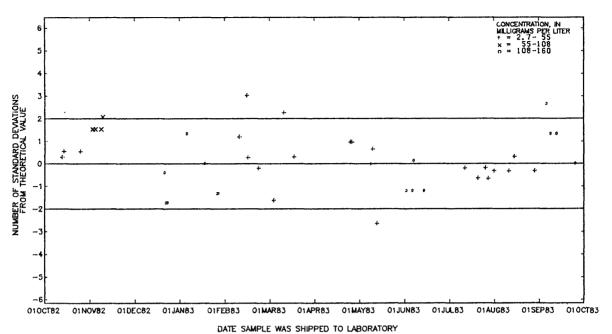


Figure 79.—Sodium, dissolved (atomic absorption spectrometry), data from the Atlanta laboratory.

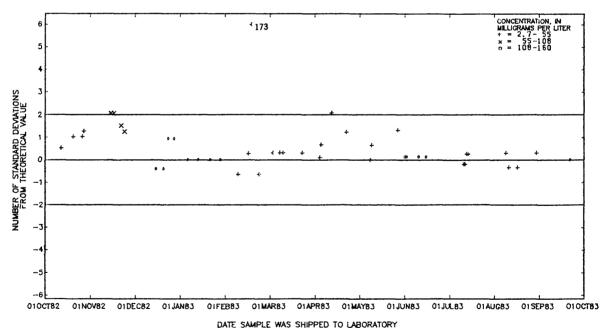


Figure 80.—Sodium, dissolved (atomic absorption spectrometry), aata from the Denver laboratory.

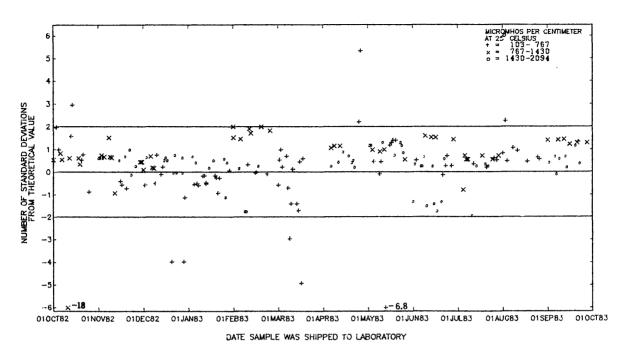


Figure 81.——Specific conductance, data from the Atlanta laboratory.

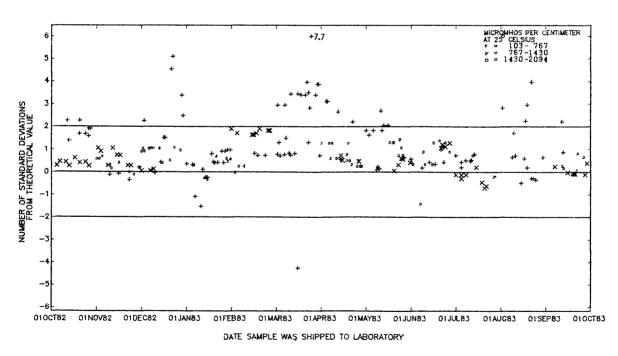


Figure 82.——Specific conductance, data from the Denver laboratory.

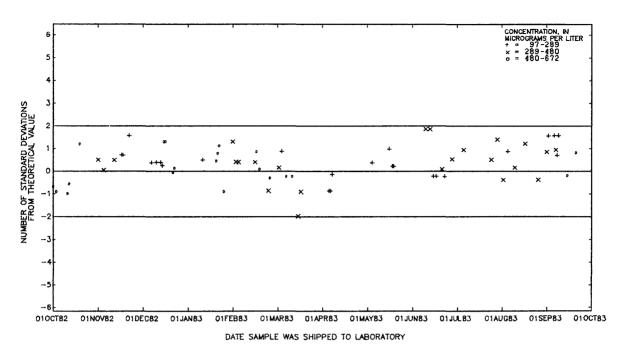


Figure 83.——Strontium, dissolved, data from the Atlanta laboratory.

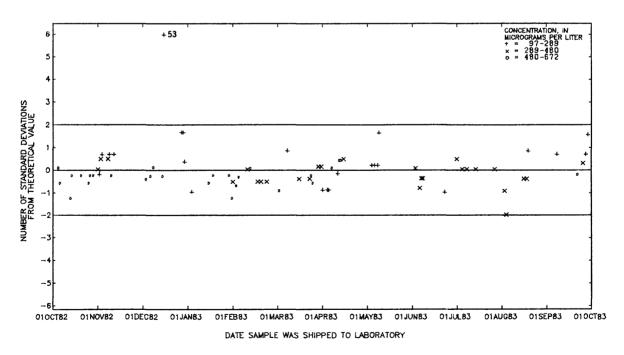


Figure 84.——Strontium, dissolved, data from the Denver laboratory.

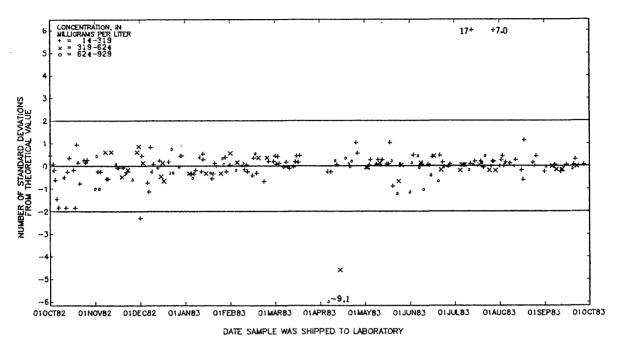


Figure 85.——Sulfate, dissolved, data from the Atlanta laboratory.

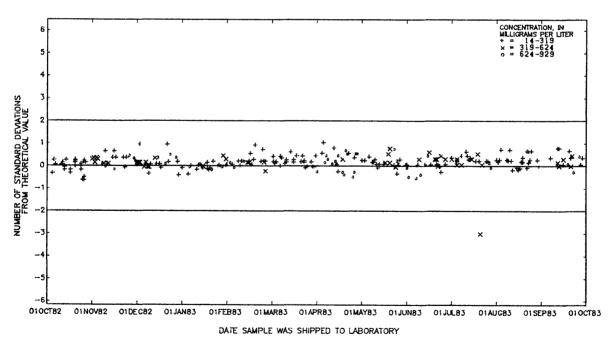


Figure 86.—Sulfate, dissolved, data from the Denver laboratory.

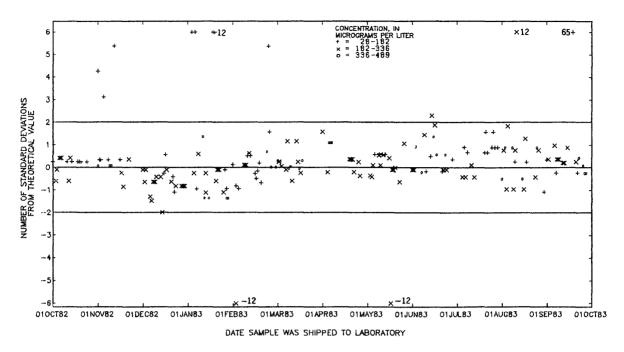


Figure 87.—Zinc, dissolved, data from the Atlanta laboratory.

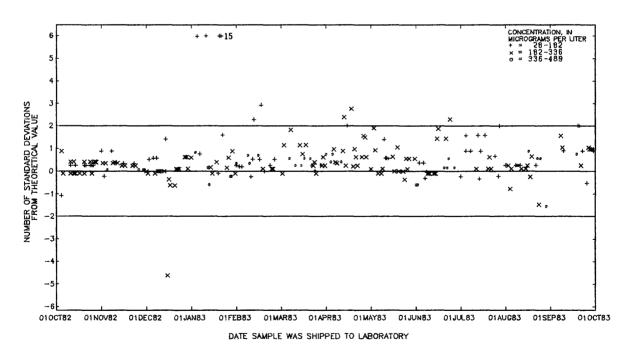


Figure 88.—Zinc, dissolved, data from the Denver laboratory.

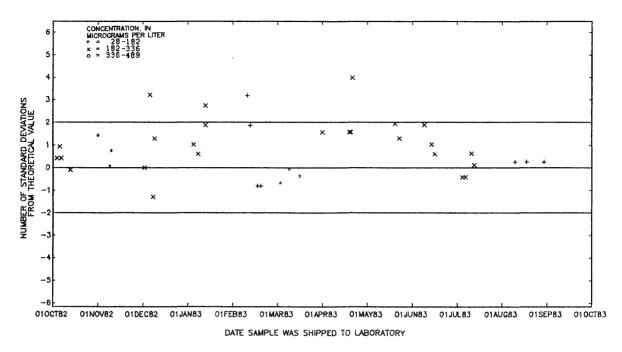


Figure 89.—Zinc, total recoverable, data from the Atlanta laboratory.

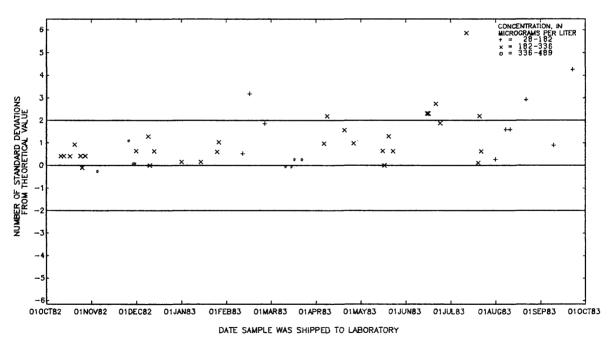
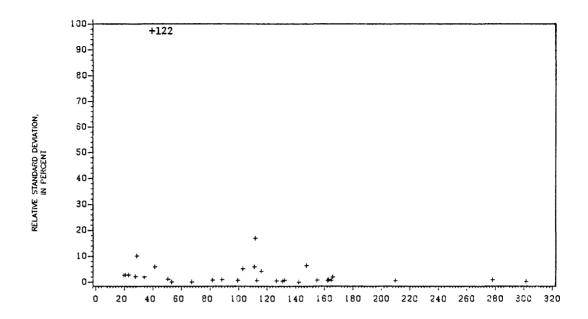
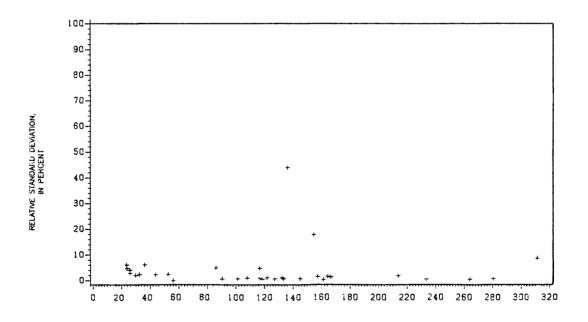


Figure 90.—Zinc, total recoverable, data from the Denver laboratory.



