QUALITY-ASSURANCE DATA FOR ROUTINE WATER ANALYSIS IN THE LABORATORIES OF THE U.S. GEOLOGICAL SURVEY FOR WATER-YEAR 1984

U.S. Geological Survey

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By Dale B. Peart and Hoyt B. Sutphin

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CONTENTS

FIGURES

Figures 1–214. Graphs showing: Page

Figures 1–214. Graphs showing--Continued:

Figures 1–214. Graphs showing--Continued: Page

TABLES

QUALITY-ASSURANCE DATA FROM ROUTINE WATER ANALYSIS IN THE LABORATORIES OF THE U.S. GEOLOGICAL SURVEY FOR WATER-YEAR 1984

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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, 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 1984 water year. Nutrient samples, simulated-precipitation (low-concentration level) samples, and selected pesticide samples also were submitted as samples of unknown concentrations. The results of these determinations were statistically analyzed for comparability and these data are presented.

An overall evaluation of the data for water year 1984 indicated a lack of precision in the Atlanta laboratory for the determination of five constituents and in the Denver laboratory for seven constituents. A biased condition existed in the determination of twenty common constituents at both laboratories. Finally, if any constituent determined by ICP indicated bias, it tended to be positive.

INTRODUCTION

The water-quality laboratories of the U.S. Geological Survey, located in Atlanta, Georgia, and Denver, Colorado, routinely analyze water, suspended sediment, streambed and lakebed 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, 1984) document results from February 1981 through September 1983.

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 in order 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 reported for one, actually belong to the other, the collecting office usually 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 figures show that an analytical process has been in statistical control for the majority of the

year, but out of statistical control for a period long enough so that the statistical tests applied indicated lack of precision or significant bias 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 1984 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 solids (residue on evaporation), fluoride, iron, lead, lithium, magnesium, manganese, molybdenum, nickel, potassium, selenium, silica, silver, sodium, strontium, sulfate, and zinc.

Nutrients--ammonia; ammonia plus organic nitrogen; carbon organic dissolved; carbon organic, total; nitrite plus nitrate; orthophosphate; and phosphorus.

Physical property--specific conductance.

Property and constituents in simulated-precipitation samples--specific conductance and minute concentrations of: ammonia, bromide, calcium, chloride, fluoride, magnesium, nitrate, orthophosphate, phosphorous, potassium, sodium, and sulfate.

Pesticides--organophosphate and organochlorine insecticides and chlorophenoxyacid herbicides.

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 because of 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 environmental 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, 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. Simulated-precipitation and pesticide samples were submitted once each week.

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, undergoing the normal 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 will 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 obvious which corrective measures were appropriate, so that the laboratories' data were preserved as they produced them. 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.

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 conductance values less than 2,100 µS/cm (microsiemens 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 markedly different specific conductance values 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 obtained 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 statistically in or out of control. The standard deviations are specific to the analytical methods used in the two subject laboratories and are documented in Friedman and Fishman (in press). 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 of these constituents 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 µg/L (micrograms per liter) is set to 7.5 µg/L; the minimum standard deviation for silver, reported to the nearest 1 µg/L, is 0.75 µg/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 108 in the Supplemental Data section at the back of this report. Three symbols are used in 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 28.2 µg/L (figs. 31 and 32) and still allow a value to be reported to the nearest 10 µg/L (for example, 30 µg/L) which is greater than the maximum MPV. 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 standard deviations), 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 statistically in or out of control. Figures 1-108 represent control charts.

Calculation of means and relative standard deviations (Miller and Freund, 1977) were made for each major constituent with sufficient data. 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 109 through 214 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. For example, the precision of the alkalinity values from the Atlanta laboratory are estimated from figure 109 to be ±2 percent. The precision of the alkalinity values from the Denver laboratory are estimated from figure 110 to be ±5 percent.

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-grade chemicals in the Ocala facility. Preparation methods used for these samples are virtually the same as those used for preparing samples for the SRWS program. Simulated-precipitation samples were either SRWS prepared with minute constituent concentrations or were regular SRWS that were diluted so that the constituent concentrations were similar to those in natural precipitation. 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-percent confidence level.

To determine a measure of comparability between the two laboratories for nutrient, simulated-precipitation, and pesticide samples, the analytical 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.

COMPARISON OF STATISTICAL DATA FOR INORGANIC-CONSTITUENT SAMPLES BETWEEN LABORATORIES

Initially, 1984 water-year data were presented statistically in four unpublished reports for the following periods: October 1-December 31, 1983; January 1-March 31, 1984; April 1-June 30, 1984; and July

1–September 30, 1984. Results of binomial–distribution tests for these four periods, as well as overall results for the year, are presented in tables 1 through 4.

Precision

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

Iron, total recoverable, failed the precision criteria three out of four quarters in the Atlanta laboratory. Barium inductively coupled plasma emission spectroscopy (ICP), dissolved solids, and molybdenum atomic–absorption spectrometry (AA) failed the precision criteria two out of four quarters in the Atlanta laboratory. Barium (ICP), lead (AA), molybdenum (AA), and selenium failed the precision criteria two out of four quarters in the Denver laboratory. Iron, total recoverable had recurring LOP problems in the Atlanta laboratory during water years 1982 and 1983 (Peart and Thomas, 1983b, 1984). Dissolved solids had recurring LOP problems in the Atlanta laboratory during water year 1983.

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

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

Constituent (dissolved except as indicated) or property	Oct.–Dec. 1983	Jan.–Mar. 1984	Apr.–Jun. 1984	Jul.–Sep. 1984	Summary Oct. 1983–Sep. 1984
Alkalinity	+	+	+	+	+
Aluminum	+	+	+	+	+
Antimony	+	+	+	+	+
Arsenic	+	+	+	+	+
Barium (ICP)	LOP	LOP	+	+	LOP
Barium (AA)	+	+	+	+	+
Barium, total recoverable	+	+	+	+	+
Beryllium	+	+	+	+	+
Boron	+	+	+	+	+
Cadmium (ICP)	+	+	+	+	+
Cadmium (AA)	+	+	+	+	+
Cadmium, total recoverable	+	+	+	+	+
Calcium (ICP)	+	+	+	+	+
Calcium (AA)	+	+	+	+	+
Chloride	+	+	+	+	+
Chromium	+	+	+	+	+
Chromium, total recoverable	+	LOP	+	+	LOP
Cobalt (ICP)	+	+	+	+	+
Cobalt (AA)	+	+	+	+	+
Cobalt, total recoverable	+	+	+	+	+
Copper (ICP)	+	+	+	+	+
Copper (AA)	+	+	+	+	+
Copper, total recoverable	+	+	+	+	+
Dissolved solids	+	+	LOP	LOP	LOP

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) or property	Oct.-Dec. 1983	Jan.-Mar. 1984	Apr.-Jun. 1984	Jul.-Sep. 1984	Summary Oct. 1983-Sep. 1984
Fluoride	+	LOP	+	+	+
Iron (ICP)	+	+	+	+	+
Iron (AA)	+	+	+	+	+
Iron, total recoverable	+	LOP	LOP	LOP	LOP
Lead (ICP)	+	+	+	+	+
Lead (AA)	+	+	+	LOP	+
Lead, total recoverable	LOP	+	+	+	+
Lithium	+	+	+	+	+
Magnesium (ICP)	+	+	+	+	+
Magnesium (AA)	+	+	+	+	+
Manganese (ICP)	+	+	+	+	+
Manganese (AA)	+	+	+	+	+
Manganese, total recoverable	+	+	+	+	+
Molybdenum (ICP)	+	+	+	+	+
Molybdenum (AA)	+	LOP	+	LOP	LOP
Nickel	+	+	+	+	+
Nickel, total recoverable	+	+	+	+	+
Potassium	+	+	+	+	+
Selenium	+	+	+	LOP	+
Silica	+	+	+	+	+
Silver	+	+	+	+	+
Silver, total recoverable	+	+	+	+	+
Sodium (ICP)	+	+	+	+	+
Sodium (AA)	+	+	+	+	+
Specific conductance	+	+	+	+	+
Strontium	+	+	+	+	+
Sulfate	+	+	+	+	+
Zinc (ICP)	+	+	+	LOP	+
Zinc (AA)	+	+	+	+	+
Zinc, total recoverable	+	+	+	+	+

When the data were evaluated as a whole for the year, barium (ICP); chromium, total recoverable; dissolved solids; iron, total recoverable and molybdenum (AA) indicated LOP in the Atlanta laboratory. Barium (ICP); copper, total recoverable; iron (AA); lead (AA); lead, total recoverable; molybdenum (AA); and nickel, total recoverable indicated LOP in the Denver laboratory.

For constituents that were determined as both dissolved (including ICP and AA) and total recoverable for identical samples, the total recoverable determinations failed the precision criteria with about the same frequency as the dissolved determinations in both the Atlanta and the Denver laboratories. These results indicate sustained improvement since water year 1982 (Peart and Thomas, 1983b). During that time, the total recoverable determinations failed the precision test twice as often as the dissolved determinations in the Atlanta laboratory, and five times as often as the dissolved determinations in the Denver laboratory.

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

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

Constituent (dissolved except as indicated) or property	Oct.-Dec. 1983	Jan.-Mar. 1984	Apr.-Jun. 1984	Jul.-Sep. 1984	Summary Oct. 1983-Sep. 1984
Alkalinity	+	+	+	+	+
Aluminum	+	+	+	+	+
Antimony	+	+	+	+	+
Arsenic	+	+	+	+	+
Barium (ICP)	LOP	+	LOP	+	LOP
Barium (AA)	+	+	+	+	+
Barium, total recoverable	+	+	+	+	+
Beryllium	+	+	+	+	+
Boron	+	+	+	+	+
Cadmium (ICP)	+	+	+	+	+
Cadmium (AA)	+	+	+	+	+
Cadmium, total recoverable	+	+	+	+	+
Calcium (ICP)	+	+	+	+	+
Calcium (AA)	LOP	+	+	+	+
Chloride	+	+	+	+	+
Chromium	+	+	+	+	+
Chromium, total recoverable	+	+	+	+	+
Cobalt (ICP)	+	+	+	+	+
Cobalt (AA)	+	+	+	+	+
Cobalt, total recoverable	+	+	+	+	+
Copper (ICP)	LOP	+	+	+	+
Copper (AA)	+	+	+	+	+
Copper, total recoverable	LOP	+	+	+	LOP
Dissolved solids	+	+	+	+	+
Fluoride	+	+	+	+	+
Iron (ICP)	+	+	+	+	+
Iron (AA)	+	+	+	+	LOP
Iron, total recoverable	+	+	+	+	+
Lead (ICP)	+	+	+	+	+
Lead (AA)	+	LOP	LOP	+	LOP
Lead, total recoverable	+	+	LOP	+	LOP
Lithium	+	+	+	+	+
Magnesium (ICP)	+	+	+	+	+
Magnesium (AA)	+	+	+	+	+
Manganese (ICP)	+	+	+	+	+
Manganese (AA)	+	+	+	+	+
Manganese, total recoverable	+	+	+	LOP	+
Molybdenum (ICP)	+	+	+	+	+
Molybdenum (AA)	LOP	+	+	LOP	LOP
Nickel	+	+	+	+	+

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 as indicated) or property	Oct.-Dec. 1983	Jan.-Mar. 1984	Apr.-Jun. 1984	Jul.-Sep. 1984	Summary Oct. 1983-Sep. 1984
Nickel, total recoverable	+	+	LOP	+	LOP
Potassium	+	+	+	+	+
Selenium	+	+	LOP	LOP	+
Silica	+	+	+	+	+
Silver	+	+	+	+	+
Silver, total recoverable	+	+	+	+	+
Sodium (ICP)	+	+	+	+	+
Sodium (AA)	LOP	+	+	+	+
Specific conductance	+	+	+	+	+
Strontium	+	+	+	+	+
Sulfate	+	+	+	+	+
Zinc (ICP)	+	+	+	+	+
Zinc (AA)	+	+	+	+	+
Zinc, total recoverable	LOP	+	+	+	+

Sodium determined by ICP in the Atlanta laboratory during water year 1984 consistently had acceptable results. This was a great improvement compared to water years 1982-83 when the constituent consistently indicated lack of precision (Peart and Thomas, 1983b, 1984). Analyses for aluminum also improved at the Atlanta laboratory. During water year 1984, the laboratory produced consistently acceptable results, whereas, for water year 1983, the laboratory produced acceptable results for only one of the four quarters. Analyses for silver improved markedly at both laboratories; results for all four quarters of water year 1984 were acceptable. During the previous water year, silver had a lack of precision for three out of the four quarters at the Atlanta laboratory, and for two out of the four quarters at the Denver laboratory.

Bias

Results of the statistical tests for bias are shown in tables 3 and 4. Using the method described previously, it was not possible to determine bias where results from less than eight samples were available. This situation occurred for antimony at both laboratories throughout the year.

The number of constituents at each laboratory showing bias is higher this year than for 1983. Arsenic, boron, nickel, and potassium indicated a negative bias for all four quarters at the Atlanta laboratory; chloride and specific conductance indicated a positive bias for all four quarters. Lead (ICP) showed positive bias for three of the four quarters of the year. Alkalinity, dissolved solids, iron (both ICP and total recoverable), selenium, sodium (ICP), sulfate, and zinc (ICP) had a positive bias for two of the four quarters. No constituents showed negative bias for two of the four quarters.

The bias results for nickel and potassium at the Atlanta laboratory during water year 1984 were similar to those for the two previous water years, although results for both constituents had more bias during water year 1984. The consistent negative bias for arsenic was a marked contrast to the acceptable bias results for water year 1983 (Peart and Thomas, 1984). Bias for alkalinity and specific conductance were the same as those for the previous water year. Several of the constituents showing positive bias for one-half of the year had acceptable results for the previous water year.

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

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

Constituent (dissolved except as indicated) or property	Oct.–Dec. 1983	Jan.–Mar. 1984	Apr.–Jun. 1984	Jul.–Sep. 1984	Summary Oct. 1983–Sep. 1984
Alkalinity	P	P	+	+	P
Aluminum	N	+	+	+	N
Antimony	*	*	*	*	+
Arsenic	N	N	N	N	N
Barium (ICP)	+	P	+	+	+
Barium (AA)	+	+	+	+	+
Barium, total	N	+	+	+	+
Beryllium	+	+	+	+	+
Boron	N	N	N	N	N
Cadmium (ICP)	+	+	+	+	+
Cadmium (AA)	+	+	+	+	+
Cadmium, total recoverable	+	+	+	+	+
Calcium (ICP)	P	+	+	+	+
Calcium (AA)	+	+	+	+	+
Chloride	P	P	P	P	P
Cobalt(ICP	+	+	+	+	+
Cobalt (AA)	+	+	+	+	+
Cobalt, total recoverable	+	+	+	+	+
Copper (ICP)	+	+	+	+	+
Copper (AA)	+	+	+	+	+
Copper, total recoverable	+	+	+	+	+
Dissolved solids	+	+	P	P	P
Fluoride	+	+	+	+	P
Iron (ICP)	P	+	P	+	P
Iron (AA)	+	+	+	+	+
Iron, total recoverable	+	P	+	P	P
Lead (ICP)	P	P	P	+	P
Lead (AA)	+	+	+	+	+
Lead, total recoverable	+	+	+	+	+
Lithium	+	+	+	+	+
Magnesium (ICP)	P	+	+	N	+
Magnesium (AA)	+	+	+	+	+
Manganese (ICP)	+	P	+	+	P
Manganese (AA)	+	+	+	+	+
Manganese, total recoverable	+	+	+	+	+
Molybdenum (ICP)	+	+	P	N	+
Molybdenum (AA)	+	+	+	+	+
Nickel	N	N	N	N	N
Nickel, total	N	+	+	+	N
Potassium	N	N	N	N	N

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) or property	Oct.-Dec. 1983	Jan.-Mar. 1984	Apr.-Jun. 1984	Jul.-Sep. 1984	Summary Oct. 1983-Sep. 1984
Selenium	+	+	P	P	P
Silica	P	+	+	+	P
Silver	+	+	+	+	+
Silver, total recoverable	+	+	+	+	+
Sodium (ICP)	P	P	+	+	P
Sodium (AA)	+	+	P	+	+
Specific conductance	P	P	P	P	P
Strontium	+	+	+	P	P
Sulfate	P	P	+	+	P
Zinc (ICP)	+	P	P	+	P
Zinc (AA)	+	N	+	+	+
Zinc, total recoverable	+	+	+	+	+

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

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

Constituent (dissolved except as indicated) or property	Oct.-Dec. 1983	Jan.-Mar. 1984	Apr.-Jun. 1984	Jul.-Sep. 1984	Summary Oct. 1983-Sep. 1984
Alkalinity	P	P	+	+	P
Aluminum	N	N	N	+	N
Antimony	*	*	*	*	+
Arsenic	N	N	N	N	N
Barium (ICP)	N	+	N	N	N
Barium (AA)	N	P	+	+	+
Barium, total recoverable	+	P	+	+	+
Beryllium	+	+	+	+	P
Boron	N	N	N	N	N
Cadmium (ICP)	+	+	+	+	+
Cadmium (AA)	+	N	+	+	+
Cadmium, total recoverable	+	+	+	+	+
Calcium (ICP)	+	+	+	+	+
Calcium (AA)	+	+	+	N	+
Chloride	P	P	+	+	P
Chromium	+	P	P	+	P
Chromium, total recoverable	+	P	+	+	P
Cobalt (ICP)	+	+	+	+	+

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

Constituent (dissolved except as indicated) or property	Oct.–Dec. 1983	Jan.–Mar. 1984	Apr.–Jun. 1984	Jul.–Sep. 1984	Summary Oct. 1983–Sep. 1984
Cobalt (AA)	N	+	+	+	N
Cobalt, total recoverable	N	+	+	+	N
Copper (ICP)	+	+	+	P	+
Copper (AA)	+	+	+	P	+
Copper, total recoverable	P	+	P	+	P
Dissolved solids	+	N	+	N	N
Fluoride	P	P	P	P	P
Iron (ICP)	+	+	+	P	+
Iron (AA)	P	P	P	+	P
Iron, total recoverable	P	P	P	+	P
Lead (ICP)	P	P	P	P	P
Lead (AA)	+	+	+	+	+
Lead, total recoverable	+	+	+	+	+
Lithium	+	+	+	+	+
Magnesium (ICP)	+	P	P	P	P
Magnesium (AA)	+	+	N	+	+
Manganese (ICP)	+	+	N	+	N
Manganese (AA)	+	+	+	+	+
Manganese, total recoverable	N	+	+	+	+
Molybdenum (ICP)	+	+	P	+	+
Molybdenum (AA)	N	+	N	N	N
Nickel	+	N	N	N	N
Nickel, total recoverable	+	*	+	+	P
Potassium	+	N	N	+	N
Selenium	P	+	+	+	P
Silica	P	P	P	+	P
Silver	+	N	+	N	N
Silver, total recoverable	+	+	+	+	N
Sodium (ICP)	P	P	P	P	P
Sodium (AA)	+	+	+	+	P
Specific conductance	+	P	P	P	P
Strontium	+	+	+	+	+
Sulfate	P	P	P	P	P
Zinc (ICP)	+	P	P	+	P
Zinc (AA)	+	P	P	+	P
Zinc, total recoverable	P	P	*	+	P

For the Denver laboratory during water year 1984, arsenic and boron had a negative bias, and fluoride, lead (ICP), sodium (ICP), and sulfate had a positive bias for all four quarters. Aluminum; barium (ICP); molybdenum (AA); and nickel indicated negative bias for three of the four quarters; whereas iron (AA); iron, total recoverable; magnesium (ICP); silica; and specific conductance showed positive bias for three of the four quarters. Dissolved solids, potassium, and silver were negatively biased for two of the four quarters. Alkalinity; chloride; chromium; copper, total recoverable; zinc (ICP); zinc (AA); and zinc, total recoverable were positively biased for two of the four quarters.

For the Denver laboratory, negatively biased constituents, consistent with results for water year 1984, were: barium (ICP), boron, dissolved solids, molybdenum, nickel, potassium, and silver.Additional constituents with negative bias that indicated none during the previous water year were aluminum and arsenic.Positively biased constituents consistent with data for water year 1983 were: alkalinity, fluoride, iron, sodium (ICP), specific conductance, sulfate, and zinc. Additional positively biased constituents that indicated no or little bias during water year 1984 were: copper, total recoverable; iron, total recoverable; lead (ICP); magnesium (ICP); silica; and zinc, total recoverable.

There were no predominant patterns for bias between dissolved versus total recoverable analyses for either laboratory. However, there were some patterns for bias between ICP and AA determinations. Bias for ICP determinations were similar for the two laboratories. Combined, 39 constituents determined by ICP had bias, only 7 of which were negatively biased. Thus, a constituent determined by ICP had bias, it tended to be positive. There were only 2 constituents determined by AA at the Atlanta laboratory that indicated bias during any quarter compared to 14 at the Denver laboratory.

When the data for the entire year from the Atlanta laboratory were considered, alkalinity; chloride; chromium, total recoverable; dissolved solids; fluoride; iron (ICP); iron, total recoverable; lead (ICP); manganese (ICP); selenium; silica; sodium (ICP); specific conductance; strontium; sulfate and zinc (ICP) indicated significant positive bias, whereas aluminum; arsenic; boron; nickel; nickel, total recoverable; and potassium indicated negative bias. For the Denver laboratory, the following indicated significant positive bias: alkalinity; beryllium; chloride; chromium; chromium, total recoverable; copper, total recoverable; fluoride; iron (AA); iron, total recoverable; lead (ICP); magnesium (ICP); nickel, total recoverable; selenium; silica; sodium (ICP); sodium (AA); specific conductance; sulfate; zinc (ICP); zinc (AA); zinc, total recoverable. For the Denver laboratory, the following indicated significant negative bias: aluminum; arsenic; barium (ICP); boron; cobalt; cobalt, total recoverable; dissolved solids; manganese (ICP); molybdenum (AA); nickel; potassium; silver and silver, total recoverable.

Because the Denver laboratory has many more constituents with persistent bias than the Atlanta laboratory, it seems unlikely that the problems related to bias are inherent in the methods used for determination of these constituents, except where that bias is persistent in both laboratories. Given the recurrence data presented previously, a biased condition exists for alkalinity, potassium, sodium (ICP), and specific conductance; that is, only these three constituents and specific conductance have failed the bias test consistently on a recurring basis for the past 2 years in both laboratories.

Several factors may be involved where other constituents indicate 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.

COMPARISON OF STATISTICAL DATA FOR NUTRIENT, SIMULATED–PRECIPITATION, AND PESTICIDE SAMPLES BETWEEN LABORATORIES

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

Table 5.--*Results of statistical evaluation for comparison of means for nutrient samples*

[A, no significant difference; --, insufficient data for determination]

Constituent	Oct.–Dec. 1983	Jan.–Mar. 1984	Apr.–Jun. 1984	Jul.–Sep. 1984	Summary Oct. 1983–Sep. 1984
Ammonia	A	A	A	A	A
Ammonia plus organic nitrogen	A	A	A	A	A
Carbon, organic dissolved	A	A	A	A	A
Carbon, organic total	--	--	--	--	A
Nitrite plus nitrate	A	A	A	A	A
Nitrite	A	A	A	A	A
Orthophosphate	A	A	A	A	A
Phosphorus	A	A	A	A	A

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

[A, no significant difference; B, significant difference; --, insufficient data for determination]

Constituent	Oct.–Dec. 1983	Jan.–Mar. 1984	Apr.–Jun. 1984	Jul.–Sep. 1984	Summary Oct. 1983–Sep. 1984
Ammonia	B	A	B	A	A
Ammonia plus organic nitrogen	A	B	B	A	B
Carbon, organic dissolved	A	A	A	A	A
Carbon, organic total	--	--	--	--	B
Nitrite plus nitrate	B	A	A	A	A
Nitrite	A	A	A	A	A
Orthophosphate	A	A	A	A	A
Phosphorus	A	A	A	A	A

Data for simulated–precipitation samples are summarized in table 7. No significant difference occurs in the mean values produced by the two laboratories for any constituents in this category except bromide and orthophosphate. The pesticide data in table 8 show that all constituents, with the exception of mirex, compare well between the laboratories.

Table 7.--*Results of statistical evaluation for comparison of means for simulated-precipitation samples*

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

Constituent	Comparison of means
Ammonia	A
Bromide	B
Calcium	A
Chloride	A
Fluoride	A
Magnesium	A
Nitrate,	A
Orthophosphate	B
Phosphorus	A
Potassium	A
Sodium	A
Specific conductance	A
Sulfate	A

Table 8.--*Results of statistical evaluation for comparison of means for pesticide samples*

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

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

SUMMARY AND CONCLUSIONS

Reference samples with known MPV are disguised as regular samples and submitted with environmental samples by selected offices of the U.S. Geological Survey to the two water-quality laboratories operated by the Survey, 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). Inorganic-constituent data then are analyzed statistically for precision and bias by using a binomial-probability-distribution equation. Analytical data for nutrient, simulated-precipitation, and pesticide samples are tested for comparability by using a modified Wilcoxon Rank-Sum test (Mann-Whitney test).

Recurring problems during the year with lack of precision existed in the Atlanta laboratory for barium (ICP); dissolved solids; iron, total recoverable; and molybdenum (AA). Similar problems existed in the Denver laboratory for barium (ICP); lead (AA); molybdenum (AA); nickel, dissolved total recoverable; selenium; and zinc, total recoverable. Dissolved solids and iron, total recoverable, also had recurring problems with lack of precision in the Atlanta laboratory during water year 1982. In the Denver laboratory, total recoverable zinc had recurring problems with lack of precision for both water years 1983 and 1984.

An overall evaluation of the data for water year 1984 indicates a lack of precision in the Atlanta laboratory for barium (ICP); chromium, total recoverable; dissolved solids; iron, total recoverable; and molybdenum (AA). Similar problems existed in the Denver laboratory for barium (ICP); copper, total recoverable; iron (AA); lead (AA); lead, total recoverable; molybdenum (AA); nickel, total recoverable.

Significant bias recurred during water year 1984 in the Atlanta laboratory for alkalinity, arsenic; boron; chloride; dissolved solids; iron (ICP) and total recoverable; lead (ICP); magnesium (ICP); manganese (ICP); molybdenum (ICP); nickel; potassium; selenium; sodium (ICP); specific conductance; sulfate; and zinc (ICP). Similar problems existed in the Denver laboratory for alkalinity; aluminum; arsenic; barium (ICP) and (AA); boron; chloride; chromium; copper, total recoverable; dissolved solids; fluoride; iron (AA) and total recoverable; lead (ICP); magnesium (ICP); molybdenum (AA); nickel; potassium; silica; silver; sodium (ICP); specific conductance; sulfate; and zinc (AA) and total recoverable. Both nickel and potassium also had similar recurring bias during water years 1982 and 1983 in the Atlanta laboratory. Recurring bias during water year 1983 also occurred for alkalinity; manganese; sodium (ICP); and specific conductance. Recurring bias in the Denver laboratory since water year 1982 occurred for barium; dissolved solids; fluoride; molybdenum; silver; sodium (ICP); specific conductance; and zinc. Alkalinity, iron (AA), potassium, and sulfate had recurring bias for water year 1983 in the Denver laboratory. In contrast to results for water year 1983, in which no constituents indicated bias in both laboratories for the two previous water years (Peart and Thomas, 1984), results for water year 1984 indicate that alkalinity, potassium, sodium (ICP) and specific conductance had biased results for the past 2 years in both laboratories.

An overall evaluation of the data for water year 1984 indicates a significant bias in the Atlanta laboratory for alkalinity; aluminum; arsenic; boron; chloride; chromium, total recoverable; dissolved solids; fluoride; iron (ICP); iron, total recoverable; lead (ICP); manganese (ICP); nickel, dissolved; nickel, total recoverable; potassium; selenium; silica; sodium (ICP); specific conductance; strontium; sulfate; and zinc (ICP). The yearly evaluation of data from the Denver laboratory indicates that almost two-thirds of the constituents had significant bias. Those constituents with overall acceptable results were: antimony; barium (AA); barium, total recoverable; all cadmium; all calcium; cobalt (ICP); copper (ICP); copper (AA); iron (ICP); lead (AA); lead, total recoverable; lithium; magnesium (AA); manganese (AA); manganese, total recoverable; molybdenum (ICP) and strontium.

Both laboratories performed similarly for all constituents in nutrient samples, except ammonia plus organic nitrogen and total organic carbon for which the standard deviations were significantly different.

Both laboratories performed comparably for constituents in simulated–precipitation samples, except for bromide and orthophosphate, which indicated a significant difference in the means. Both laboratories performed comparably for constituents in pesticide samples with the exception of mirex for which the means were significantly different.

REFERENCES

American Society for Testing and Materials, 1980, Annual book of ASTM standards, part 41: Philadelphia, p. 206–232.

Crawford, C.G., Slack, J.R. and Hirsch, R.M., 1983, Non–parametric tests for trends in water–quality data using the statistical analysis system: U.S. Geological Survey Open–File Report 83–550, 102 p.

Friedman, L.C., Bradford, W.L., and Peart, D.B., 1983, Application of binomial distributions to quality–assurance of quantitative chemical analyses: Journal of Environmental Science and Health, v. A18, no. 4, p.561–570.

Friedman, L.C., and Fishman, M.J., in press, Evaluation of methods used from 1965 through 1982 to determine inorganic constituents in water samples: U.S. Geological Survey Water–Supply Paper 2293.

Keith, L.H., and Telliard, W.A., 1979, Priority pollutants, I. a perspective view: Environmental Science and Technology, v. 13 no. 4, p. 416–423.

Miller, I. and Freund, J., 1977, Probability and Statistics for Engineers, 2 ed.: Prentice–Hall, Inc., Englewood Cliffs, New Jersey, 529 p.

Peart, D.B., and Thomas, Nancy, 1983a; Quality–assurance data for routine water analysis in the laboratories of the U.S. Geological Survey––1981 annual report:U.S. Geological Survey Water–Resources Investigations Report 83–4090, 137 p.

—————— 1983b, Quality–assurance data for routine water analysis in the laboratories of the U.S. Geological Survey for water year 1982: U.S. Geological Survey Water Resources Investigations Report 83–4262, 112 p.

—————— 1984, Quality–assurance data for routine water analysis in the laboratories of the U.S. Geological Survey for water year 1983; U.S. Geological Survey Water Resources Investigations Report 84–4234, 112 p.

Schroder, L.J., Fishman, M.J., Friedman, L.C., and Darlington, G.W., 1980, The use of standard reference water samples by the U.S. Geological Survey: U.S. Geological Survey Open File Report 80–738, 11 p.

Skougstad, M.W., and Fishman, M.J., 1975,Standard reference water samples: American Water Works Association Water Quality Technology Conference, Dallas, 1974, Proceedings, p. XIX–1 –XIX–6.

Skougstad, M.W., Fishman, M.J., Friedman, L.C., Erdmann, D.E., and Duncan, S.S., eds., 1979, Methods for determination of inorganic substances in water and fluvial sediment:U.S. Geological Survey Techniques of Water–Resources Investigations, Book 5, Chapter A1, p. 21–22.

SUPPLEMENTAL DATA

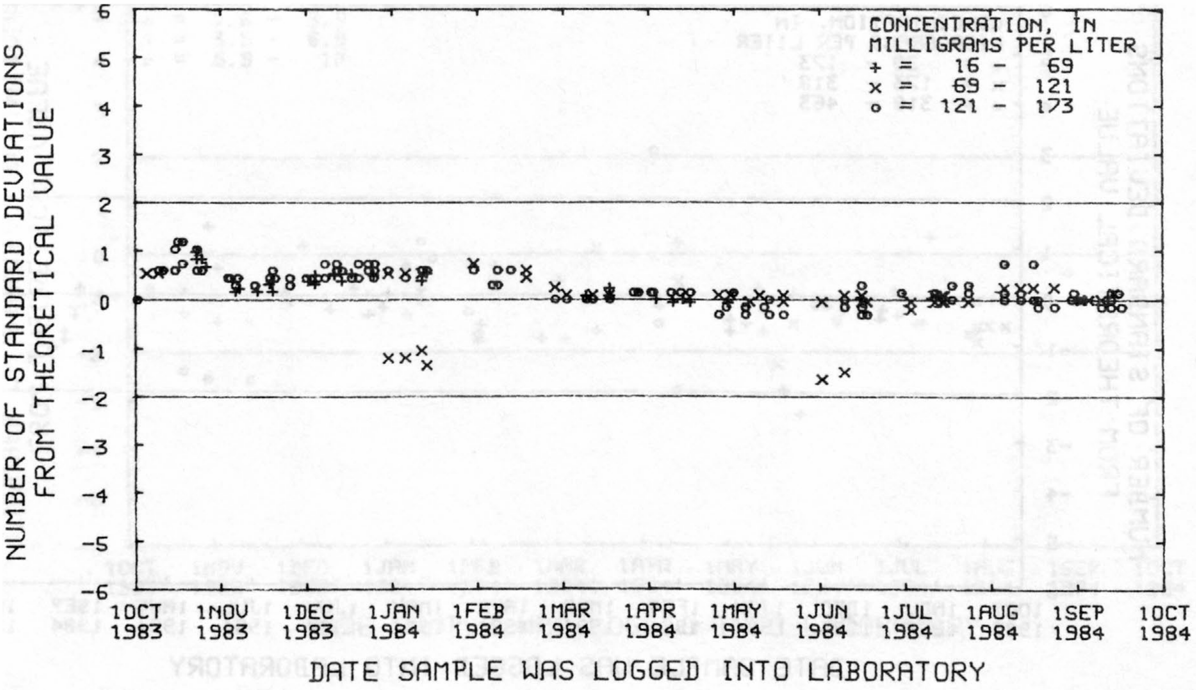

Figure 1--Alkalinity, dissolved, data from Atlanta laboratory.

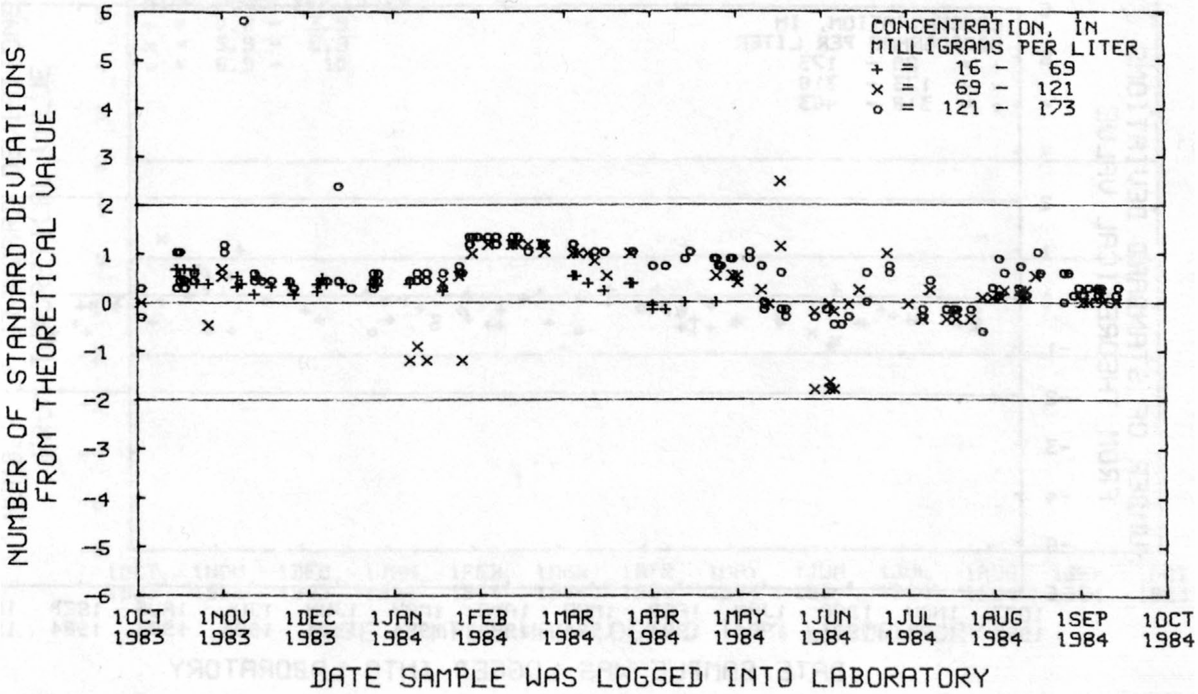

Figure 2--Alkalinity, dissolved, data from Denver laboratory.

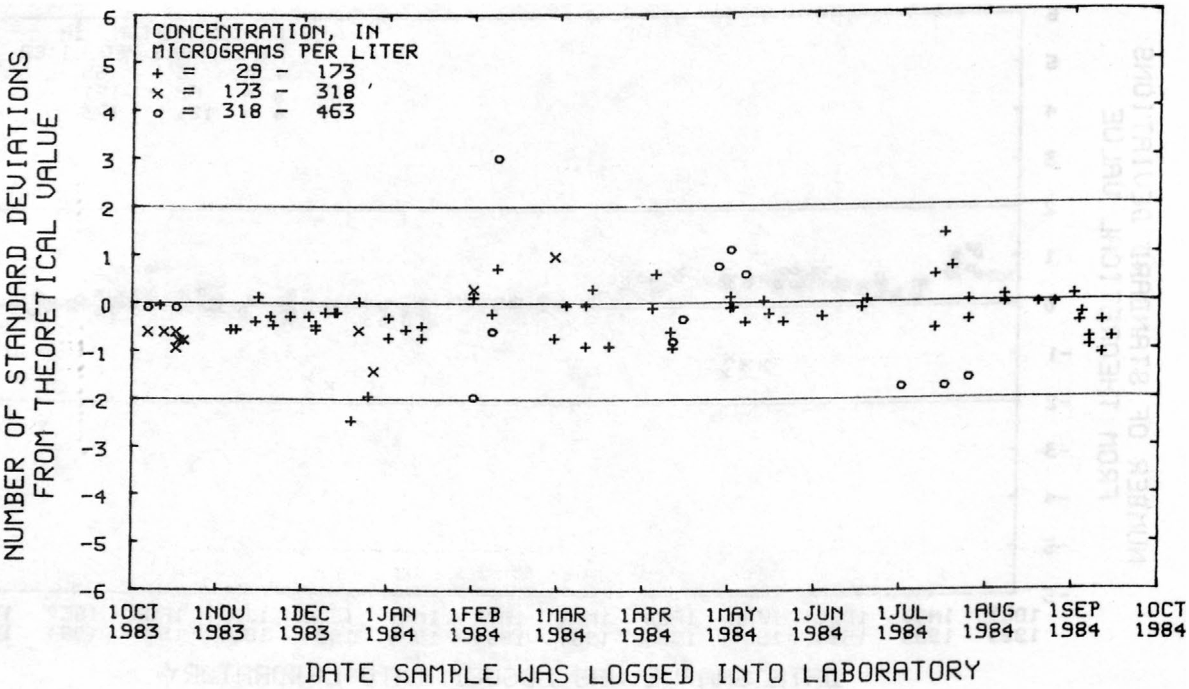

Figure 3--Aluminum, dissolved, data for the Atlanta laboratory.

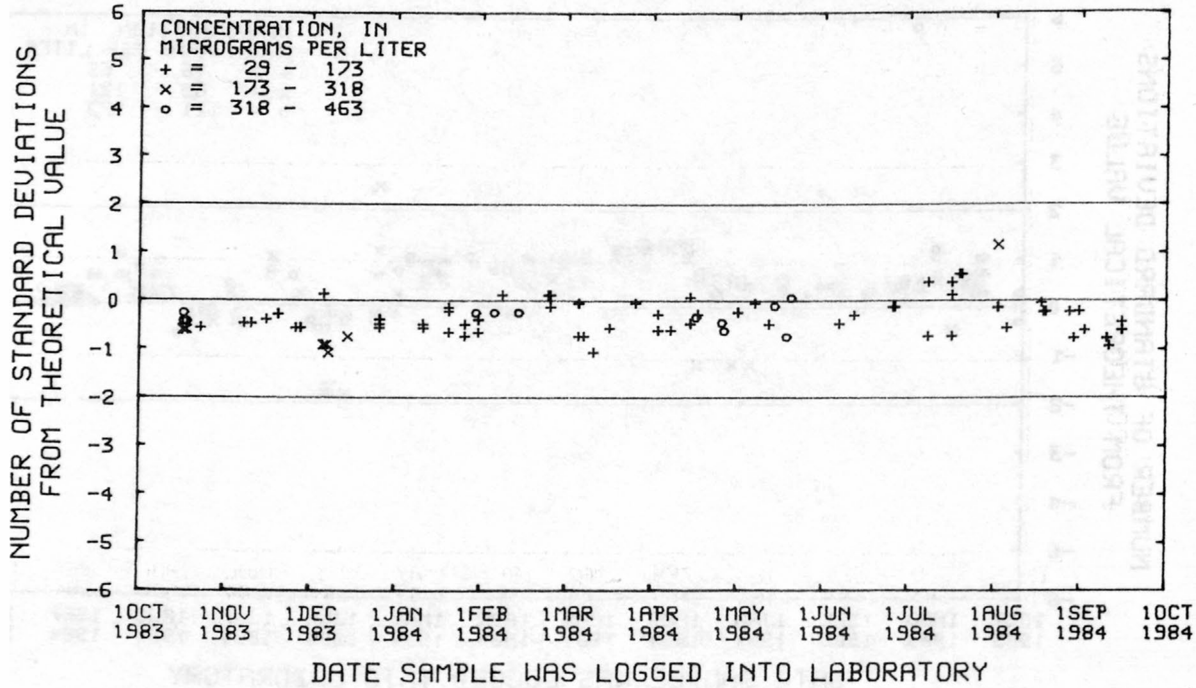

Figure 4--Aluminum, dissolved, data for the Denver laboratory.

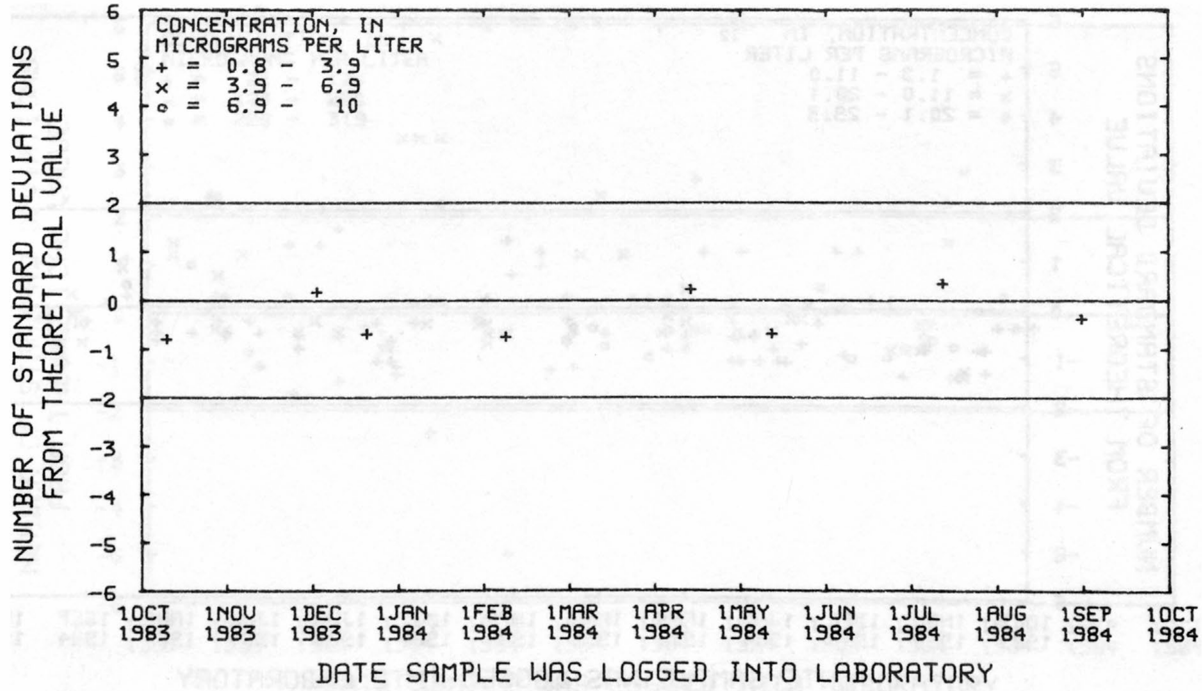

Figure 5--Antimony, dissolved, data for the Atlanta laboratory.

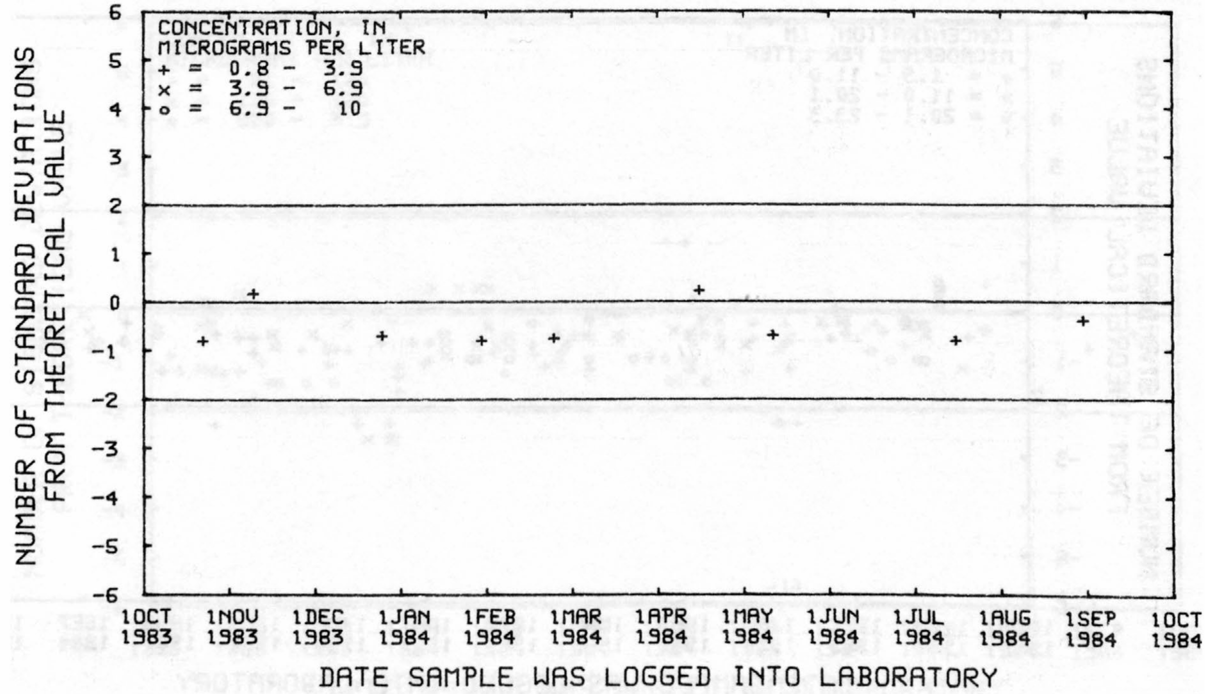

Figure 6--Antimony, dissolved, data for the Denver laboratory.