MEAN CONCENTRATION. IN MILLIGRAMS PER LITER
Figure 91.-- Precision data for alkalinity, dissolved, at the Atlanta laboratory.



MEAN CONCENTRATION. IN MILLIGRAMS PER LITER
Figure 92.— Precision data for alkalinity, dissolved, at the Denver laboratory.

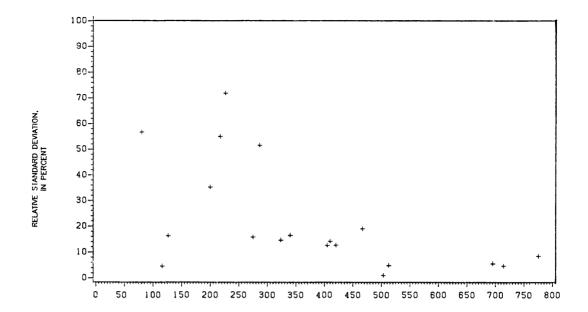
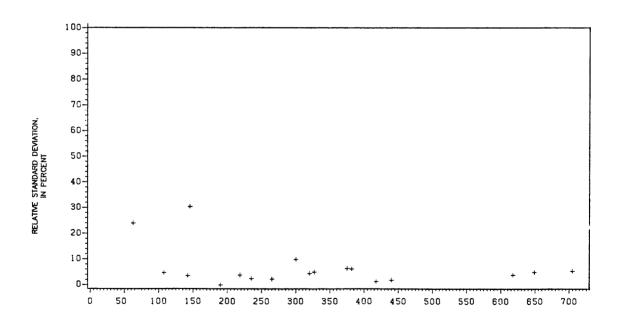


Figure 93.— Precision data for aluminum, dissolved, at the Atlanta laboratory.



MEAN CONCENTRATION, IN MICROGRAMS PER LITER

Figure 94.-- Precision data for aluminum, dissolved, at the Denver laboratory.

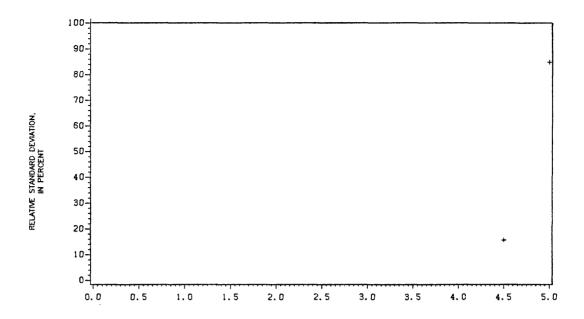
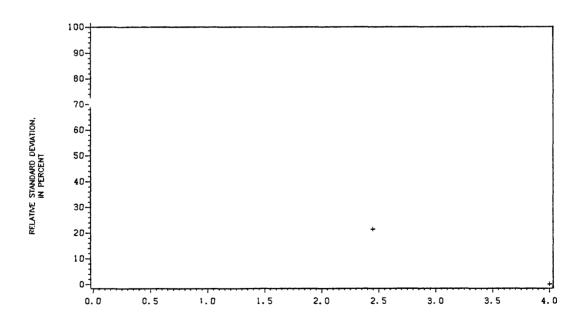
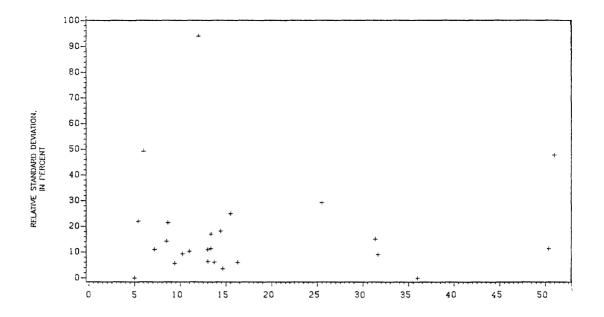


Figure 95.-- Precision data for antimony, dissolved, at the Atlanta laboratory.

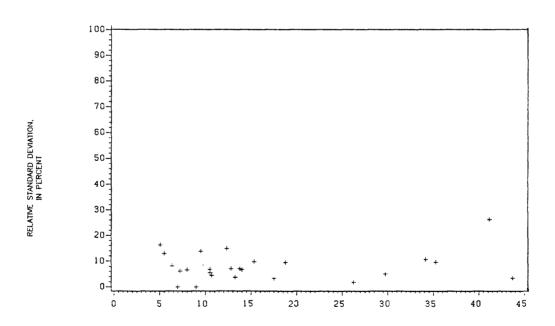


MEAN CONCENTRATION. IN MICROGRAMS PER LITER

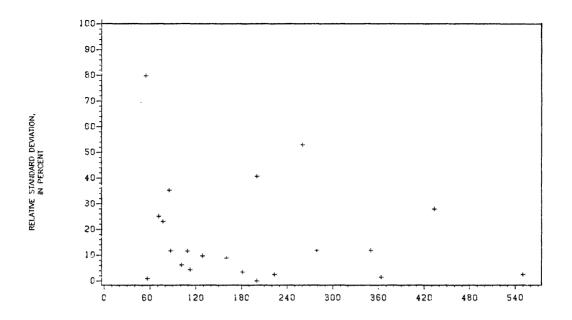
Figure 96.-- Precision data for anitmony. dissolved, at the Denver laboratory.



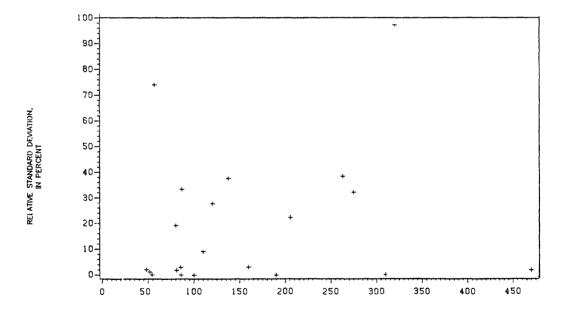
MEAN CONCENTRATION. IN MICROGRAMS PER LITER
Figure 97.-- Precision data for arsenic, dissolved, at the Altanta laboratory.



MEAN CONCENTRATION. IN MICROGRAMS PER LITER
Figure 98.-- Precision data for arsenic, dissolved, at the Denver laboratory.

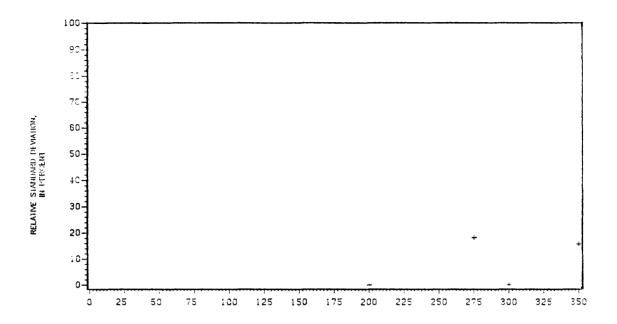


MEAN CONCENTRATION. IN MICROGRAMS PER LITER
Figure 99.-- Precision data for barium, dissolved, at the Atlanta laboratory.



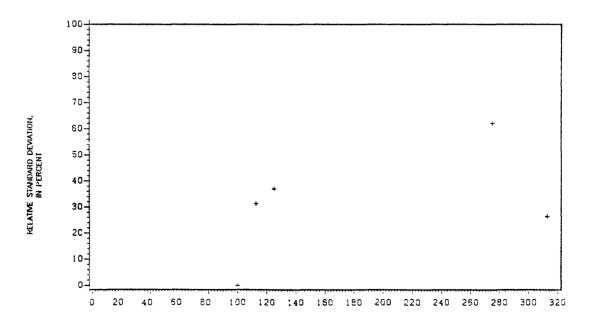
MEAN CONCENTRATION, IN MICROGRAMS PER LITER

Figure 100.-- Precision data for barium, dissolved, at the Denver laboratory.



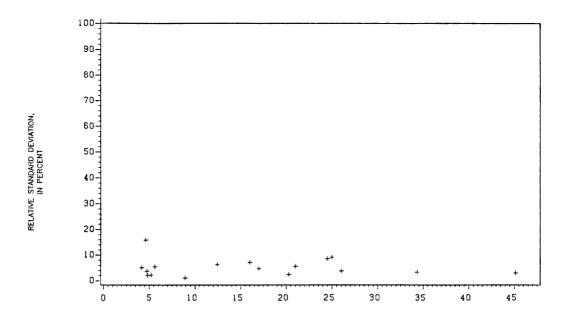
MEAN CONCENTRATION, IN MICROGRAMS PER LITER

Figure 101.— Precision data for barium, total recoverable, at the Atlanta laboratory.

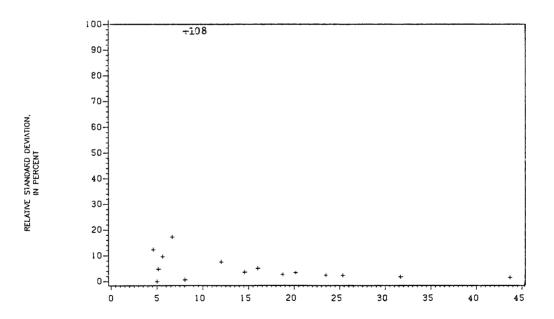


MEAN CONCENTRATION. IN MICROGRAMS PER LITER

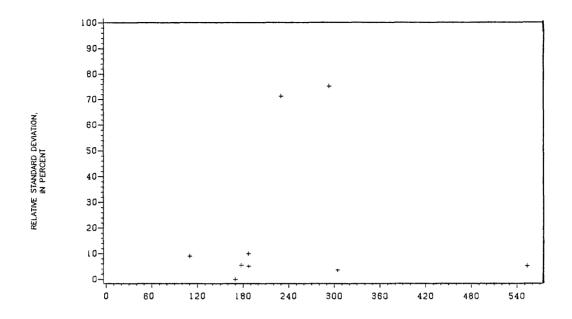
Figure 102.-- Precision data for barium, total recoverable, at the Denver laboratory.