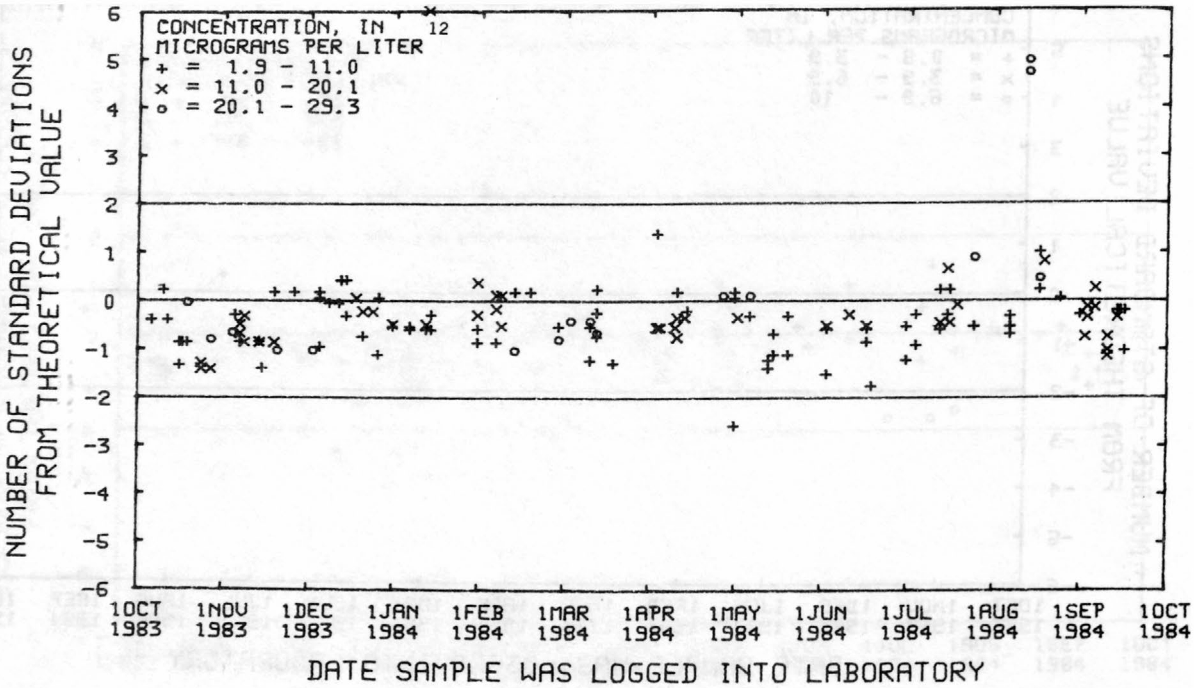

Figure 7--Arsenic, dissolved, data for the Atlanta laboratory.

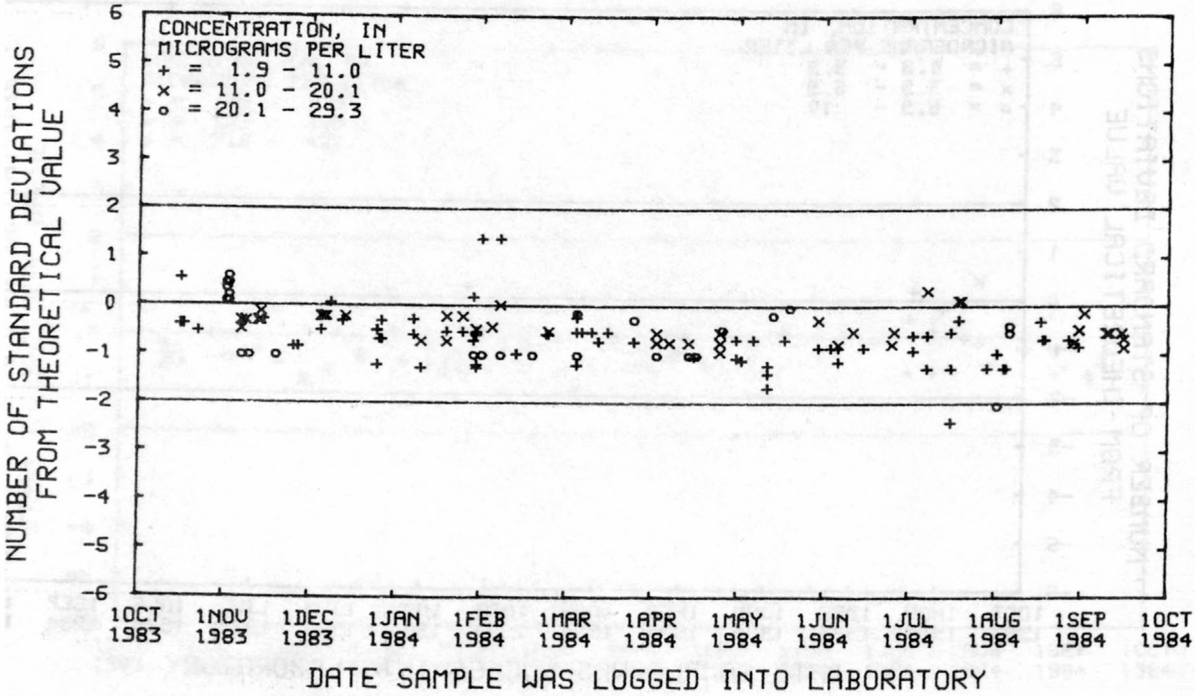

Figure 8--Arsenic, dissolved, data for the Denver laboratory.

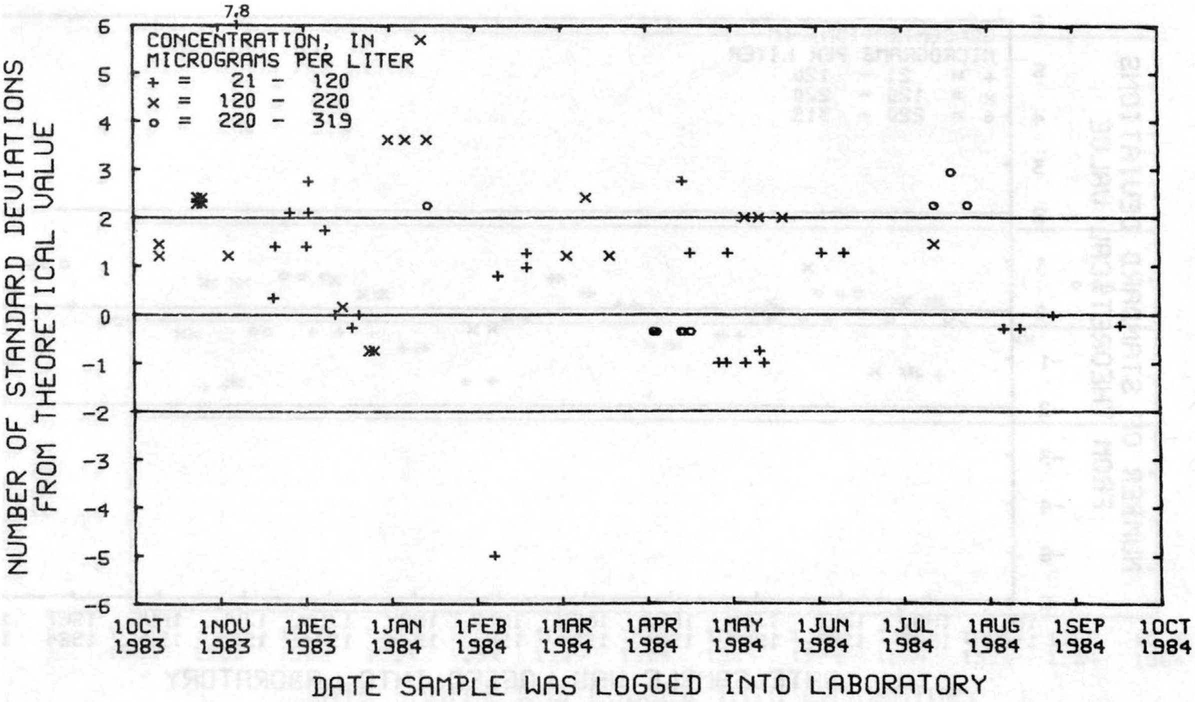

Figure 9--Barium, dissolved,
(inductively coupled plasma emission spectrometry)
data for the Atlanta laboratory.

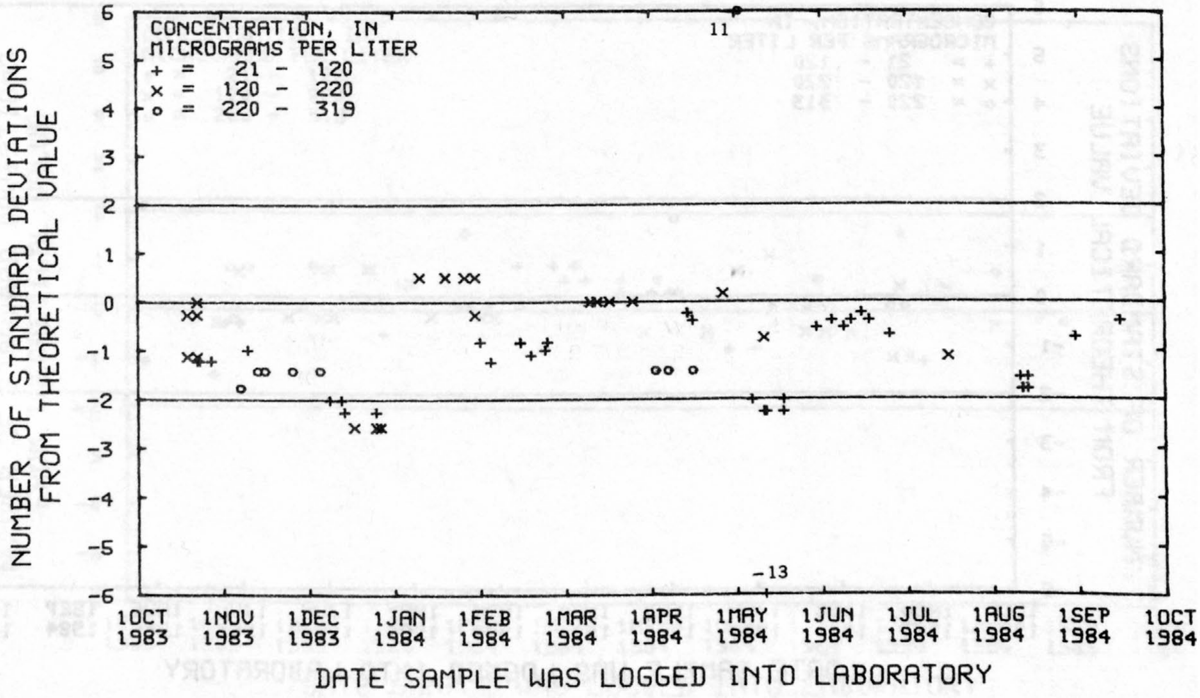

Figure 10--Barium, dissolved,
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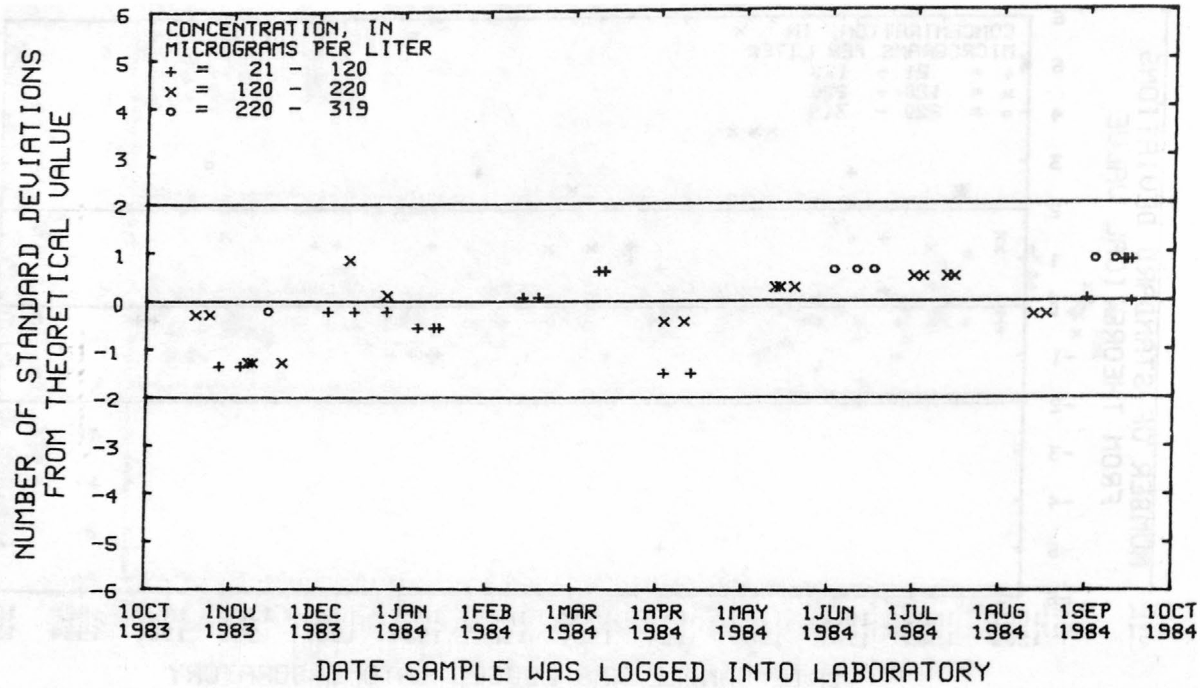

Figure 11--Barium, dissolved, (atomic absorption spectrometry) data for the Atlanta laboratory.

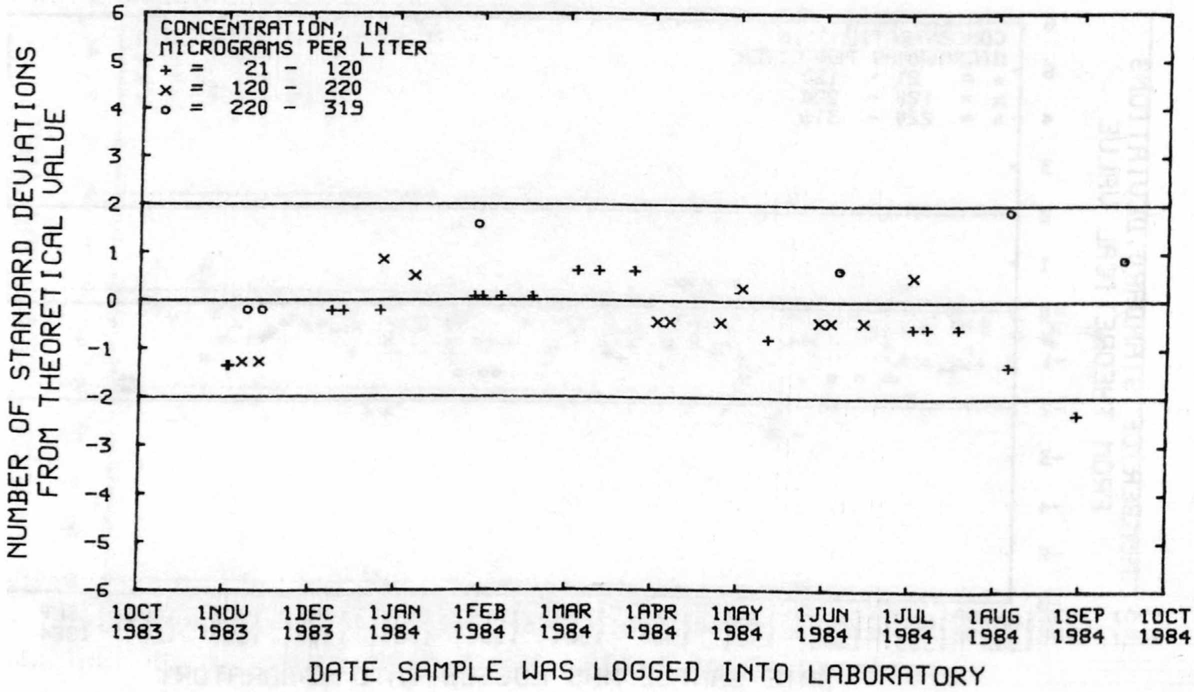

Figure 12--Barium, dissolved, (atomic absorption spectrometry) data for the Denver laboratory.

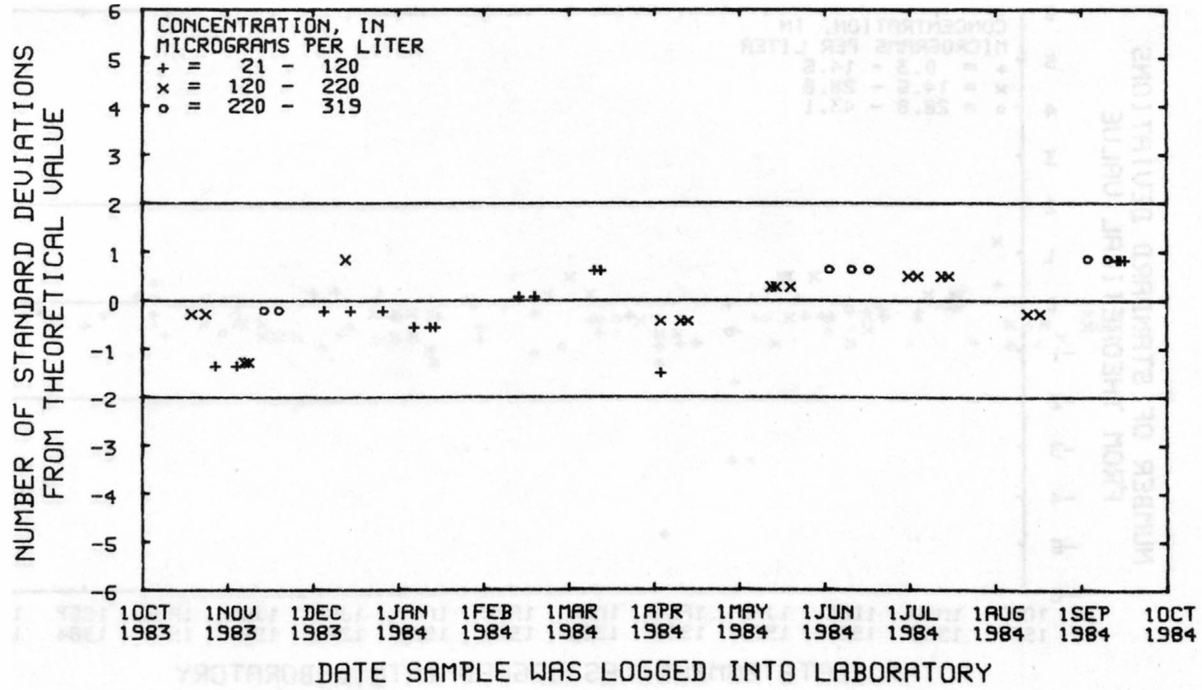

Figure 13--Barium, total recoverable, data for the Atlanta laboratory.

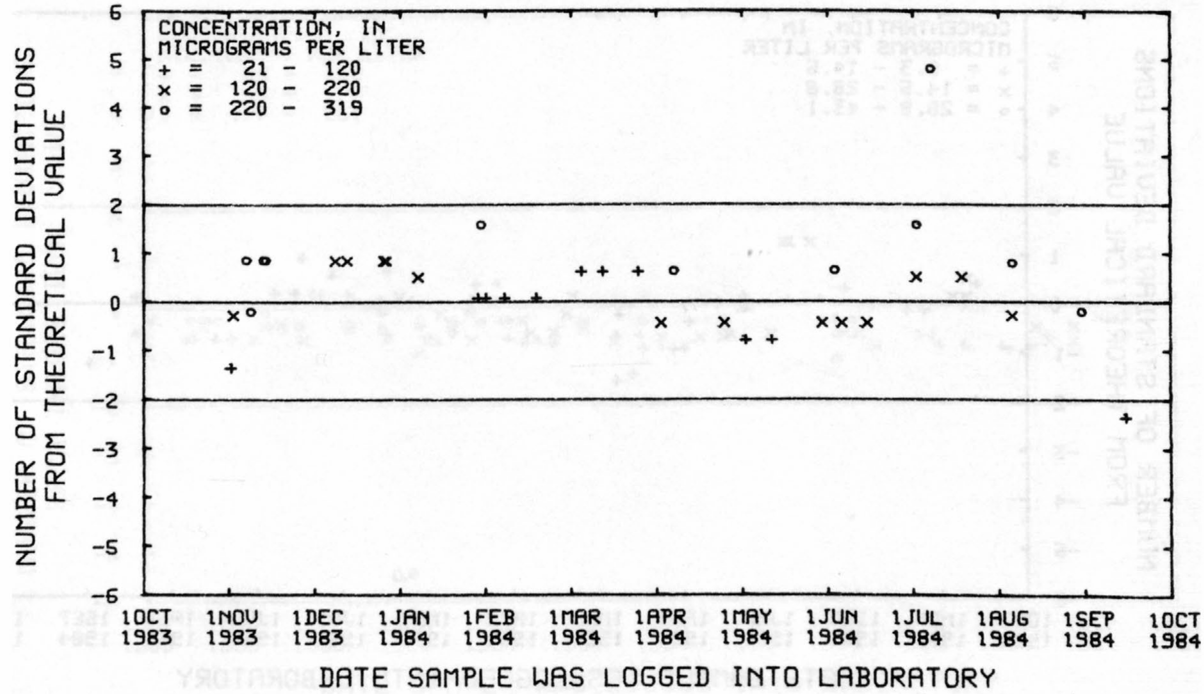

Figure 14--Barium, total recoverable, data for the Denver laboratory.

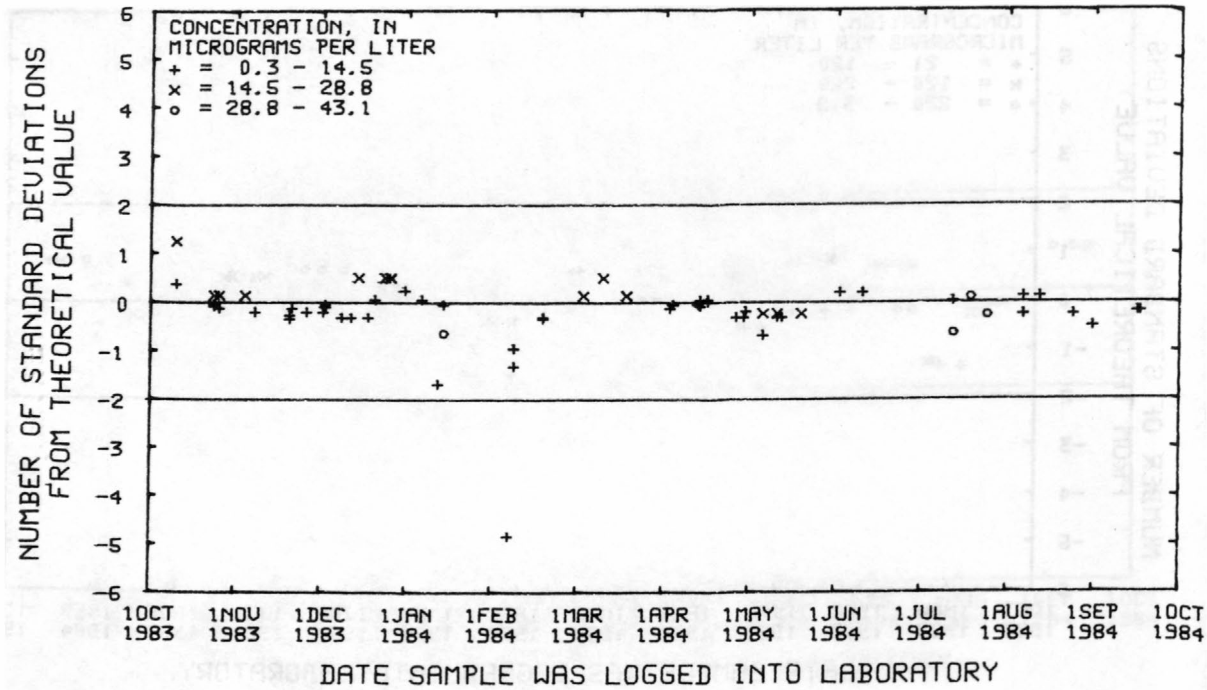

Figure 15--Beryllium, dissolved, data for the Atlanta laboratory.

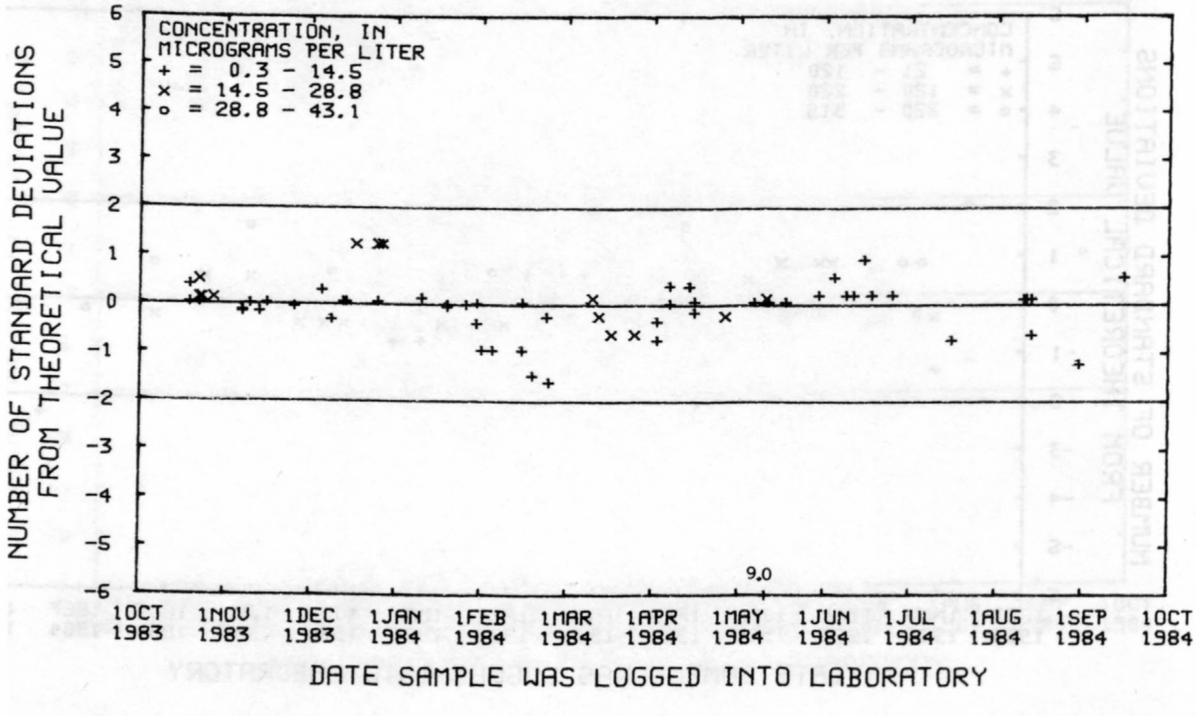

Figure 16--Beryllium, dissolved, data for the Denver laboratory.

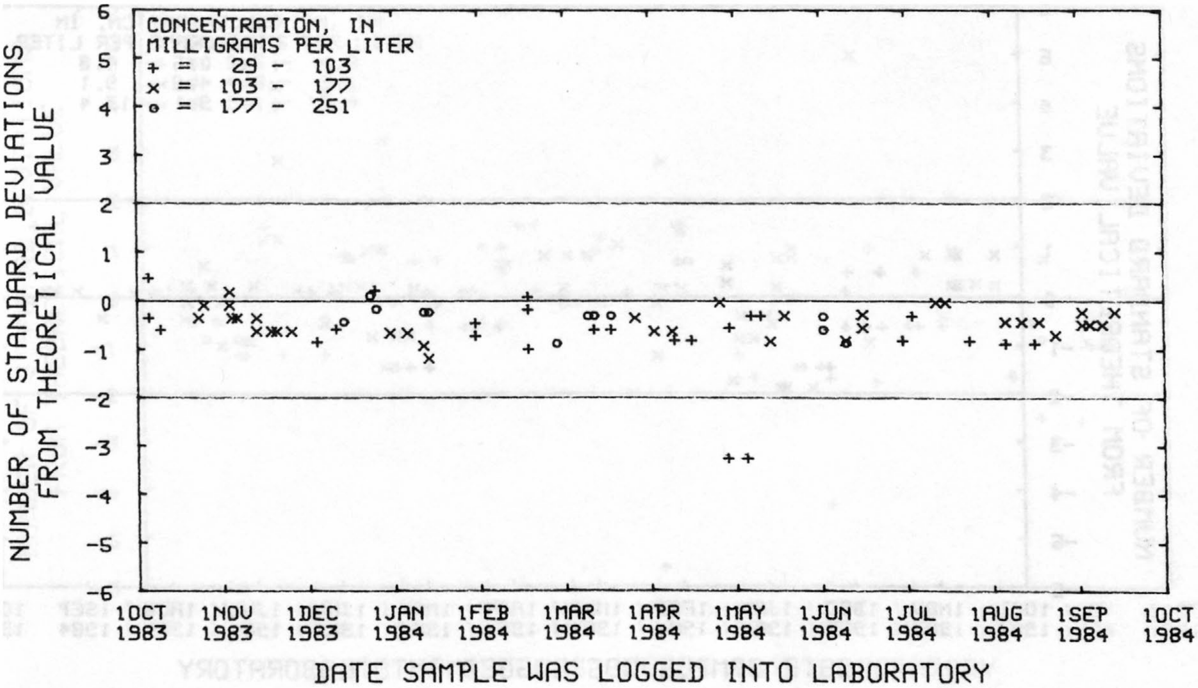

Figure 17--Boron, dissolved, data from Atlanta laboratory.

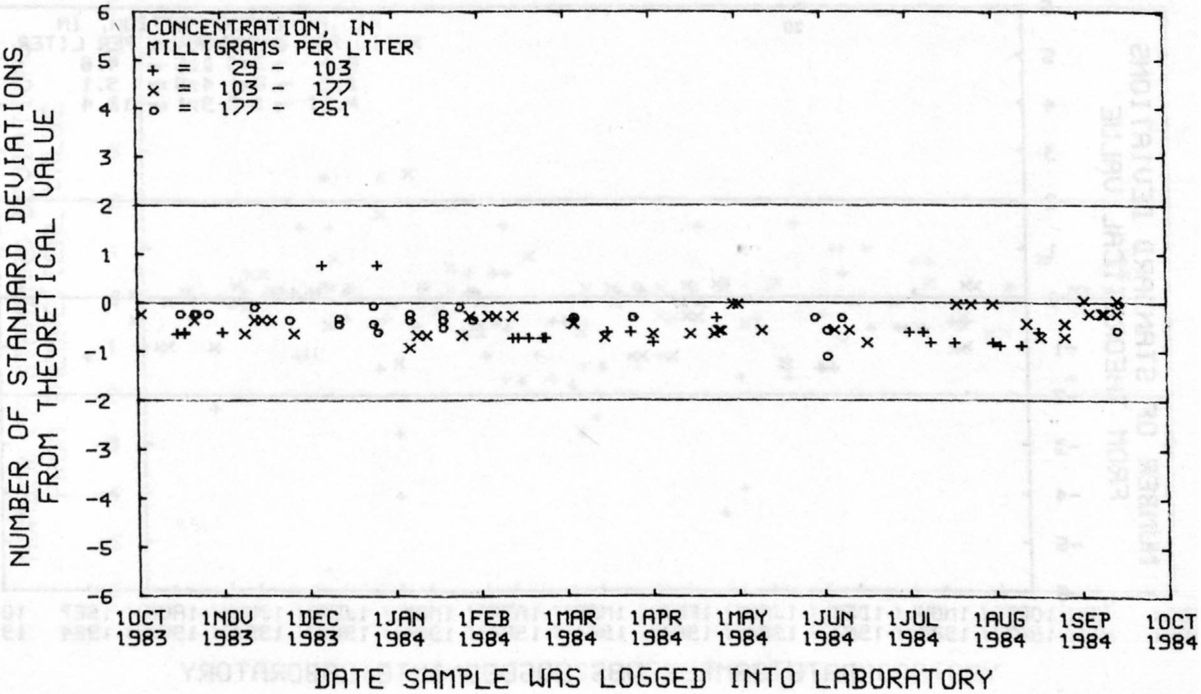

Figure 18--Boron, dissolved, data from Denver laboratory.

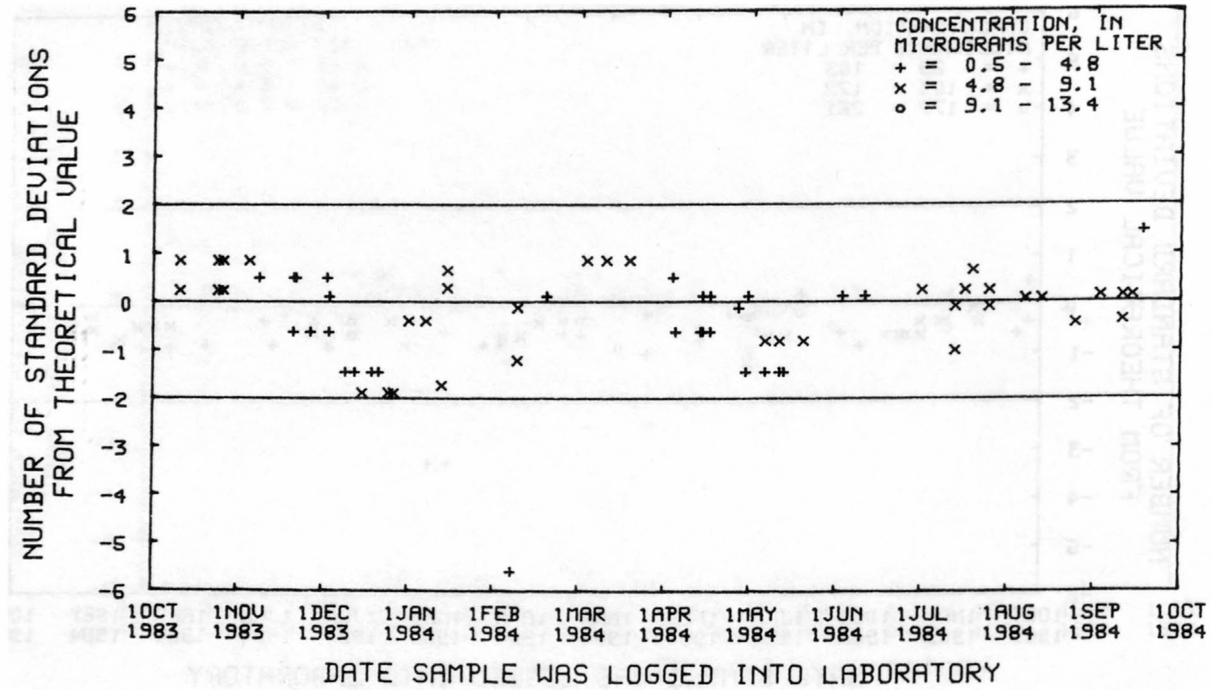

Figure 19--Cadmium, dissolved, (inductively coupled plasma emission spectrometry) data for the Atlanta laboratory.

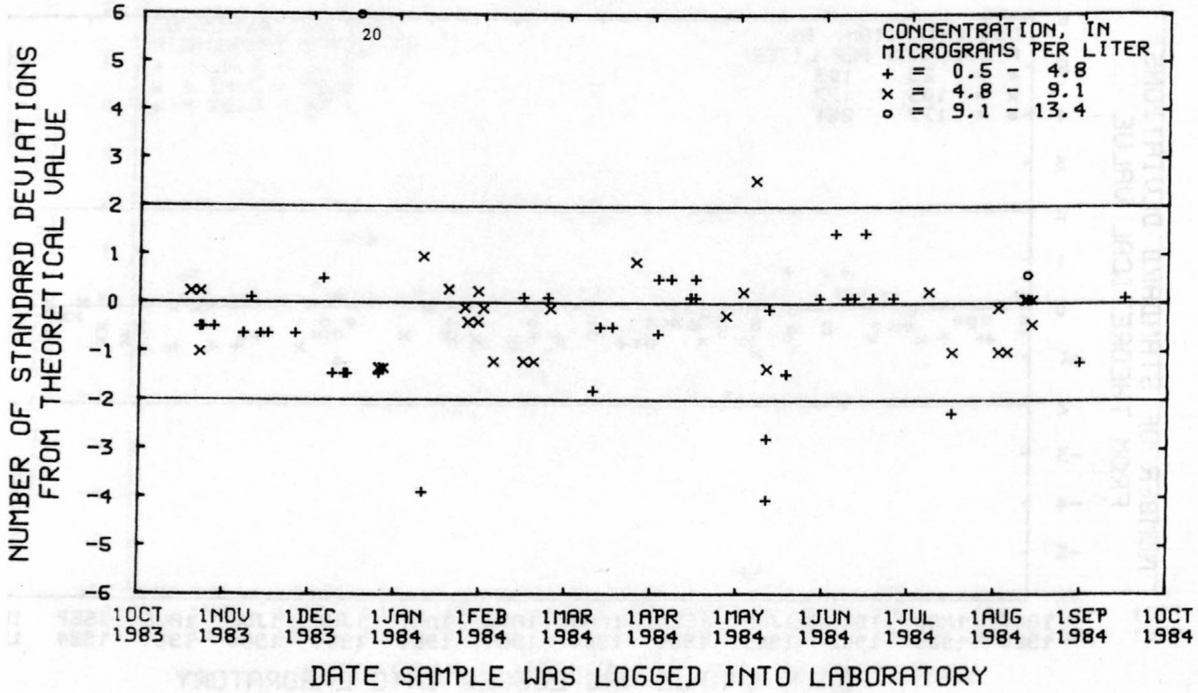

Figure 20--Cadmium, dissolved, (inductively coupled plasma emission spectrometry) data for the Denver laboratory.

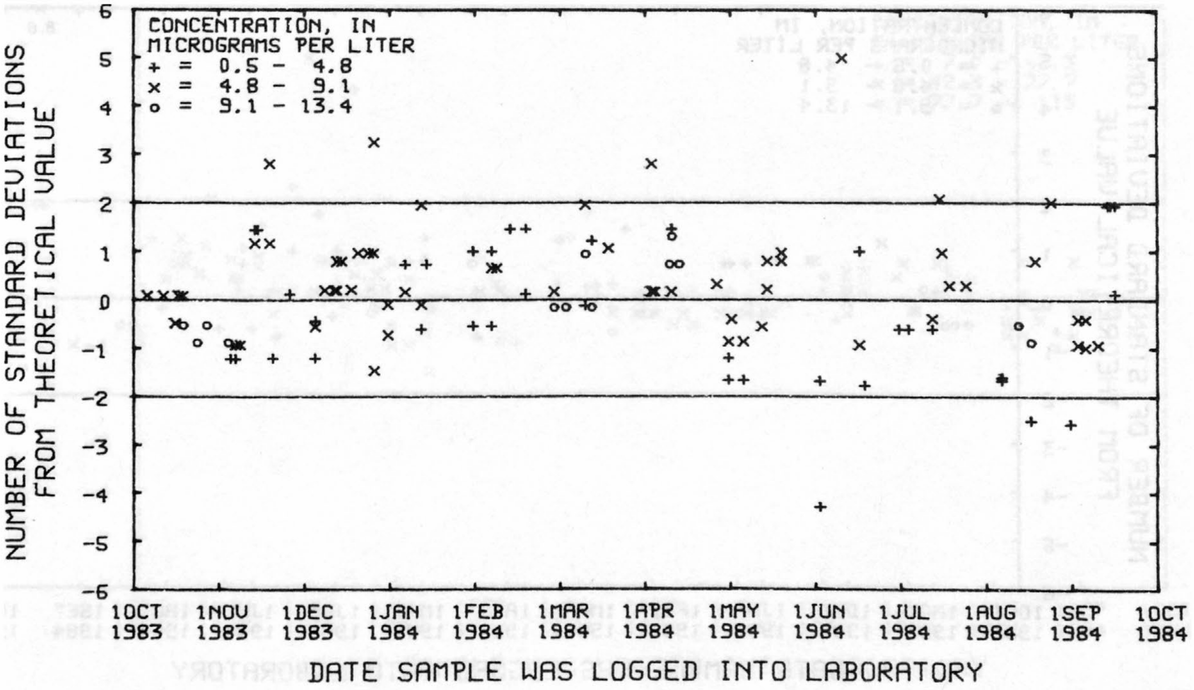

Figure 21--Cadmium, dissolved,
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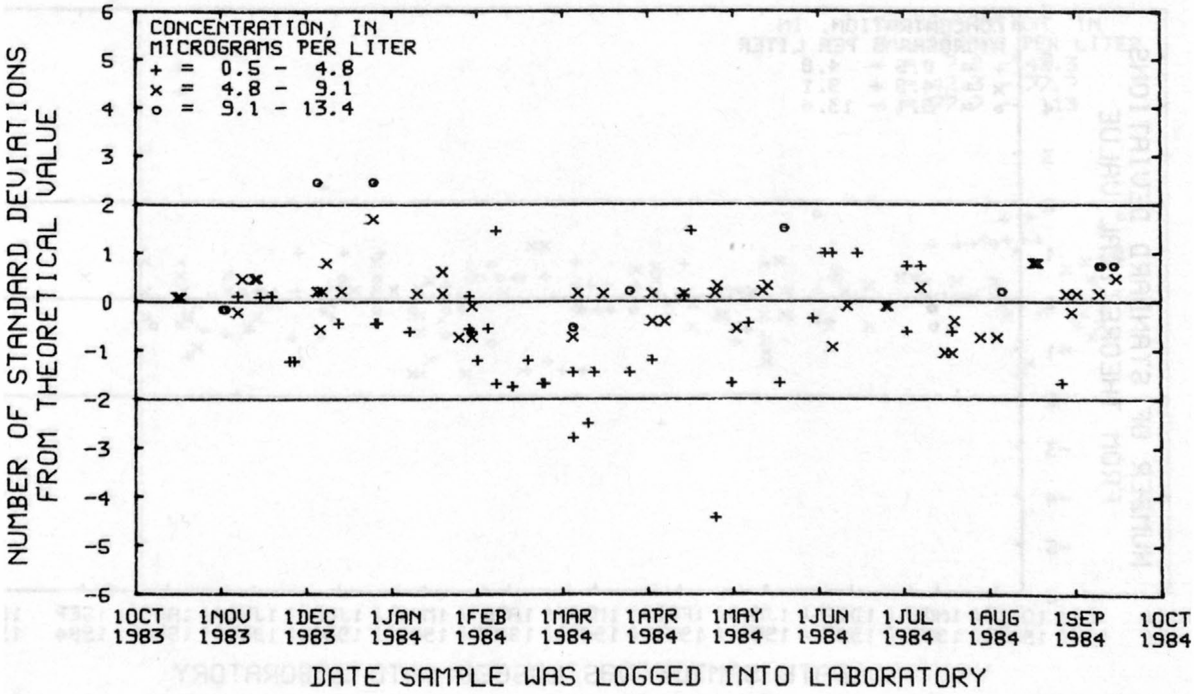

Figure 22--Cadmium, dissolved,
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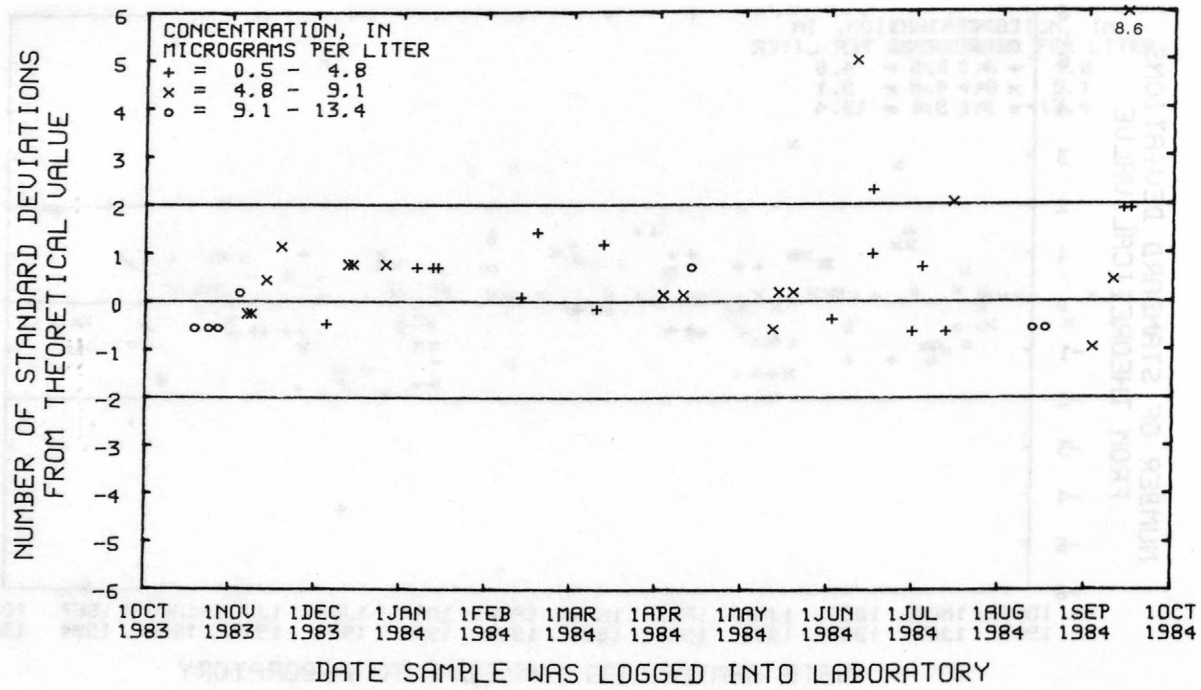

Figure 23--Cadmium, total recoverable, data for the Atlanta laboratory.

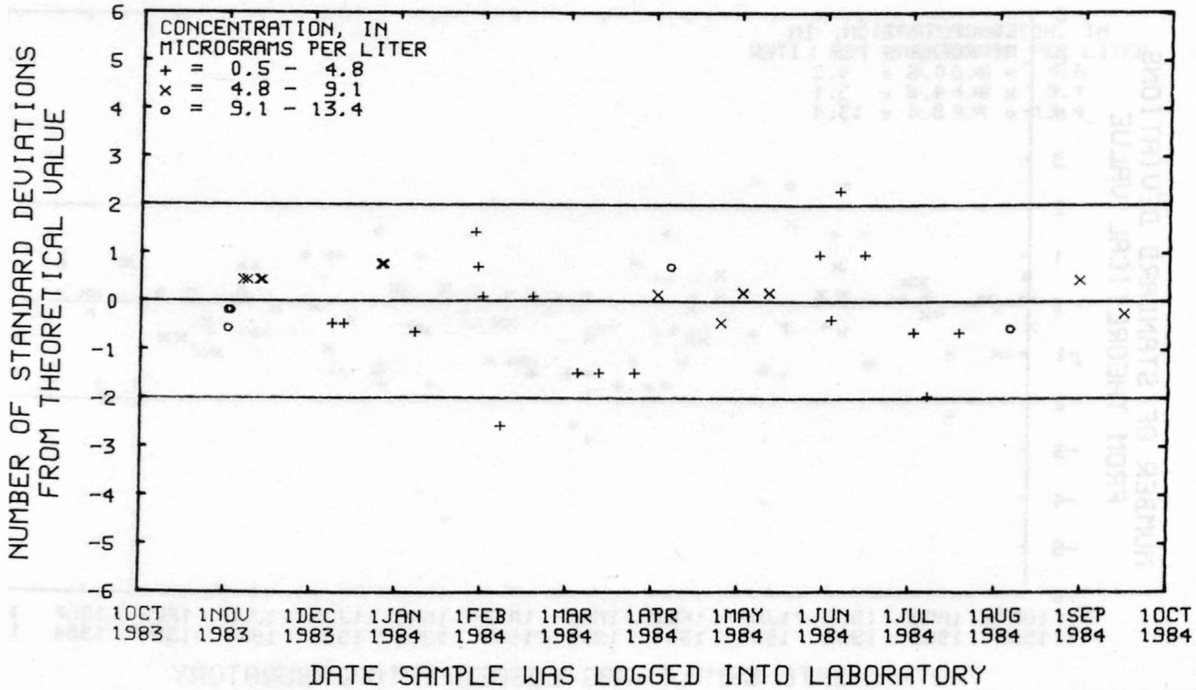

Figure 24--Cadmium, total recoverable, data for the Denver laboratory.

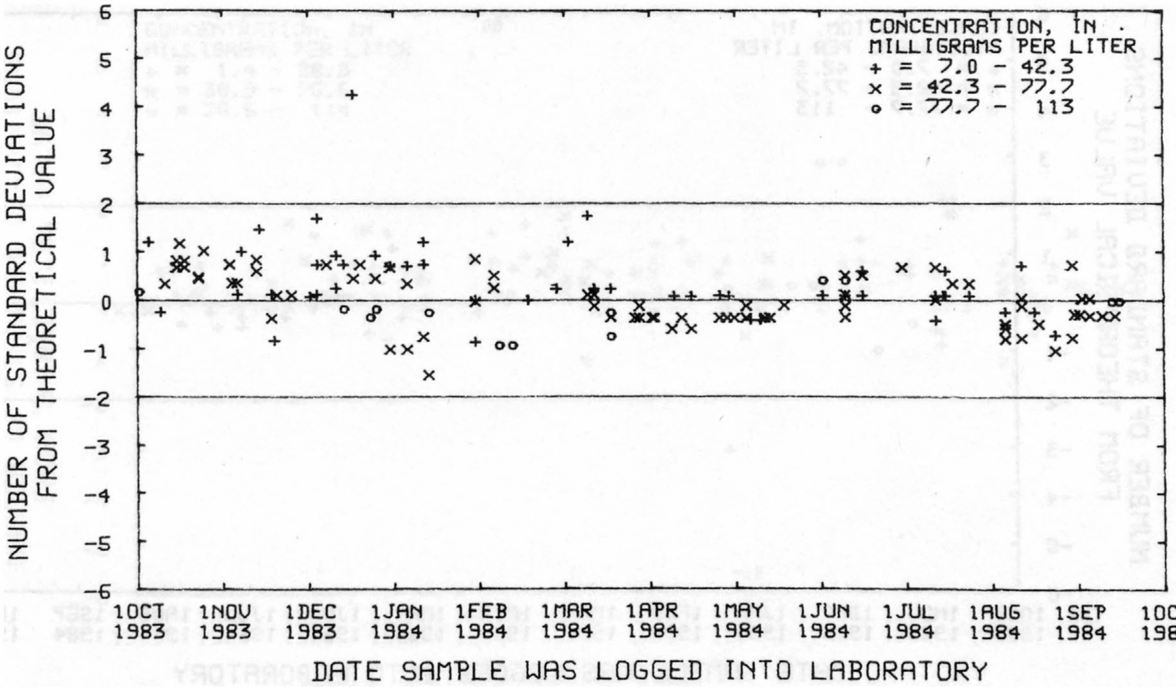

Figure 25--Calcium, dissolved, (inductively coupled plasma emission spectrometry) data from Atlanta laboratory.

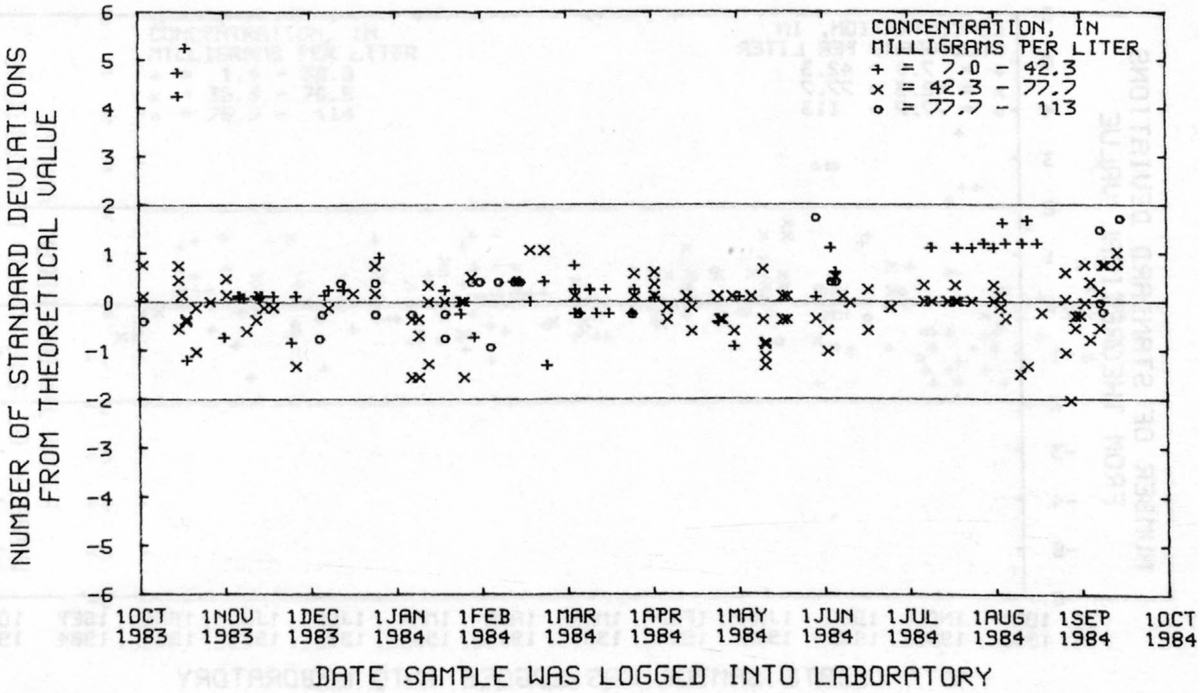

Figure 26--Calcium, dissolved, (inductively coupled plasma emission spectrometry) data from Denver laboratory.

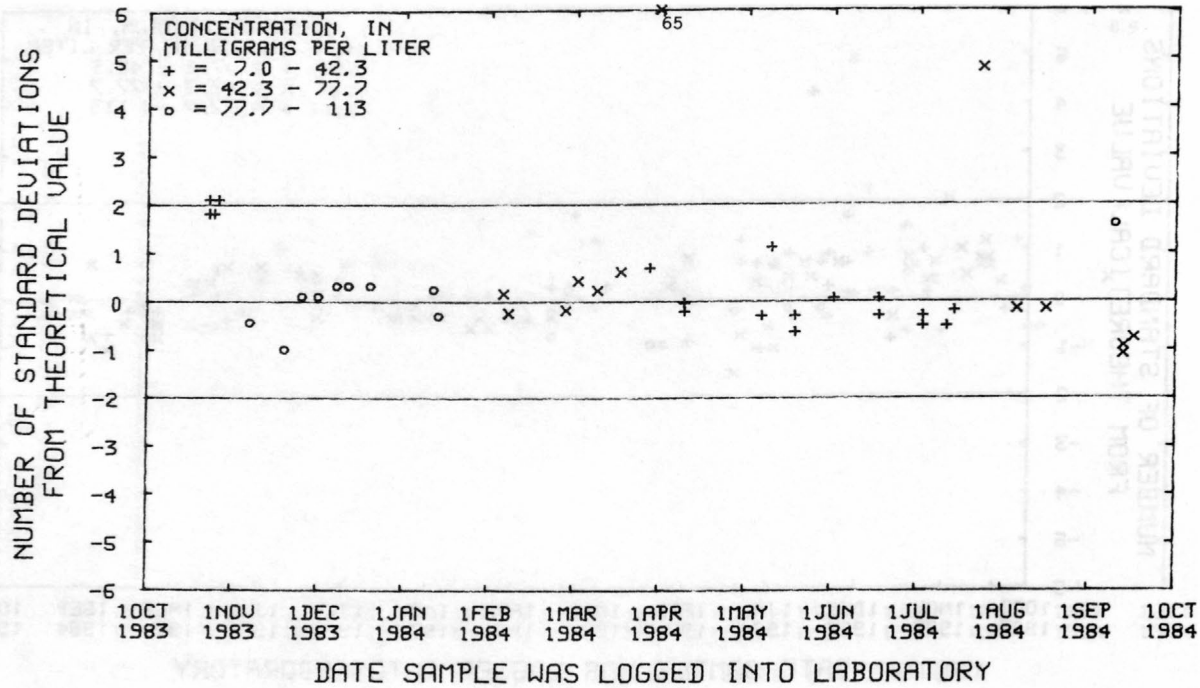

Figure 27--Calcium, dissolved,
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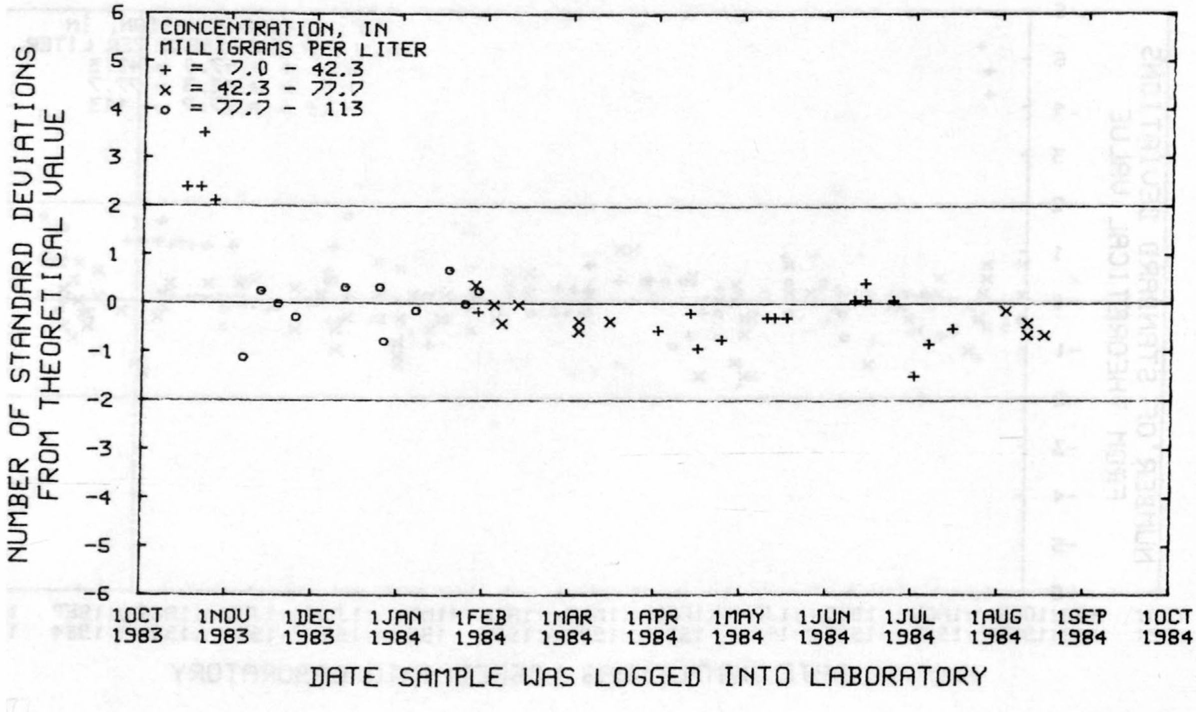

Figure 28--Calcium, dissolved,
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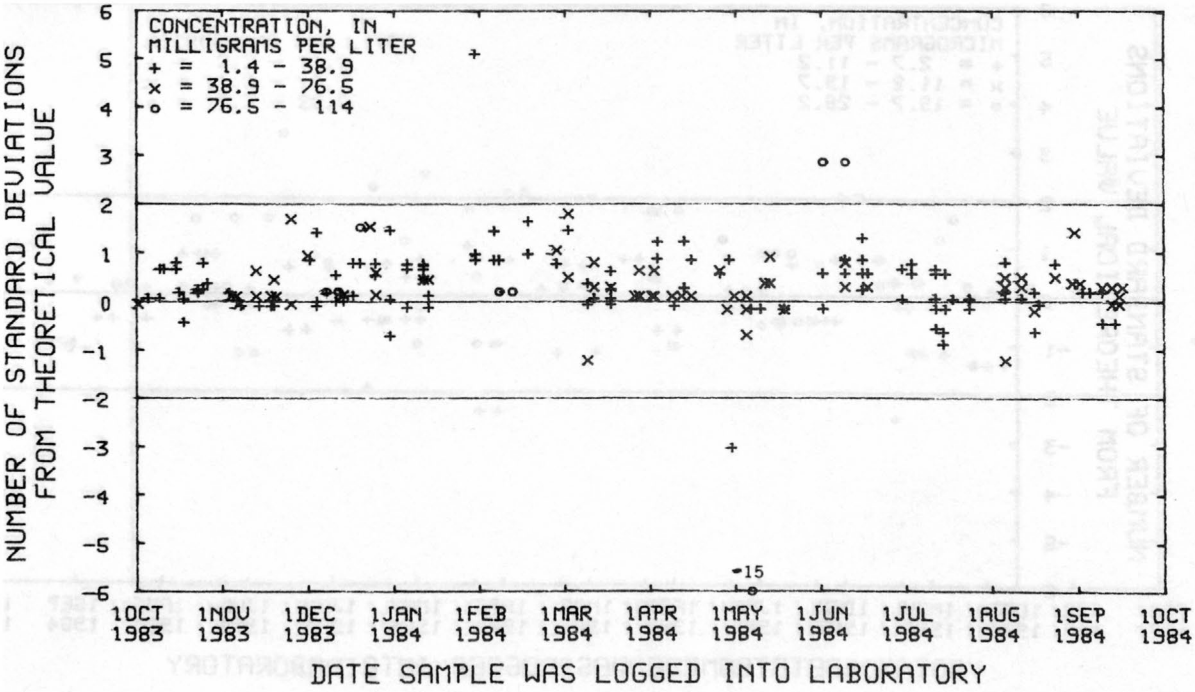

Figure 29--Chloride, dissolved, data from Atlanta laboratory.

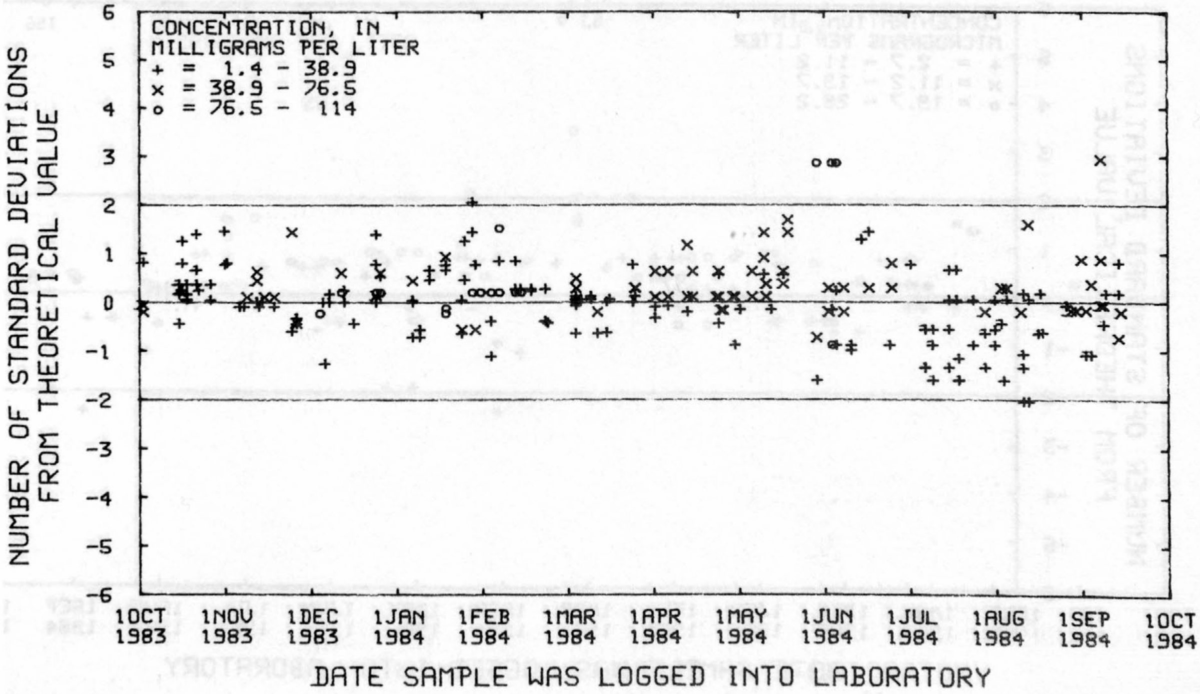

Figure 30--Chloride, dissolved, data from Denver laboratory.

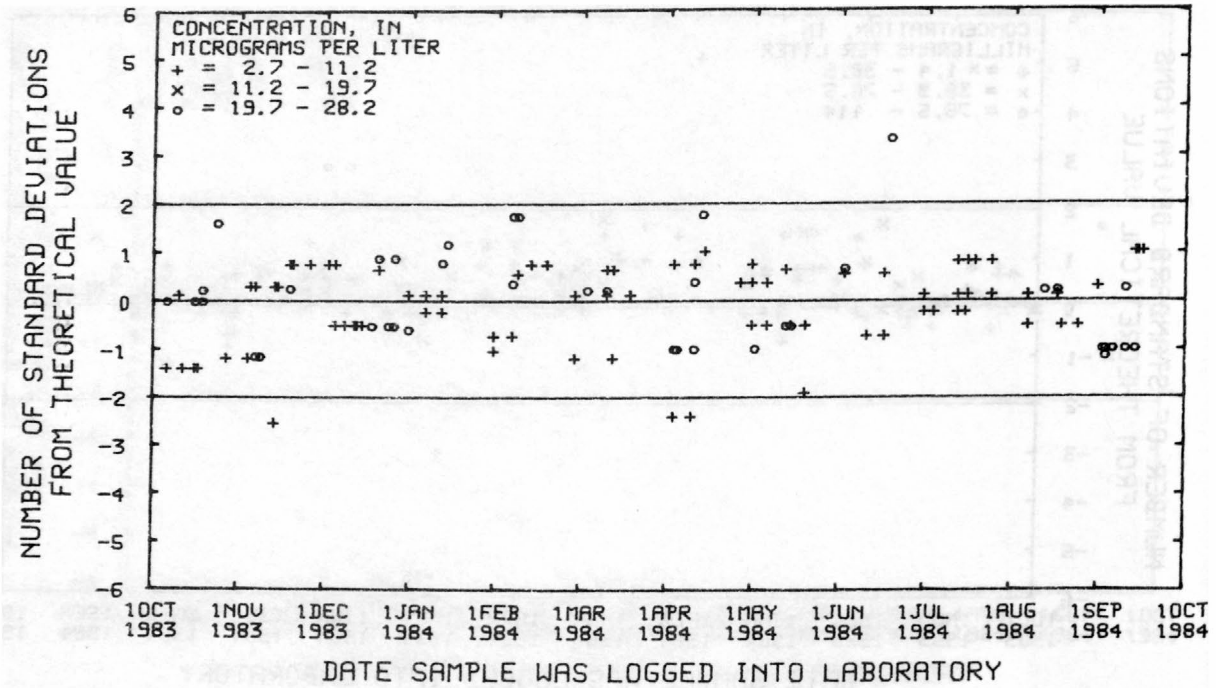

Figure 31--Chromium, dissolved, data for the Atlanta laboratory.

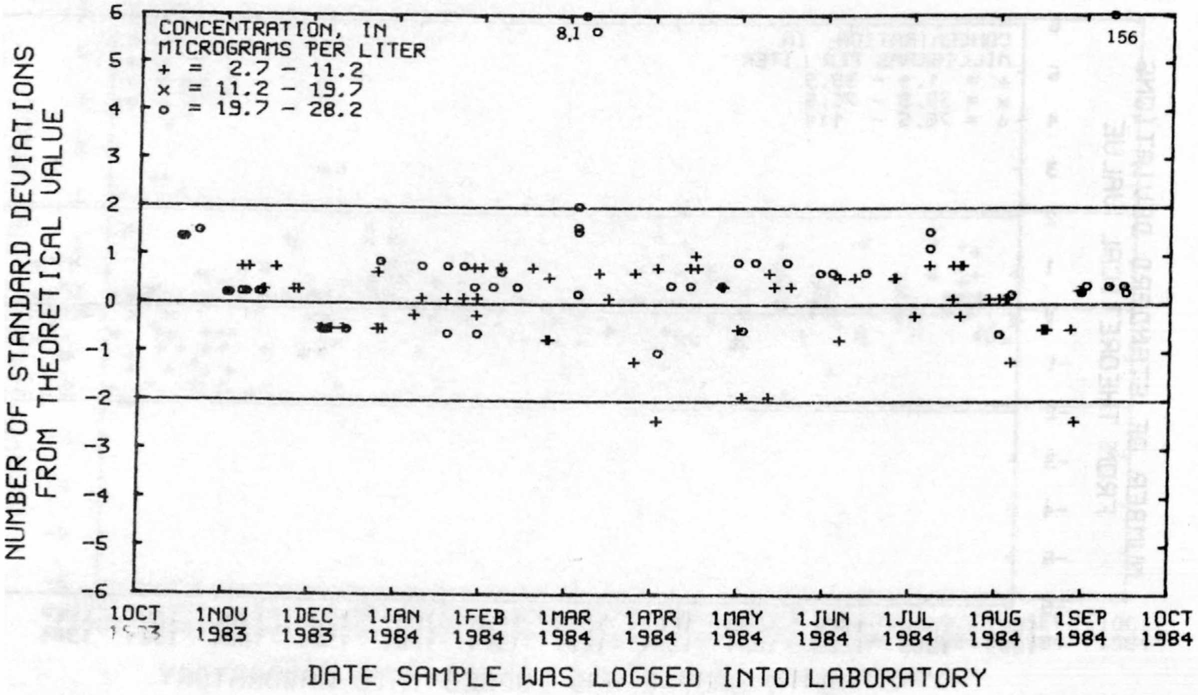

Figure 32--Chromium, dissolved, data for the Denver laboratory.

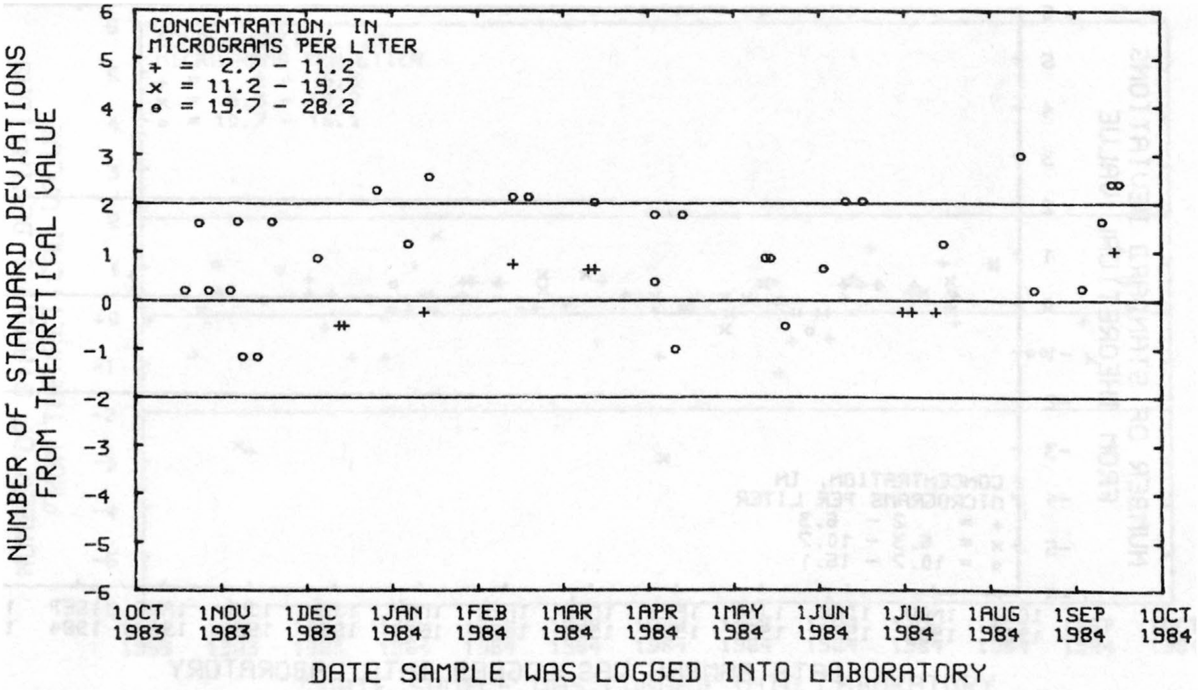

Figure 33--Chromium, total recoverable, data for the Atlanta laboratory.

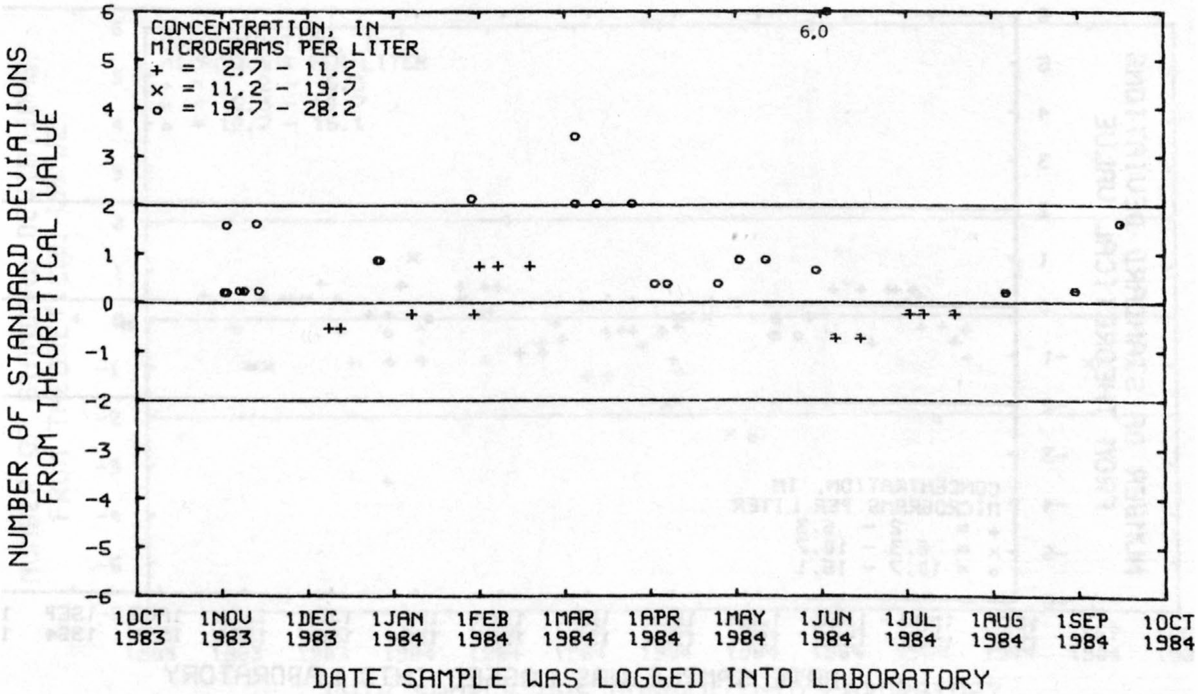

Figure 34--Chromium, total recoverable, data for the Denver laboratory.

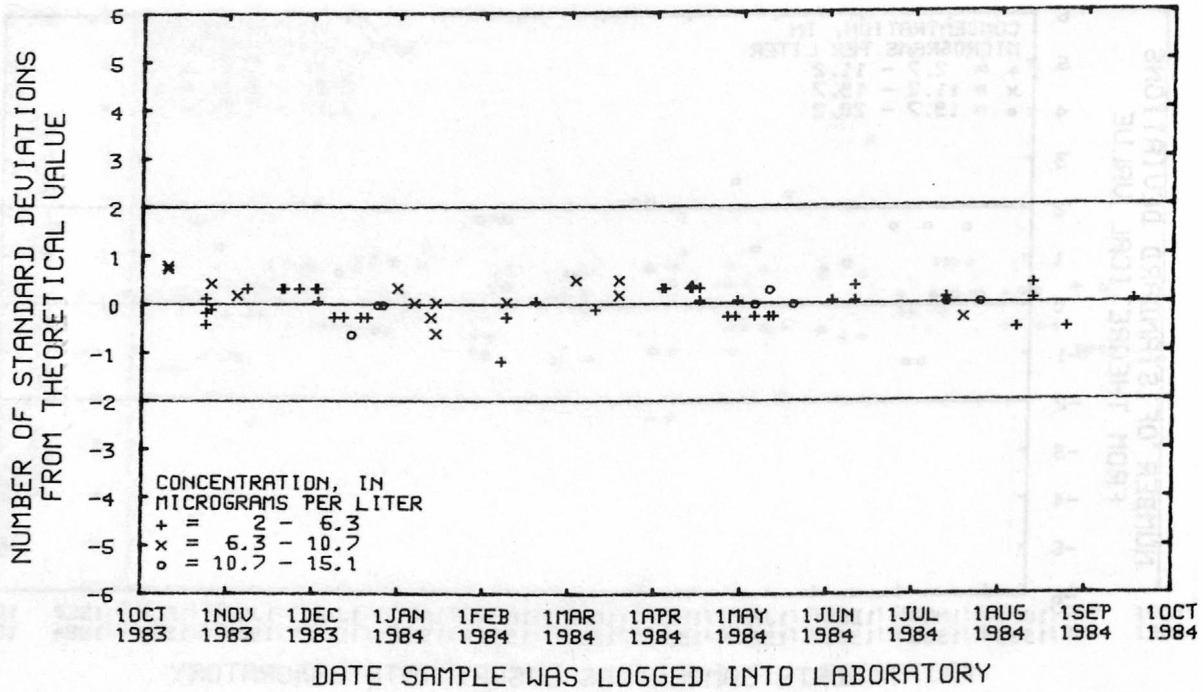

Figure 35--Cobalt, dissolved, (inductively coupled plasma emission spectrometry) data for the Atlanta laboratory.

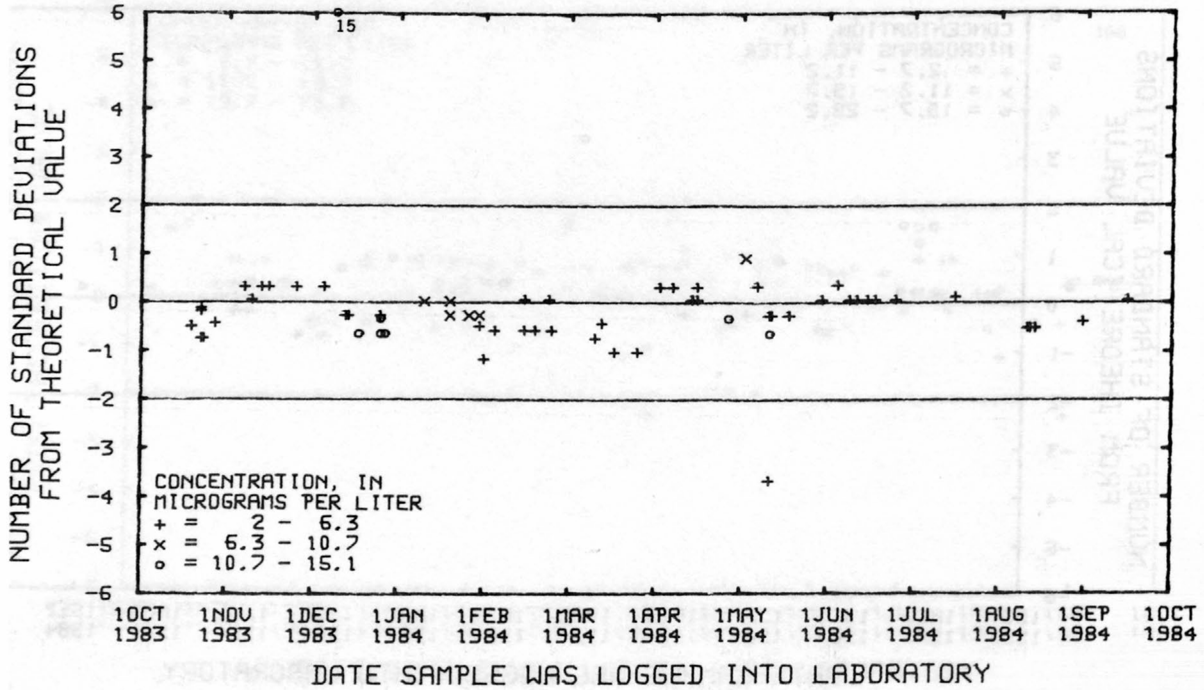

Figure 36--Cobalt, dissolved, (inductively coupled plasma emission spectrometry) data for the Denver laboratory.

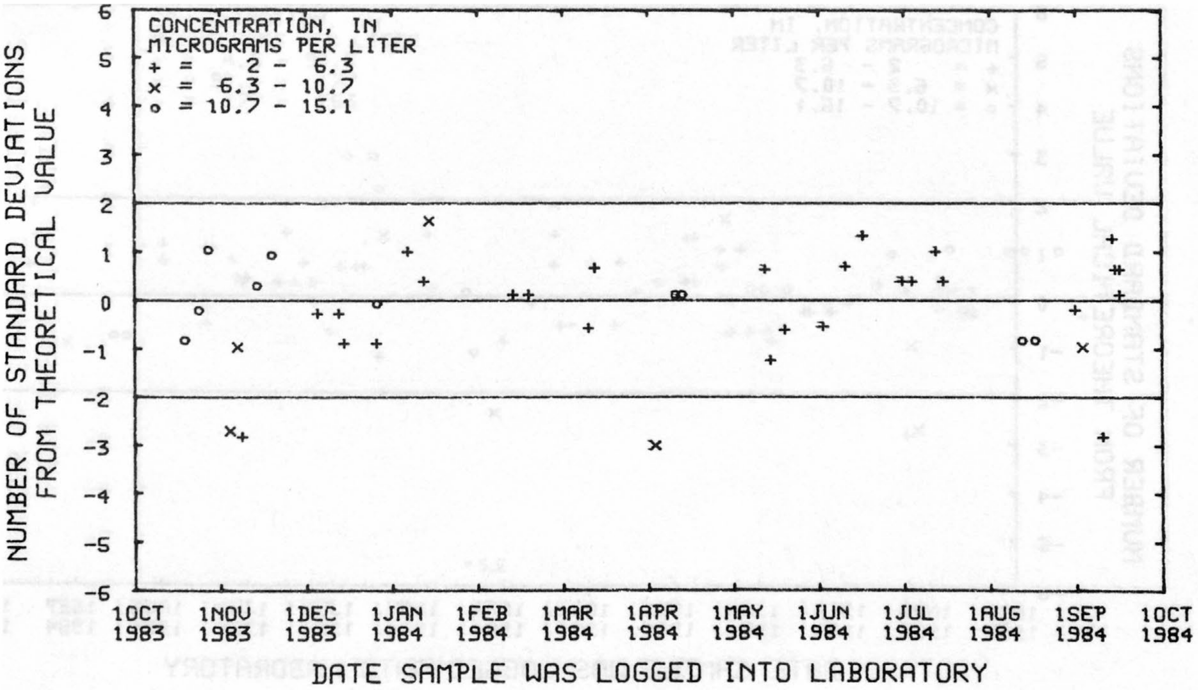

Figure 37--Cobalt, dissolved, (atomic absorption spectrometry) data for the Atlanta laboratory.

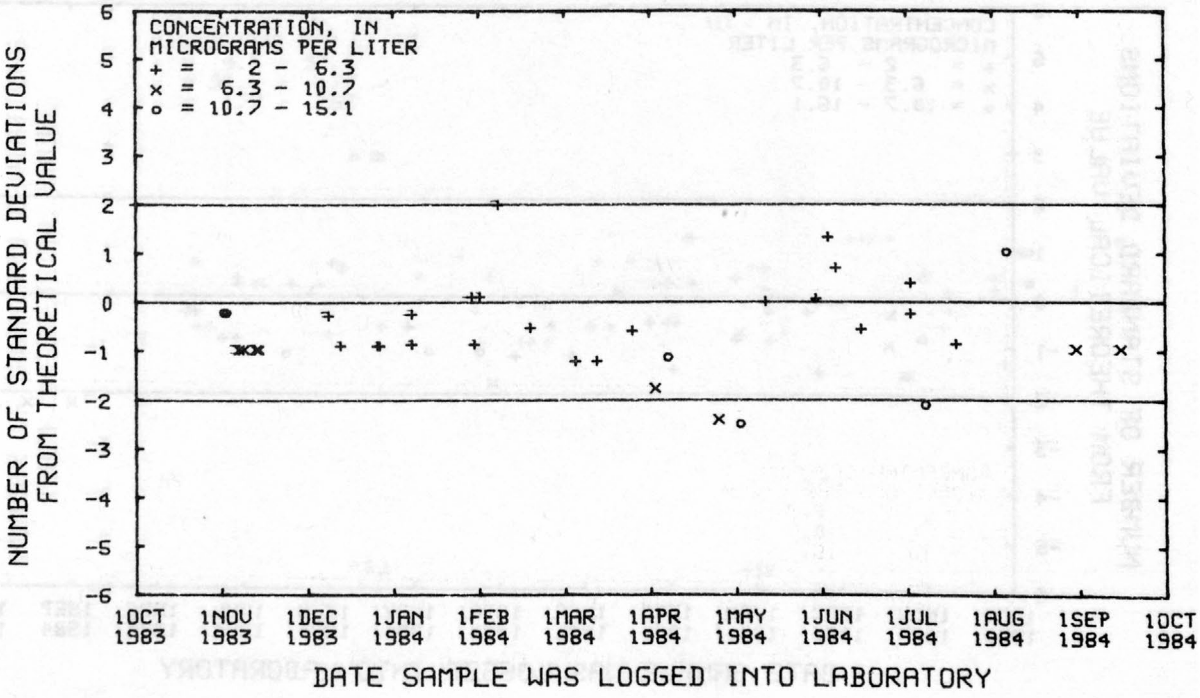

Figure 38--Cobalt, dissolved, (atomic absorption spectrometry), data for the Denver laboratory.

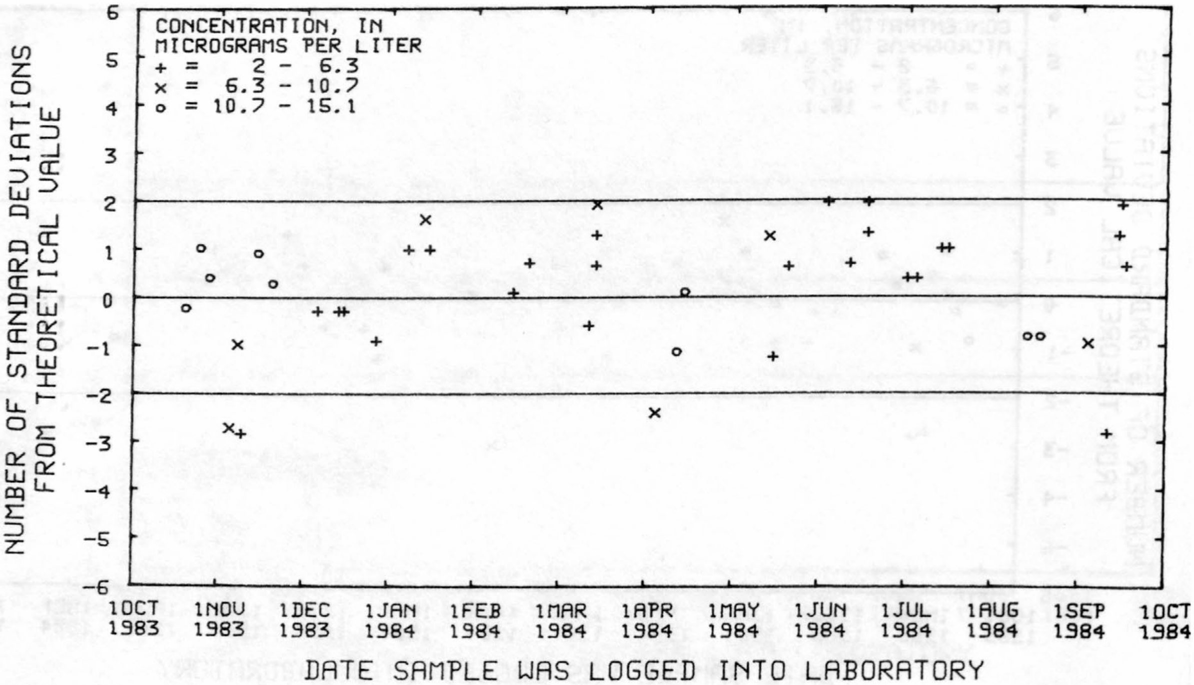

Figure 39--Cobalt, total recoverable, data for the Atlanta laboratory.

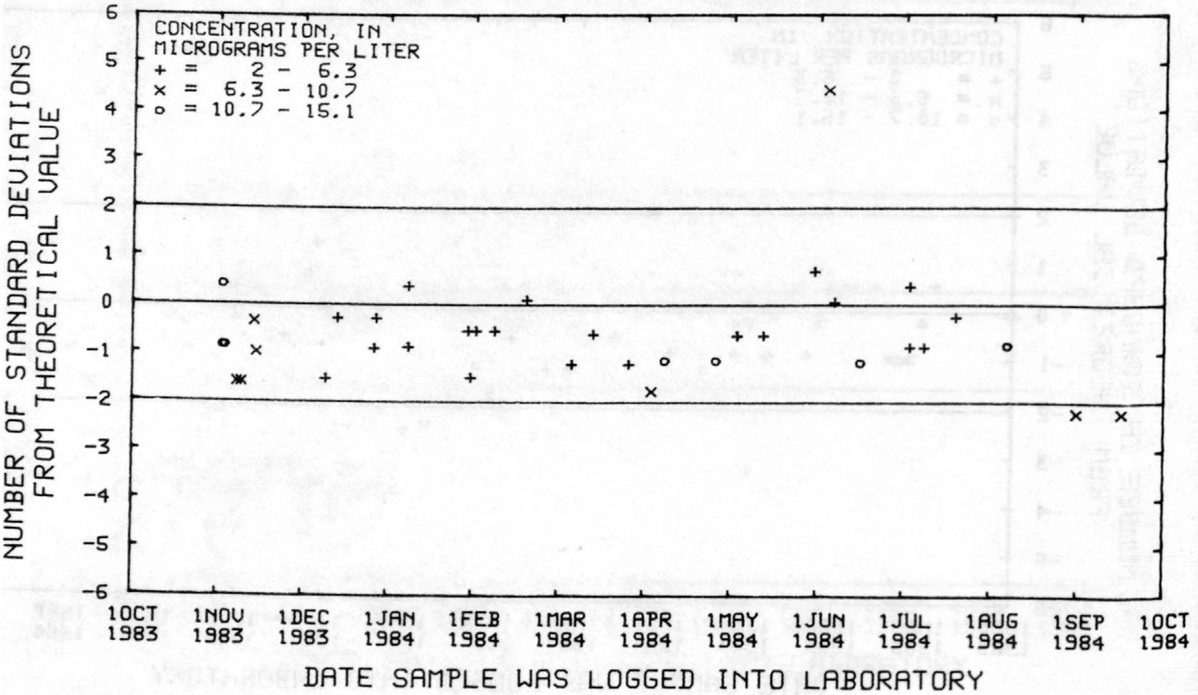

Figure 40--Cobalt, total recoverable, data for the Denver laboratory.