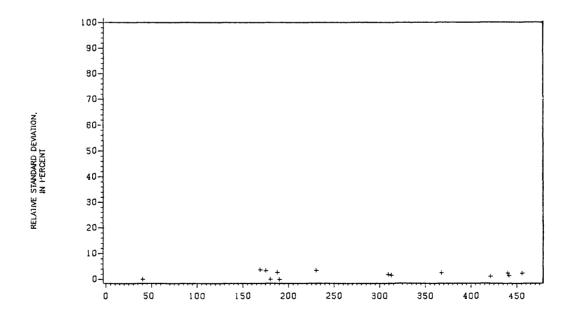
MEAN CONCENTRATION, IN MICHOGRAMS PER LITER
Figure 103.-- Precision data for beryllium, dissolved, at the Atlanta laboratory.



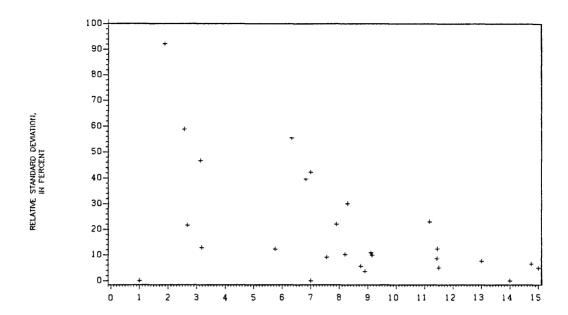
MEAN CONCENTRATION, IN MICROGRAMS PER LITER
Figure 104.-- Precision data for beryllium, dissolved, at the Denver laboratory.



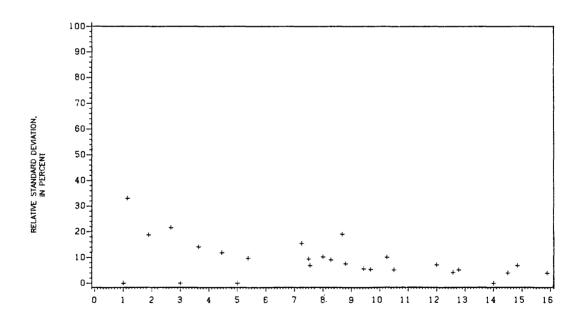
MEAN CONCENTRATION. IN MICROGRAMS PER LITER
Figure 105.-- Precision data for boron, dissolved, at the Atlanta laboratory.



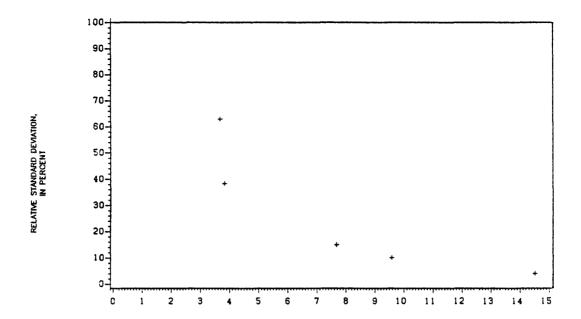
MEAN CONCENTRATION. IN MICROGRAMS PER LITER Figure 106.-- Precision data for boron, dissolved, at the Denver laboratory.



MEAN CONCENTRATION, IN MICROGRAMS PER LITER
Figure 107.-- Precision data for cadmium, dissolved, at the Atlanta laboratory.

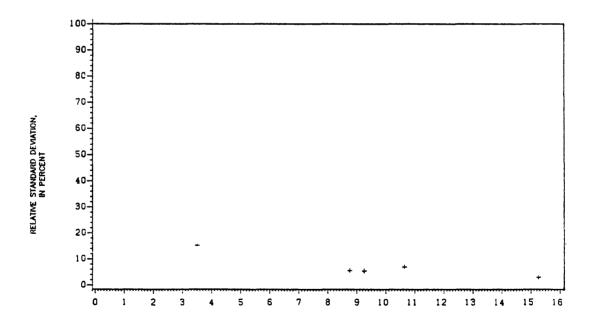


MEAN CONCENTRATION. IN MICROGRAMS PER LITER Figure 108.-- Precision data for cadmium, dissolved, at the Denver laboratory.



MEAN CONCENTRATION, IN MICROGRAMS PER LITER

Figure 109.— Precision data for cadmium, total recoverable, at the Atlanta laboratory.



MEAN CONCENTRATION, IN MICROGRAMS PER LITER

Figure 110.-- Precision data for cadmium, total recoverable, at the Denver laboratory.

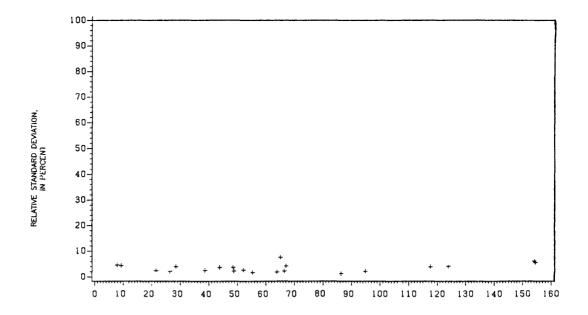
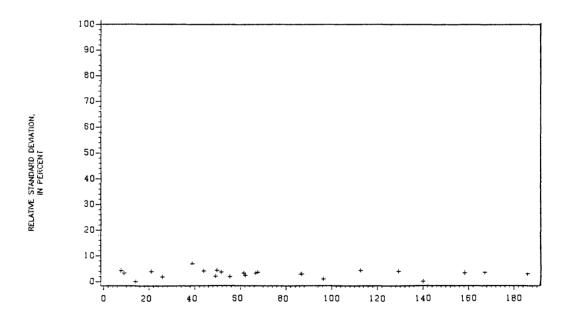


Figure 111. -- Precision data for calcium, dissolved (inductively coupled plasma emission spectrometry), at the Atlanta laboratory.



MEAN CUNCENTRATION. IN MILLIGRAMS PER LITER

Figure 112.-- Precision data for calcium, dissolved (inductively coupled plasma emission spectrometry), at the Denver laboratory.

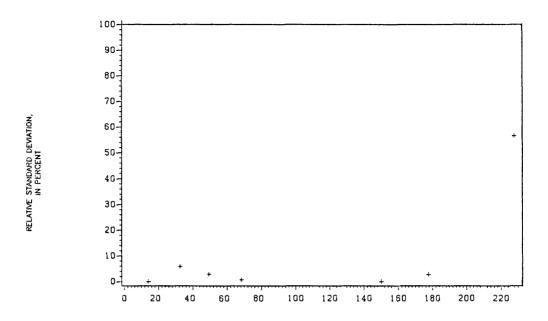
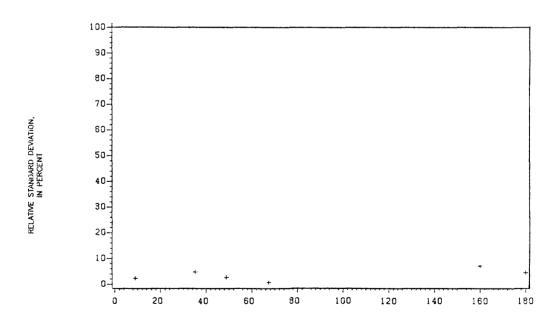


Figure 113.-- Precision data for calcium, dissolved (atomic absorption spectrometry), at the Atlanta laboratory.



MEAN CONCENTRATION, IN MILLIGRAMS PER LITER

Figure 114.-- Precision data for calcium, dissolved (atomic absorption spectrometry), at the Denver laboratory.

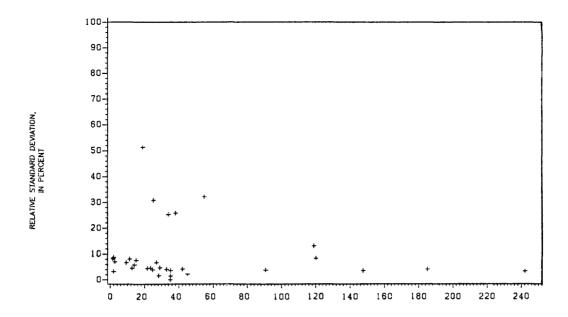
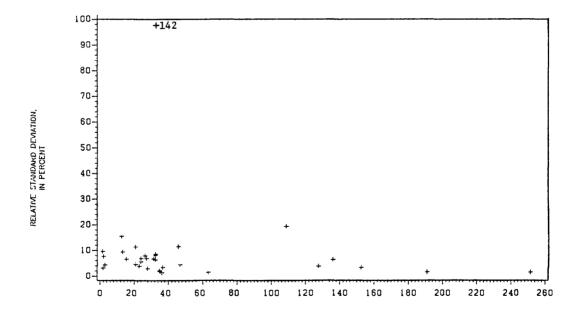
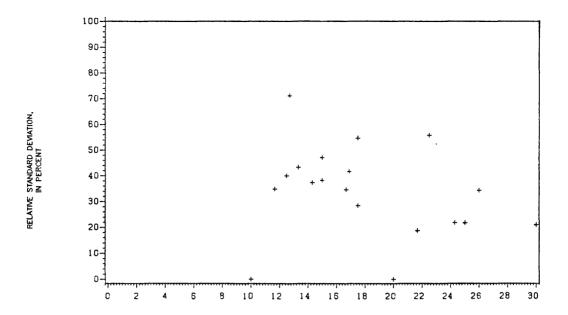


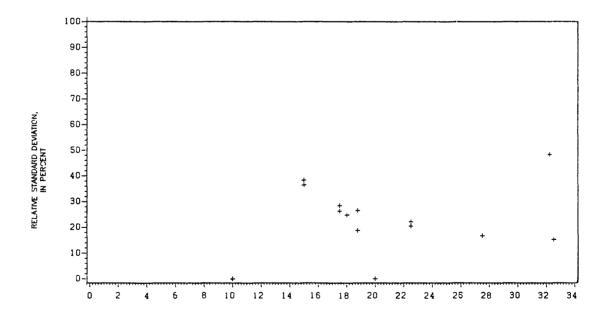
Figure 115.-- Precision data for chloride, dissolved, at the Atlanta laboratory.



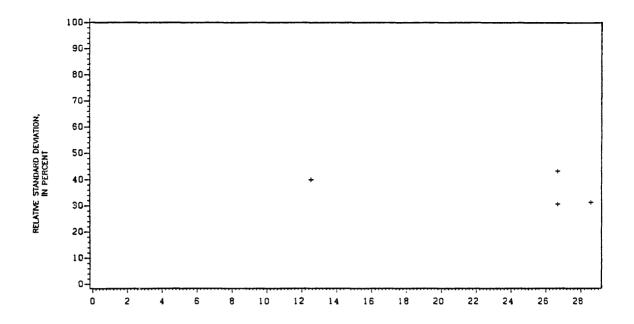
MEAN CONCENTRATION. IN MILLIGRAMS PER LITER
Figure 116.-- Precision data for chloride, dissolved, at the Denver laboratory.



MEAN CONCENTRATION. IN MICROGRAMS PER LITER
Figure 117.-- Precision data for chromium, dissolved, at the Atlanta laboratory.

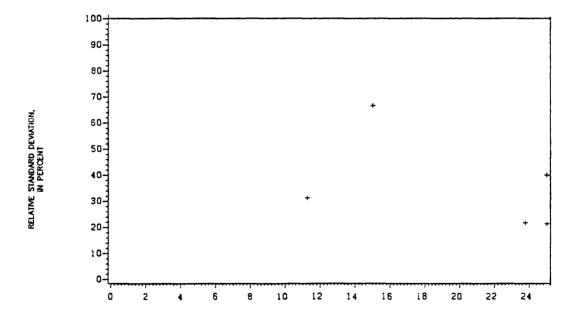


MEAN CONCENTRATION. IN MICROGRAMS PER LITER
Figure 118.-- Precision data for chromium, dissolved, at the Denver laboratory.



MEAN CONCENTRATION. IN MICROGRAMS PER LITER

Figure 119.— Precision data for chromium, total recoverable, at the Atlanta laboratory.



MEAN CONCENTRATION, IN MICROGRAMS PER LITER

Figure 120.— Precision data for chromium, total recoverable, at the Denver laboratory.

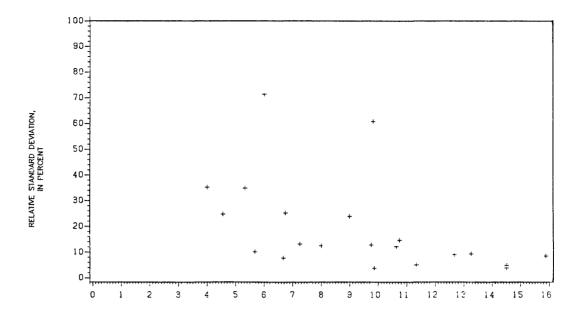
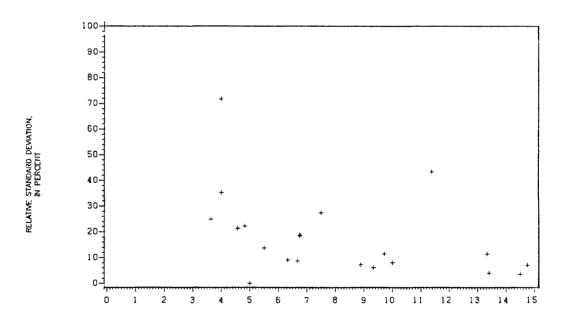
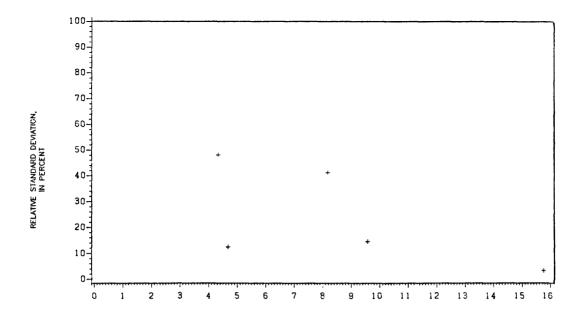


Figure 121.-- Precision data for cobalt, dissolved, at the Atlantic laboratory.

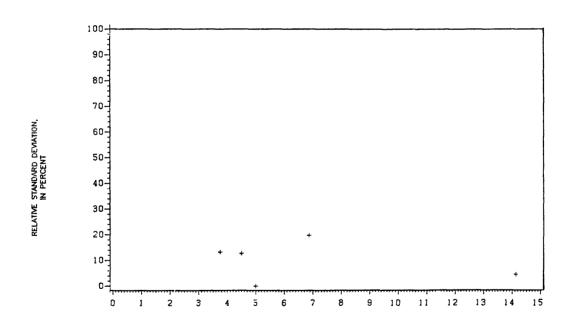


MEAN CONCENTRATION, IN MICROGRAMS PER LITER

Figure 122.-- Precision data for cobalt, dissolved, at the Denver laboratory.

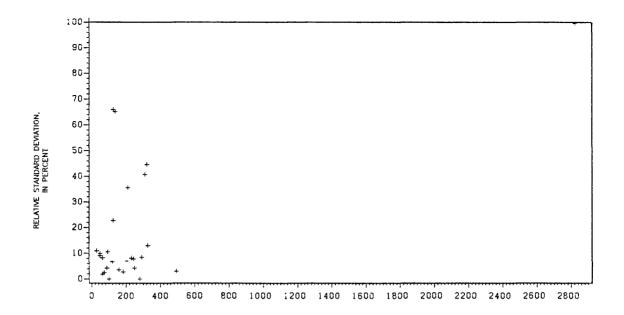


MEAN CONCENTRATION. IN MICROGRAMS PER LITER
Figure 123.-- Precision data for cobalt, total recoverable, at the Atlanta laboratory.



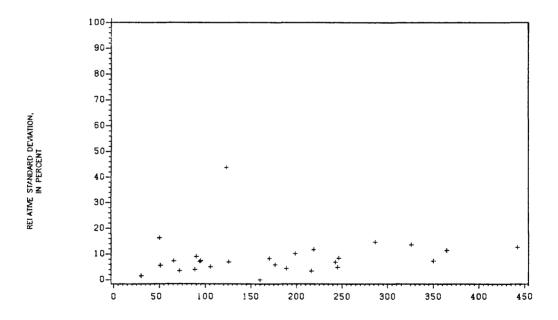
MEAN CONCENTRATION. IN MICROGRAMS PER LITER

Figure 124.— Precision data for cobalt, total recoverable, at the Denver laboratory.

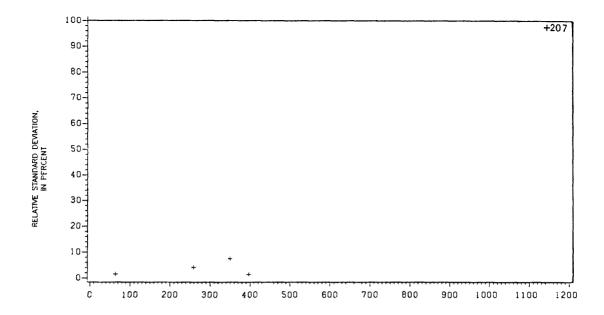


MEAN CONCENTRATION, IN MICROGRAMS PER LITER

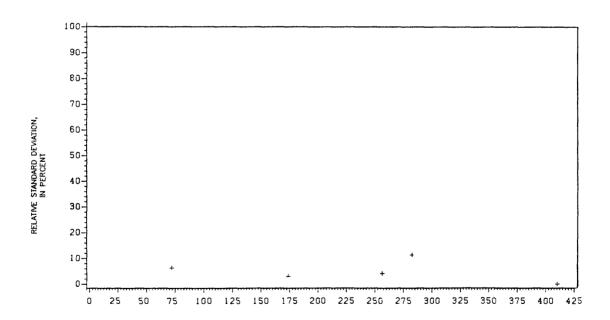
Figure 125.-- Precision data for copper, dissolved, at the Atlanta laboratory.



MEAN CONCENTRATION. IN MICROGRAMS PER LITER
Figure 126.-- Precision data for copper, dissolved, at the Denver laboratory.



MEGN CONCENTRATION, IN MICROGRAMS PER LITER
Figure 127.-- Precision data for copper, total recoverable, at the Atlanta laboratory.



MEAN CONCENTRATION. IN MICROGRAMS PER LITER

Figure 128.-- Precision data for copper, total recoverable, at the Denver laboratory.

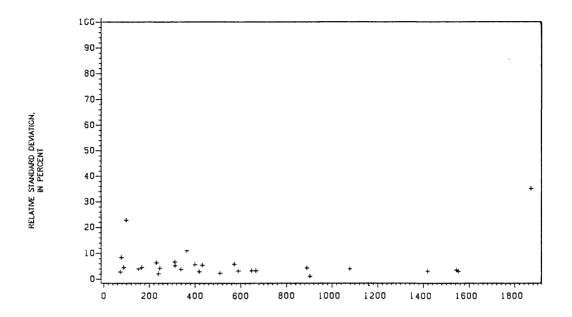
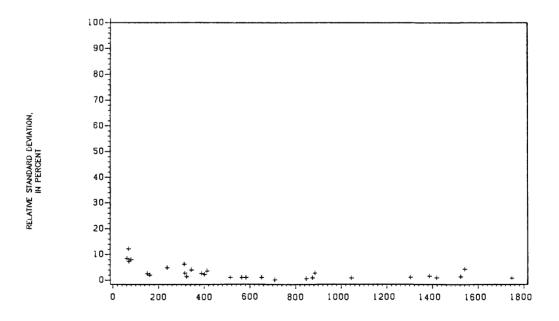
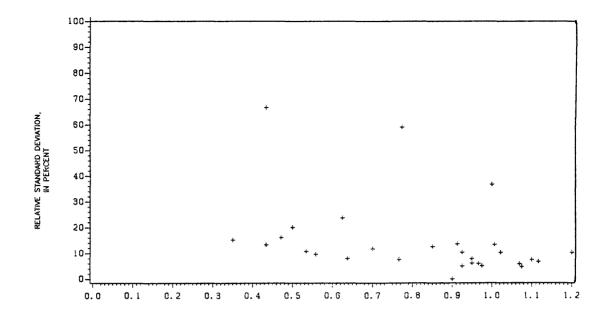


Figure 129. -- Precision data for dissolved solids at the Atlanta laboratory.