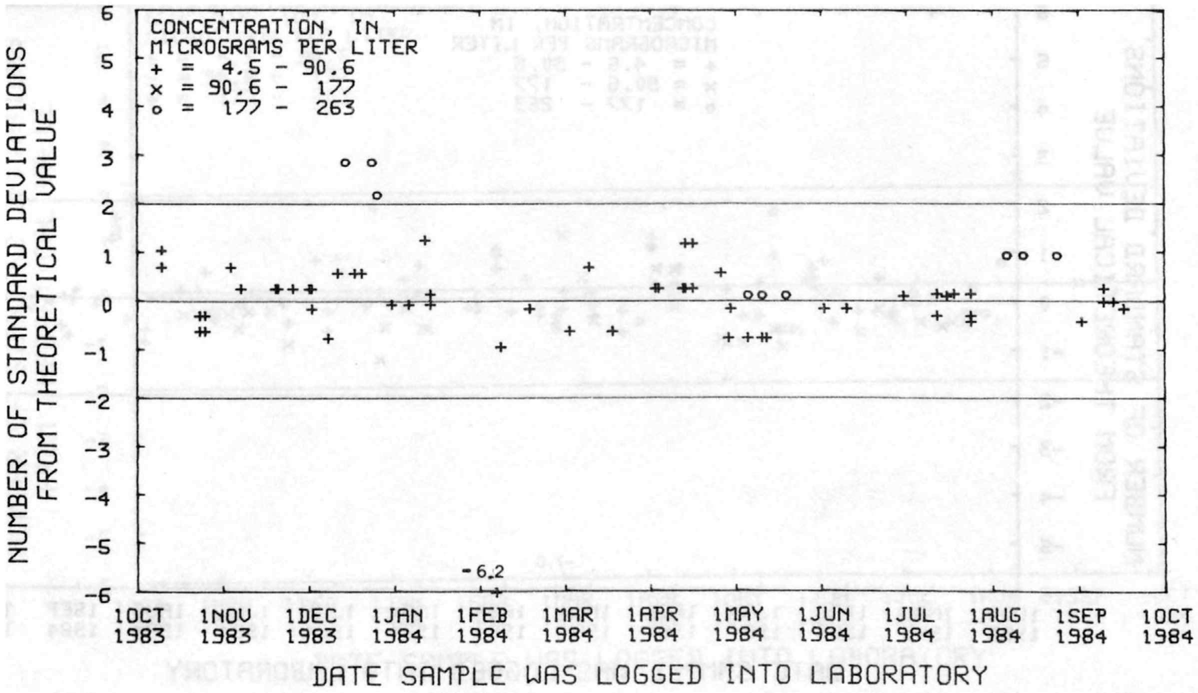

Figure 41--Copper, dissolved, (inductively coupled plasma emission spectrometry), data for the Atlanta laboratory.

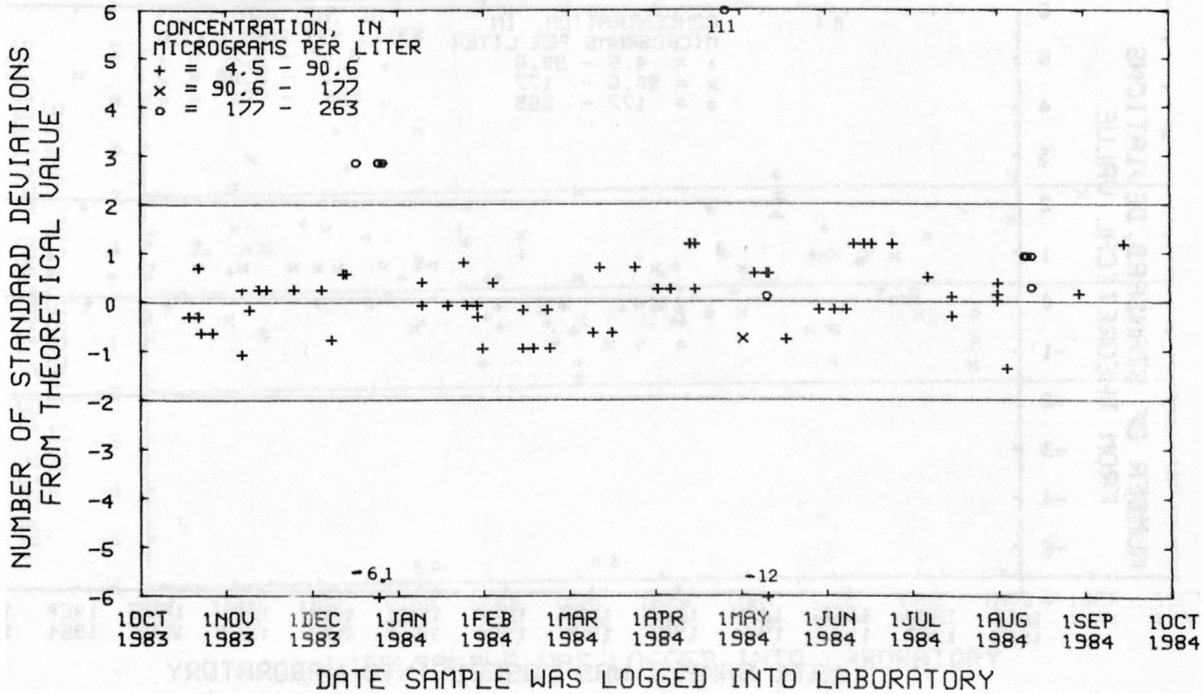

Figure 42--Copper, dissolved, (inductively coupled plasma emission spectrometry), data for the Denver laboratory.

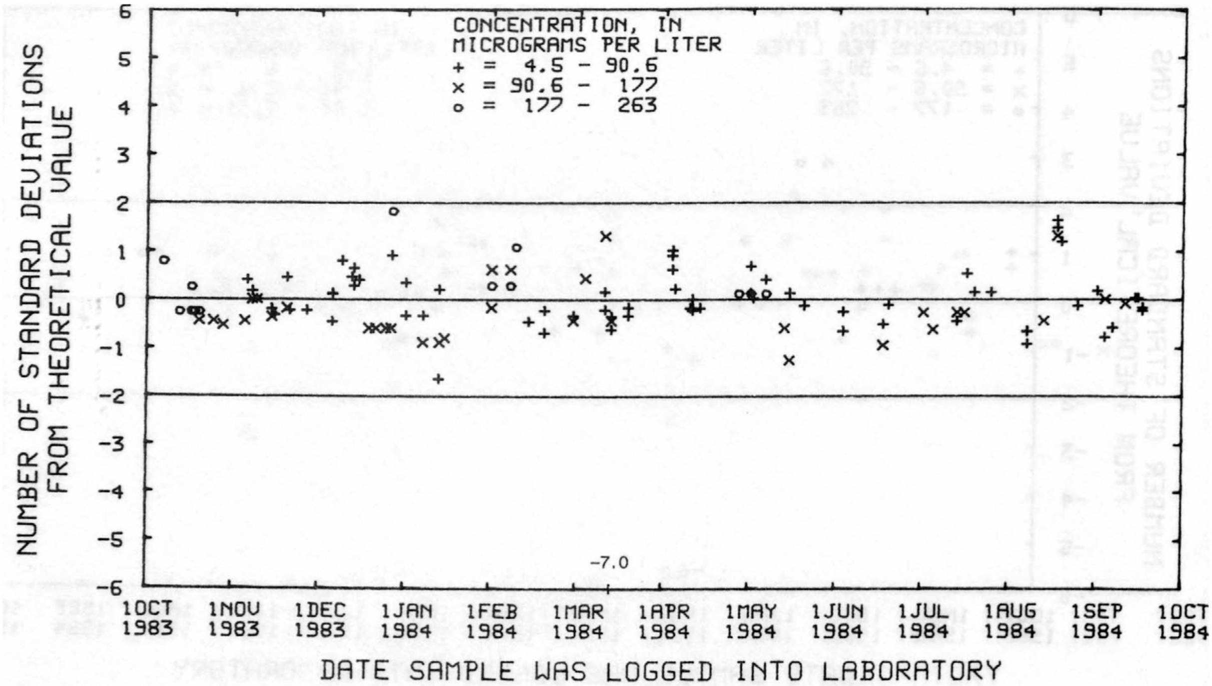

Figure 43--Copper, dissolved,
(atomic absorption spectrometry)
data for the Atlanta laboratory.

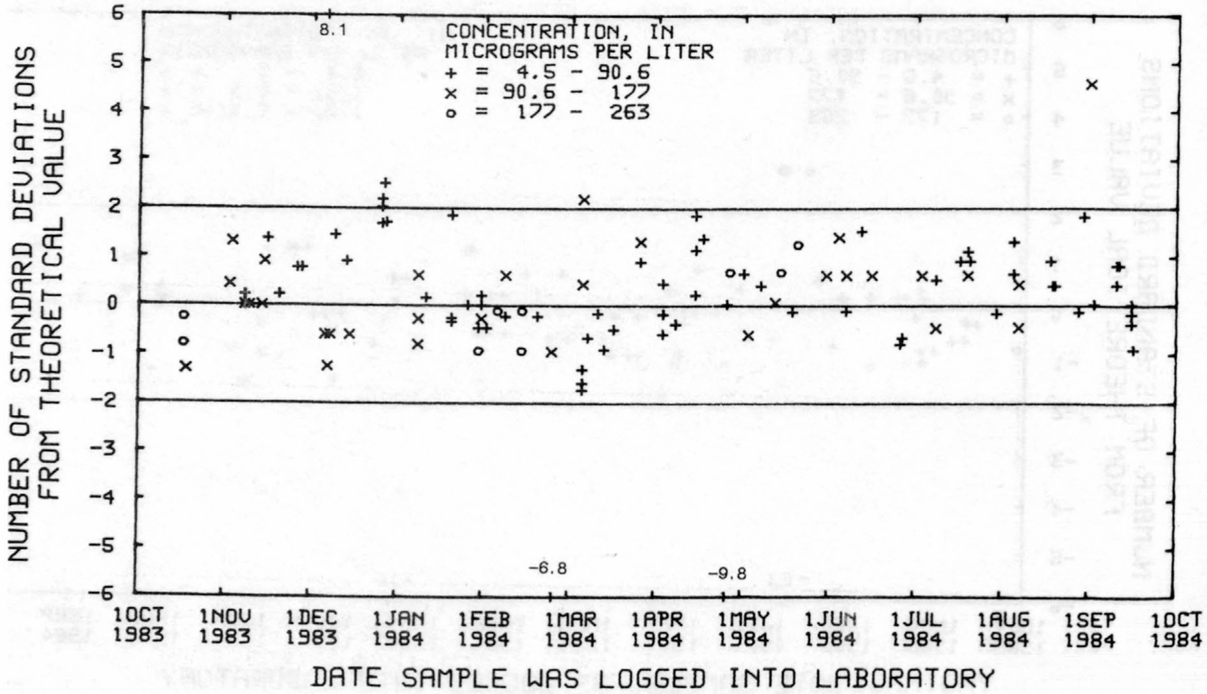

Figure 44--Copper, dissolved,
(atomic absorption spectrometry)
data for the Denver laboratory.

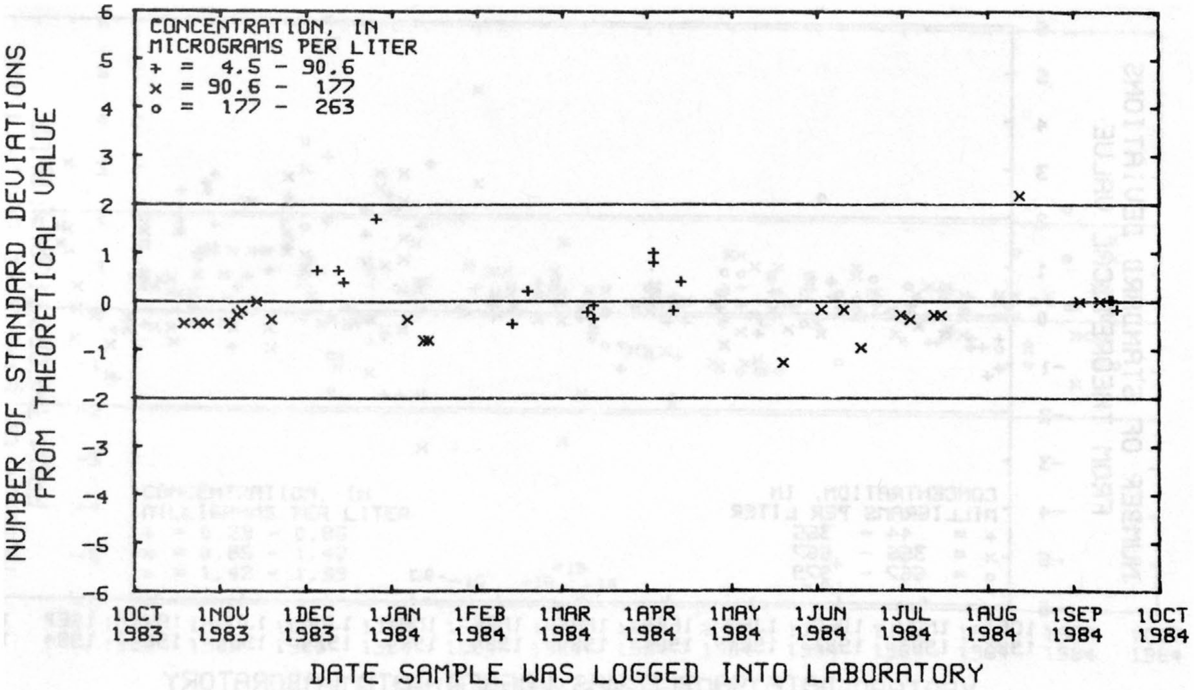

Figure 45--Copper, total recoverable, data for the Atlanta laboratory.

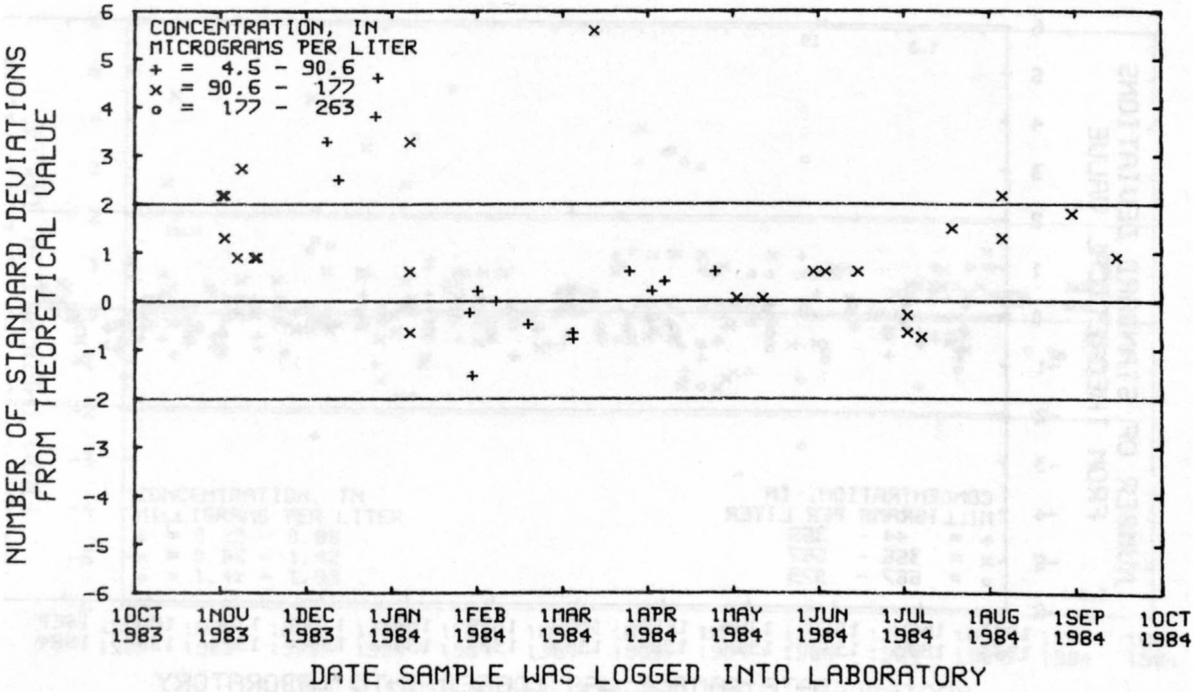

Figure 46--Copper, total recoverable, data for the Denver laboratory.

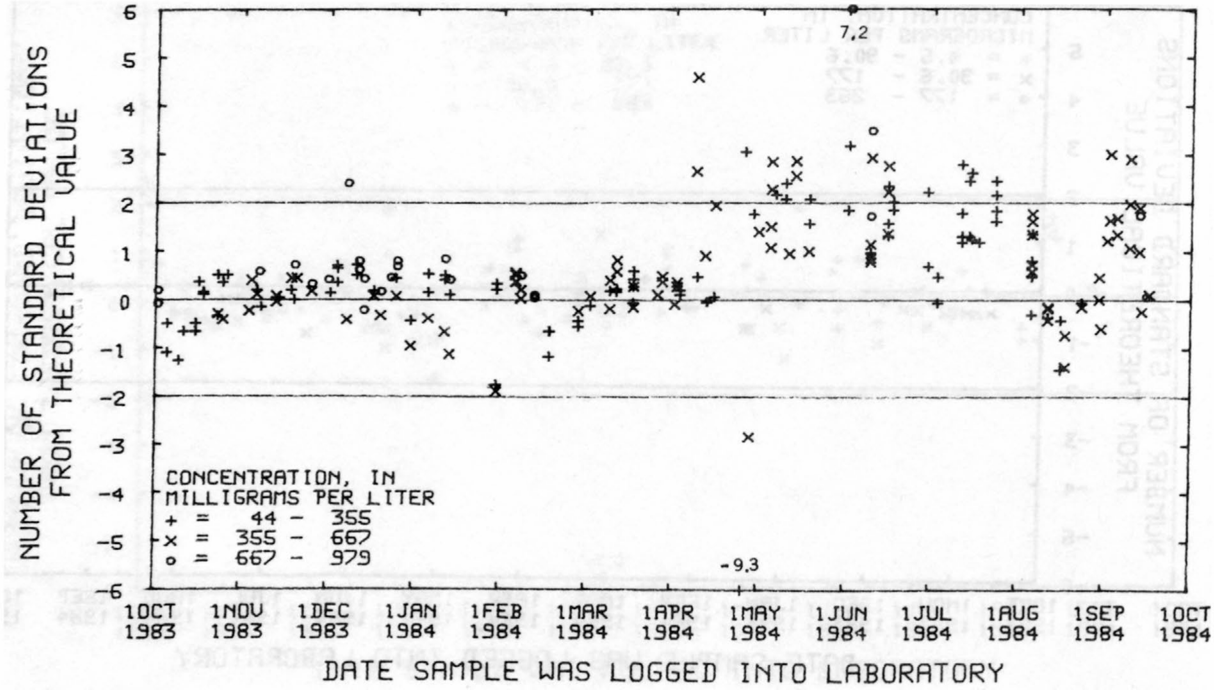

Figure 47--Dissolved solids data from Atlanta laboratory.

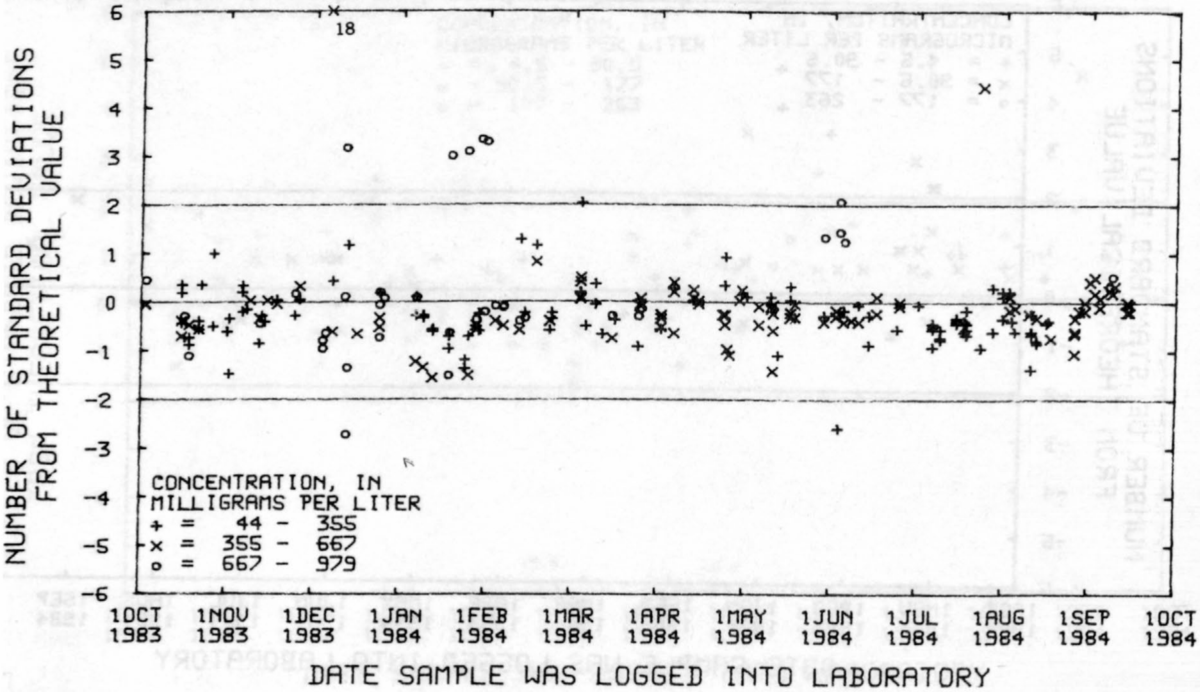

Figure 48--Dissolved solids data from Denver laboratory.

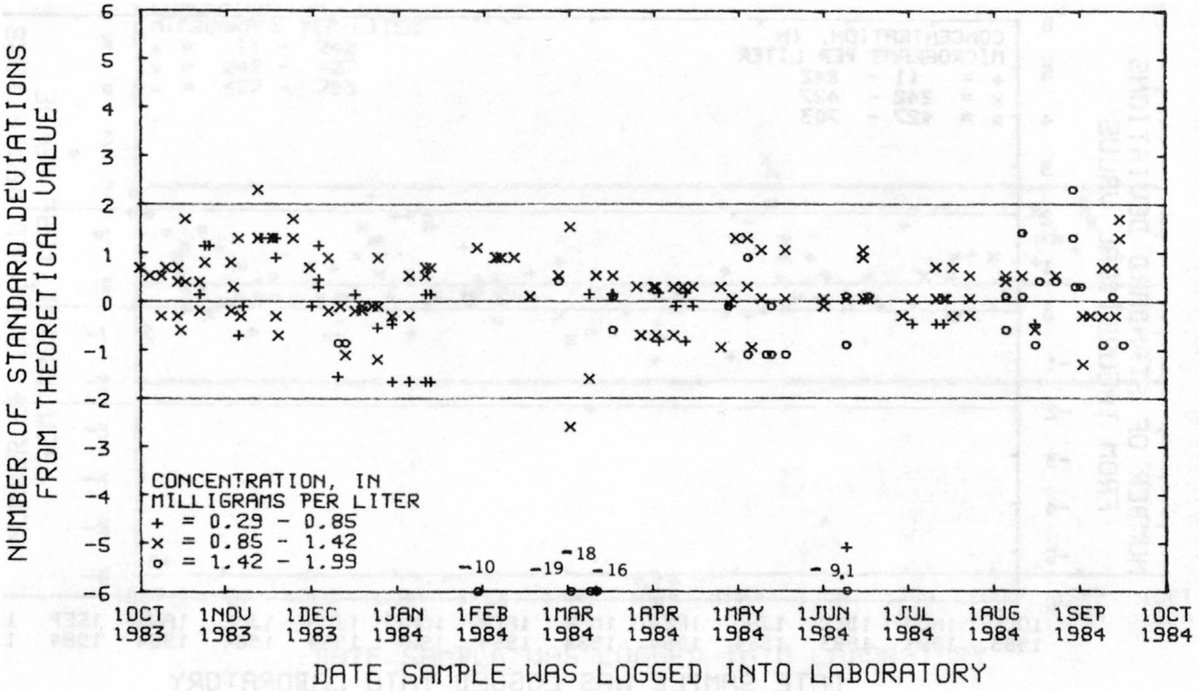

Figure 49--Flouride, dissolved, data from Atlanta laboratory.

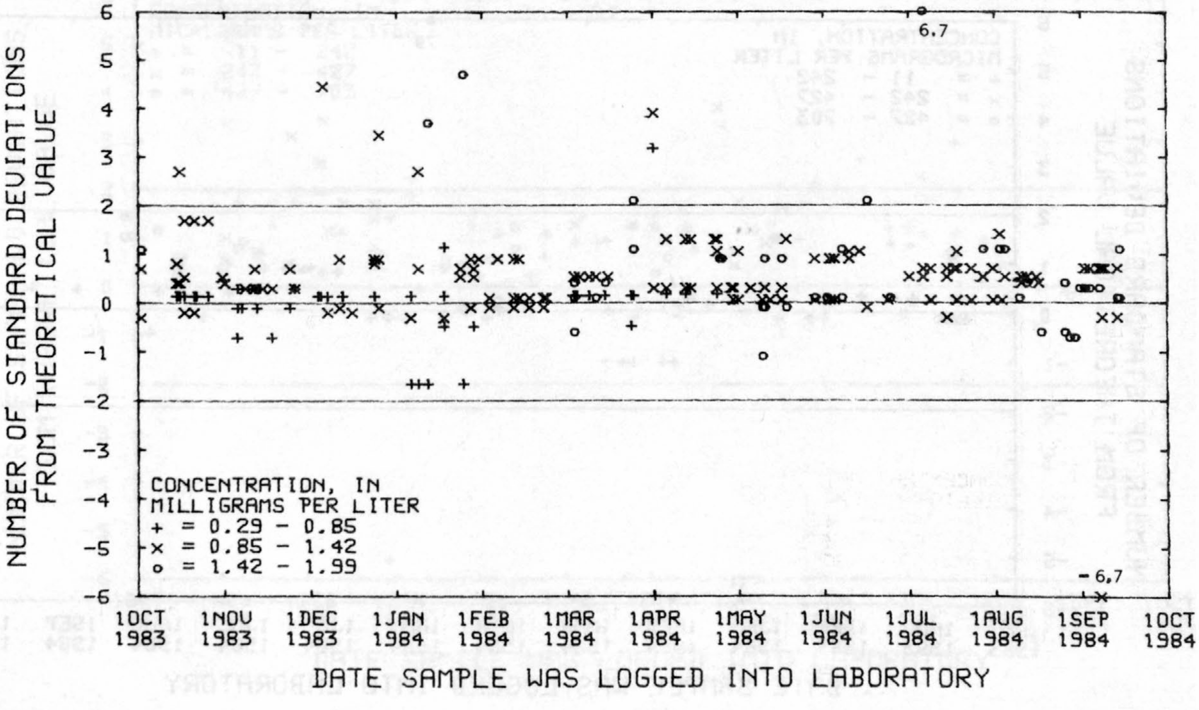

Figure 50--Flouride, dissolved, data from Denver laboratory.

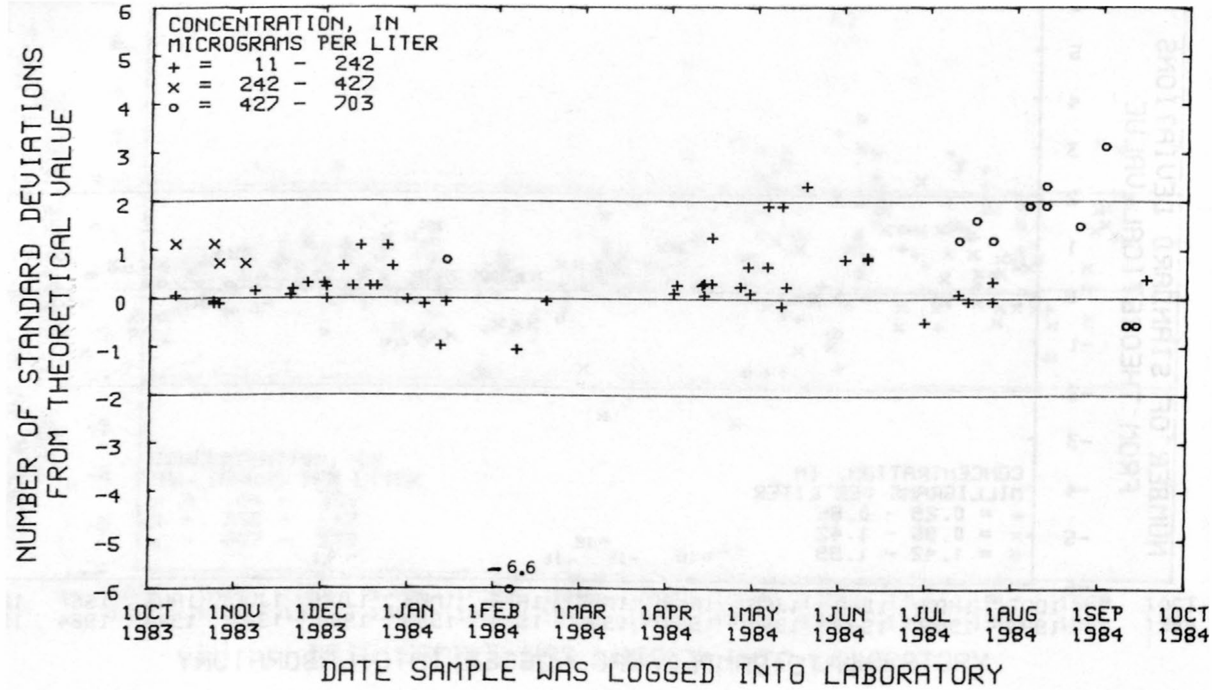

Figure 51--Iron, dissolved,
(inductively coupled plasma emission spectrometry)
data for the Atlanta laboratory.

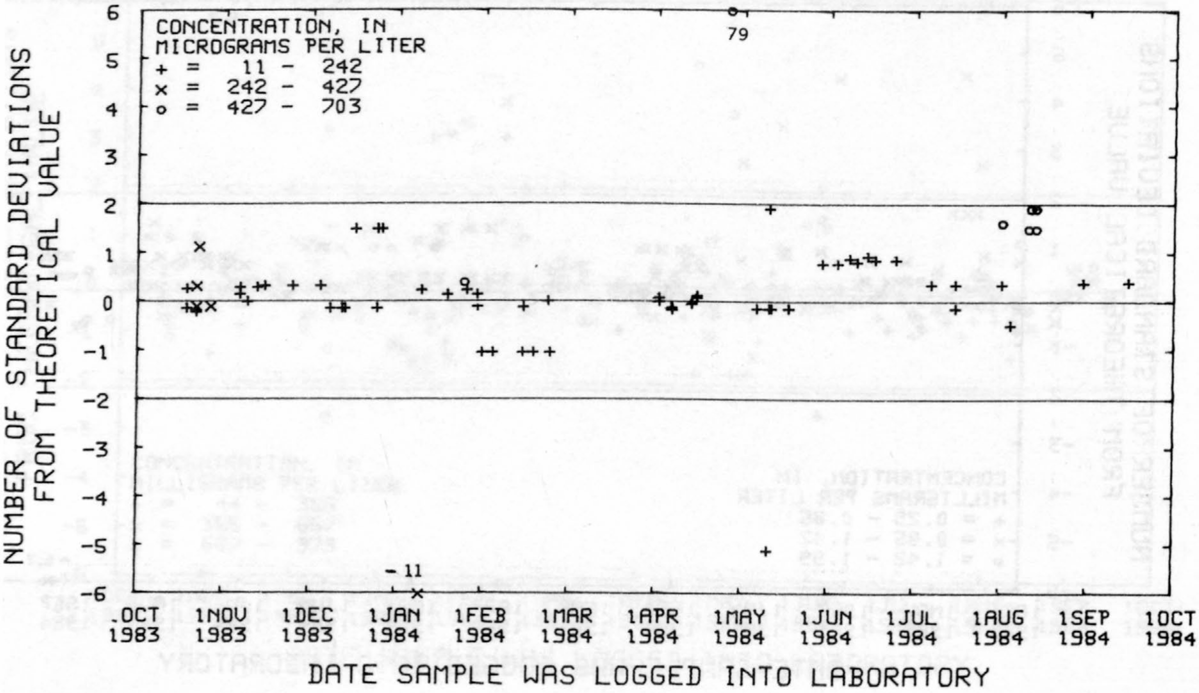

Figure 52--Iron, dissolved,
(inductively coupled plasma emission spectrometry)
data for the Denver laboratory.

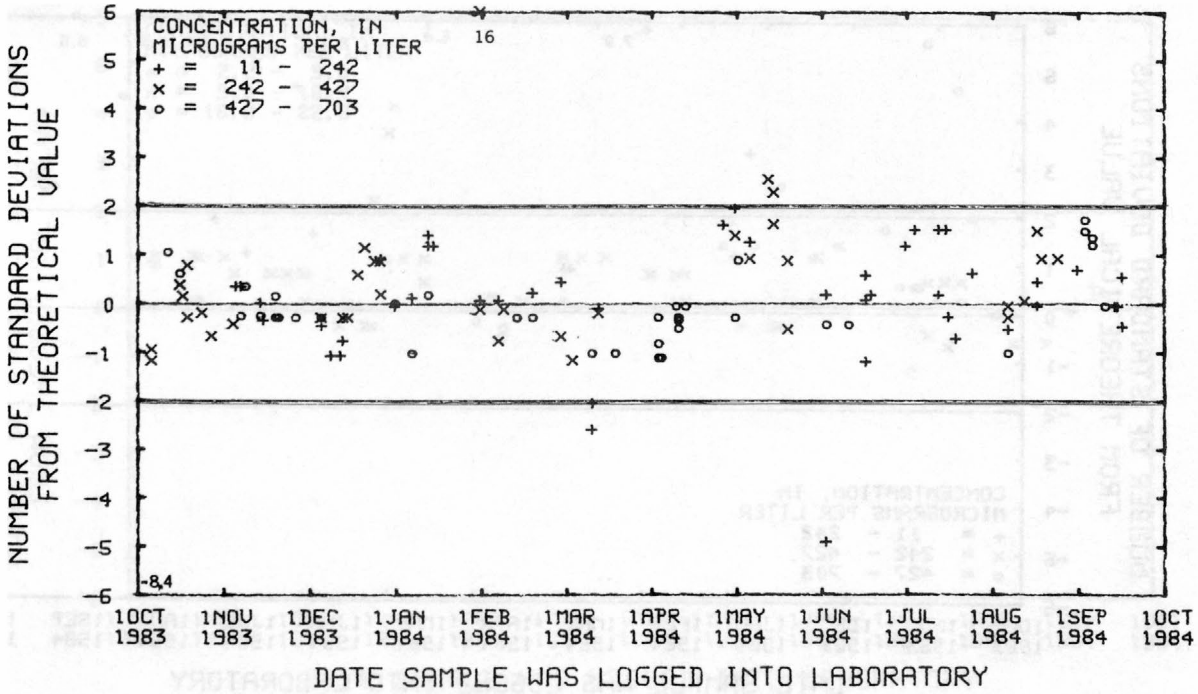

Figure 53--Iron, dissolved,
(atomic absorption spectrometry)
data for the Atlanta laboratory.

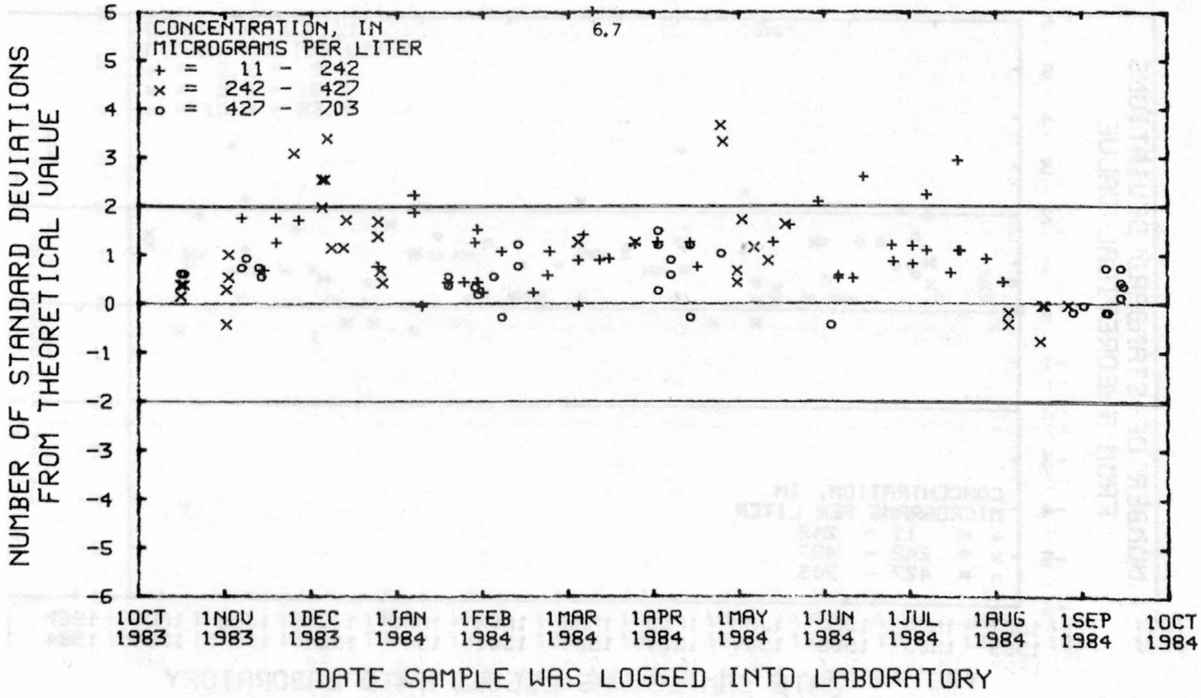

Figure 54--Iron, dissolved,
(atomic absorption spectrometry),
data for the Denver laboratory.

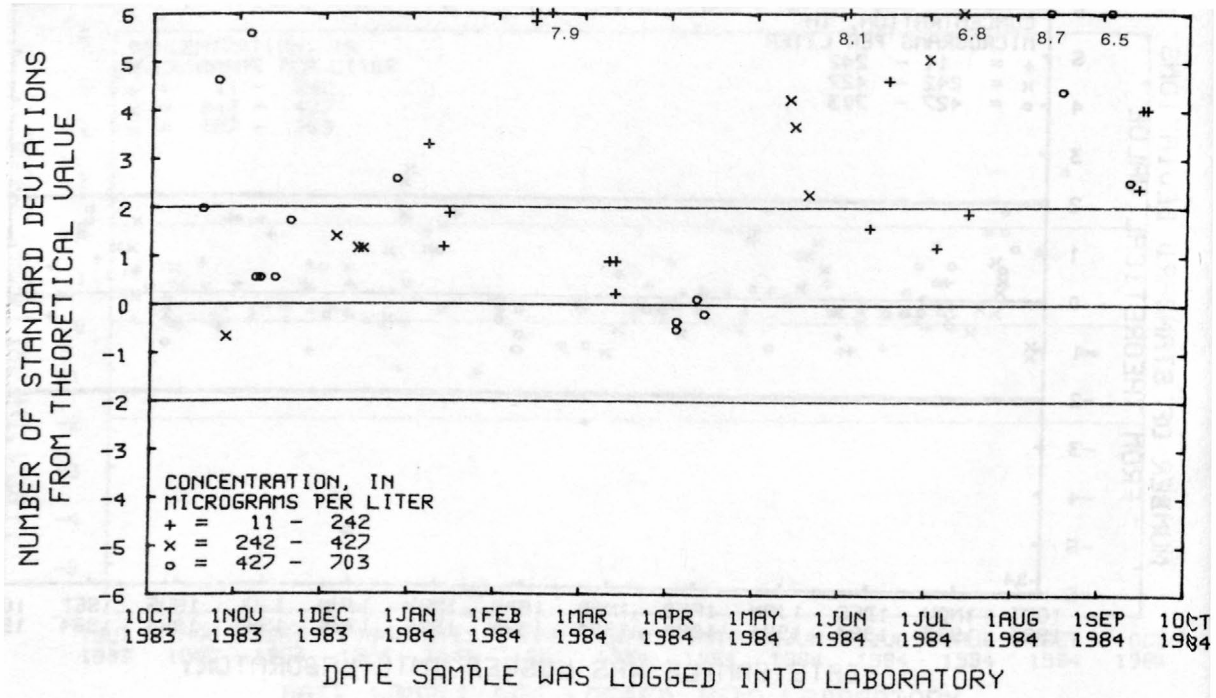

Figure 55--Iron, total recoverable, data for the Atlanta laboratory.

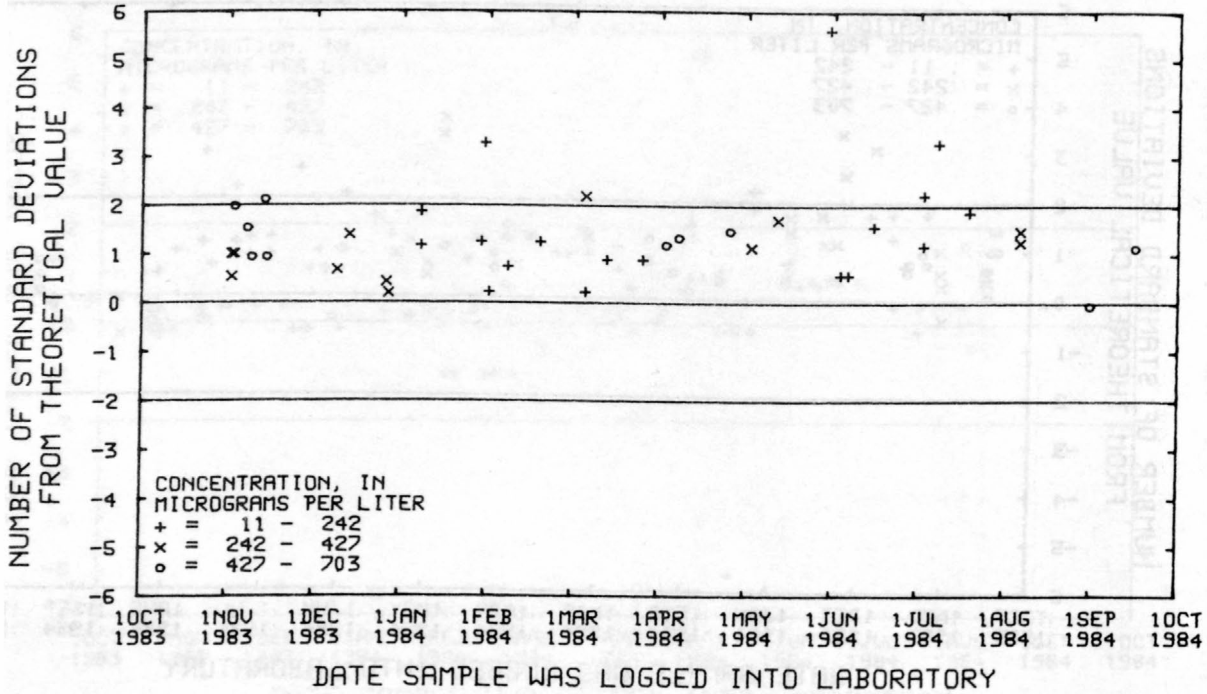

Figure 56--Iron, total recoverable, data for the Denver laboratory.

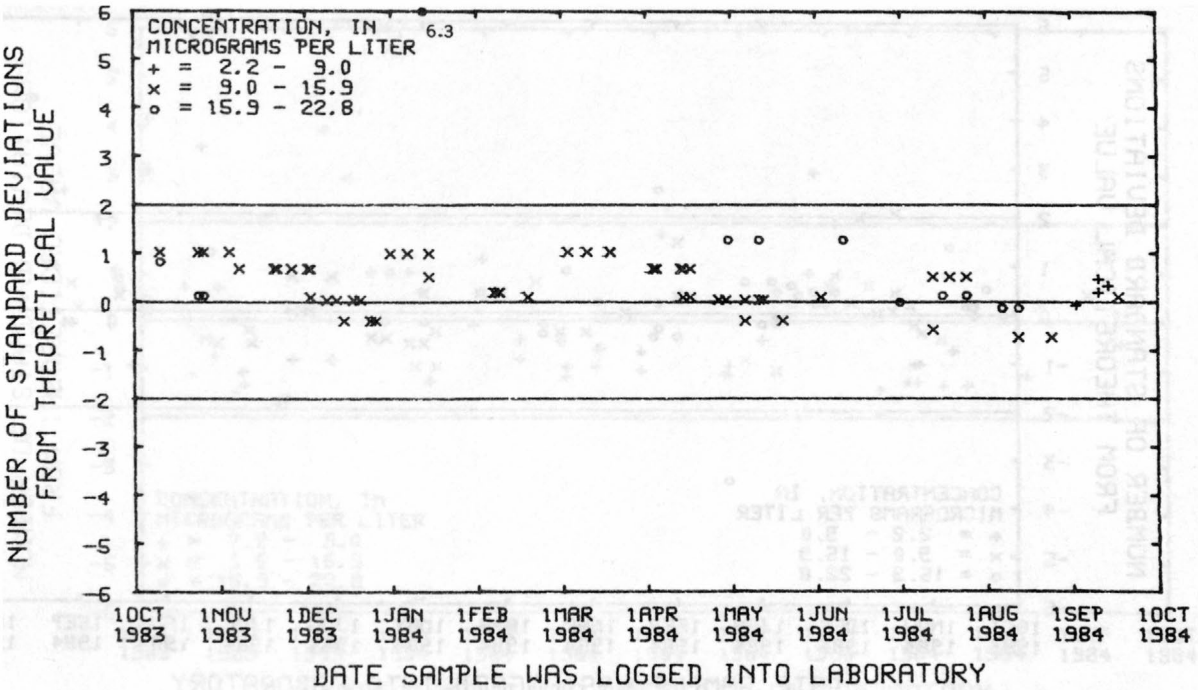

Figure 57--Lead, dissolved, (inductively coupled plasma emission spectrometry) data for the Atlanta laboratory.

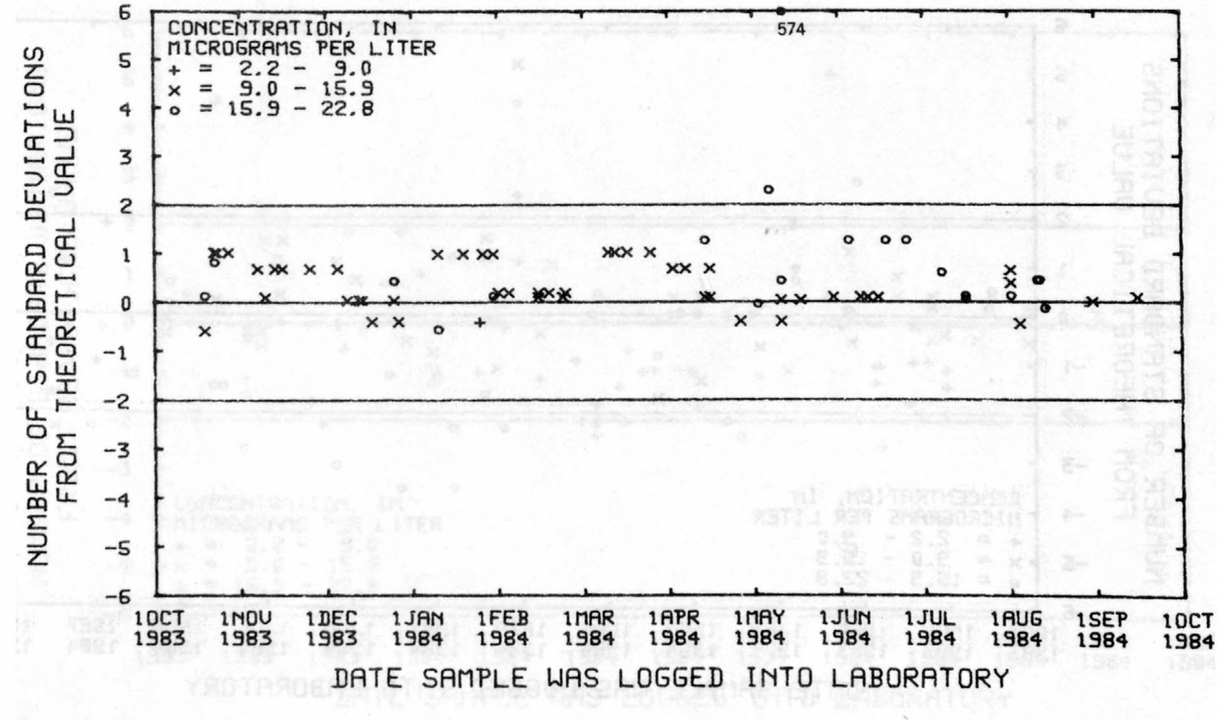

Figure 58--Lead, dissolved, (inductively coupled plasma emission spectrometry) data for the Denver laboratory.