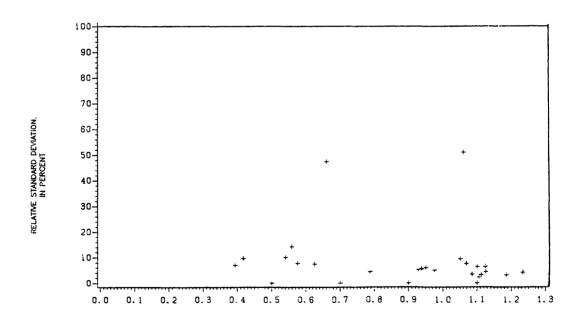


MEAN CONCENTRATION. IN MILLIGRAMS PER LITER
Figure 130.— Precision data for dissolved solids at the Denver laboratory.



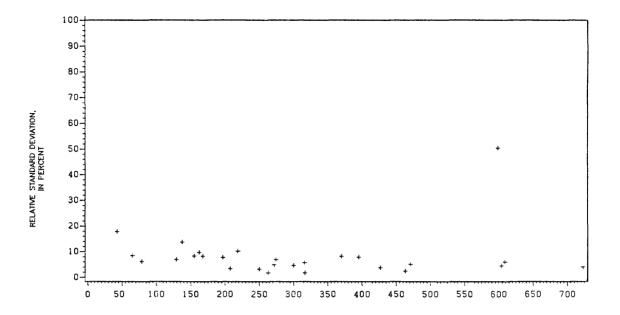
MEAN CONCENTRATION, IN MILLIGRAMS PER LITER

Figure 131.-- Precision data for fluoride, dissolved, at the Atlanta laboratory.



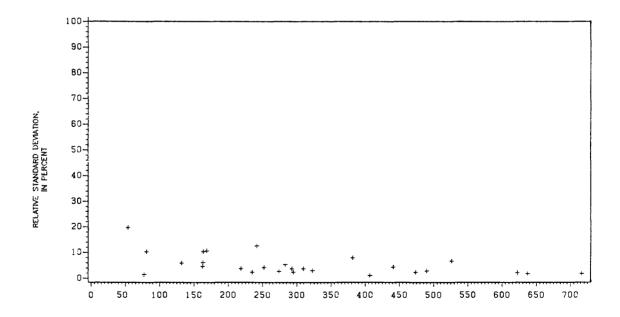
MEAN CONCENTRATION. IN MILLIGRAMS PER LITER

Figure 132.-- Precision data for fluoride, dissolved, at the Denver laboratory.

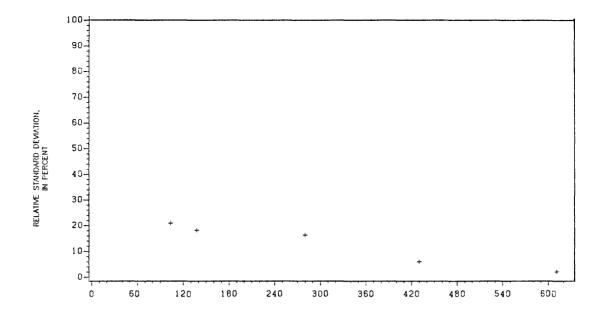


MEAN CONCENTRATION, IN MICROGRAMS PER LITER

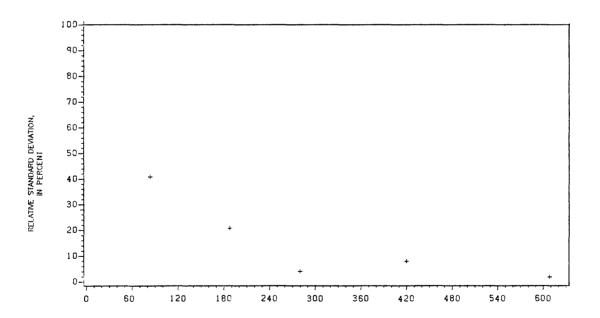
Figure 133.-- Precision data for iron, dissolved, at the Atlanta laboratory.



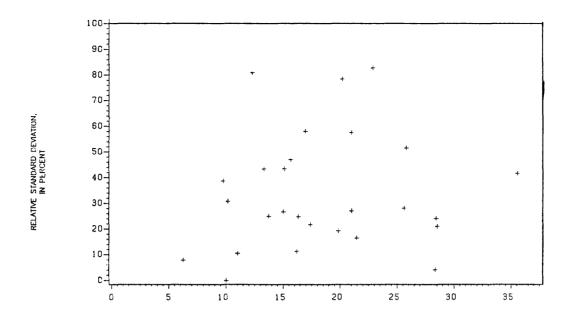
MEAN CONCENTRATION, IN MICROGRAMS PER LITER
Figure 134.-- Precision data for iron, dissolved, at the Denver laboratory.



MEAN CONCENTRATION. IN MICROGRAMS PER LITER
Figure 135.— Precision data for iron, total recoverable, at the Atlanta laboratory.

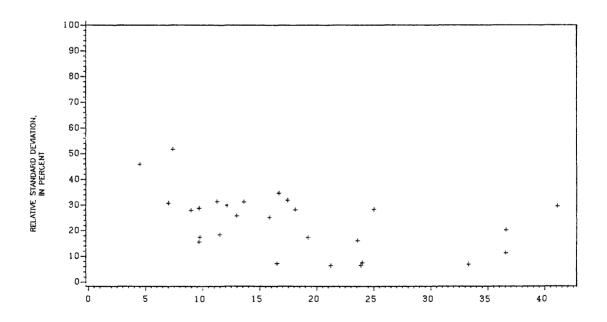


MFAN CONCENTRATION, IN MICROGRAMS PER LITER
Figure 136.-- Precision data for iron, total recoverable, at the Denver laboratory.



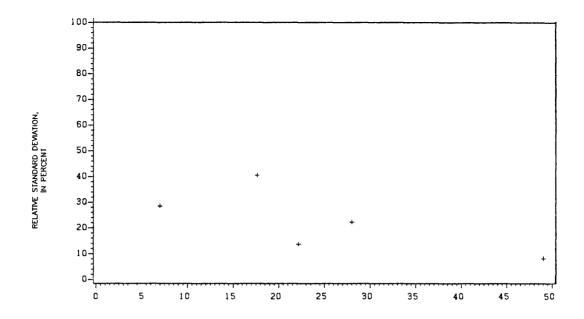
MEAN CONCENTRATION. IN MICROGRAMS PER LITER

Figure 137.— Precision data for lead, dissolved, at the Atlanta laboratory.



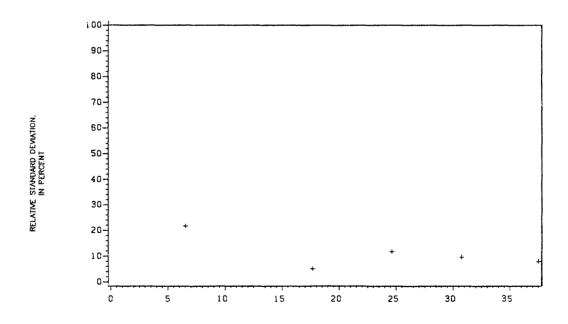
MEAN CONCENTRATION. IN MICROGRAMS PER LITER

Figure 138.— Precision data for lead, dissolved, at the Denver laboratory.



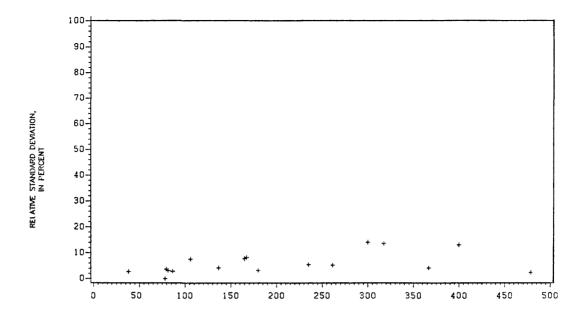
MEAN CONCENTRATION. IN MICROGRAMS PER LITER

Figure 139.-- Precision data for lead, total recoverable, at the Atlanta laboratory.



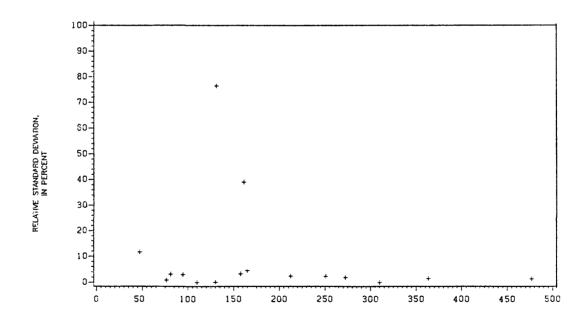
MEAN CONCENTRATION. IN MICROGRAMS PER LITER

Figure 140.— Precision data for lead, total recoverable, at the Denver laboratory.



MEAN CONCENTRATION. IN MICROGRAMS PER LITER

Figure 141.— Precision data for lithium, dissolved, at the Atlanta laboratory.



MEAN CONCENTRATION. IN MICROGRAMS PFR LITER

Figure 142.-- Precision data for lithium, dissolved, at the Denver laboratory.

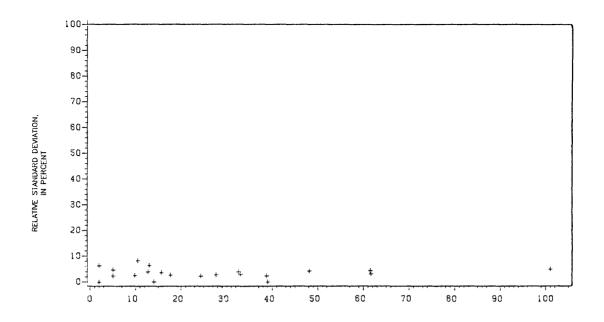
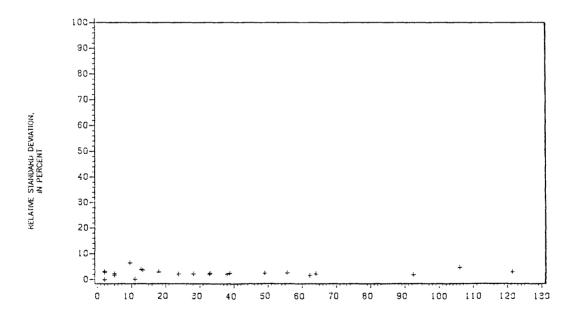


Figure 143.-- Precision data for magnesium, dissolved (inductively coupled plasma emission spectrometry), at the Atlanta laboratory.



MEAN CONCENTRATION, IN MILLIGRAMS PER LITER

Figure 144.-- Precision data for magnesium, dissolved (inductively coupled plasma spectrometry), at the Denver laboratory.

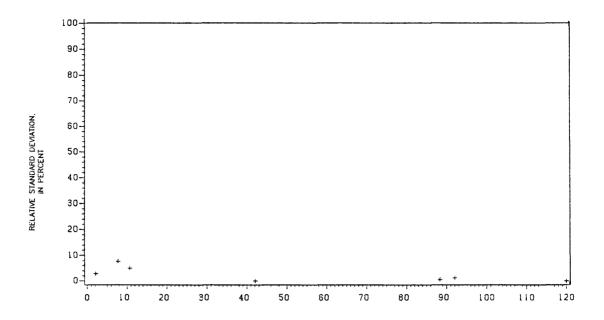
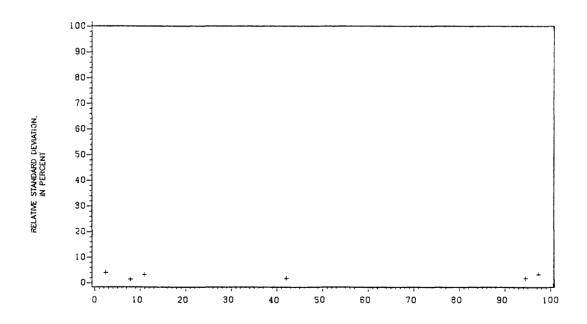
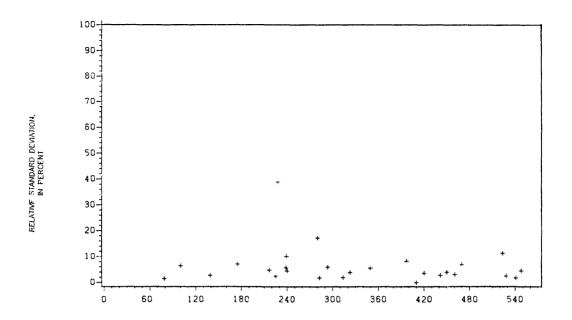


Figure 145.-- Precision data for magnesium, dissolved (atomic absorption spectrometry), at the Atlanta laboratory.



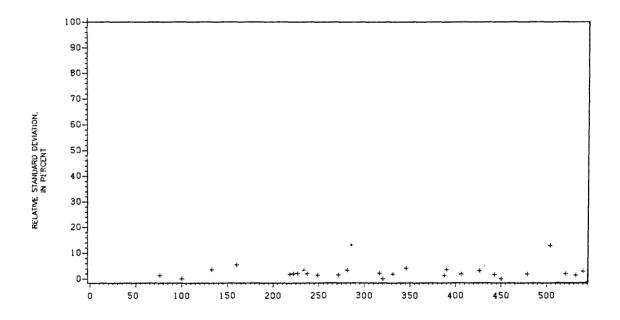
MEAN CONCENTRATION, IN MILLIGRAMS PER LITER

Figure 146.-- Precision data for magnesium, dissolved (atomic absorption spectrometry), at the Denver laboratory.



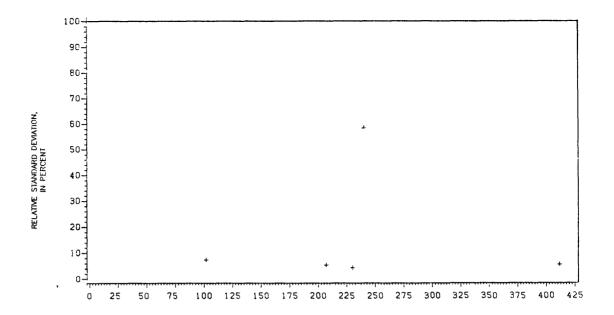
MEAN CONCENTRATION, IN MICROGRAMS PER LITER

Figure 147.-- Precision data for manganese, dissolved, at the Atlanta laboratory.

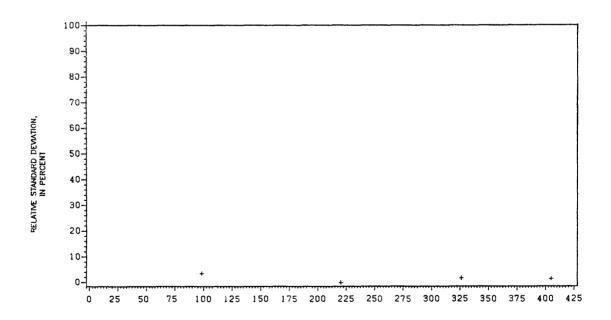


MEAN CONCENTRATION. IN MICROGRAMS PER LITER

Figure 148.-- Precision data for manganese, dissolved, at the Denver laboratory.

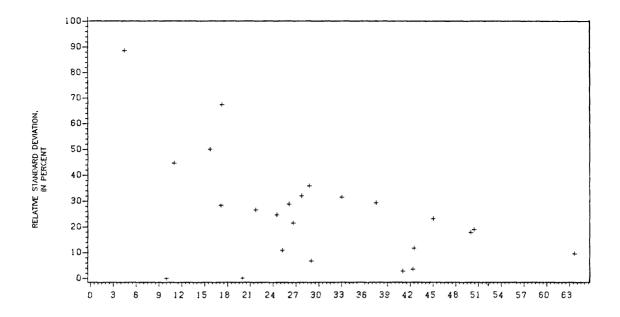


MEAN CONCENTRATION. IN MICROGRAMS PER LITER
Figure 149.-- Precision data for manganese, total recoverable, at the Atlanta laboratory.

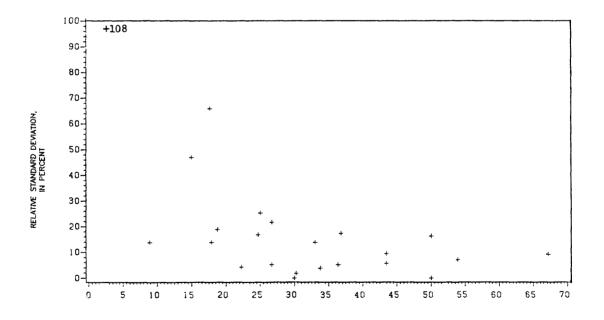


MEAN CONCENTRATION. IN MICROGRAMS PER LITER

Figure 150.— Precision data for manganese, total recoverable, at the Denver laboratory.



MEAN CONCENTRATION, IN MICROGRAMS PER LITER
Figure 151.-- Precision data for molybdenum, dissolved, at the Atlanta laboratory.



MEAN CONCENTRATION. IN MICROGRAMS PER LITER

Figure 152.— Precision data for molybdenum, dissolved, at the Denver laboratory.

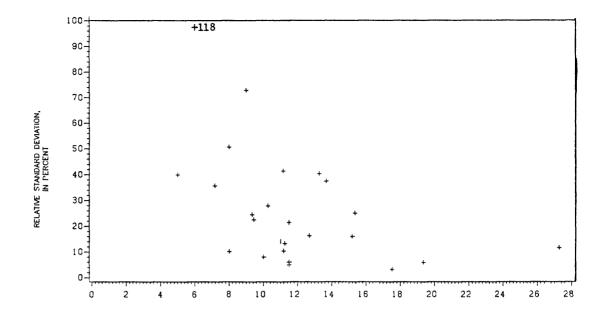
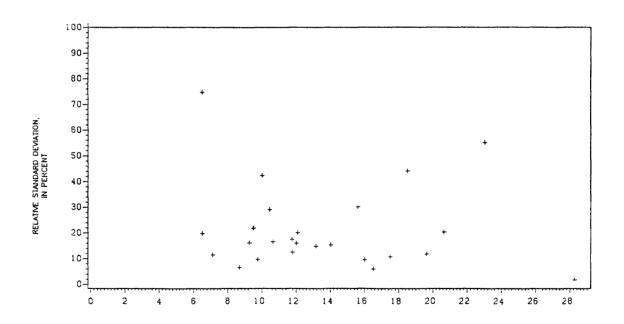
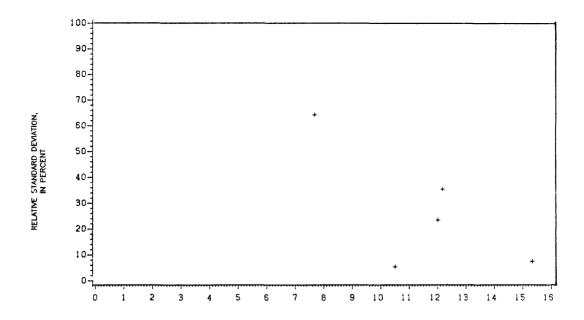


Figure 153.-- Precision data for nickel, dissolved at the Atlanta laboratory.