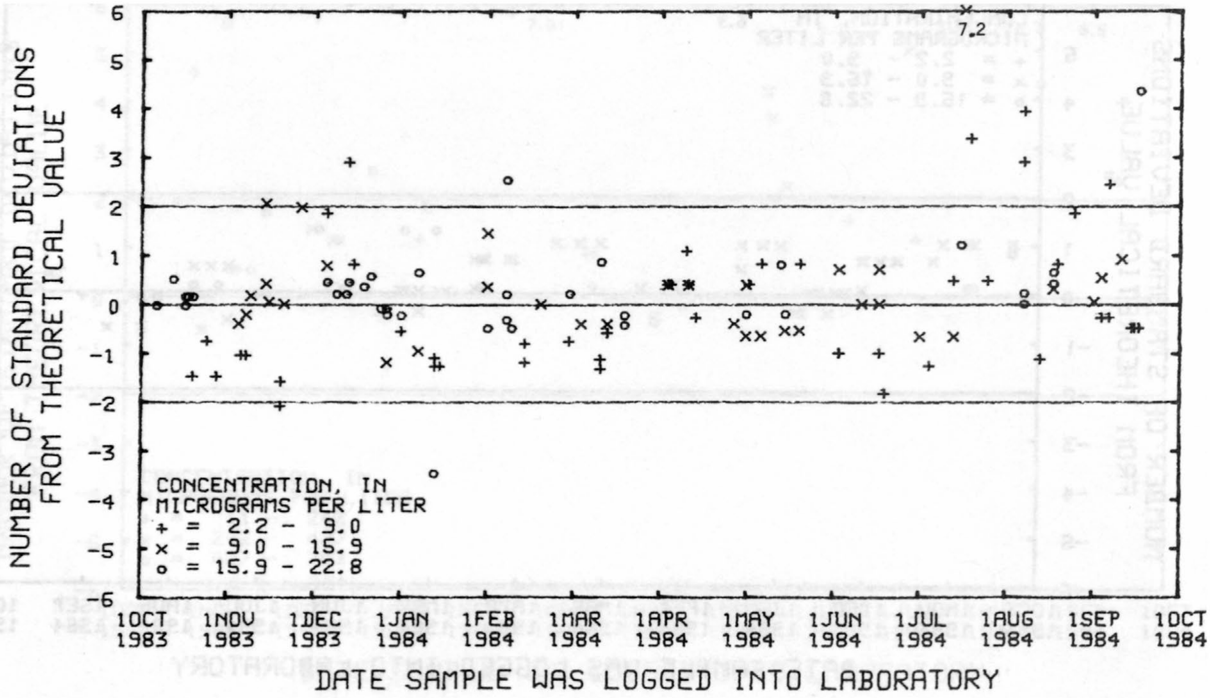

Figure 59--Lead, dissolved, (atomic absorption spectrometry) data for the Atlanta laboratory.

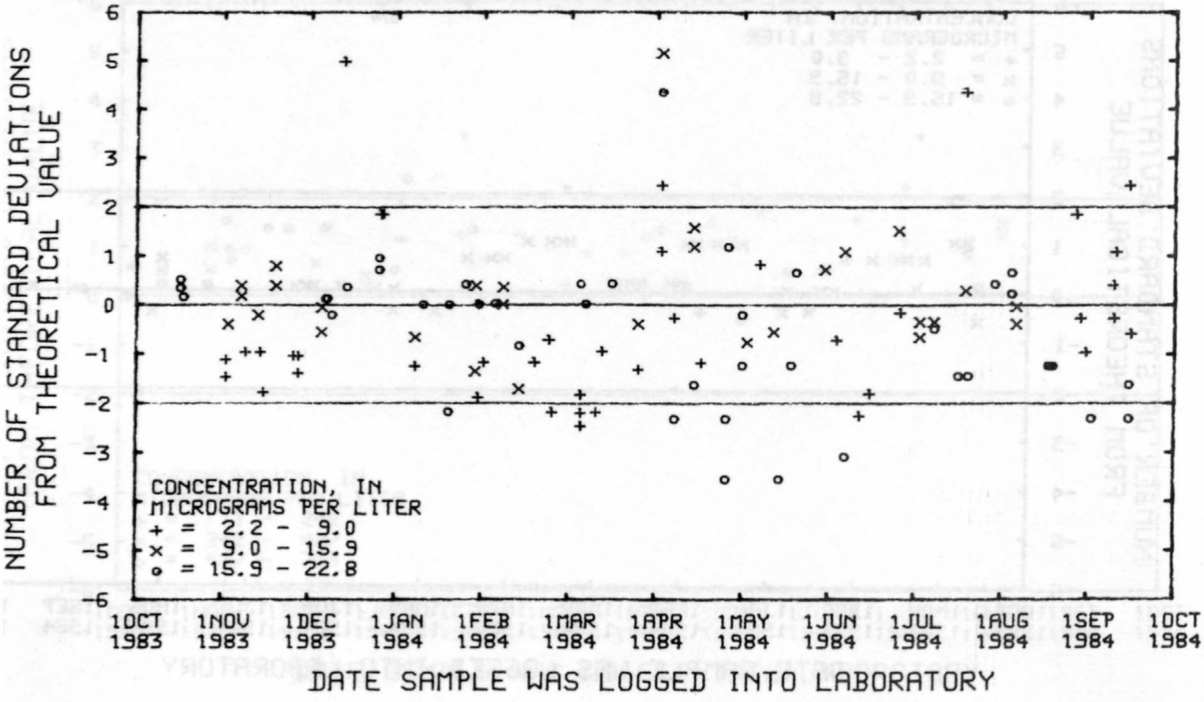

Figure 60--Lead, dissolved, (atomic absorption spectrometry) data for the Denver laboratory.

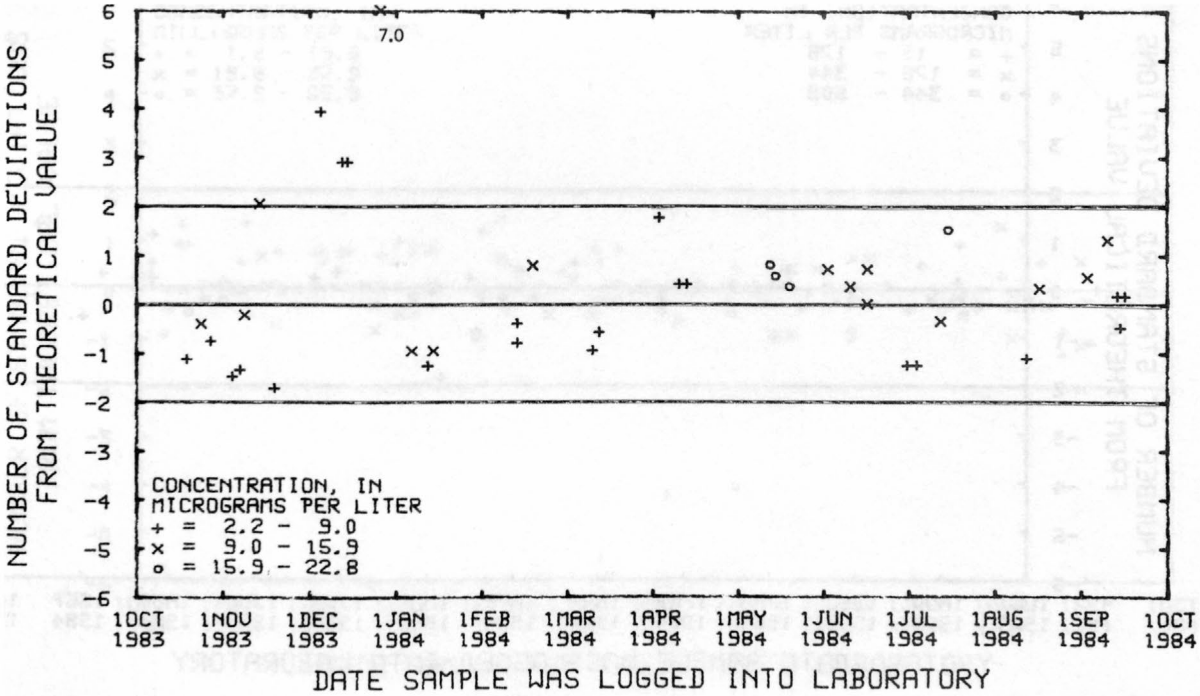

Figure 61--Lead, total recoverable, data for the Atlanta laboratory.

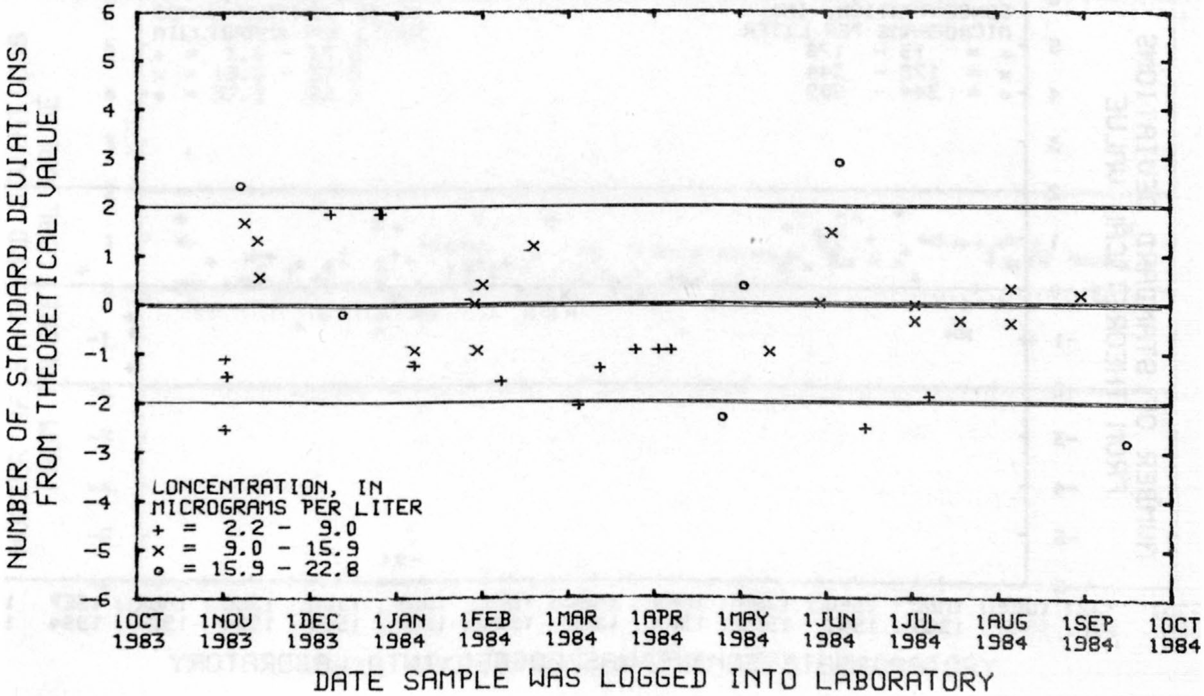

Figure 62--Lead, total recoverable, data for the Denver laboratory.

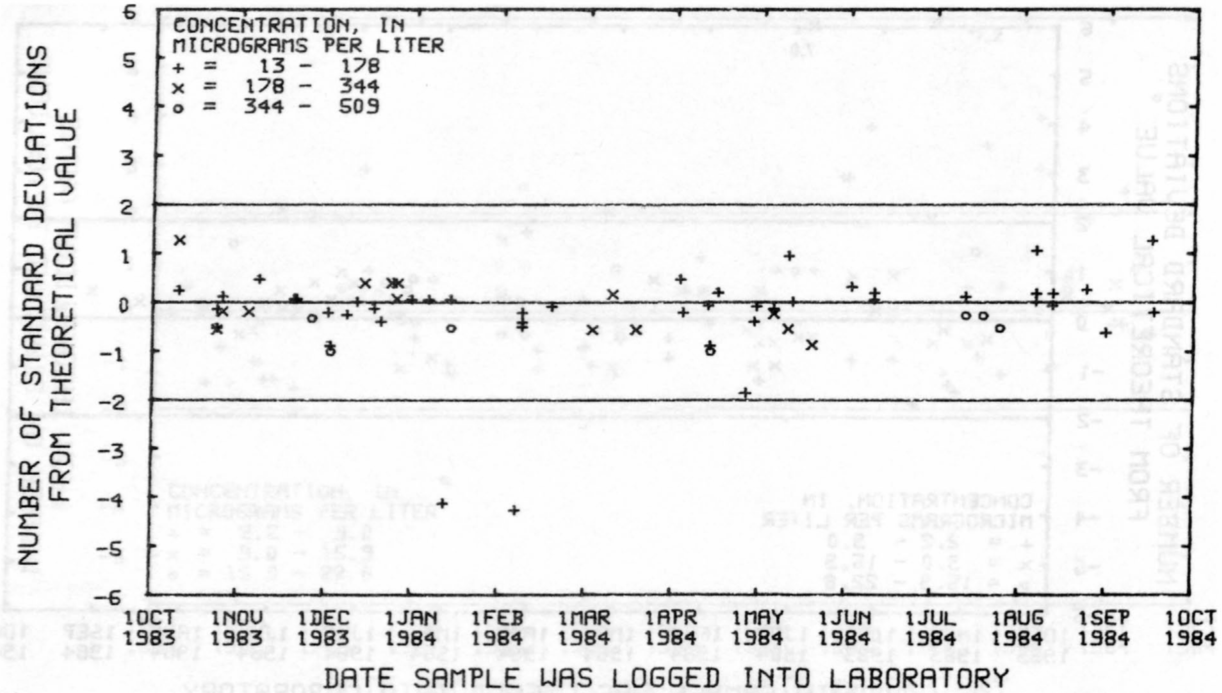

Figure 63--Lithium, dissolved, data for the Atlanta laboratory.

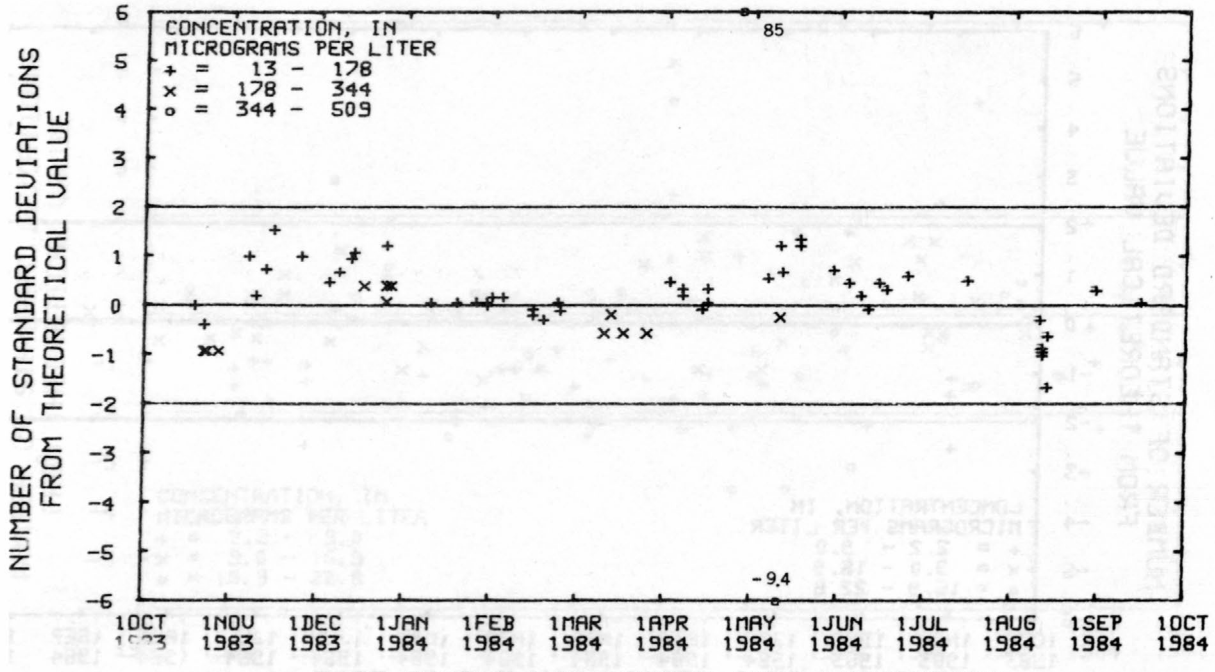

Figure 64--Lithium, dissolved, data for the Denver laboratory.

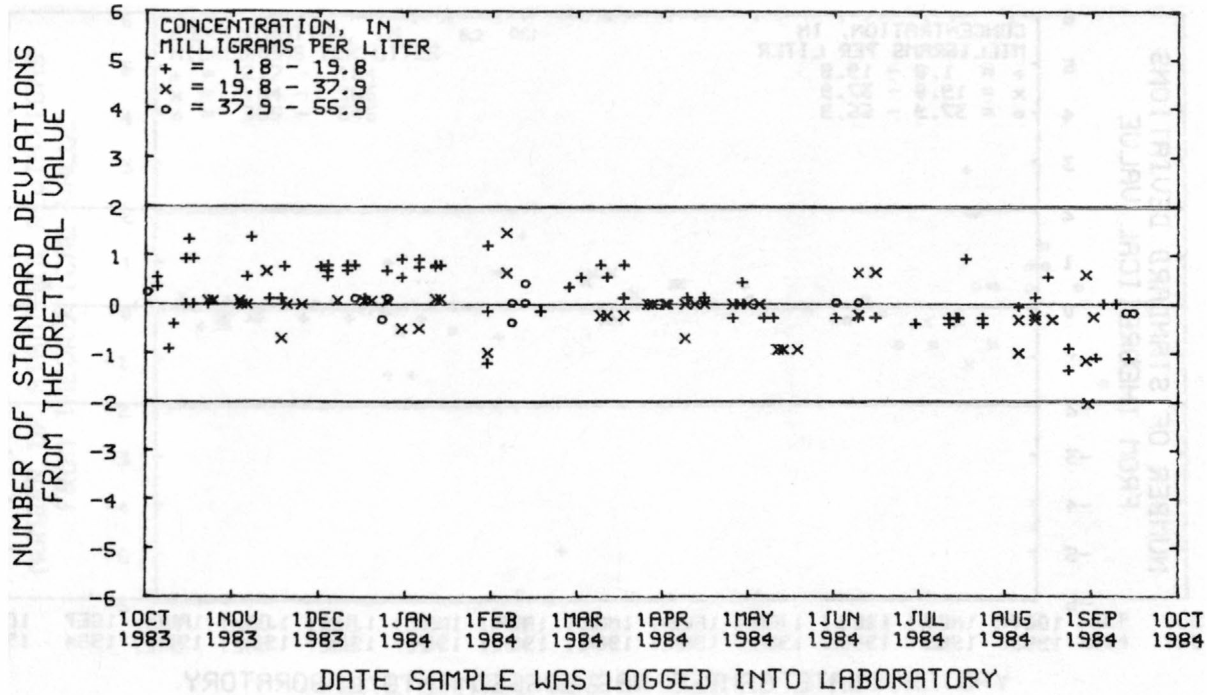

Figure 65--Magnesium, dissolved, (inductively coupled plasma emission spectrometry) data from Atlanta laboratory.

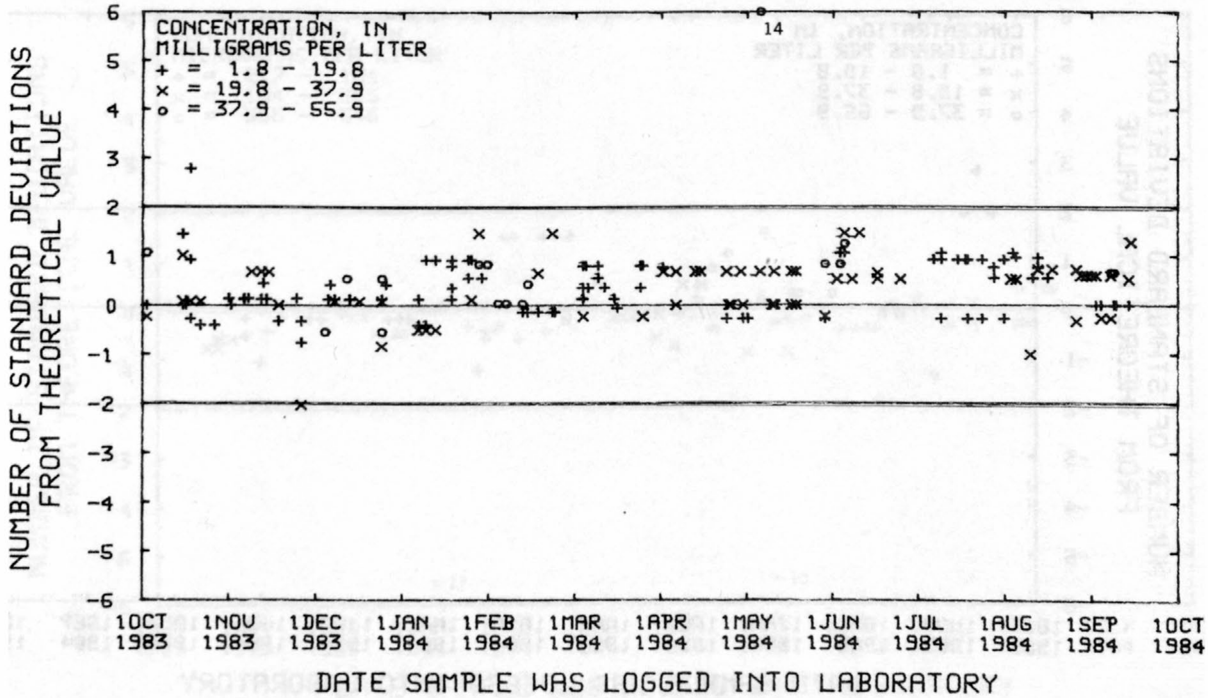

Figure 66--Magnesium, dissolved, (inductively coupled plasma emission spectrometry), data from Denver laboratory.

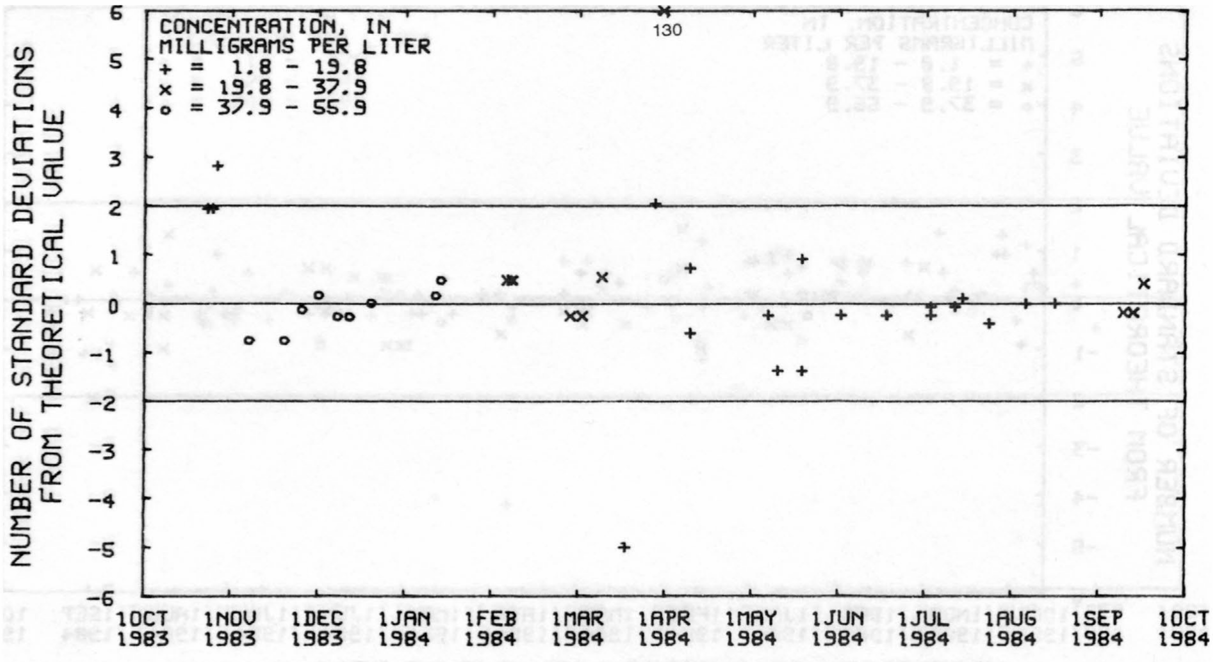

Figure 67--Magnesium, dissolved, (atomic absorption spectrometry) data from Atlanta laboratory.

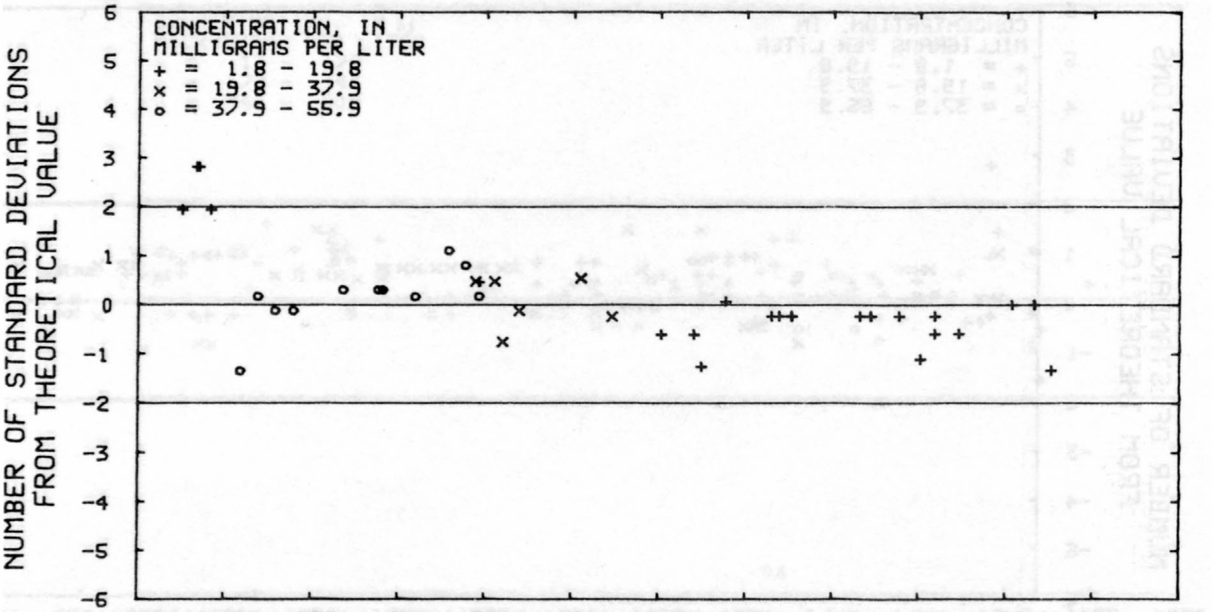

Figure 68--Magnesium, dissolved, (atomic absorption spectrometry) data from Denver laboratory.

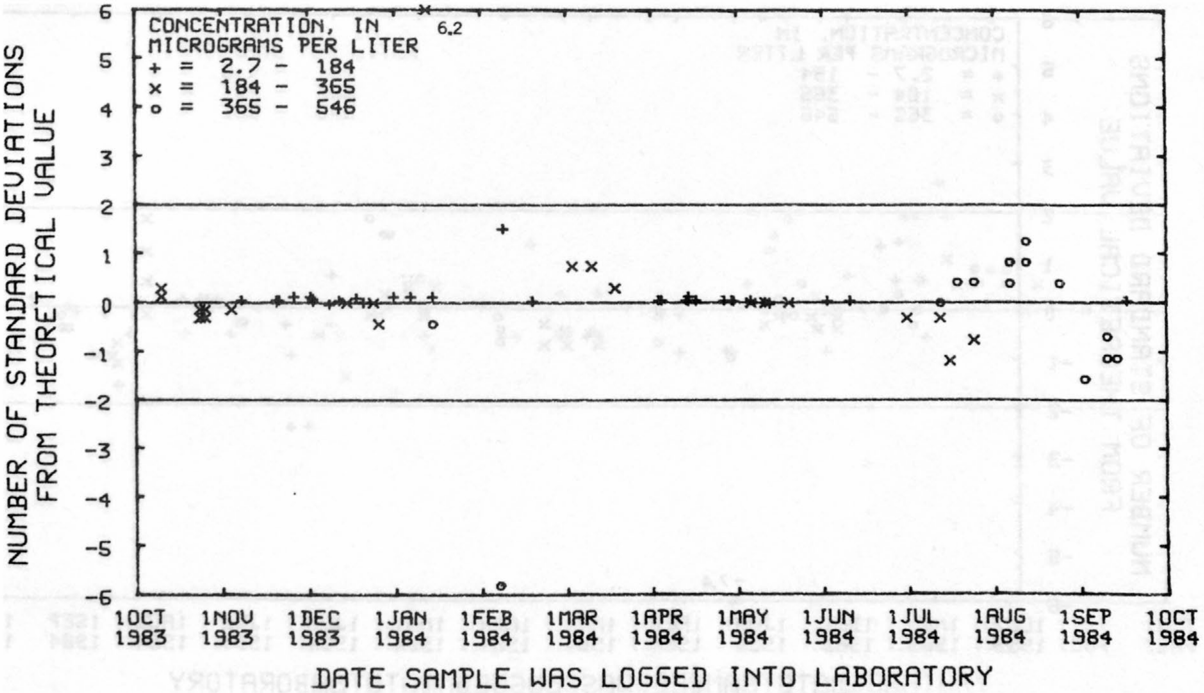

Figure 69--Manganese, dissolved,
(inductively coupled plasma emission spectrometry)
data for the Atlanta laboratory.

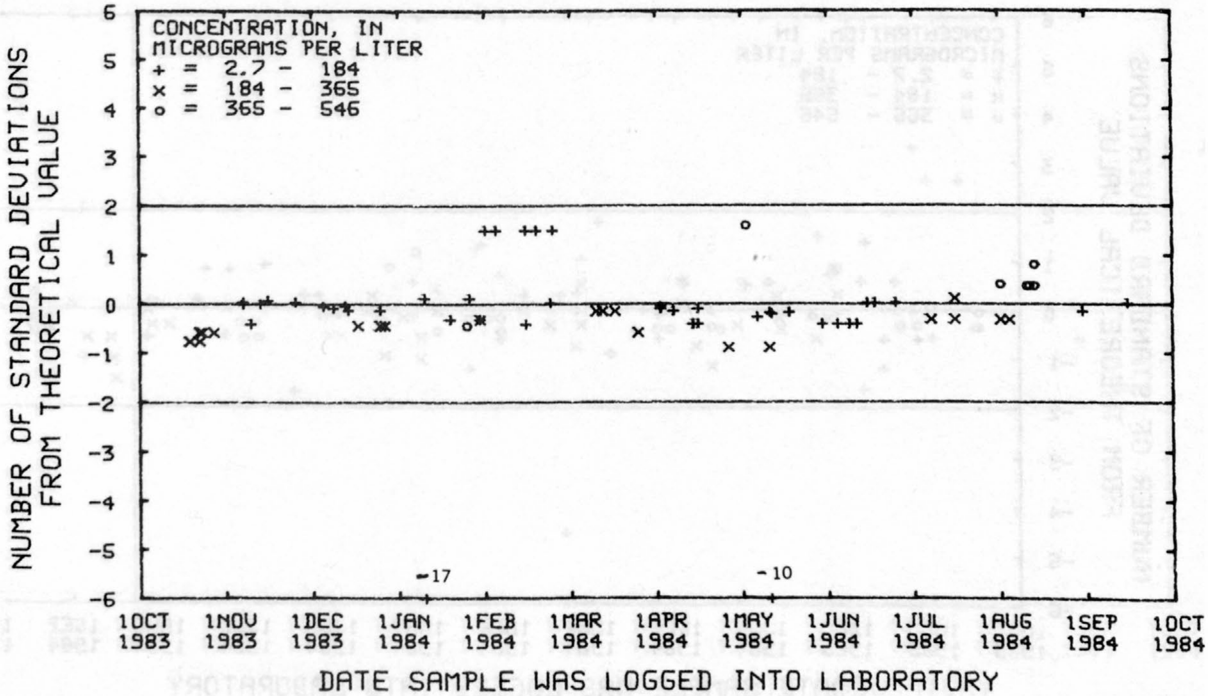

Figure 70--Manganese, dissolved,
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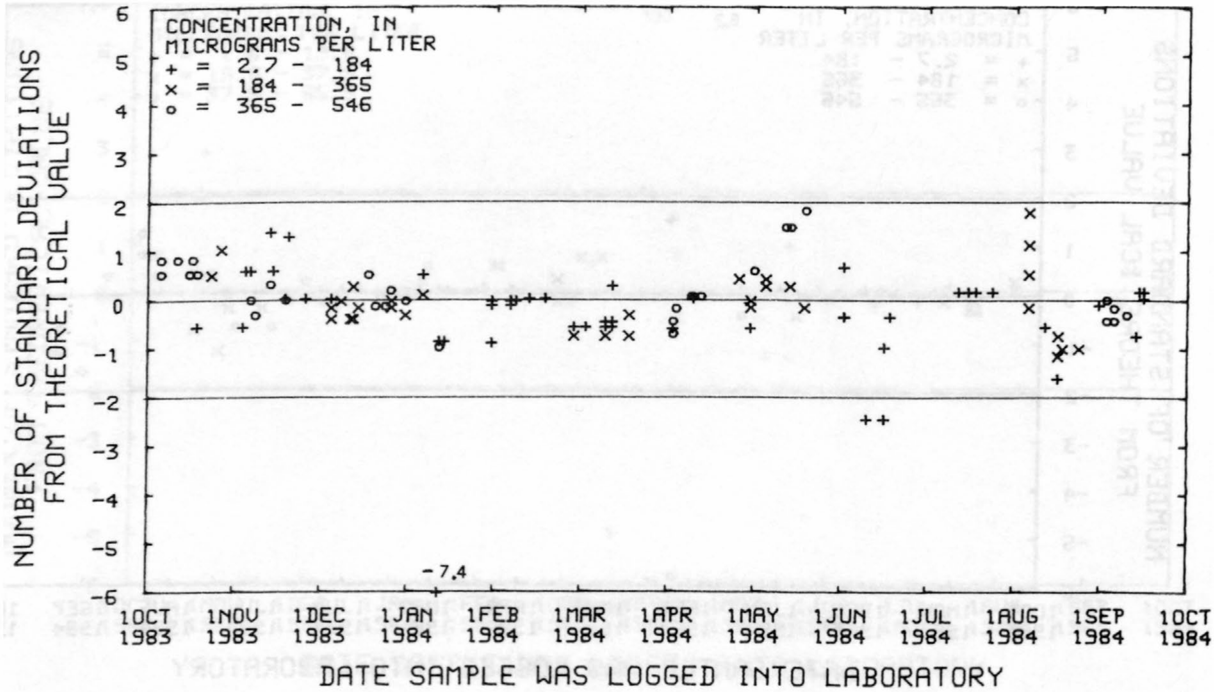

Figure 71--Manganese, dissolved, (atomic absorption spectrometry) data for the Atlanta laboratory.

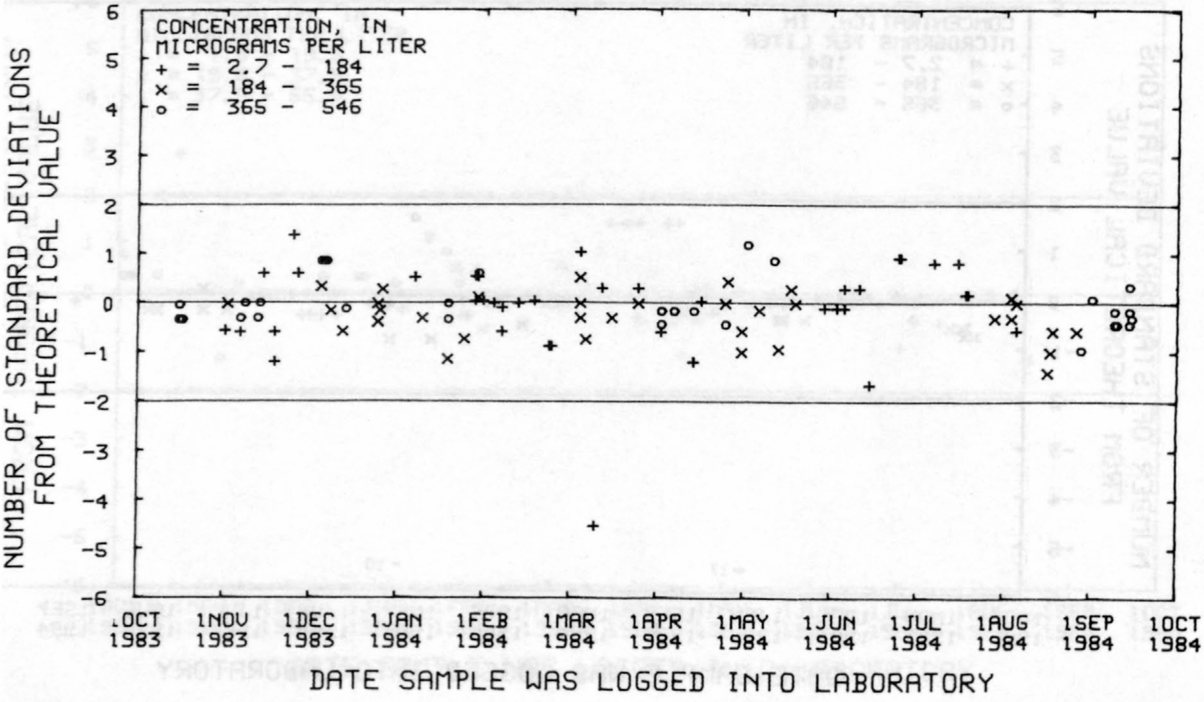

Figure 72—Manganese, dissolved, (atomic absorption spectrometry) data for the Denver laboratory.

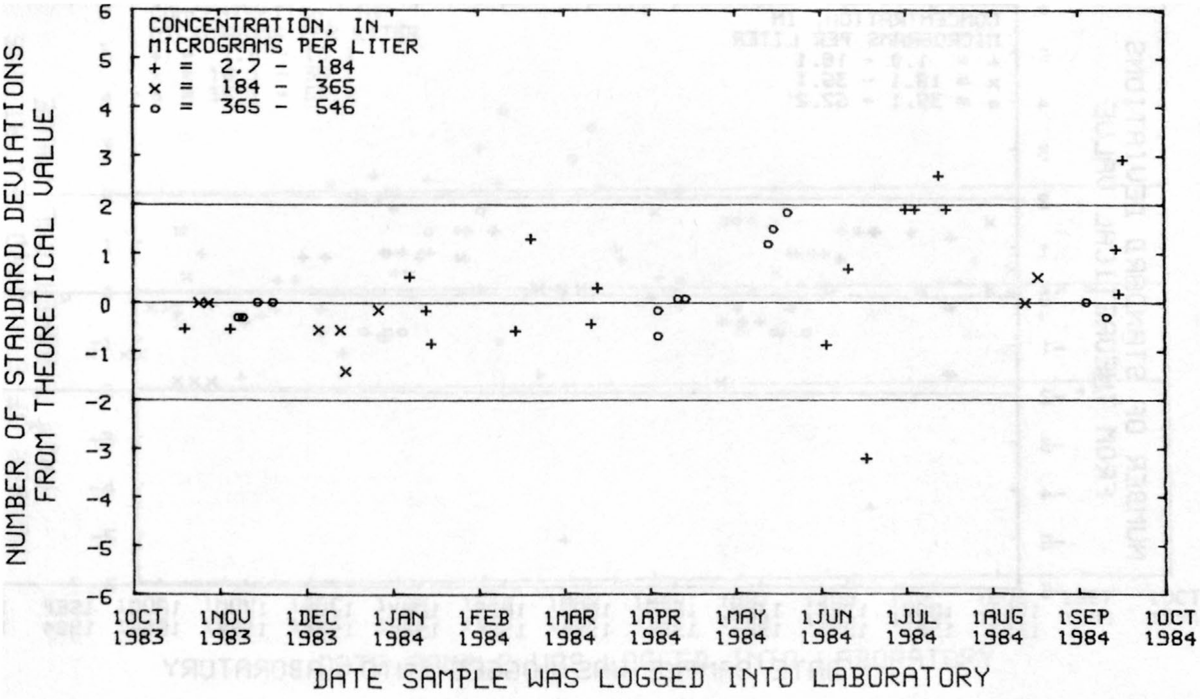

Figure 73--Manganese, total recoverable, data for the Atlanta laboratory.

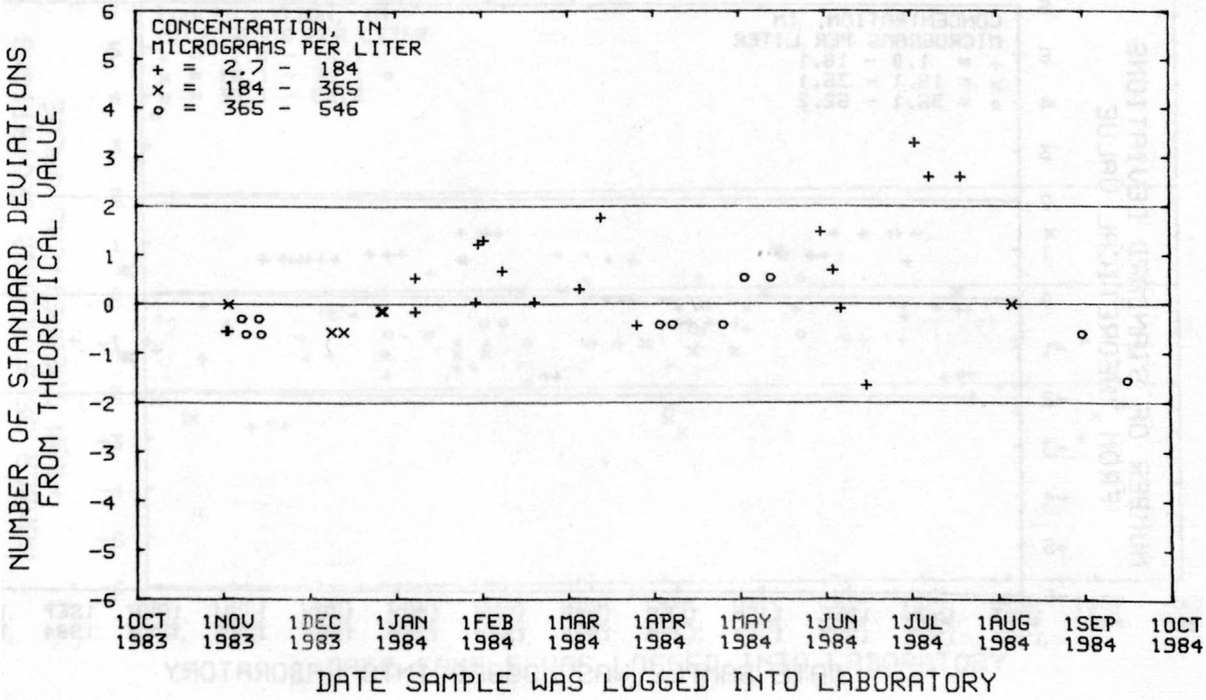

Figure 74--Manganese, total recoverable, data for the Denver laboratory.

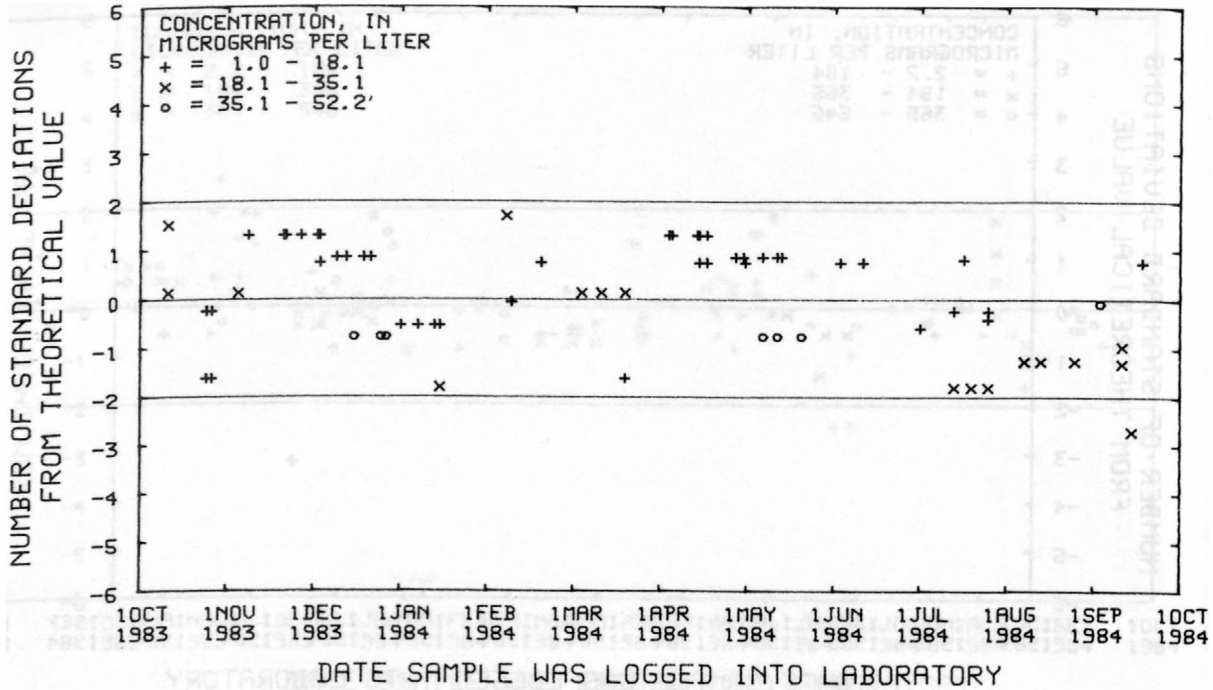

Figure 75--Molybdenum, dissolved,
(inductively coupled plasma emission spectrometry)
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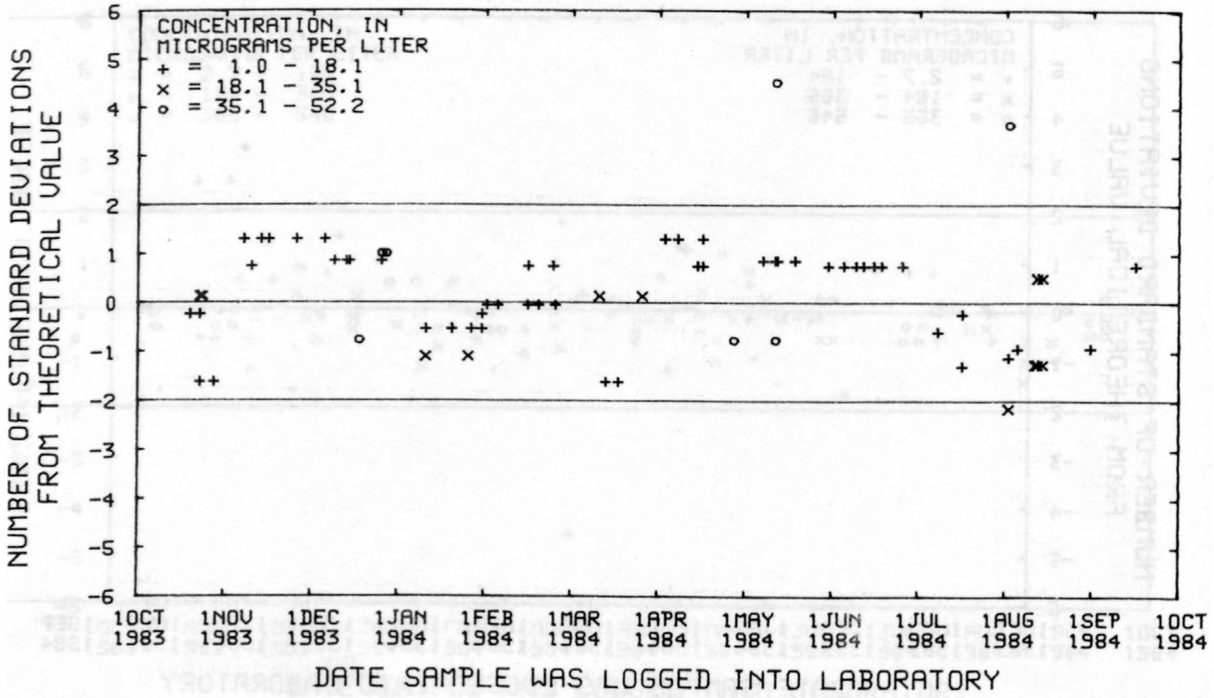

Figure 76--Molybdenum, dissolved,
(inductively coupled plasma emission spectrometry)
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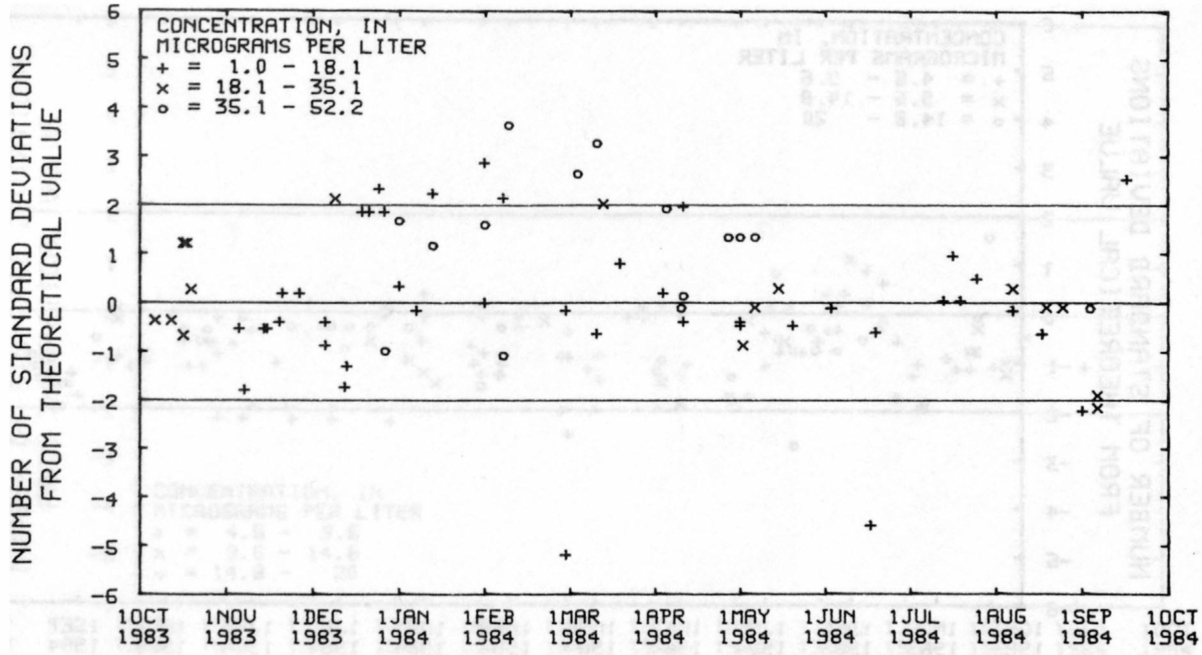

Figure 77--Molybdenum, dissolved, (atomic absorption spectrometry) data for the Atlanta laboratory.

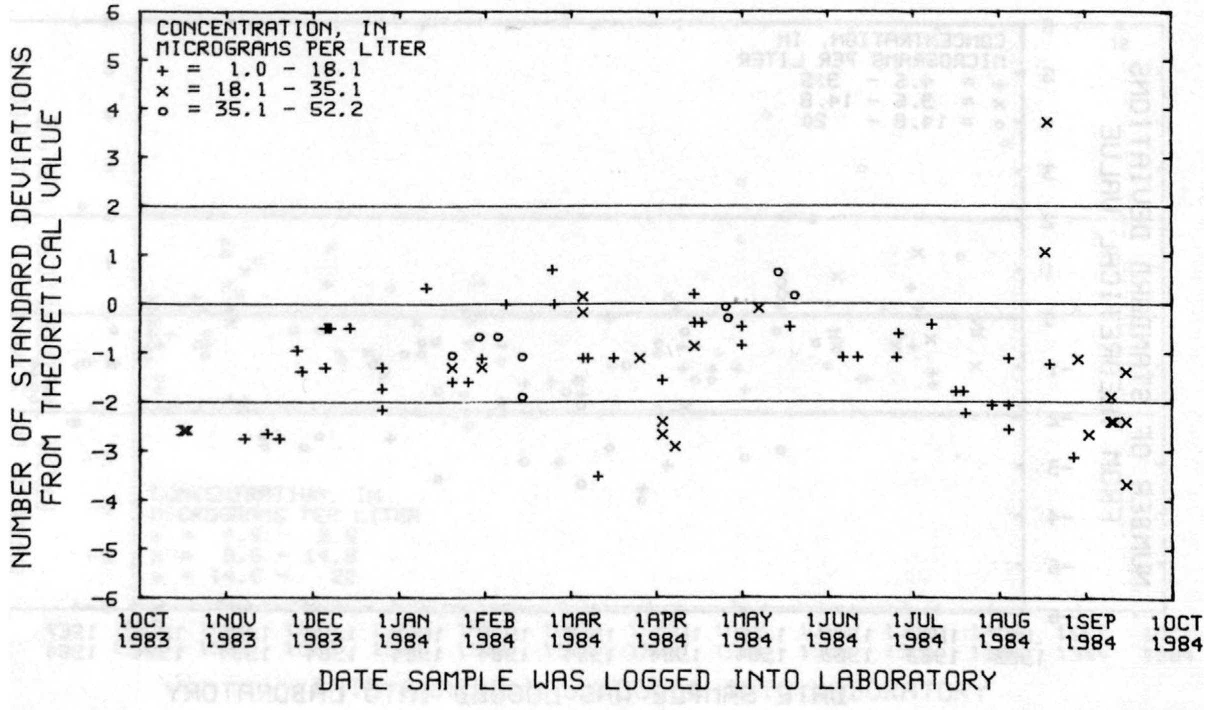

Figure 78--Molybdenum, dissolved, (atomic absorption spectrometry) data for the Denver laboratory.

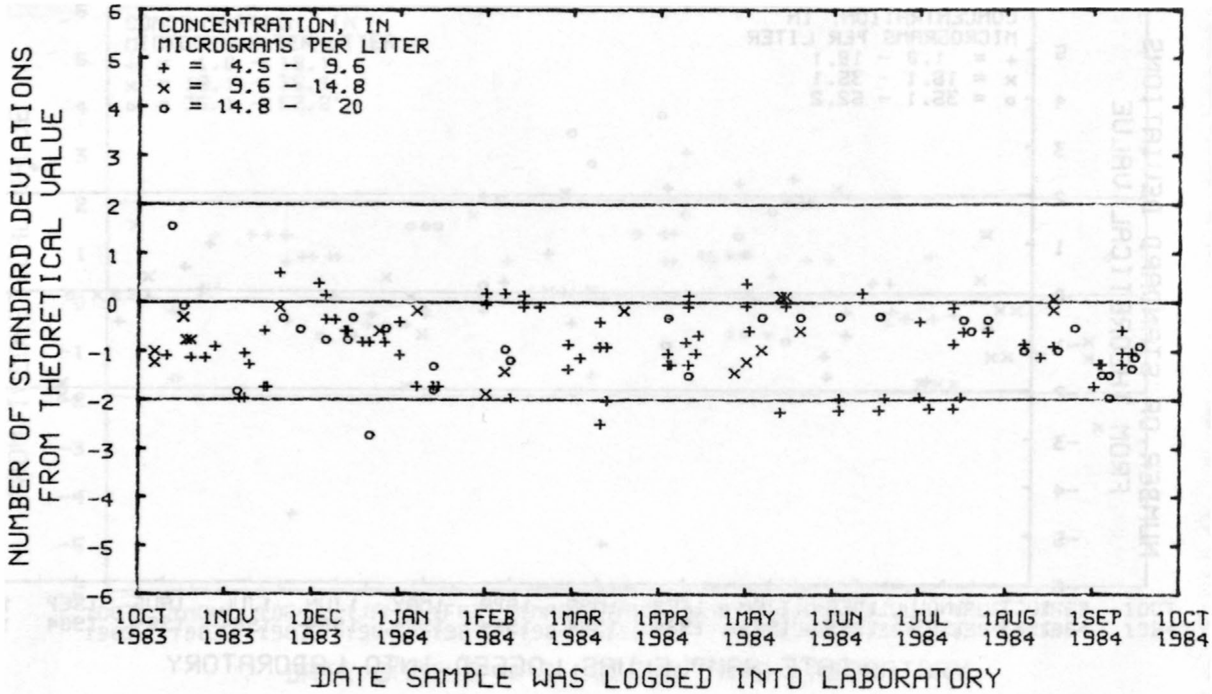

Figure 79--Nickel, dissolved, data for the Atlanta laboratory.

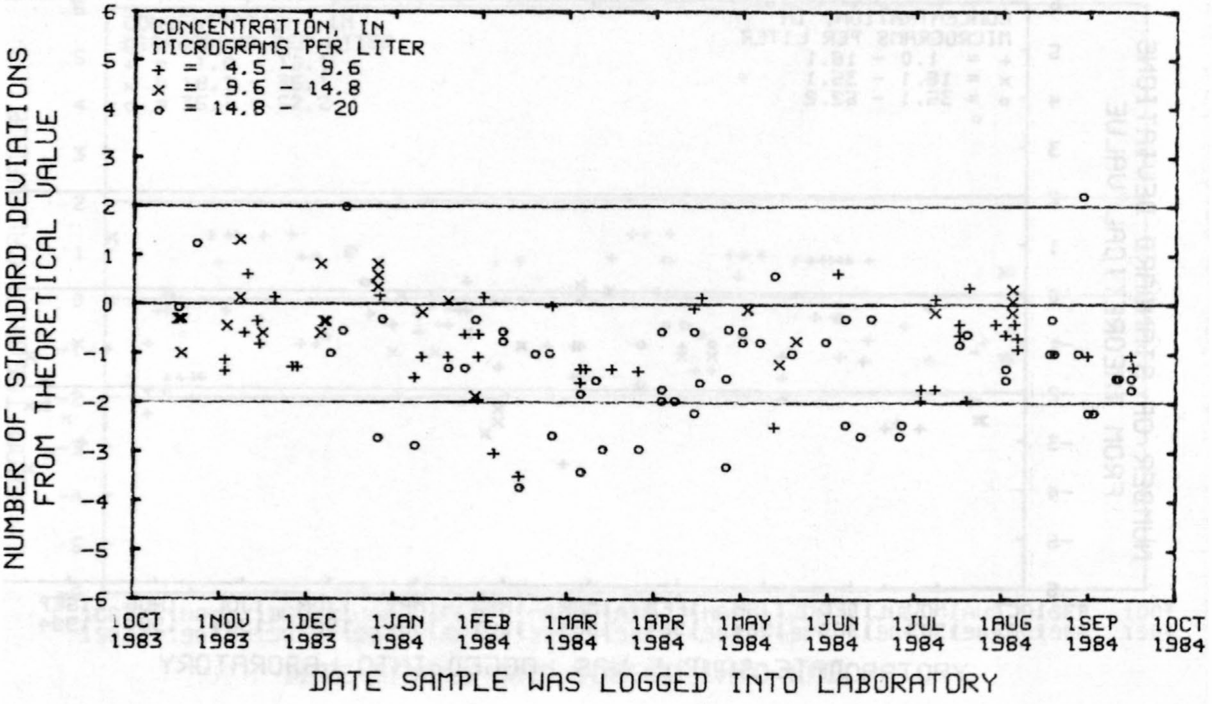

Figure 80--Nickel, dissolved, data for the Denver laboratory.

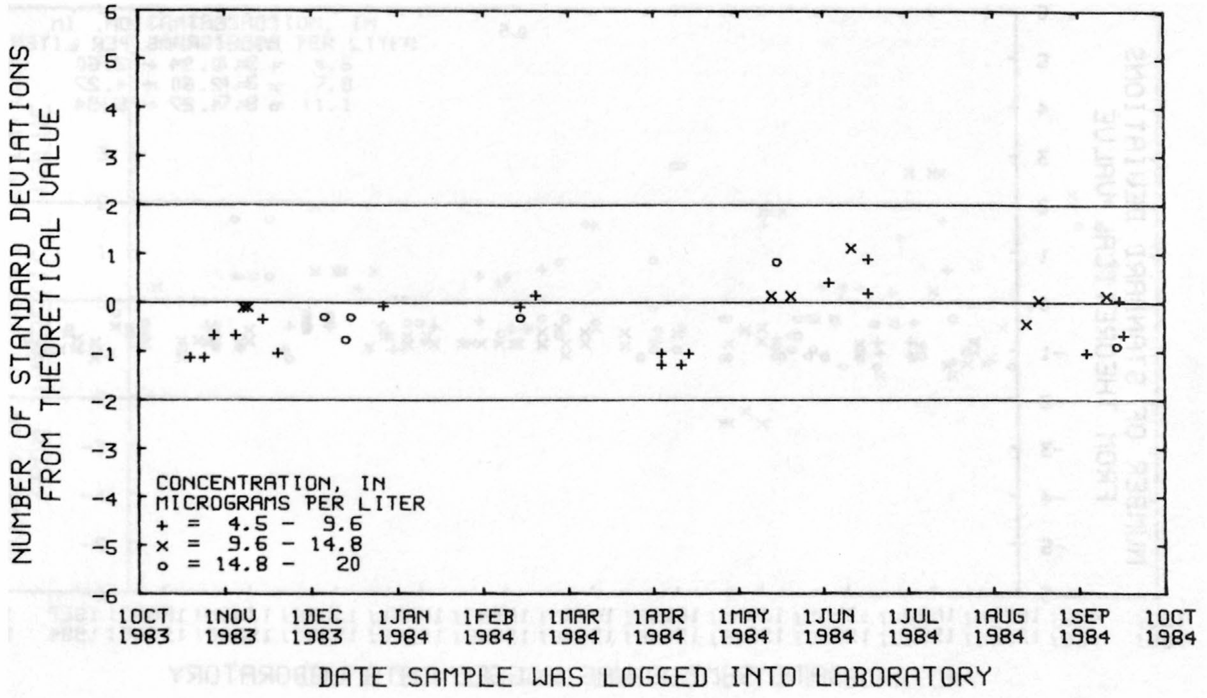

Figure 81--Nickel, total recoverable, data for the Atlanta laboratory.

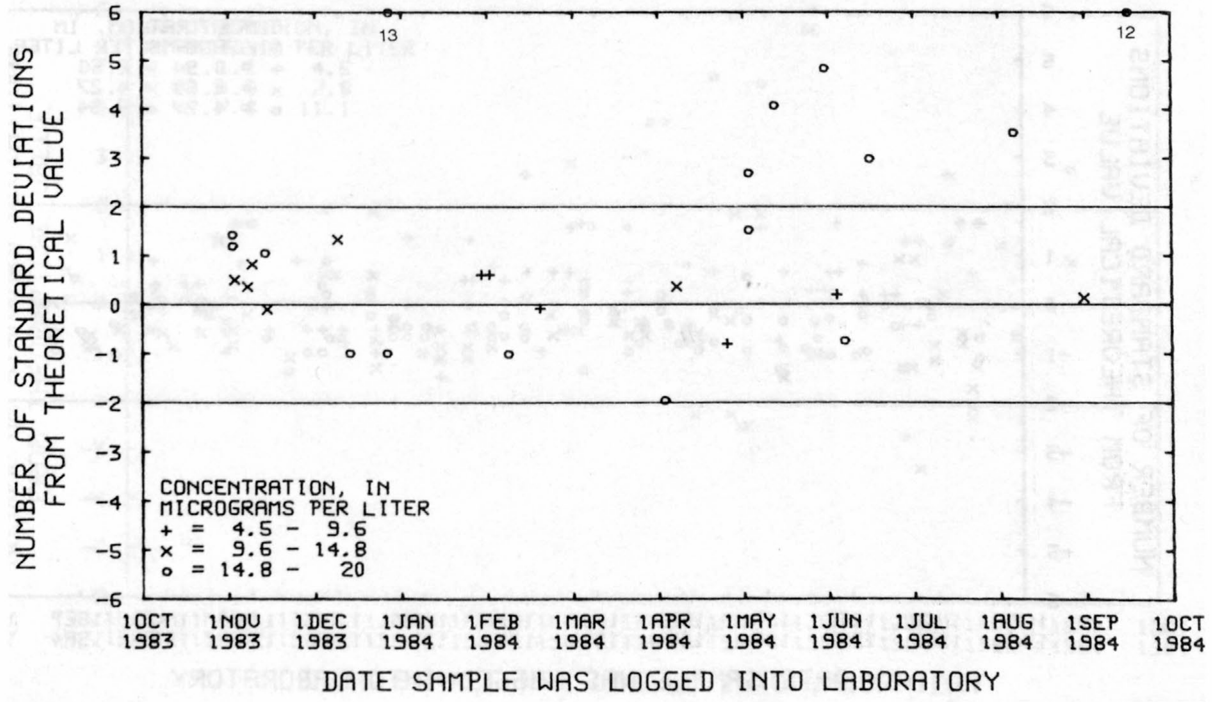

Figure 82--Nickel, total recoverable, data for the Denver laboratory.

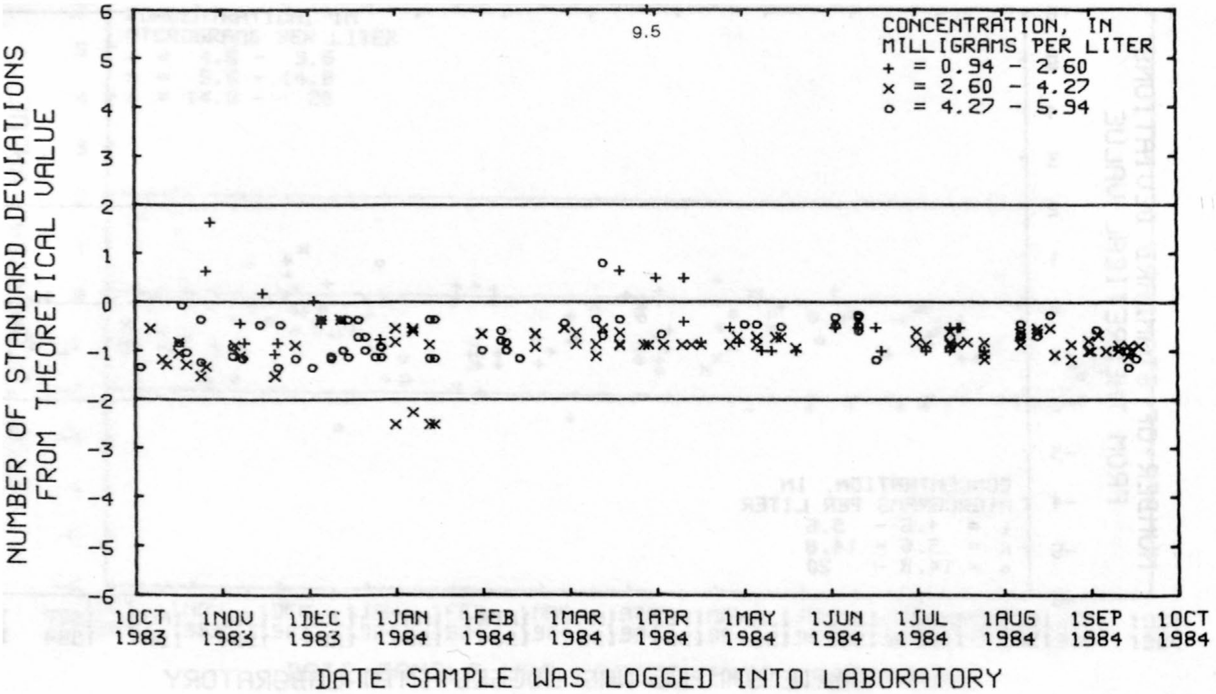

Figure 83--Potassium, dissolved, data from Atlanta laboratory.

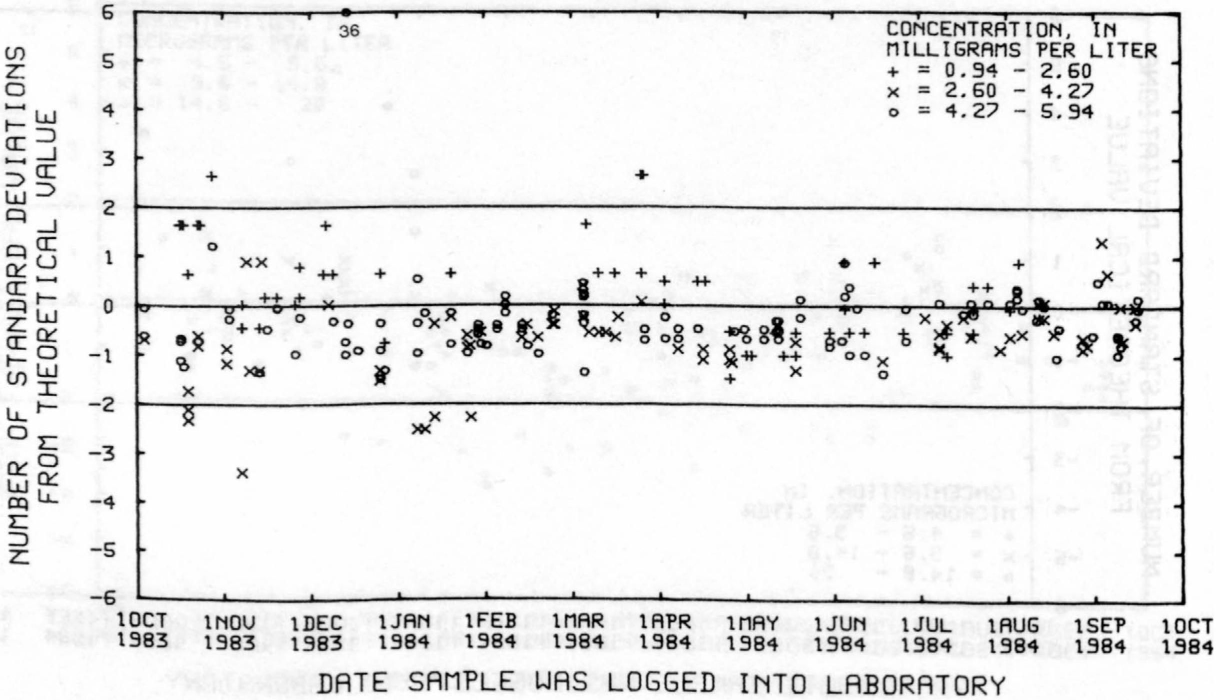

Figure 84--Potassium, dissolved, data from Denver laboratory.

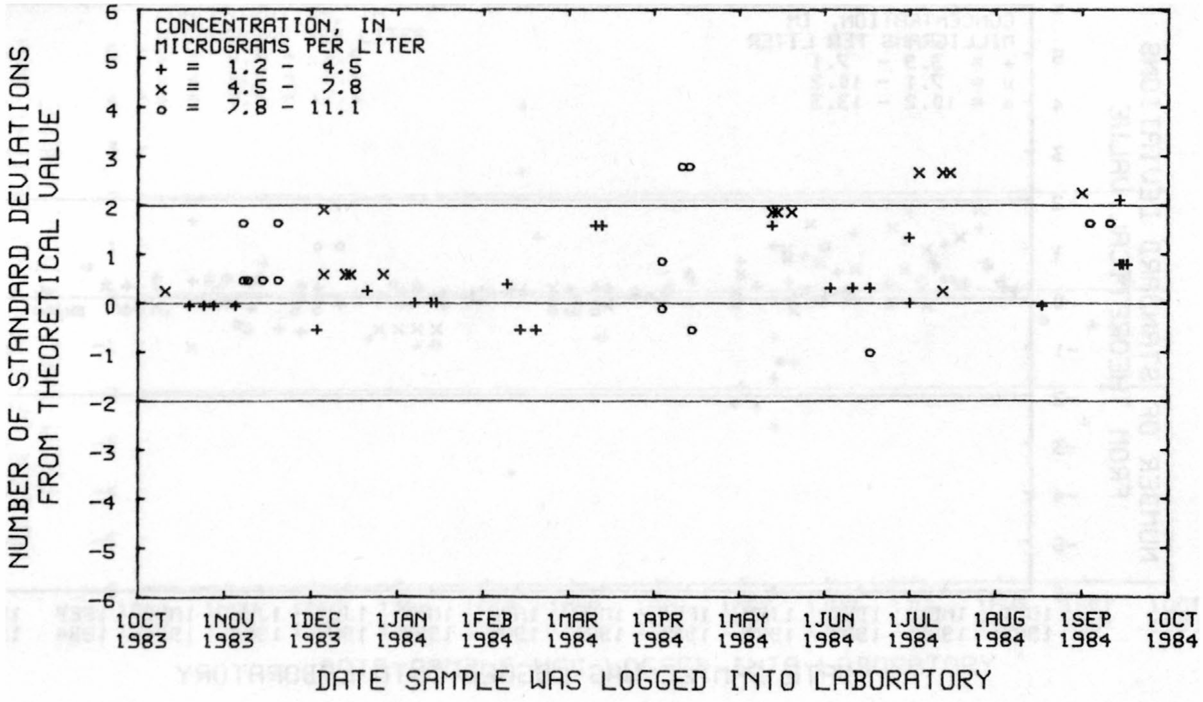

Figure 85--Selenium, dissolved, data for the Atlanta laboratory.

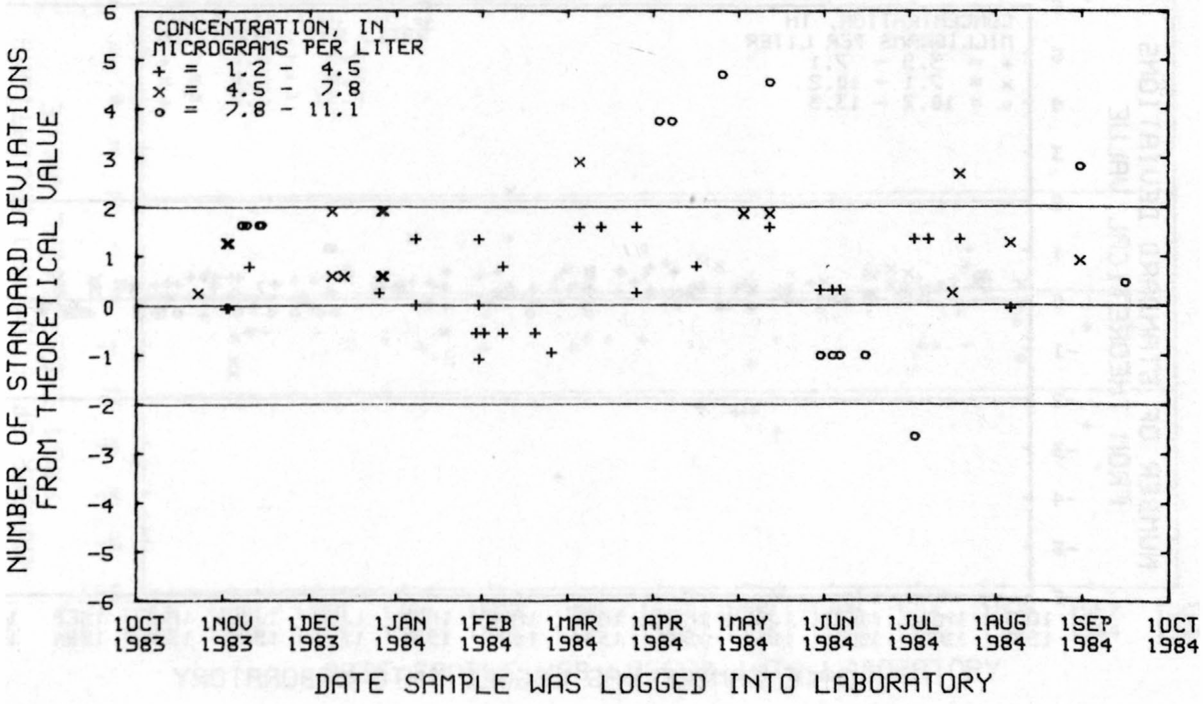

Figure 86--Selenium, dissolved, data for the Denver laboratory.

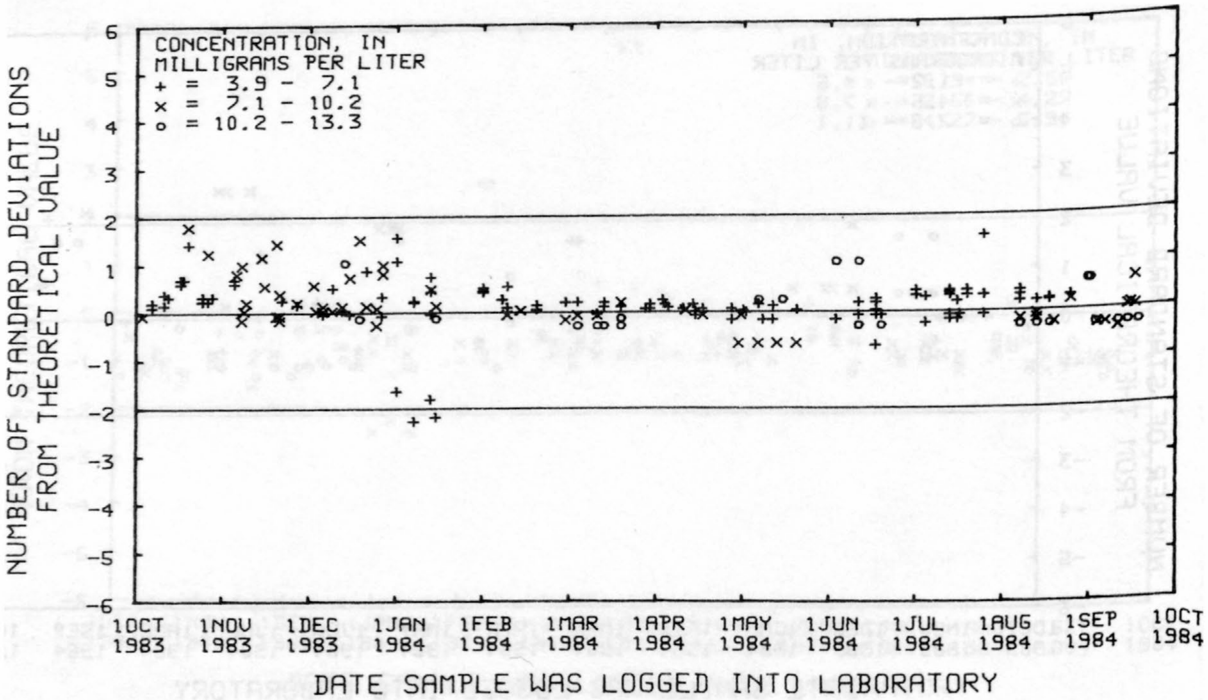

Figure 87--Silica, dissolved, data from Atlanta laboratory.

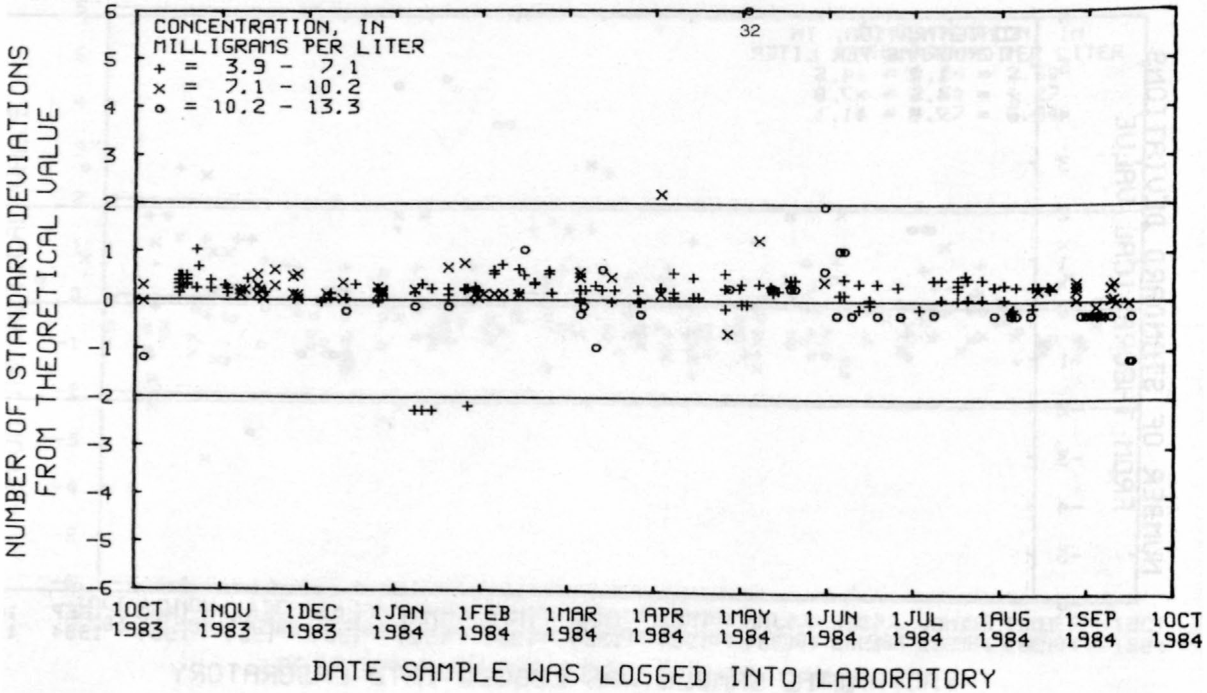

Figure 88--Silica, dissolved, data from Denver laboratory.

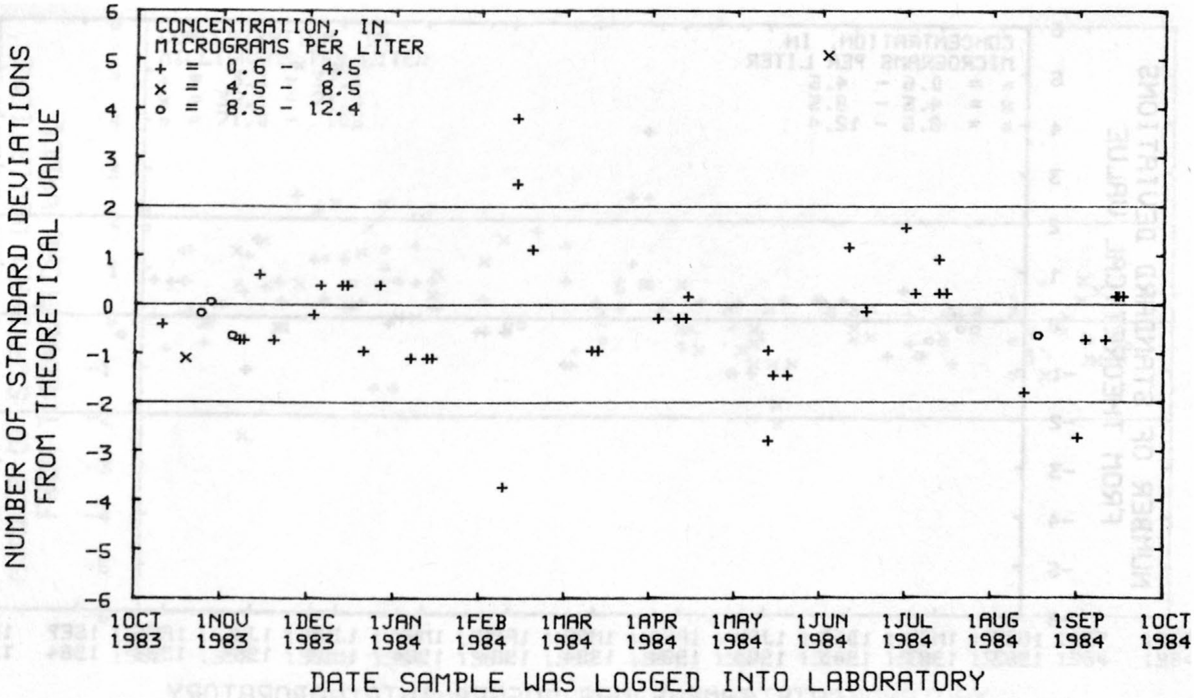

Figure 89--Silver, dissolved, data for the Atlanta laboratory.

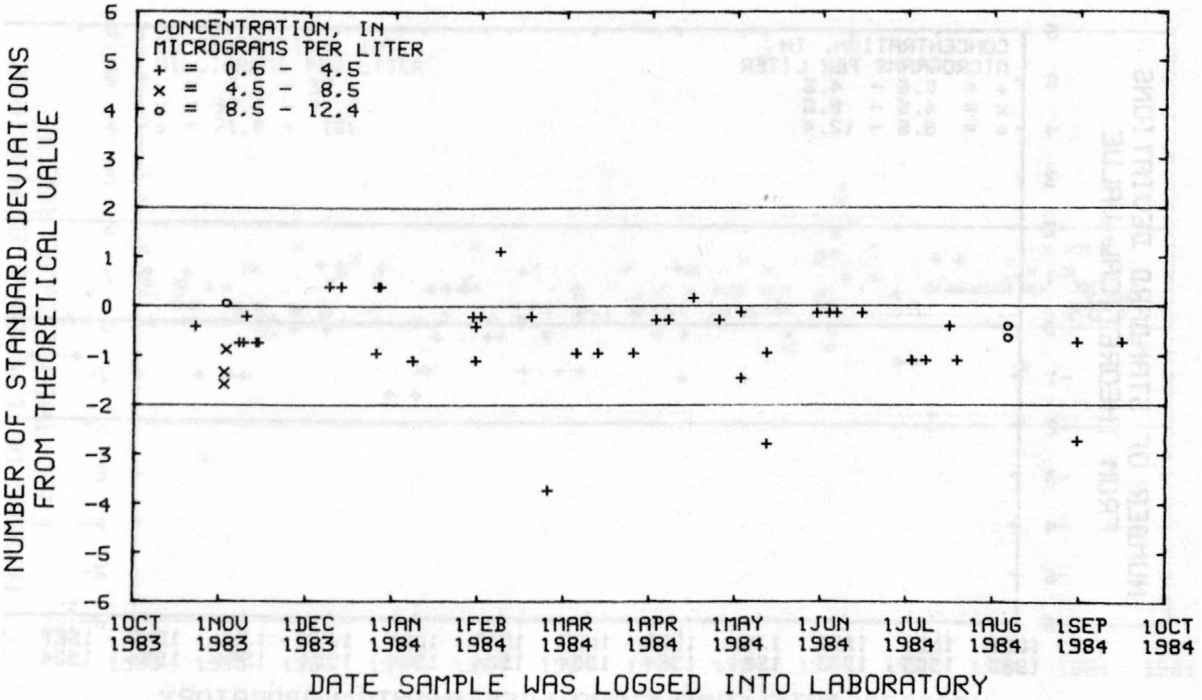

Figure 90--Silver, dissolved, data for the Denver laboratory.

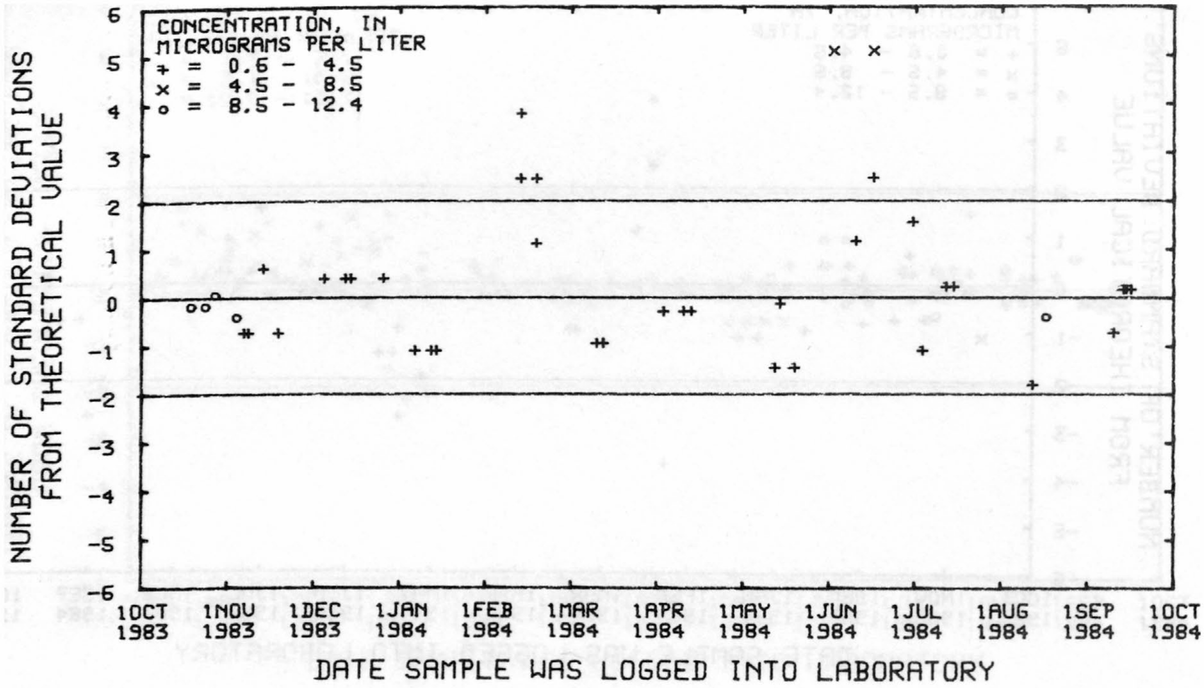

Figure 91--Silver, total recoverable, data for the Atlanta laboratory.

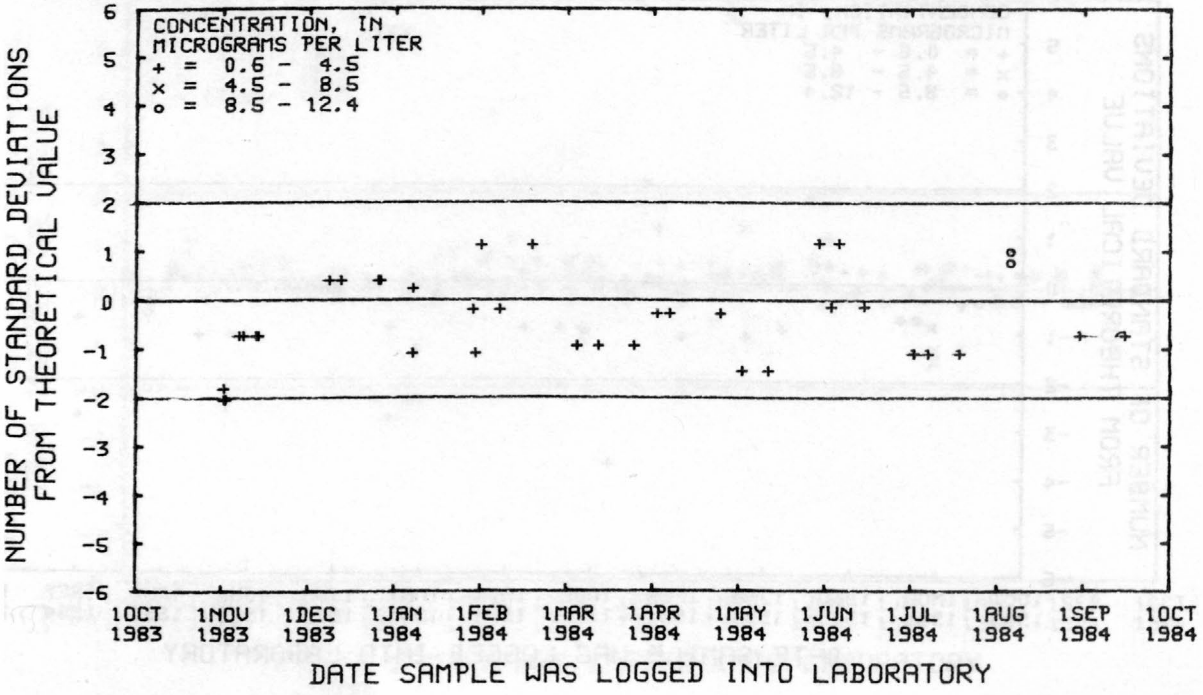

Figure 92—Silver, total recoverable, data for the Denver laboratory.