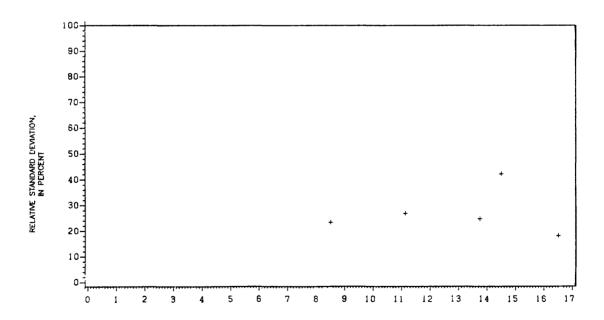
MEAN CONCENTRATION. IN MICROGRAMS PER LITER

Figure 154.-- Precision data for nickel, dissolved, at the Denver laboratory.



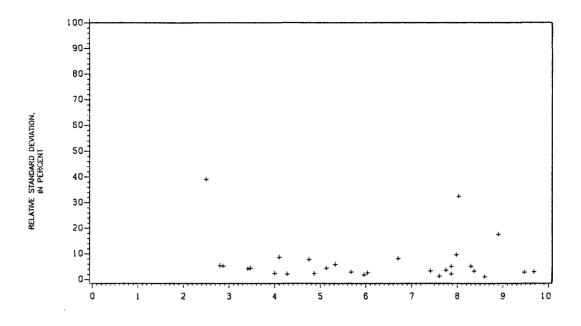
MEAN CONCENTRATION. IN MICROGRAMS PER LITER

Figure 155.-- Precision data for nickel, total recoverable, at the Atlanta laboratory.

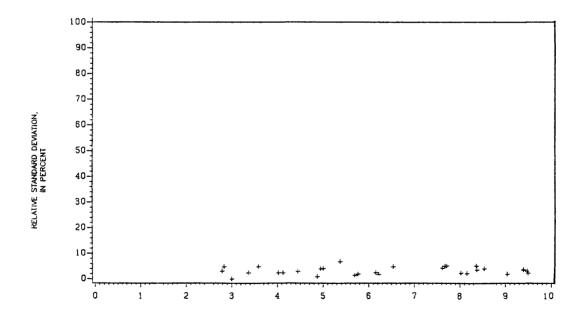


MEAN CONCENTRATION, N MICROGRAMS PER LITER

Figure 156.— Precision data for nickel, total recoverable, at the Denver laboratory.

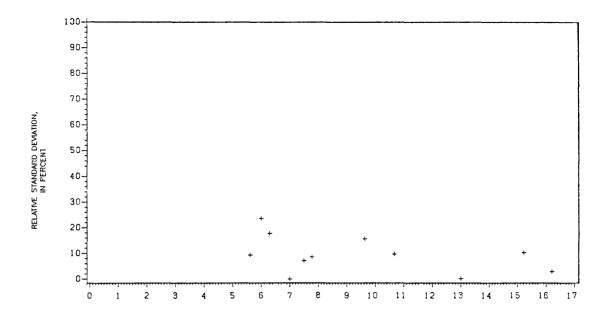


MEAN CONCENTRATION. IN MILLIGRAMS PER LITER
Figure 157.— Precision data for potassium, dissolved, at the Atlanta laboratory.



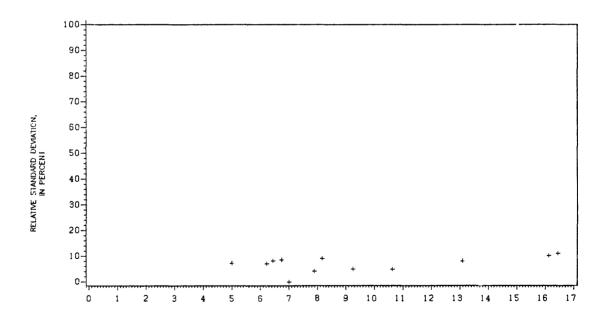
MEAN CONCENTRATION. IN MILLIGRAMS PER LITER

Figure 158.— Precision data for potassium, dissolved, at the Denver laboratory.

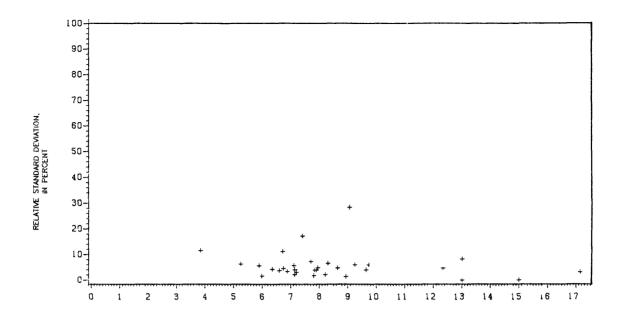


MEAN CONCENTRATION, IN MICROGRAMS PER LITER

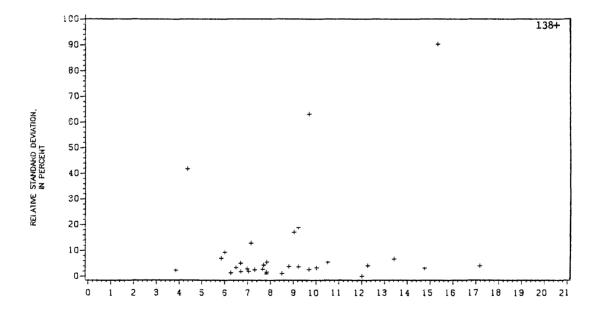
Figure 159. -- Precision data for selenium, dissolved, at the Atlanta laboratory.



MEAN CONCENTRATION. IN MICROGRAMS PER LITER
Figure 160.-- Precision data for selenium, dissolved, at the Denver laboratory.

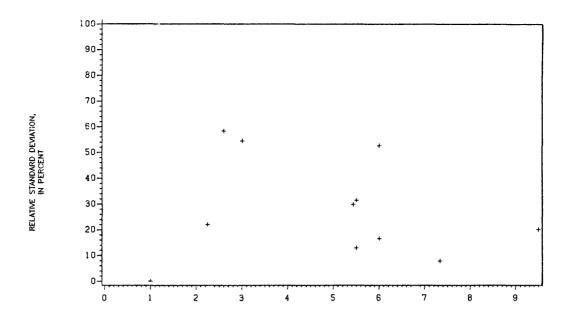


MEAN CONCENTRATION. IN MILLIGRAMS PER LITER
Figure 161.— Precision data for silica, dissolved, at the Atlanta laboratory.

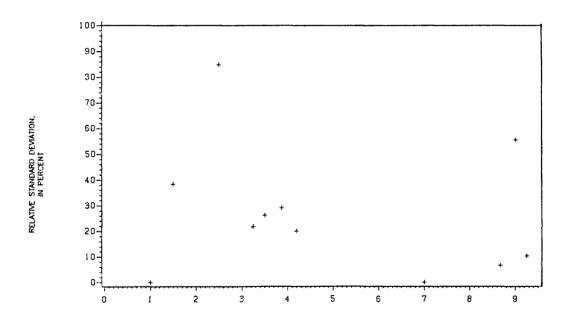


MEAN CONCENTRATION. IN MILLIGRAMS PER LITER

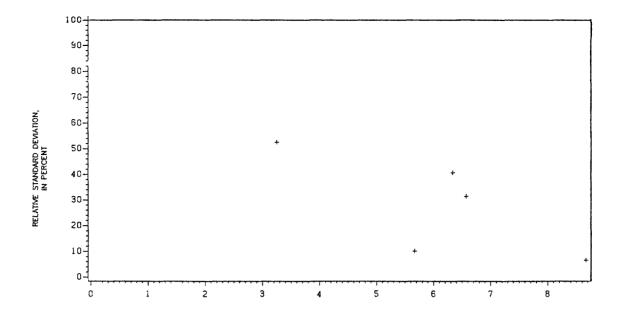
Figure 162.— Precision data for silica, dissolved, at the Denver laboratory.



MEAN CONCENTRATION. IN MICROGRAMS PER LITER
Figure 163.-- Precision data for silver, dissolved, at the Atlanta laboratory.

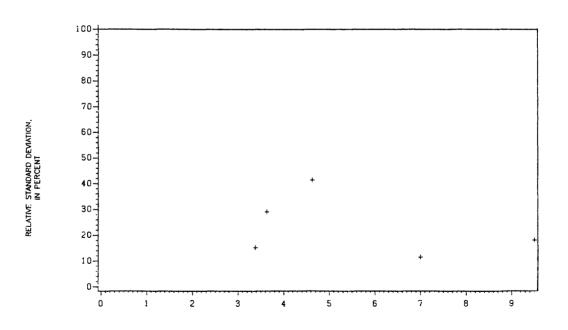


MEAN CONCENTRATION. IN MICROGRAMS PER LITER
Figure 164.— Precision data for silver, dissolved, at the Denver laboratory.



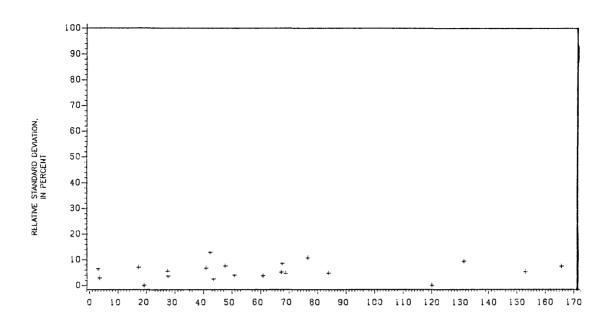
MEAN CONCENTRATION, IN MICROGRAMS PER LITER

Figure 165. -- Precision data for silver, total recoverable, at the Atlanta laboratory.



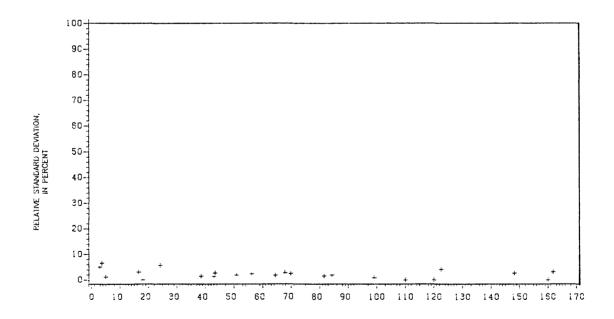
MEAN CONCENTRATION, IN MICROGRAMS PER LITER

Figure 166. -- Precision data for silver, total recoverable, at the Denver laboratory.



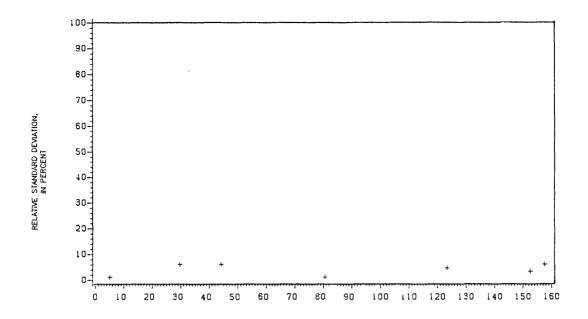
MEAN CONCENTRATION, IN MILLIGRAMS PER LITER

Figure 167.-- Precision data for sodium, dissolved (inductively coupled plasma emission spectrometry), at the Atlanta laboratory.



MEAN CONCENTRATION. IN MILLIGRAMS PER LITER

Figure 168.-- Precision data for sodium, dissolved (inductively coupled plasma emmission spectrometry), at the Denver laboratory.



MEGN CONCENTRATION. IN MILLIGRAMS PER LITER

Figure 169.-- Precision data for sodium, dissolved (atomic absorption spectrometry),
at the Atlanta laboratory.

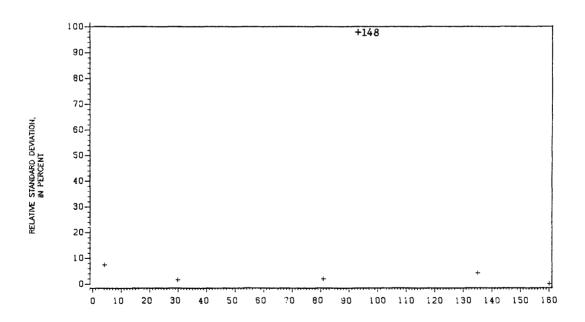
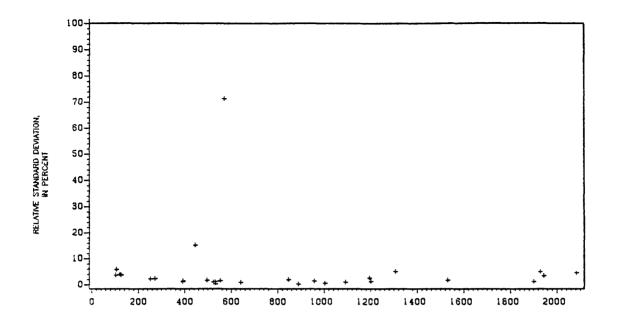


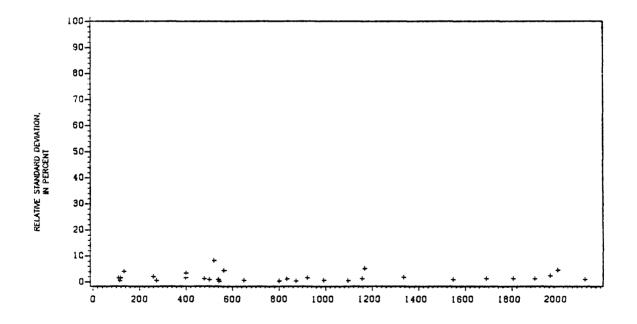
Figure 170.-- Precision data for sodium, dissolved (atomic absorption spectrometry), at the Denver laboratory.

MEAN CONCENTRATION, IN MILLIGRAMS PER LITER



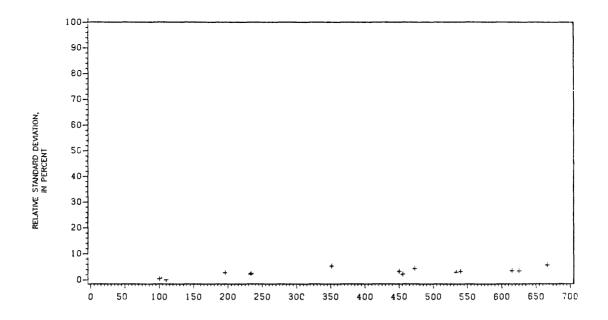
MEAN VALUE. IN MICROMHOS PER CENTIMETER AT 25° CELSIUS

Figure 171. -- Precision data for specific conductance at the Atlanta laboratory.



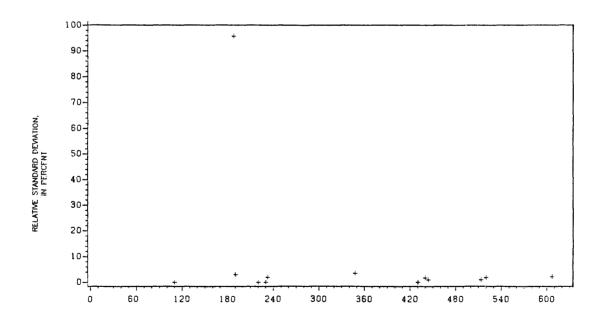
MEAN VALUE. IN MICROMHOS PER CENTIMETER AT 25° CELSIUS

Figure 172. — Precision data for specific conductance at the Denver laboratory.



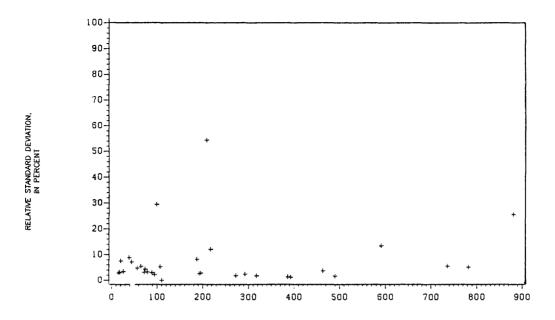
MEAN CONCENTRATION, IN MICROGRAMS PER LITER

Figure 173.-- Precision data for strontium, dissolved, at the Atlanta laboratory.



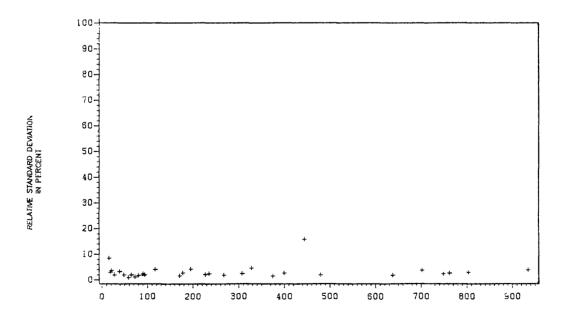
MEAN CONCENTRATION, IN MICROGRAMS PER LITER

Figure 174.— Precision data for strontium, dissolved, at the Denver laboratory.



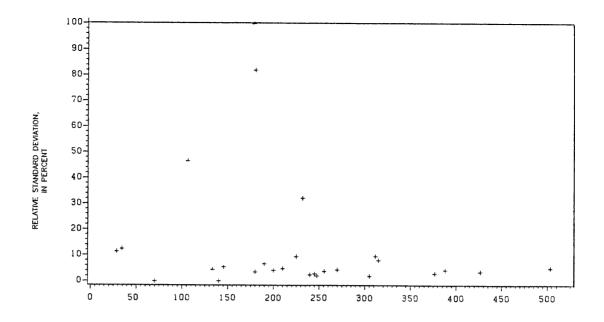
MERN CONCENTRATION. IN MILLIGRAMS PER LITER

Figure 175. -- Precision data for sulfate, dissolved, at the Atlanta laboratory.

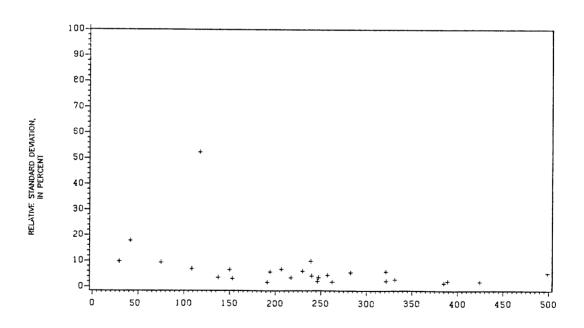


MEAN CONCENTRATION. IN MILLIGRAMS PER LITER

Figure 176.-- Precision data for sulfate, dissolved, at the Denver laboratory.

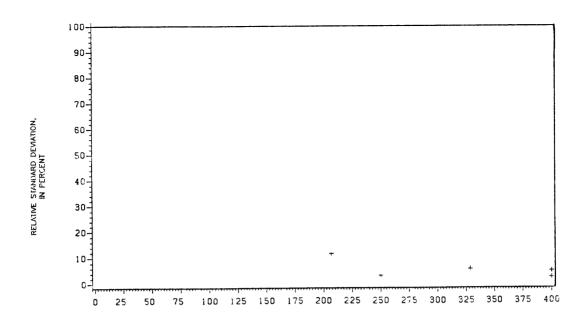


MEAN CONCENTRATION, IN MICROGRAMS PER LITER
Figure 177.-- Precision data for zinc, dissolved, at the Atlanta laboratory.



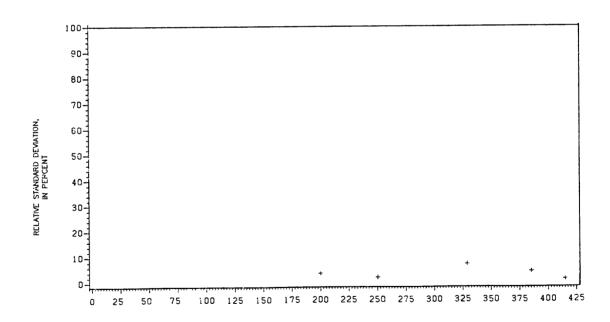
MEAN CONCENTRATION, IN MICROGRAMS PER LITER

Figure 178.-- Precision data for zinc, dissolved, at the Denver laboratory.



MEAN CONCENTRATION. IN MICROGRAMS PER LITES

Figure 179. -- Precision data for zinc, total recoverable, at the Atlanta laboratory.



MEAN CONCENTRATION. IN MICROGRAMS PER LITER

Figure 180.— Precision data for zinc, total recoverable, at the Denver laboratory.