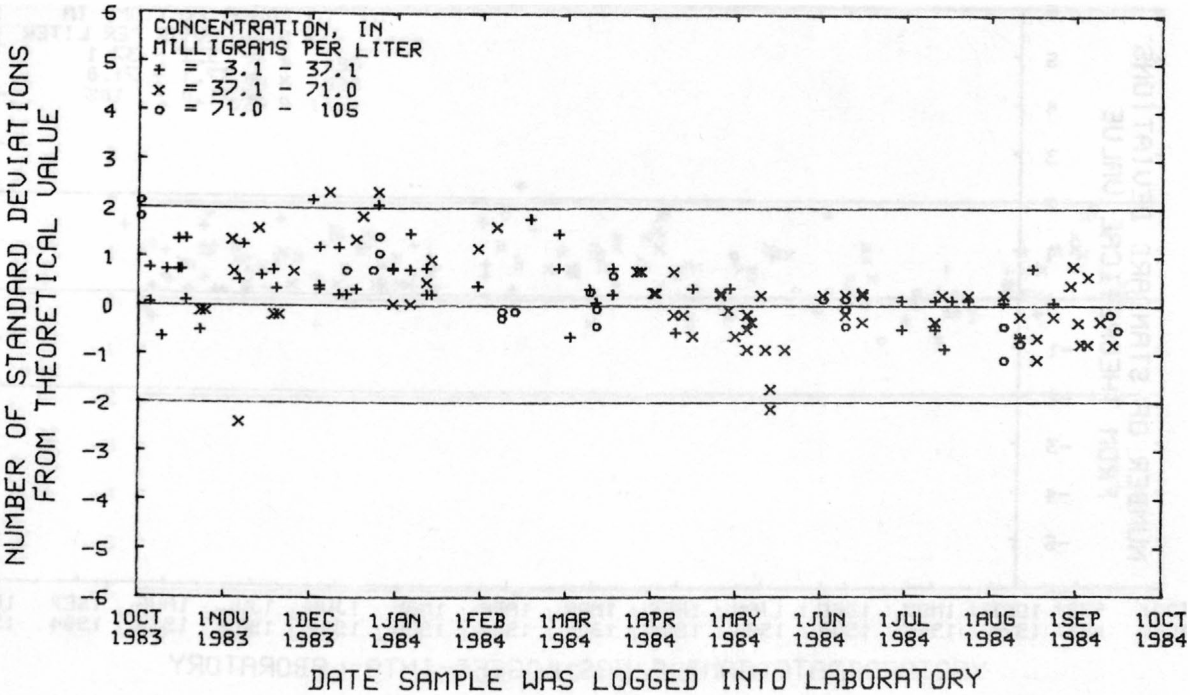

Figure 93--Sodium, dissolved, (inductively coupled plasma emission spectrometry) data from Atlanta laboratory.

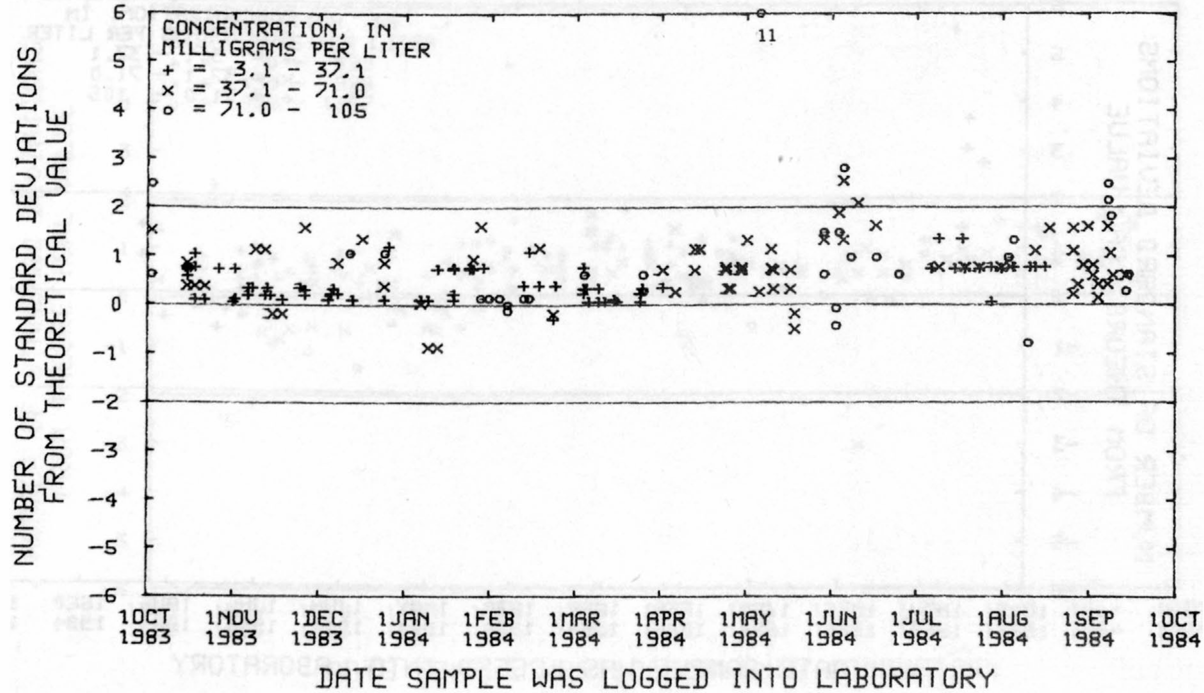

Figure 94--Sodium, dissolved, (inductively coupled plasma emission spectrometry) data from Denver laboratory.

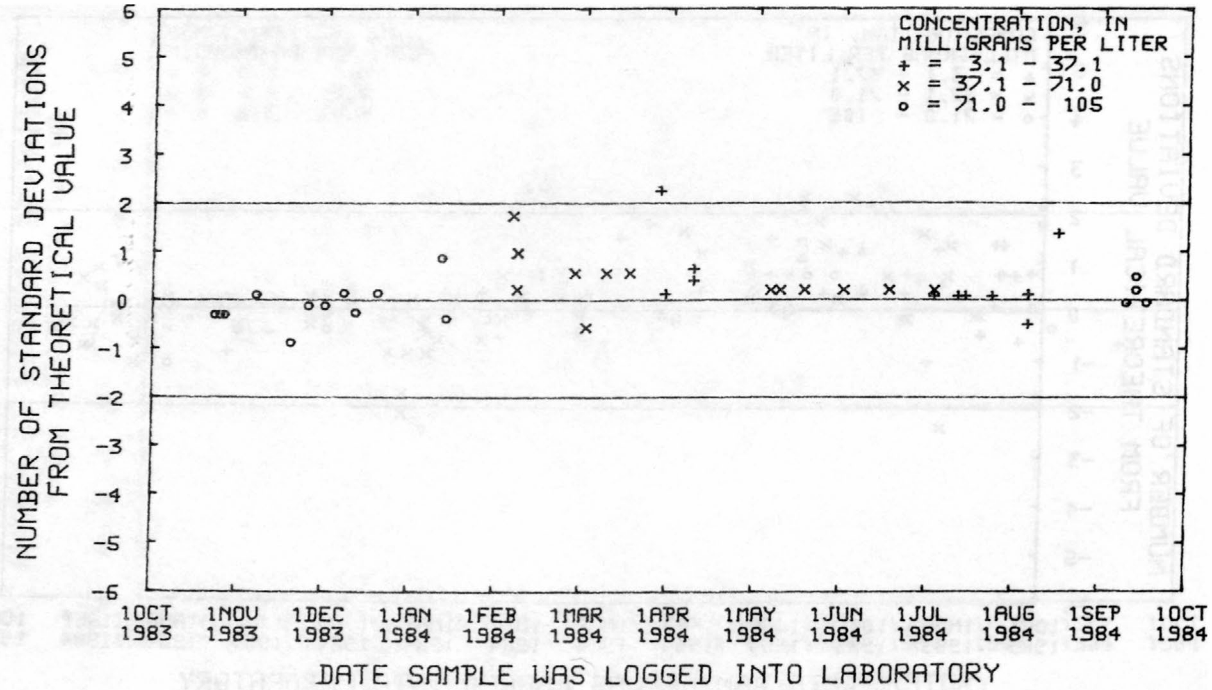

Figure 95--Sodium, dissolved, (atomic absorption spectrometry) data from Atlanta laboratory.

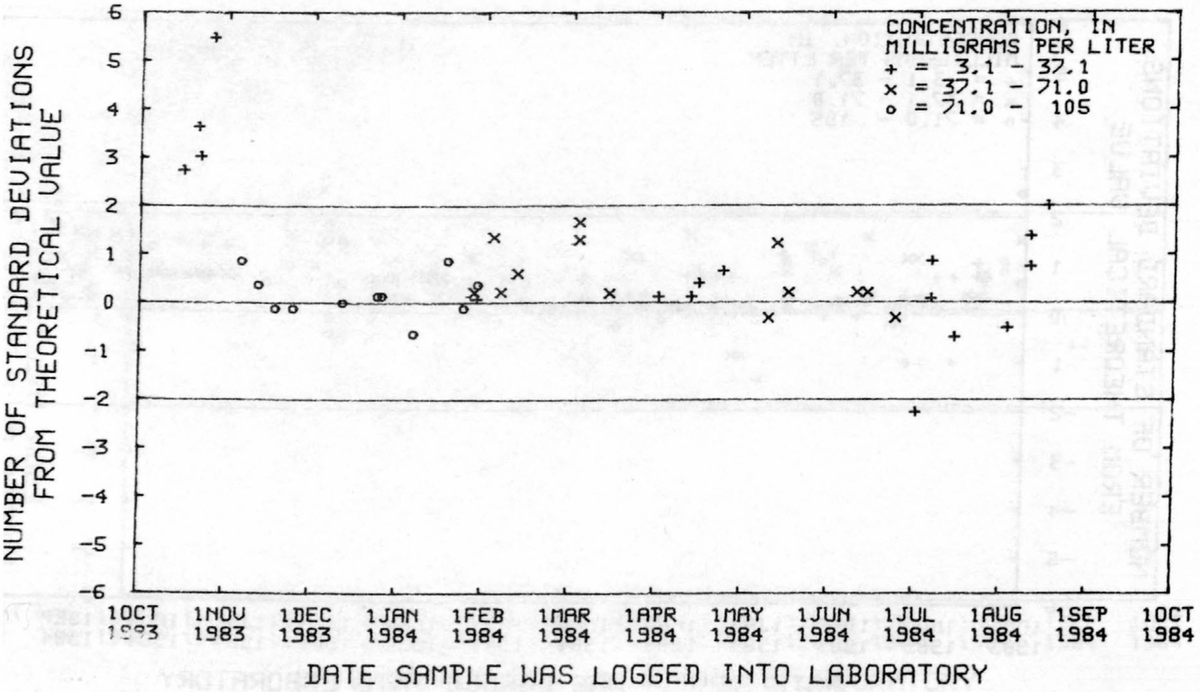

Figure 96--Sodium, dissolved, (atomic absorption spectrometry) data from Denver laboratory.

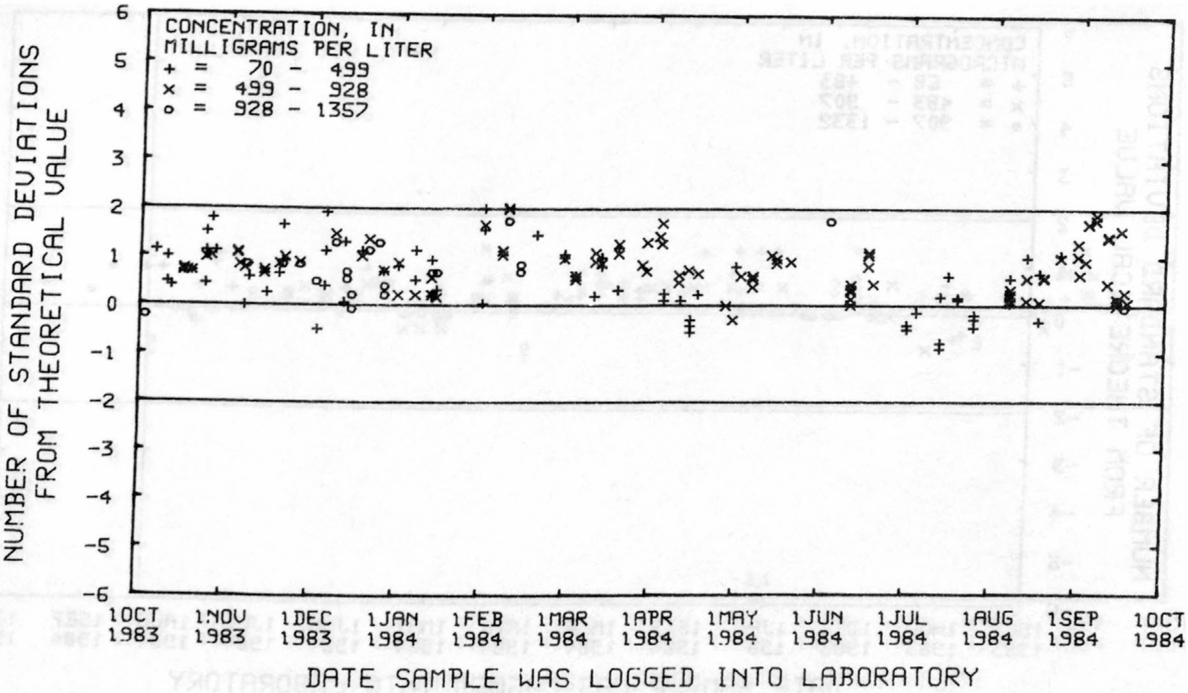

Figure 97--Specific Conductance data from Atlanta laboratory.

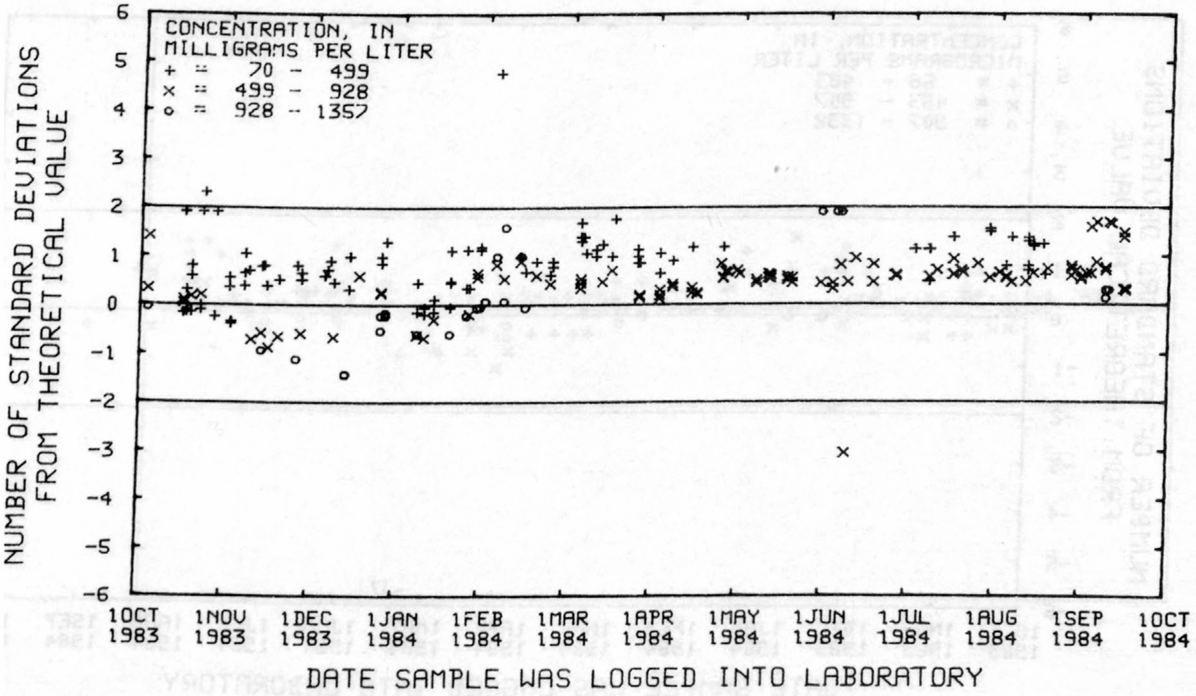

Figure 98--Specific Conductance data from Denver laboratory.

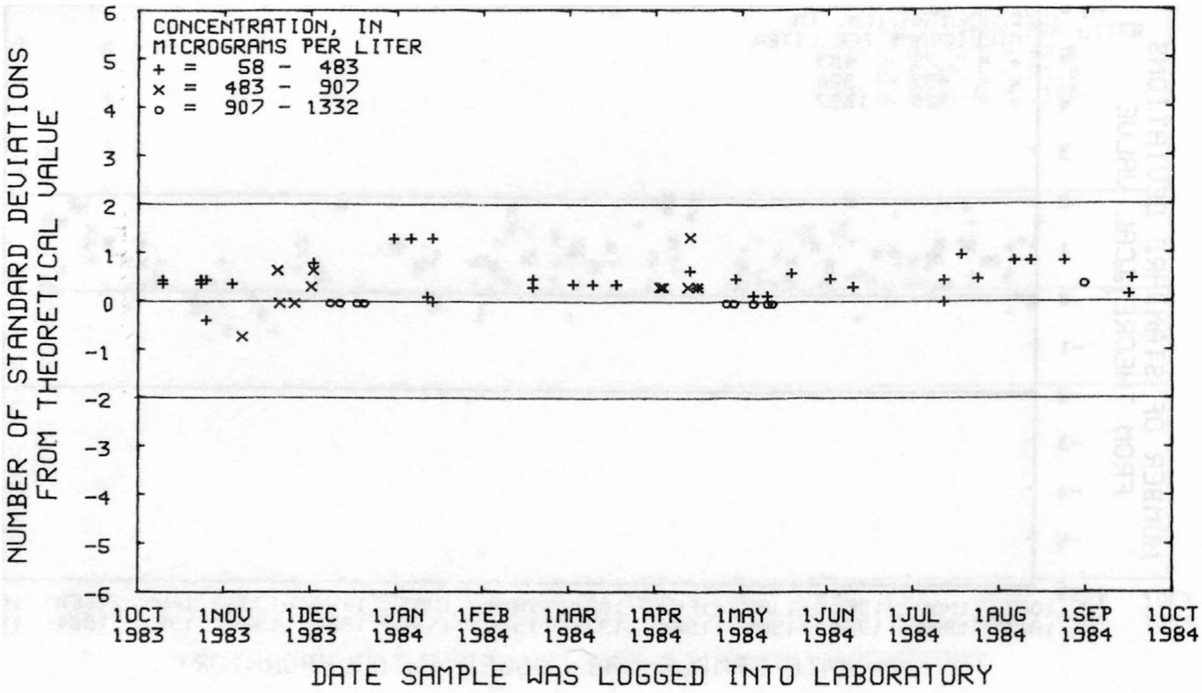

Figure 99--Strontium, dissolved, data for the Atlanta laboratory.

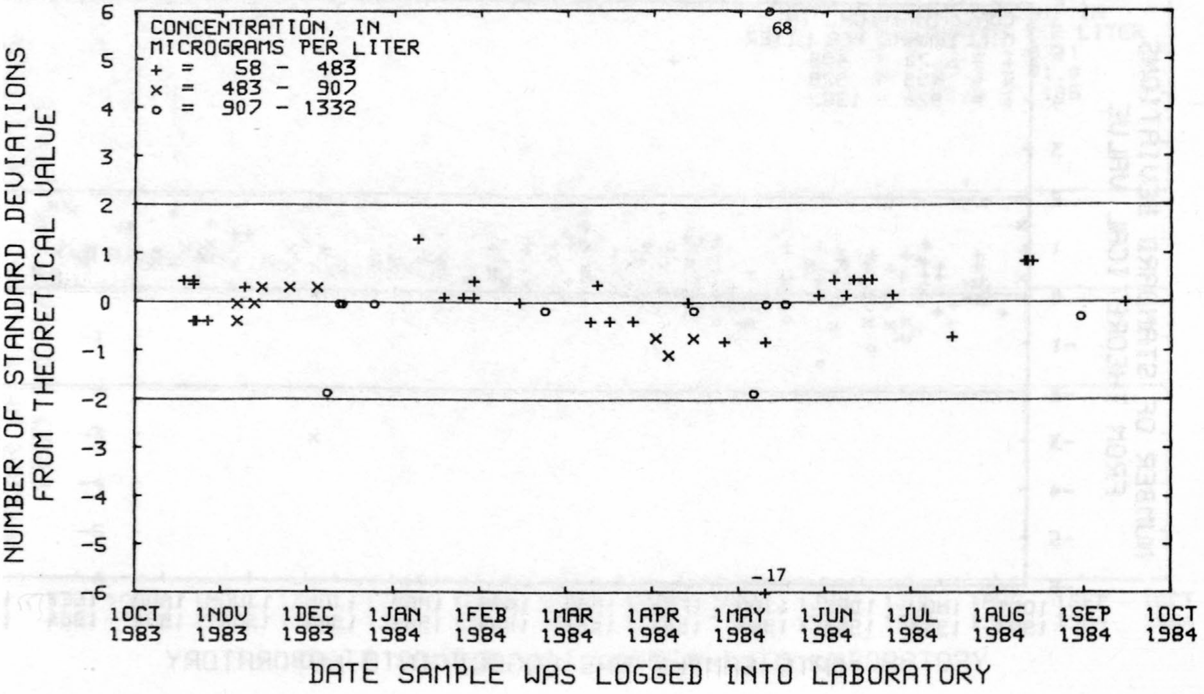

Figure 100--Strontium, dissolved, data for the Denver laboratory.

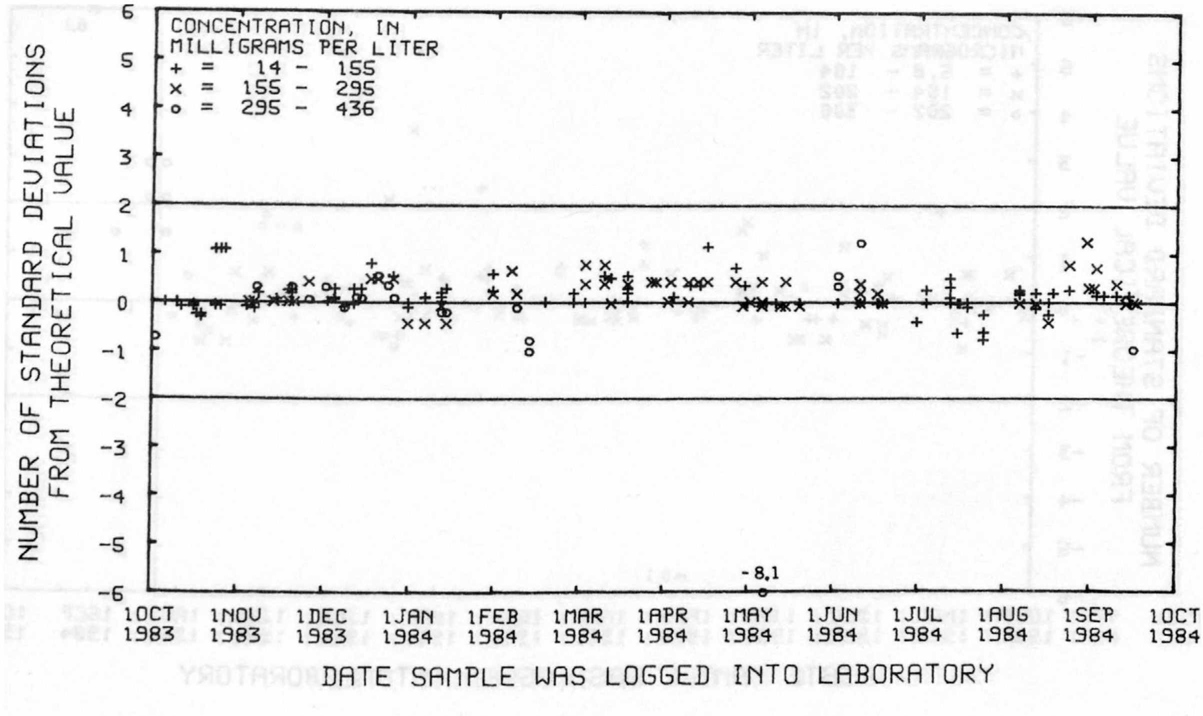

Figure 101--Sulfate, dissolved, data from Atlanta laboratory.

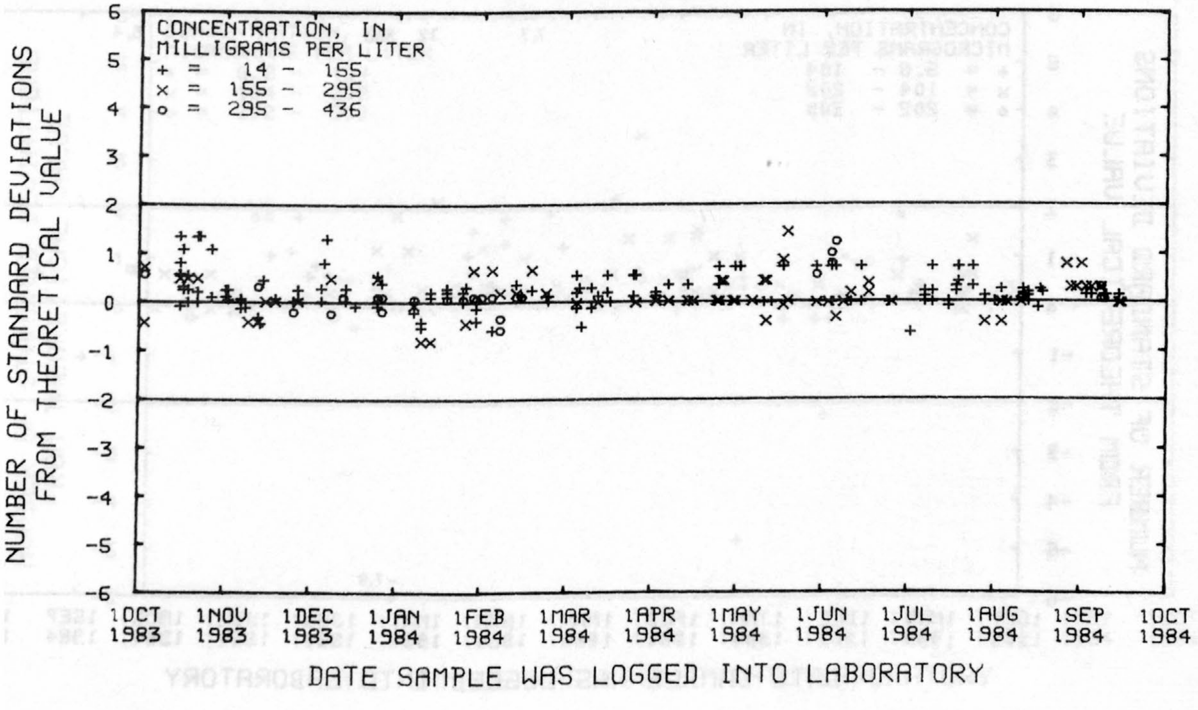

Figure 102--Sulfate, dissolved, data from Denver laboratory.

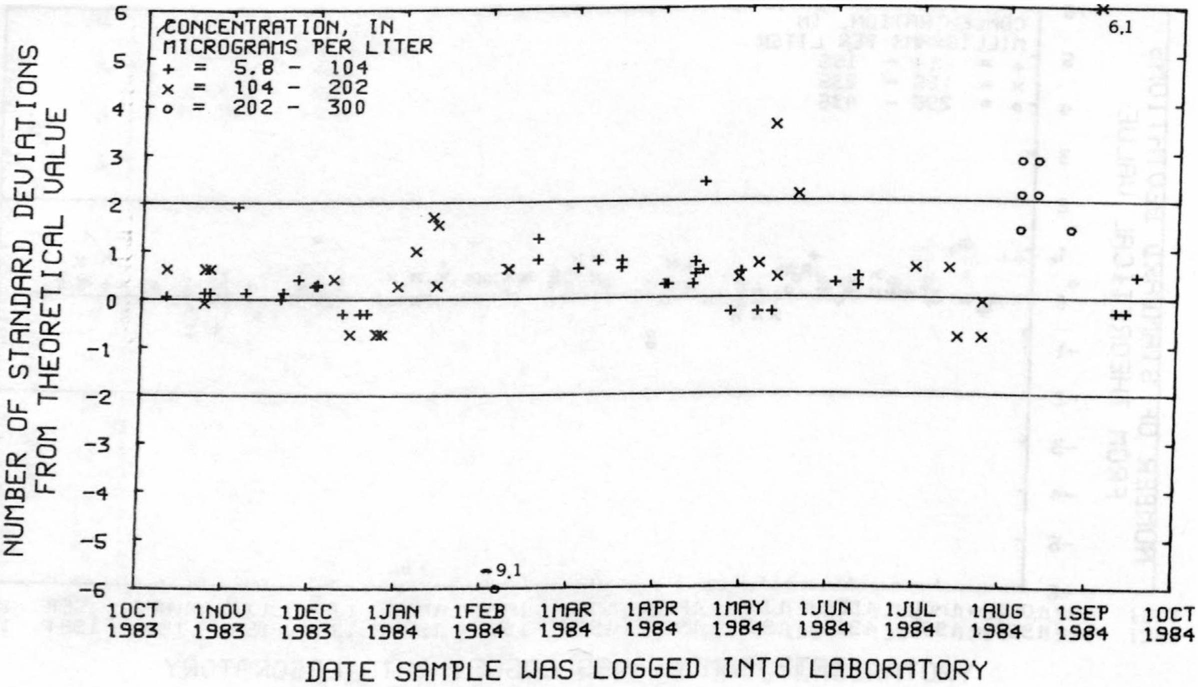

Figure 103--Zinc, dissolved, (inductively coupled plasma emission spectrometry) data for the Atlanta laboratory.

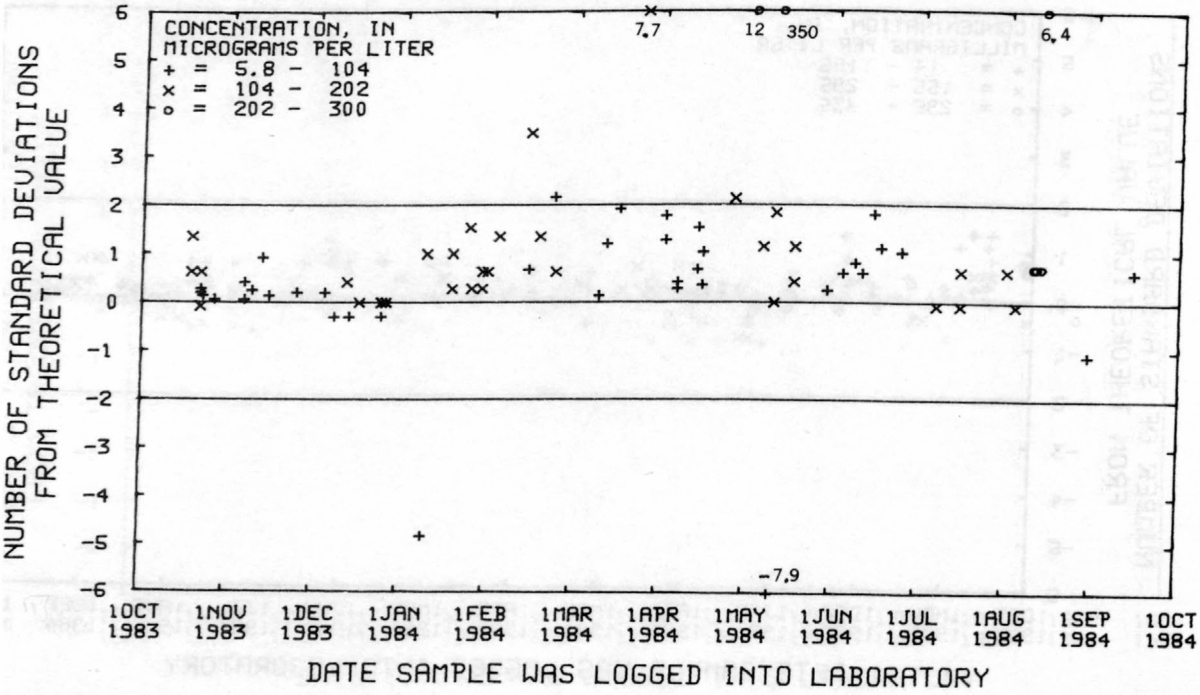

Figure 104--Zinc, dissolved, (inductively coupled plasma emission spectrometry) data for the Denver laboratory.

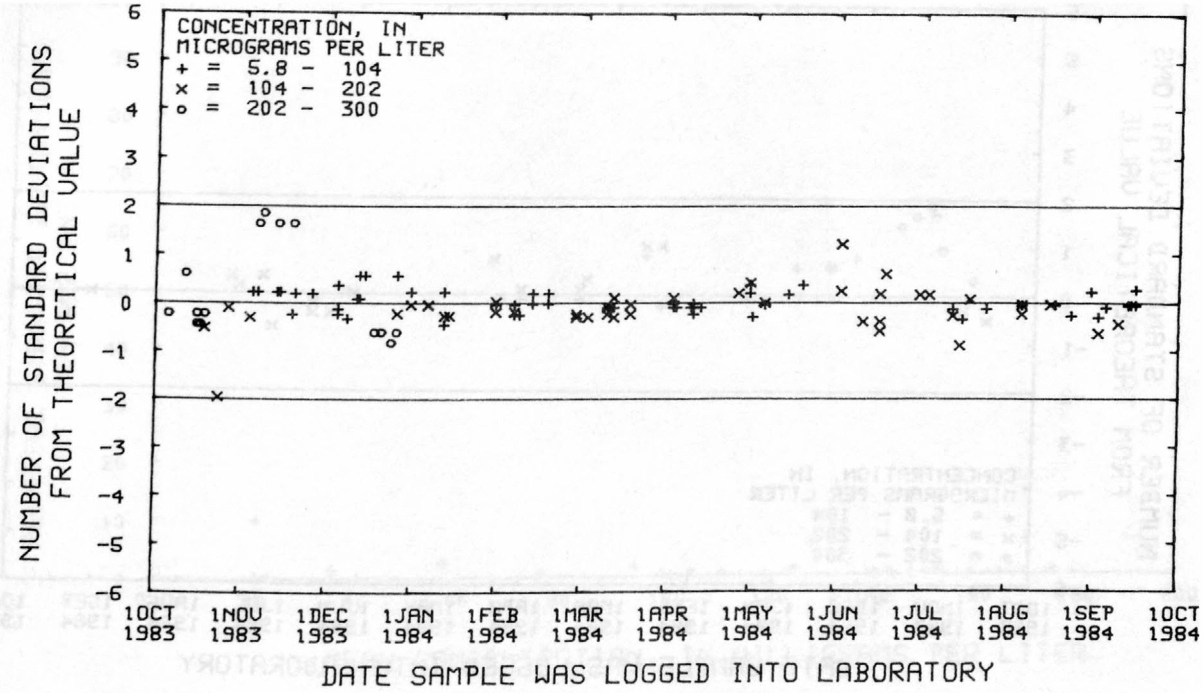

Figure 105--Zinc, dissolved, (atomic absorption spectrometry) data for the Atlanta laboratory.

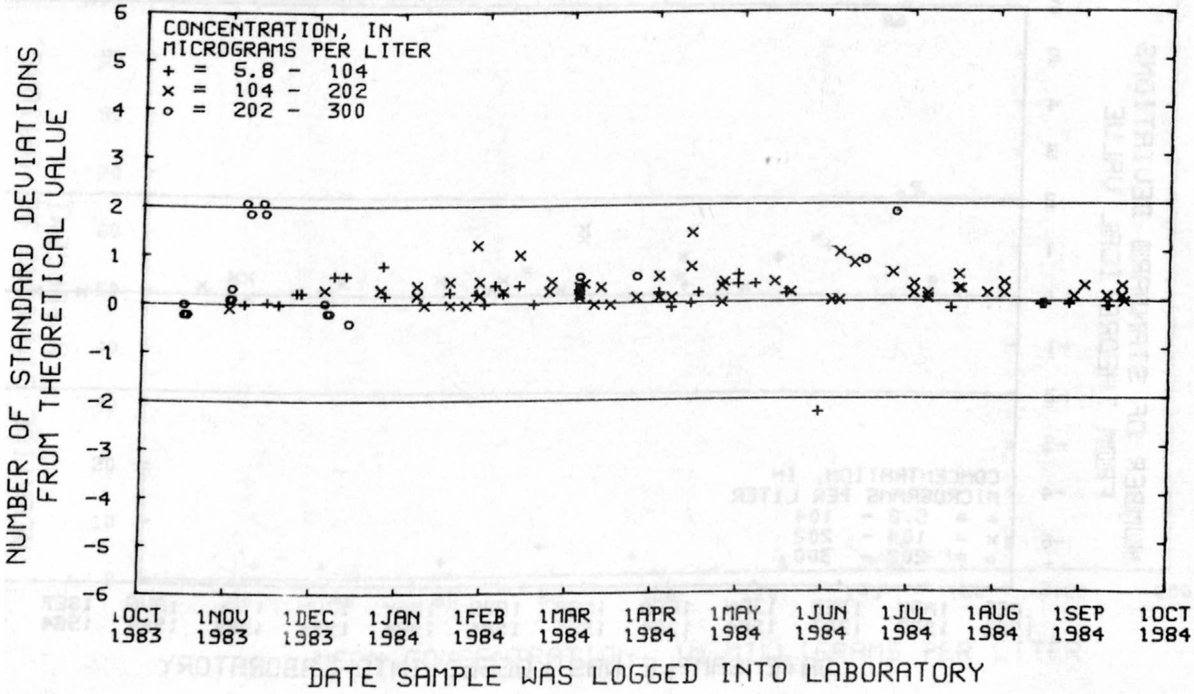

Figure 106--Zinc, dissolved, (atomic absorption spectrometry) data for the Denver laboratory.

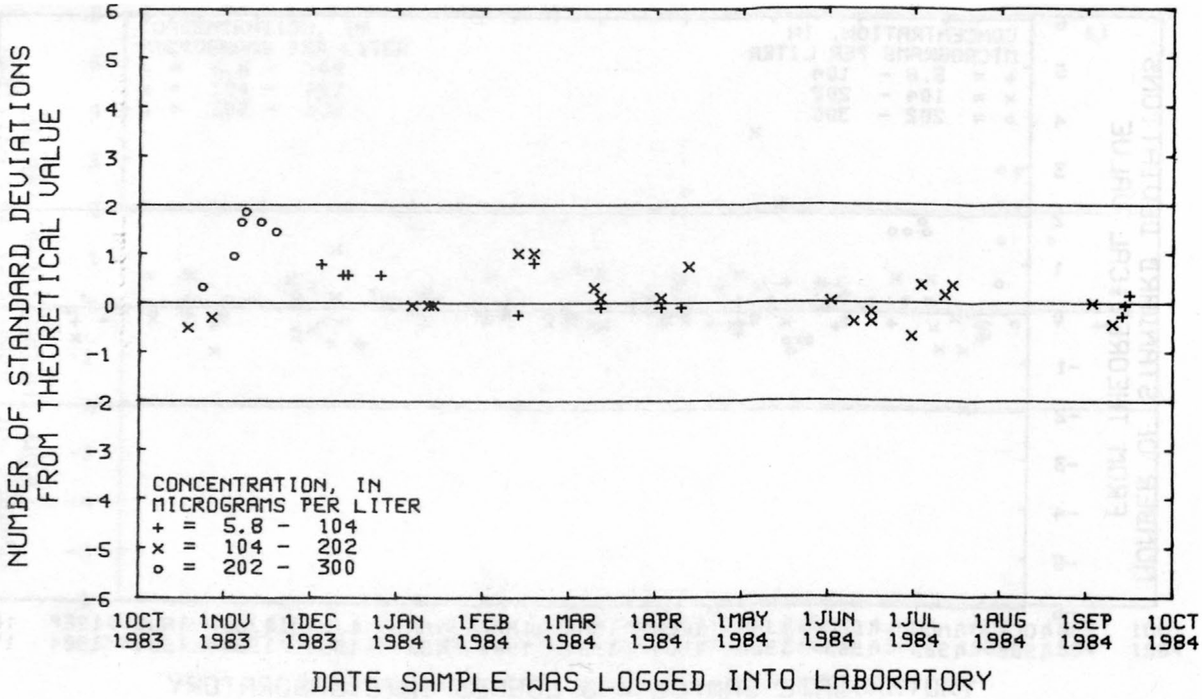

Figure 107--Zinc, total recoverable, data for the Atlanta laboratory.

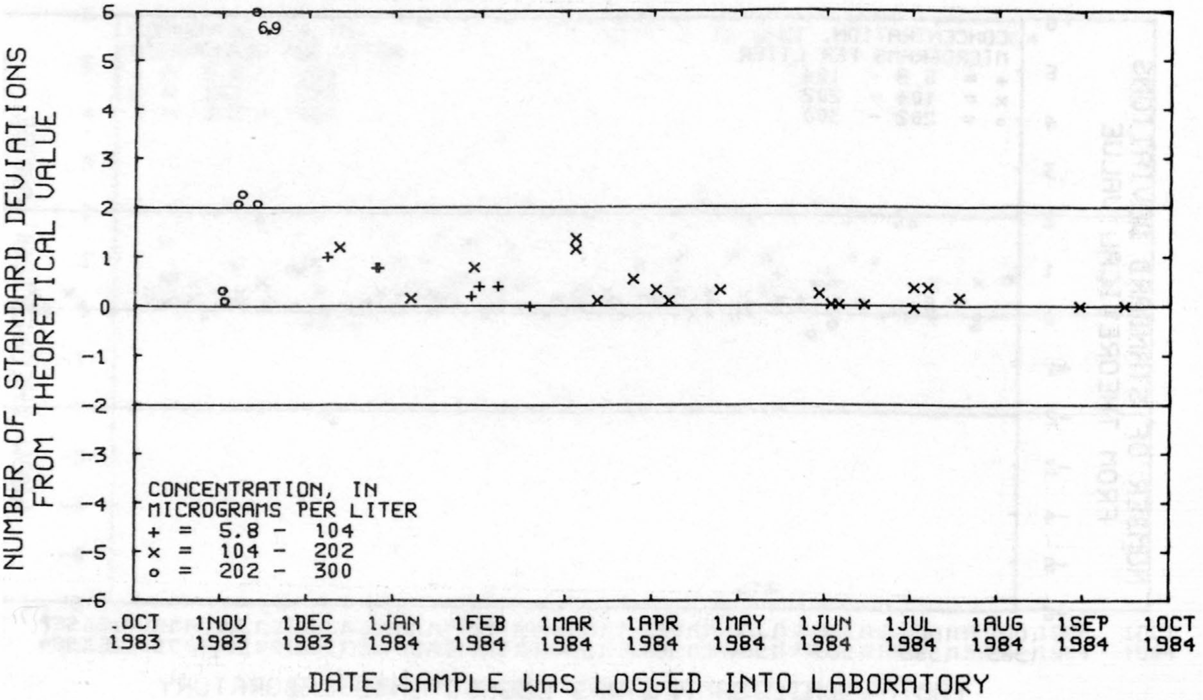

Figure 108--Zinc, total recoverable, data for the Denver laboratory.

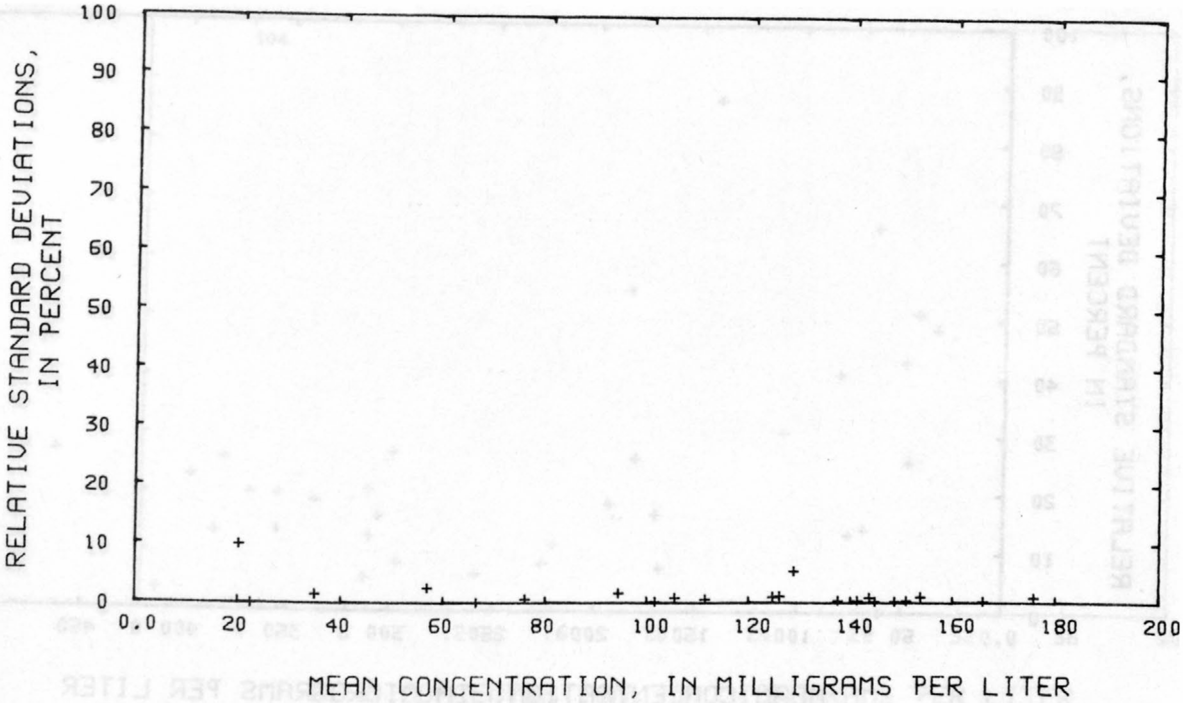

Figure 109--Precision data for alkalinity, dissolved, at the Atlanta laboratory.

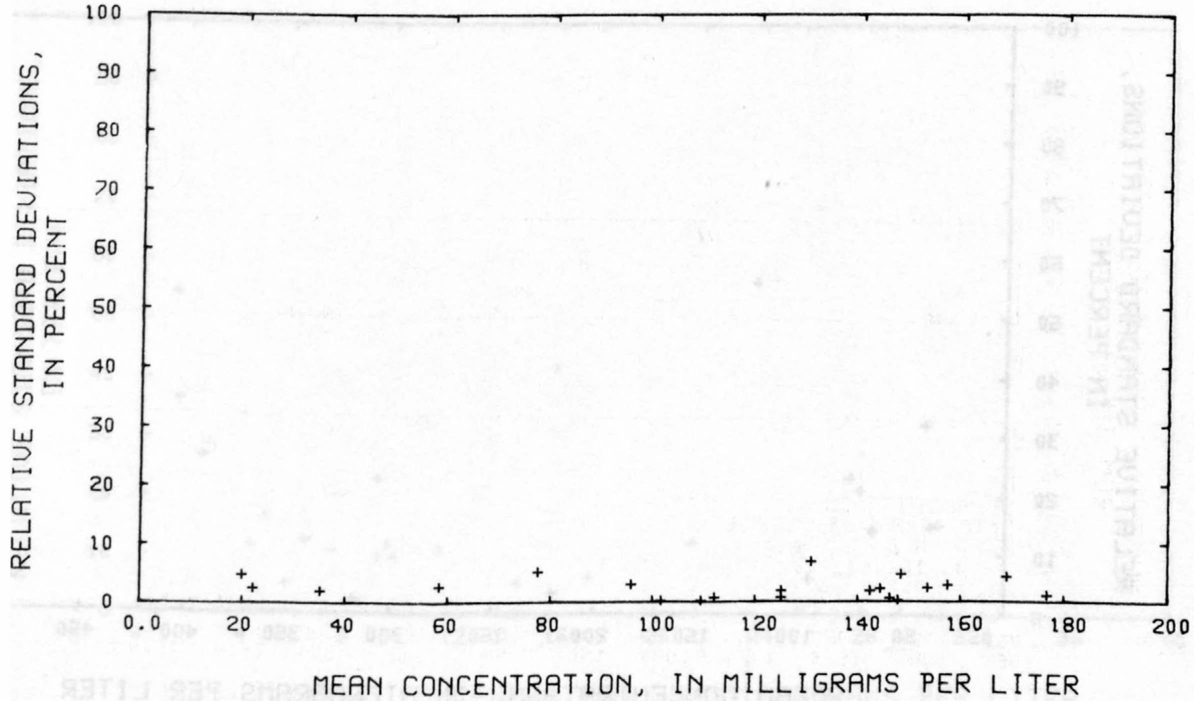

Figure 110--Precision data for alkalinity, dissolved, at the Denver laboratory.

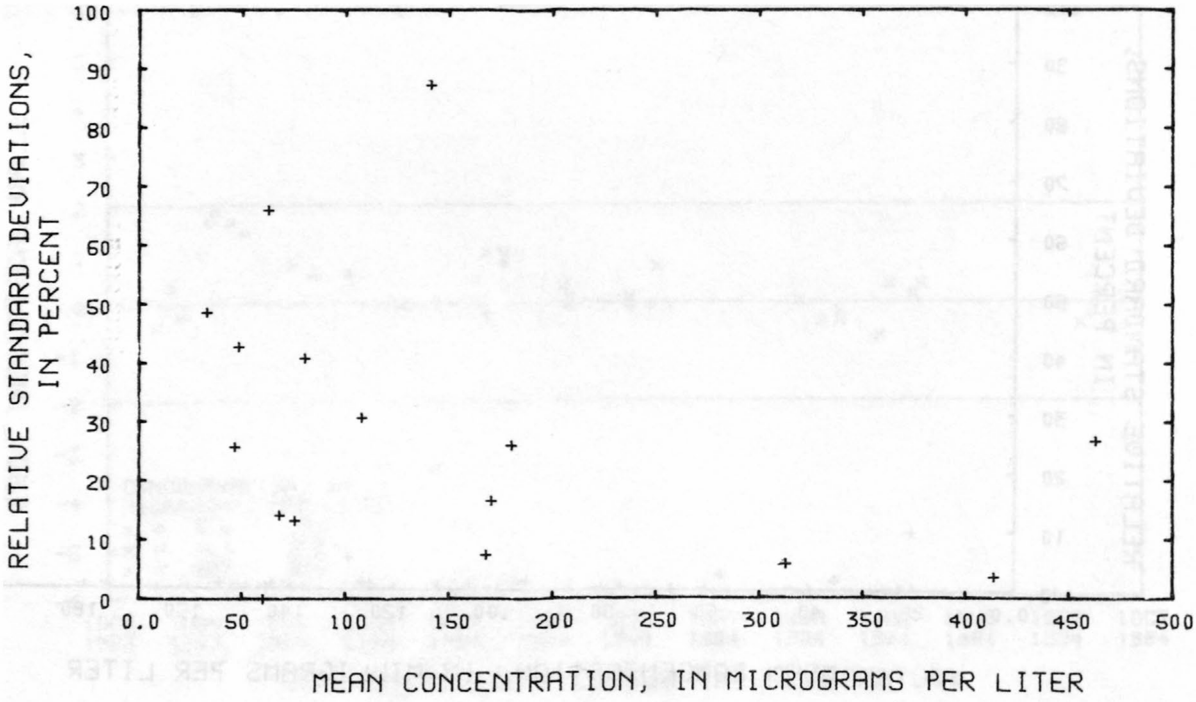

Figure 111--Precision data for aluminum, dissolved, at the Atlanta laboratory.

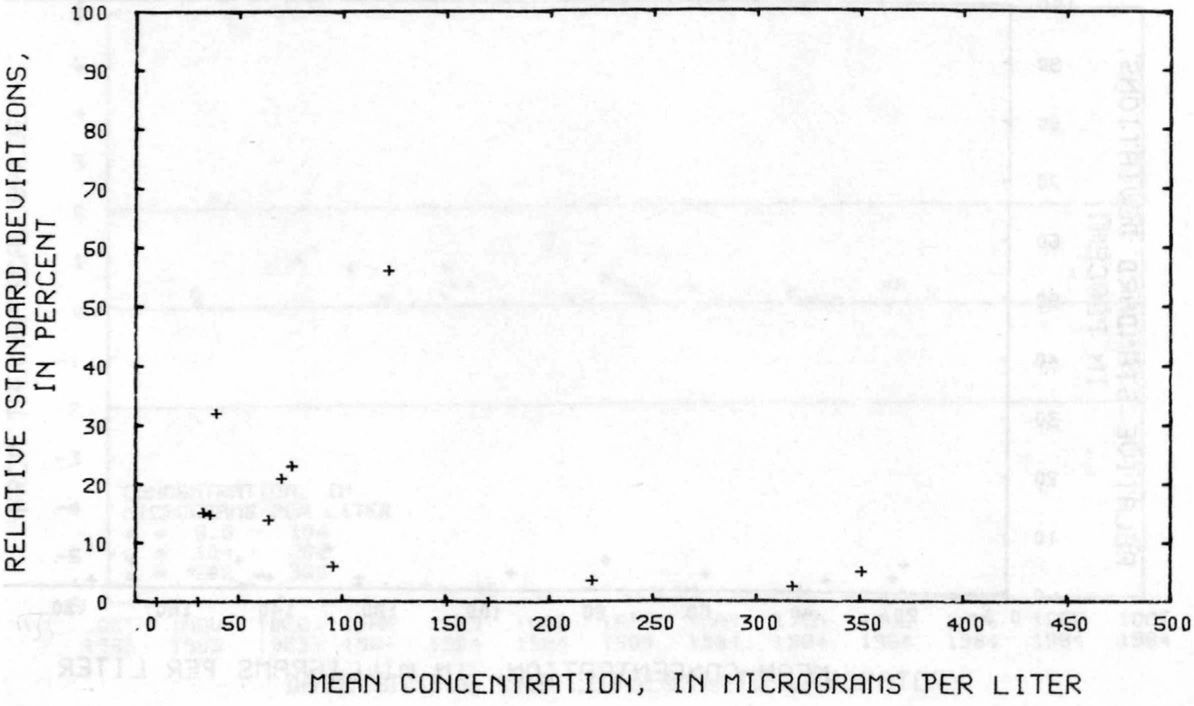

Figure 112--Precision data for aluminum, dissolved, at the Denver laboratory.

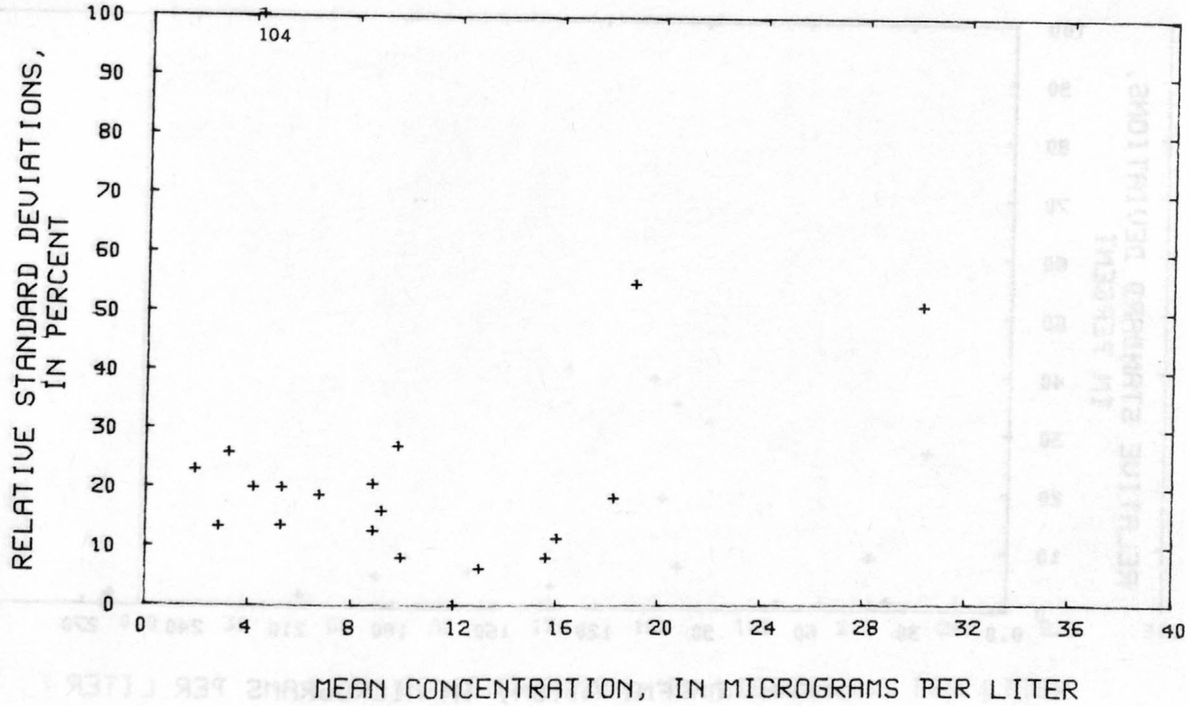

Figure 113--Precision data for arsenic, dissolved, at the Atlanta laboratory.

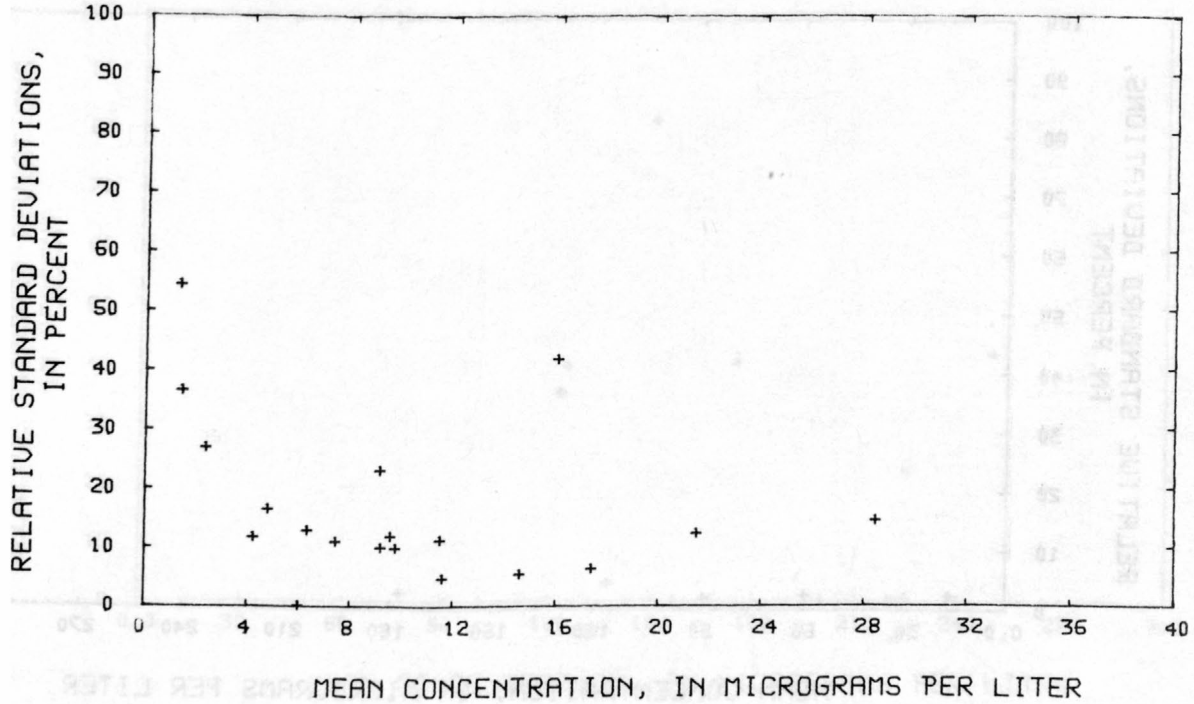

Figure 114--Precision data for arsenic, dissolved, at the Denver laboratory.

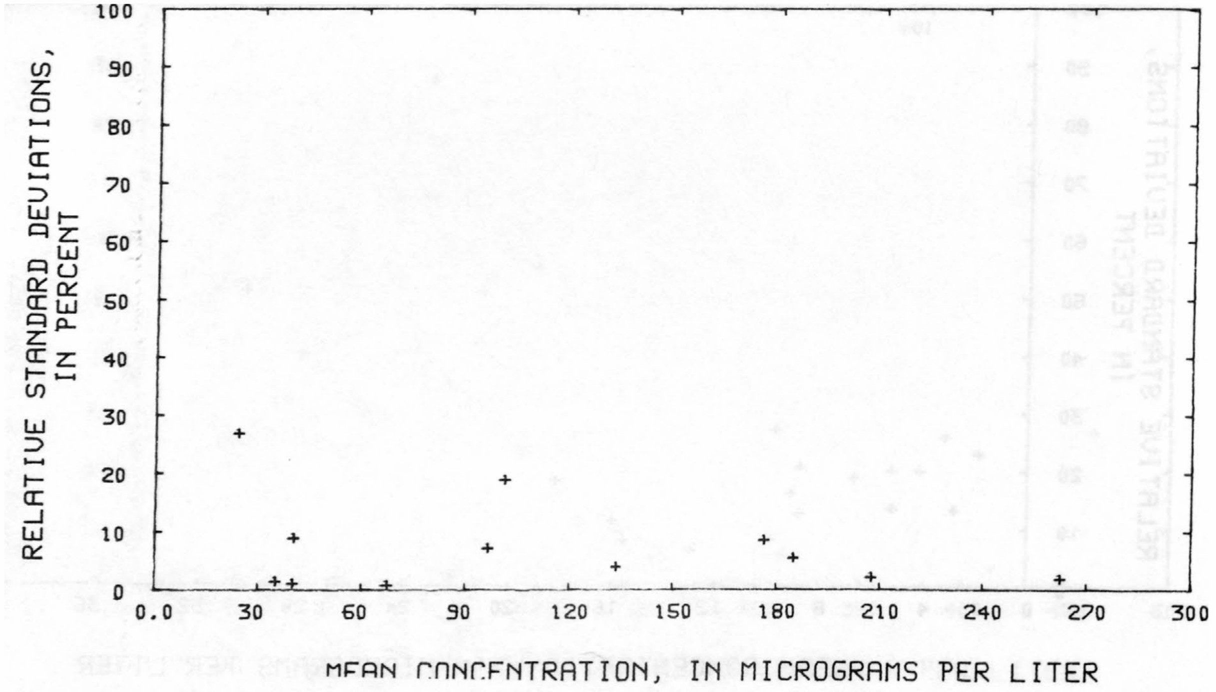

Figure 115--Precision data for barium, dissolved, (inductively coupled plasma emission spectrometry) at the Atlanta laboratory.

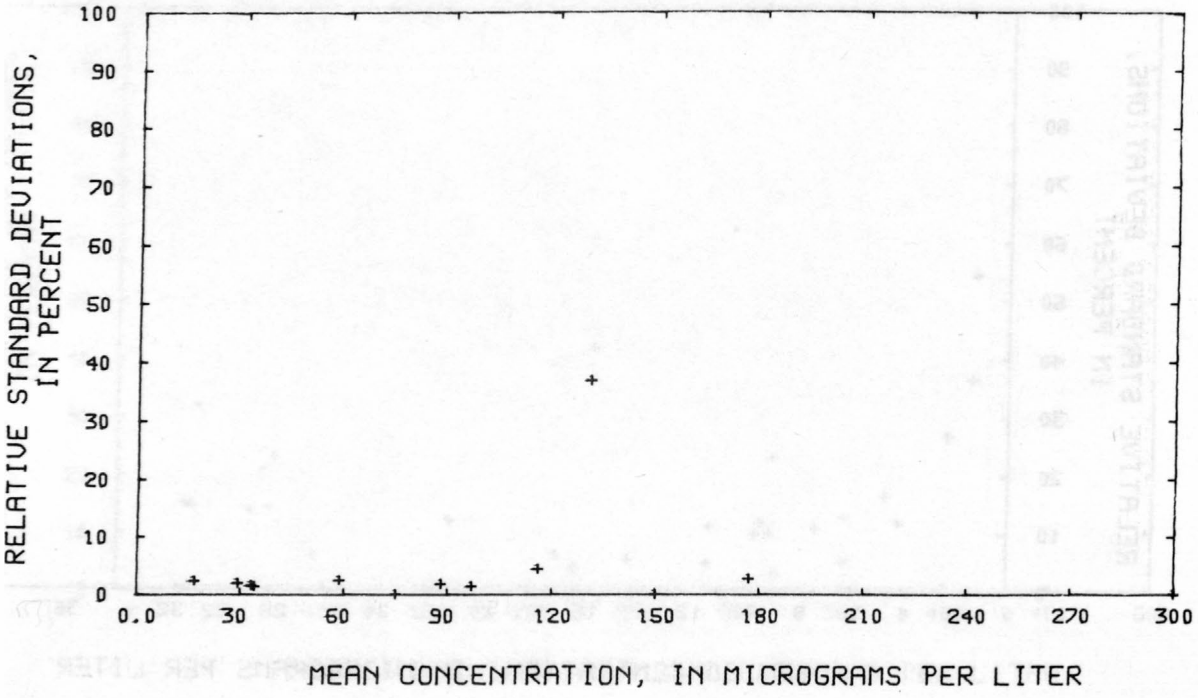

Figure 116--Precision data for barium, dissolved, (inductively coupled plasma emission spectrometry), at the Denver laboratory.

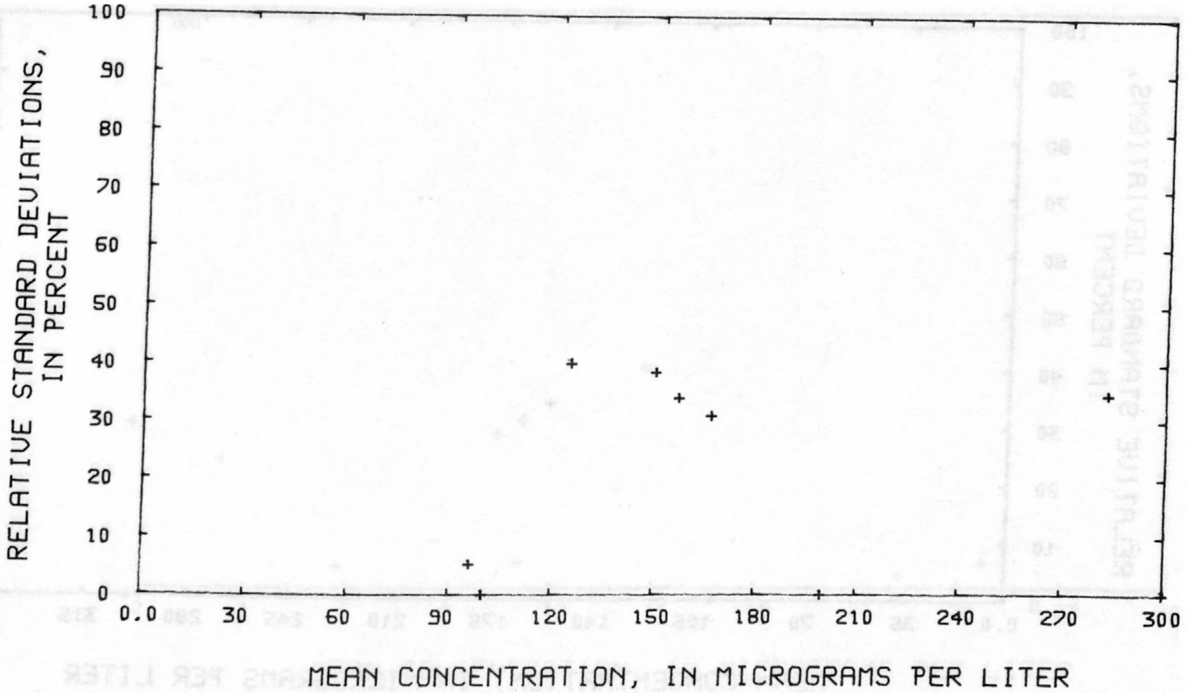

Figure 117--Precision data for barium, dissolved, (atomic absorption spectrometry) at the Atlanta laboratory.

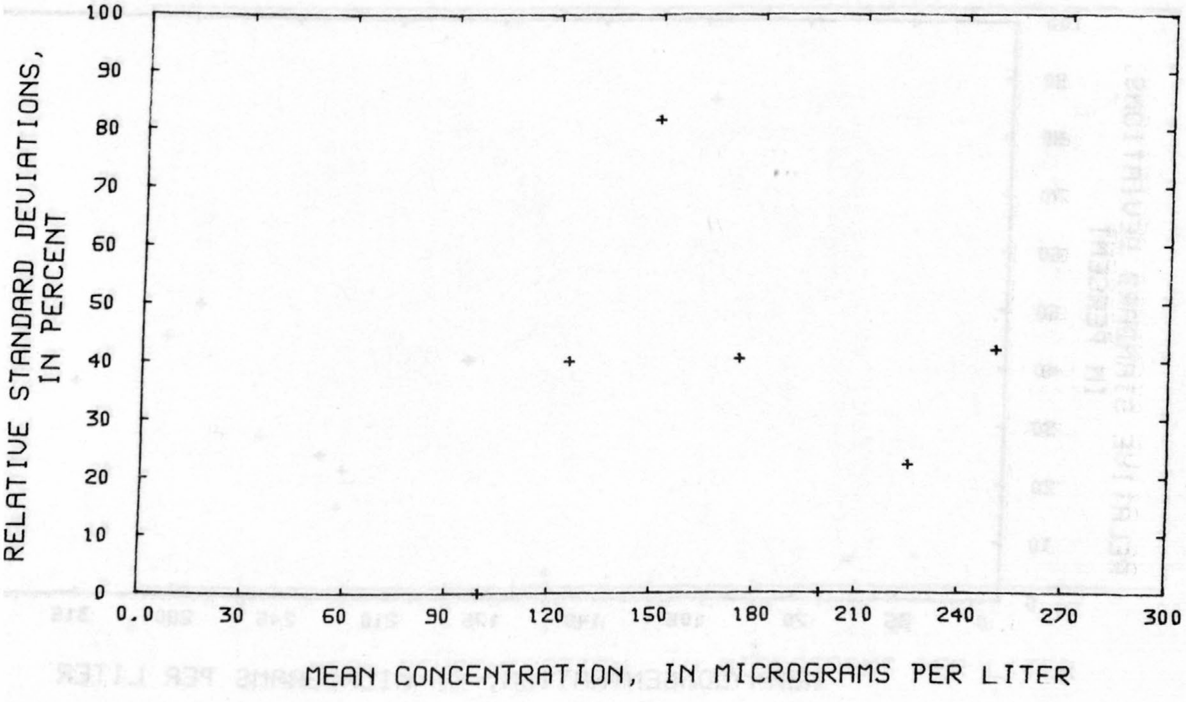

Figure 118--Precision data for barium, dissolved, (atomic absorption spectrometry) at the Denver laboratory.

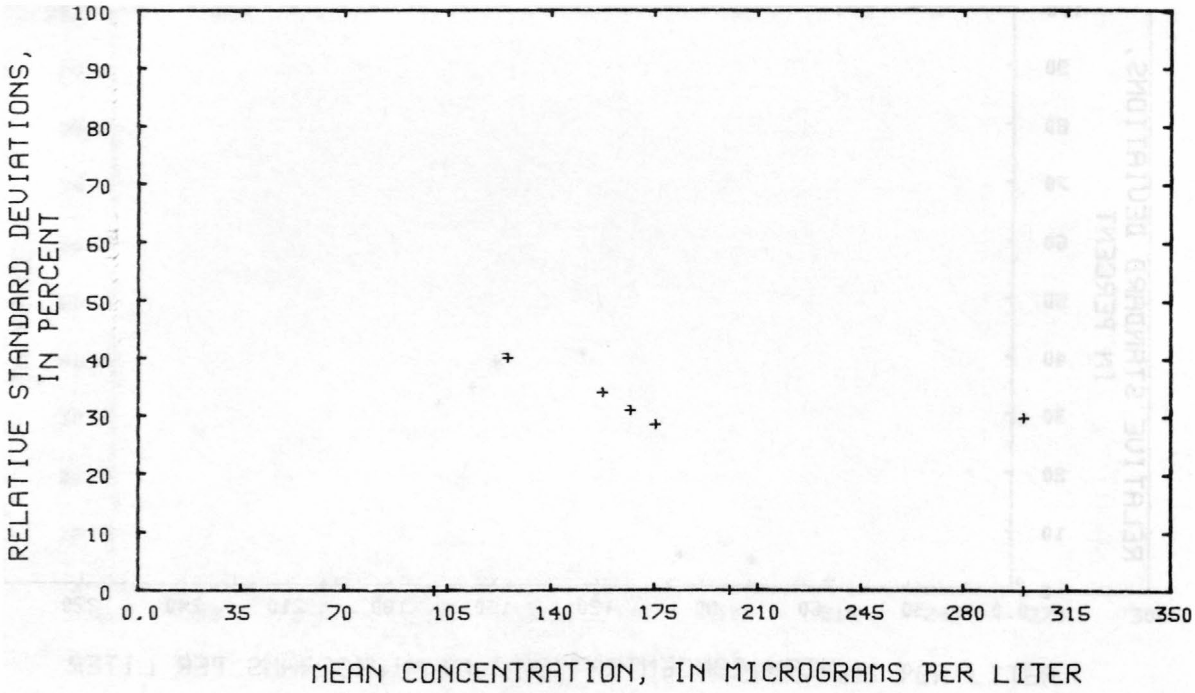

Figure 119--Precision data for barium, total recoverable, at the Atlanta laboratory.

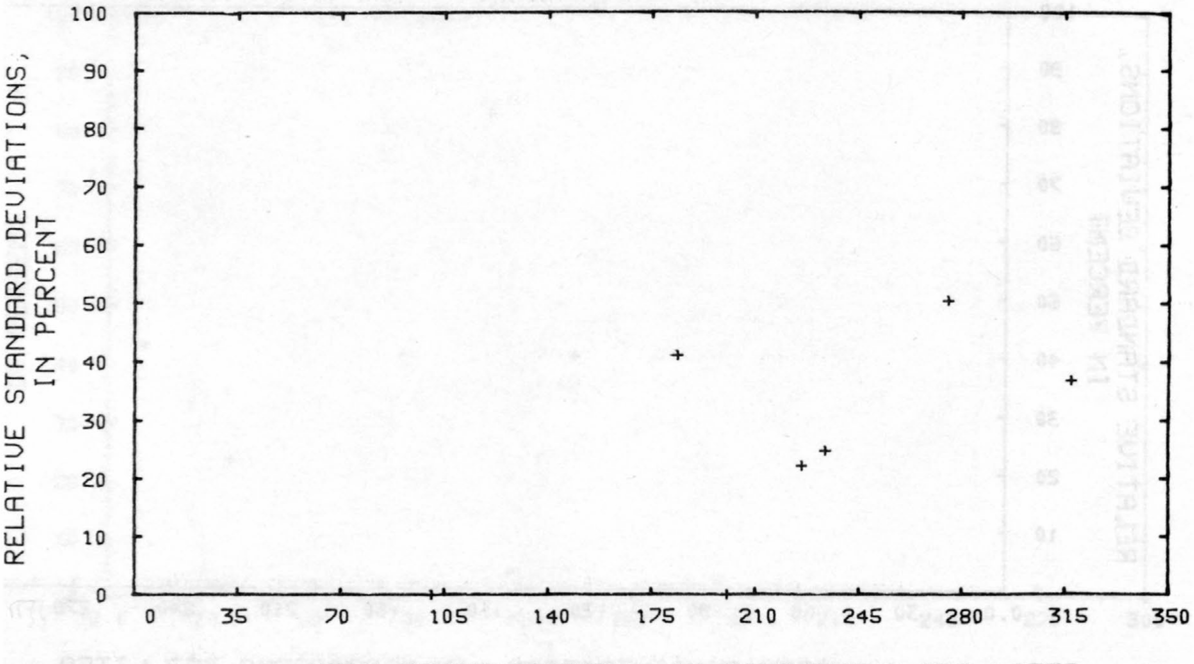

Figure 120--Precision data for barium, total recoverable, at the Denver laboratory.

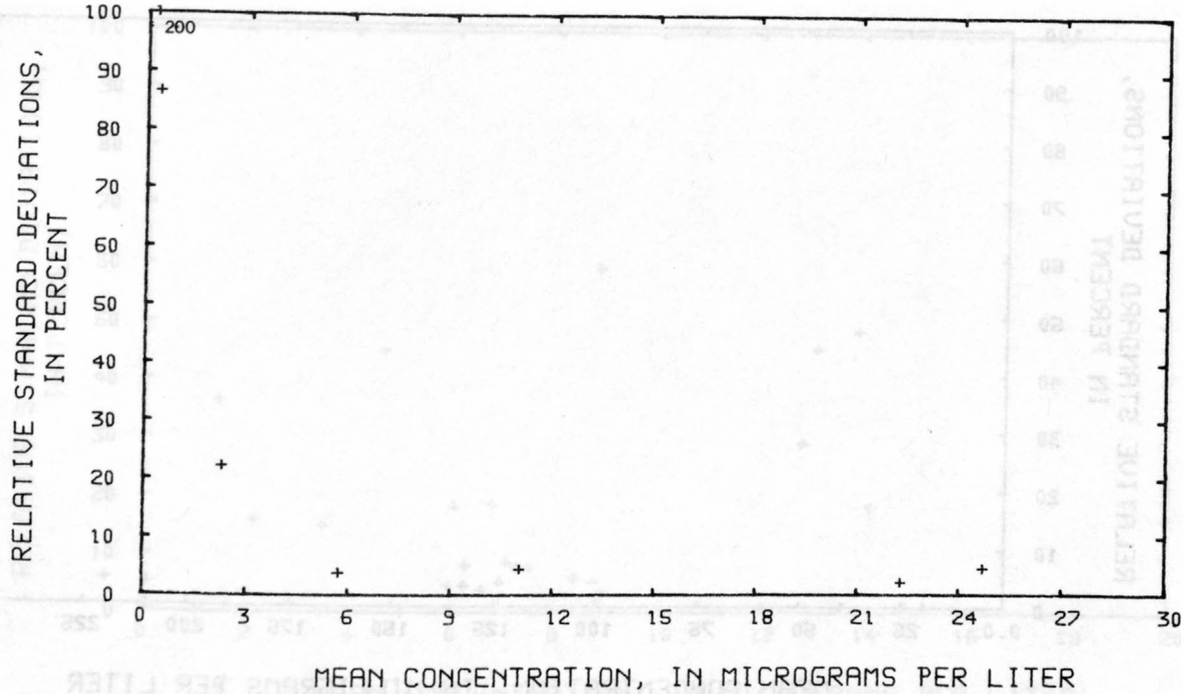

Figure 121--Precision data for beryllium, dissolved, at the Atlanta laboratory.

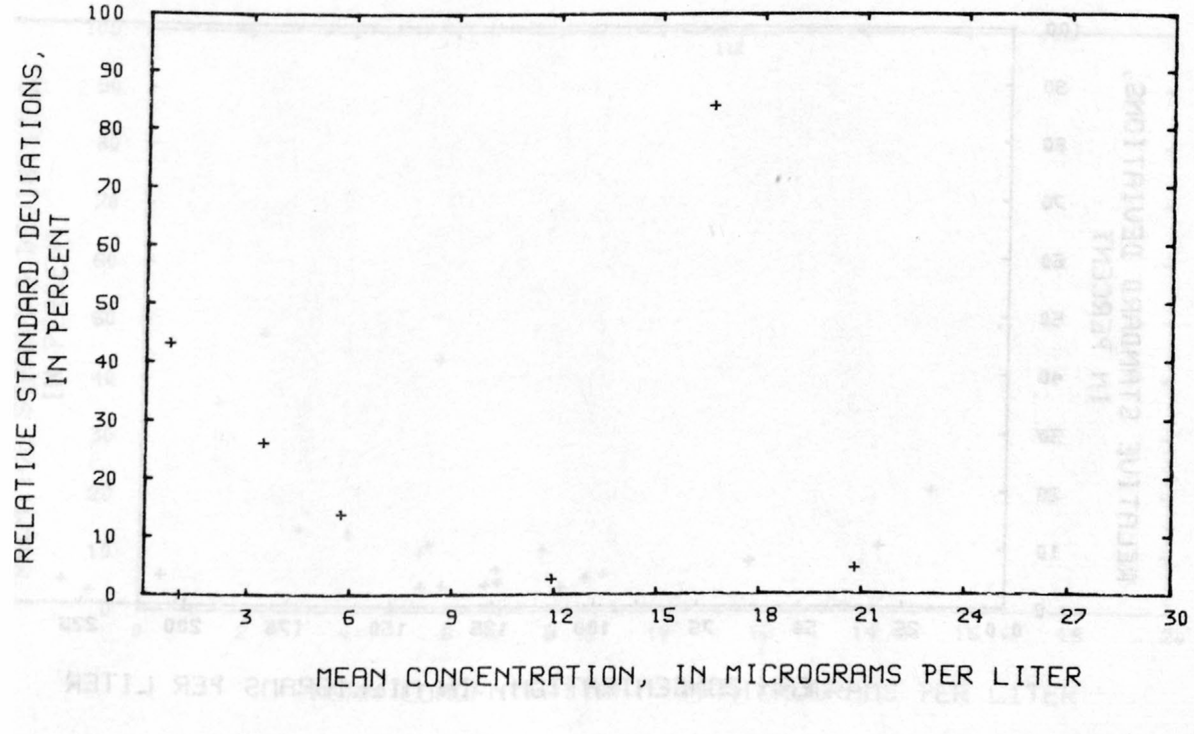

Figure 122--Precision data for beryllium, dissolved, at the Denver laboratory.

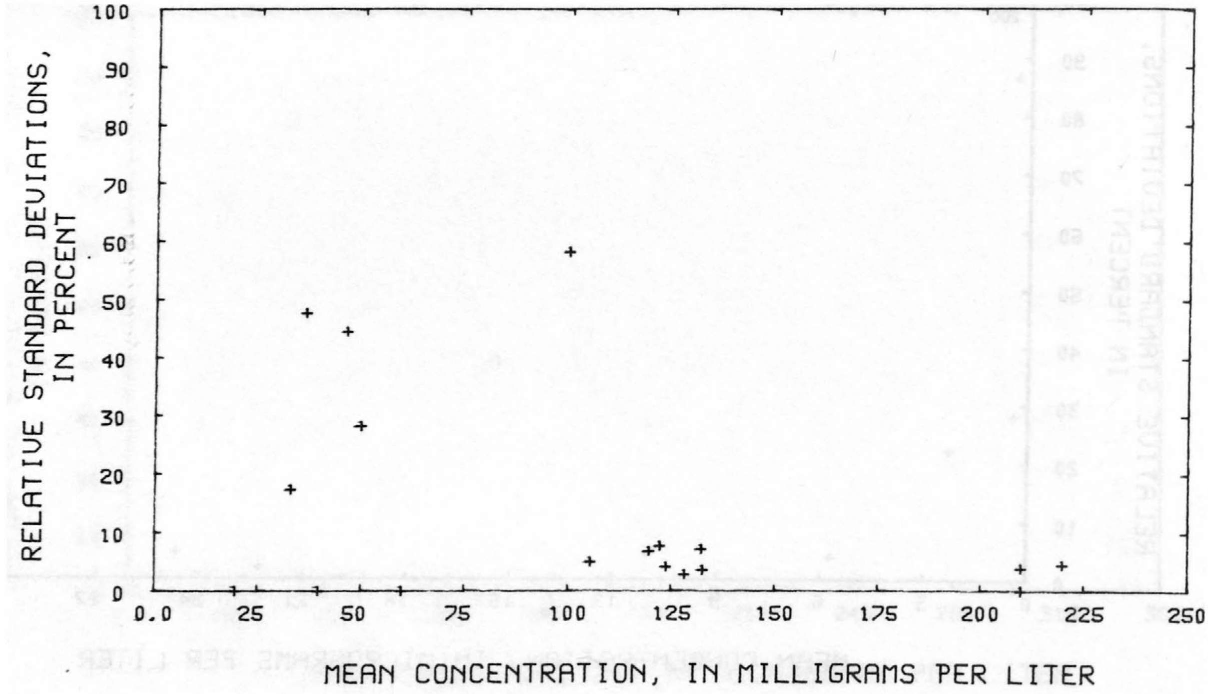

Figure 123--Precision data for boron, dissolved, at the Atlanta laboratory.

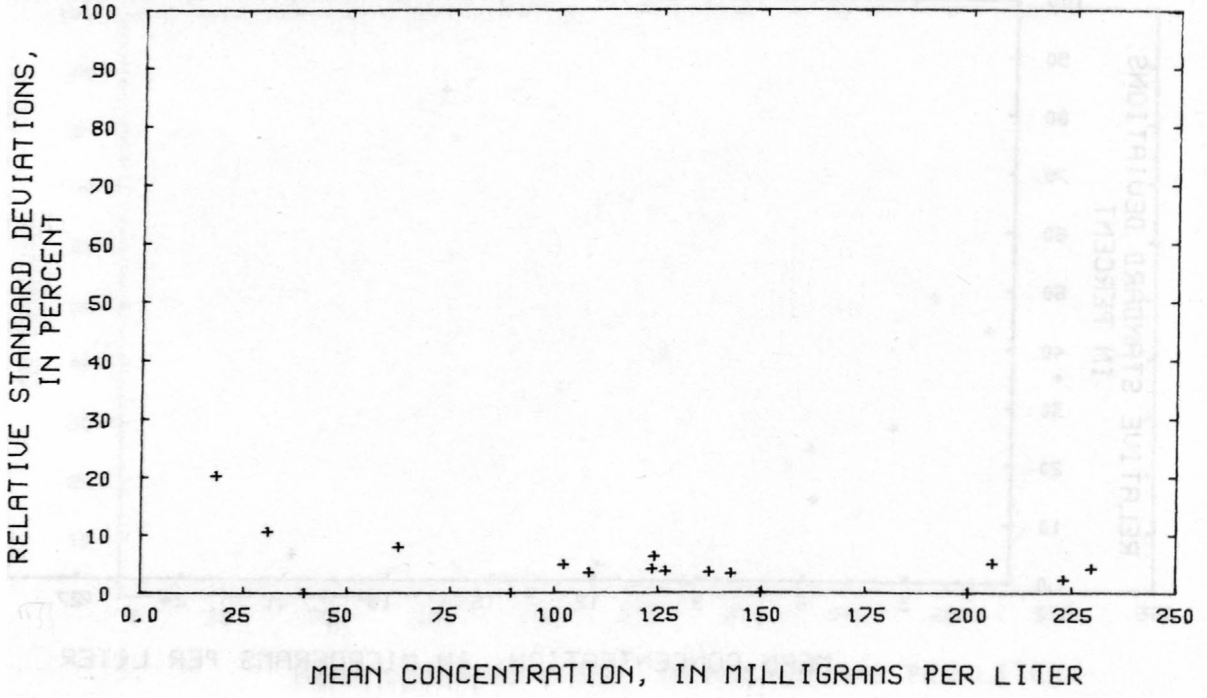

Figure 124--Precision data for boron, dissolved, at the Denver laboratory.

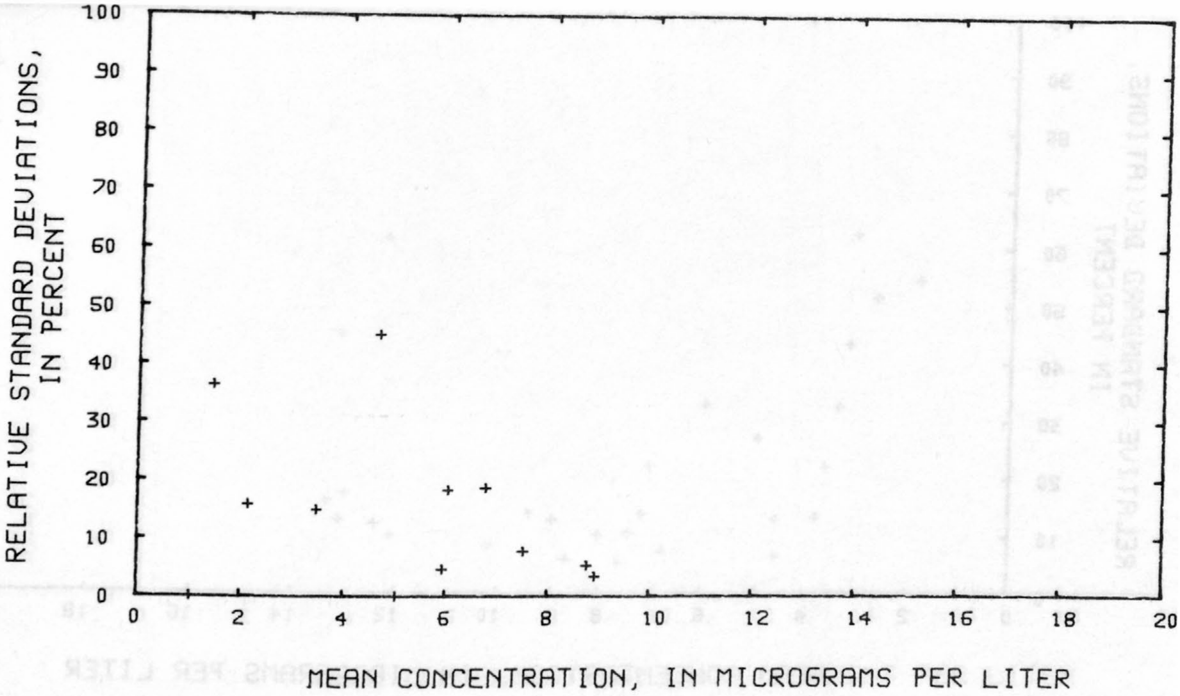

Figure 125--Precision data for cadmium, dissolved, (inductively coupled plasma emission spectrometry) at the Atlanta laboratory.

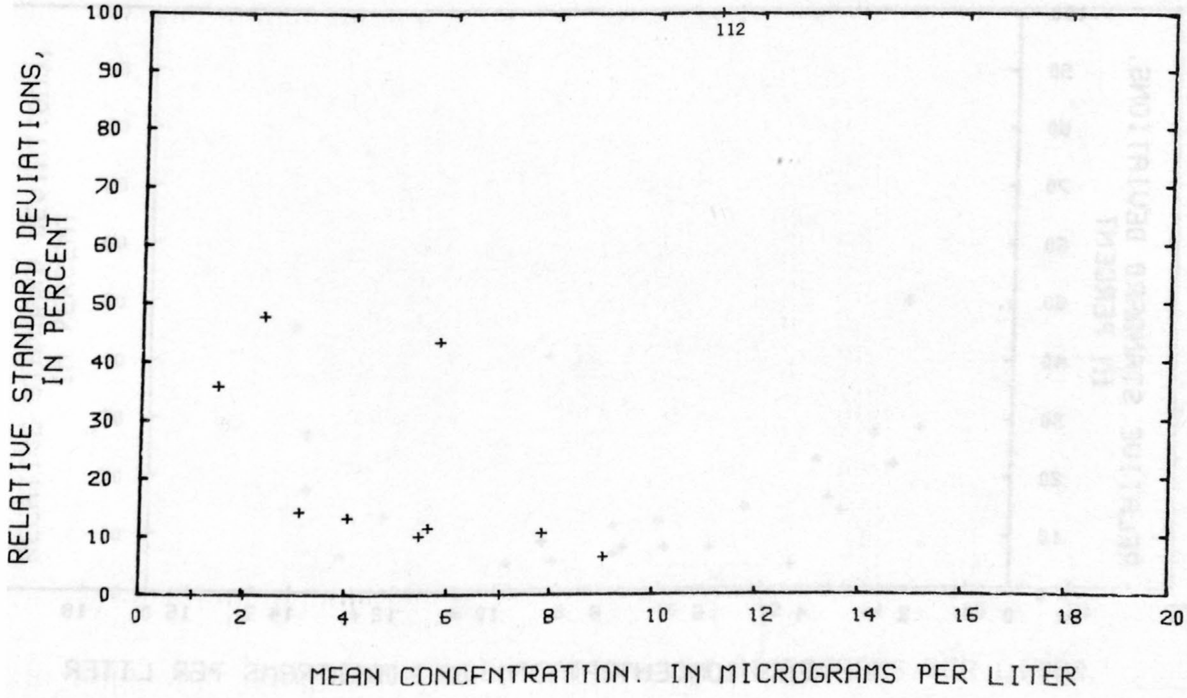

Figure 126--Precision data for cadmium, dissolved, (inductively coupled plasma emission spectrometry) at the Denver laboratory.

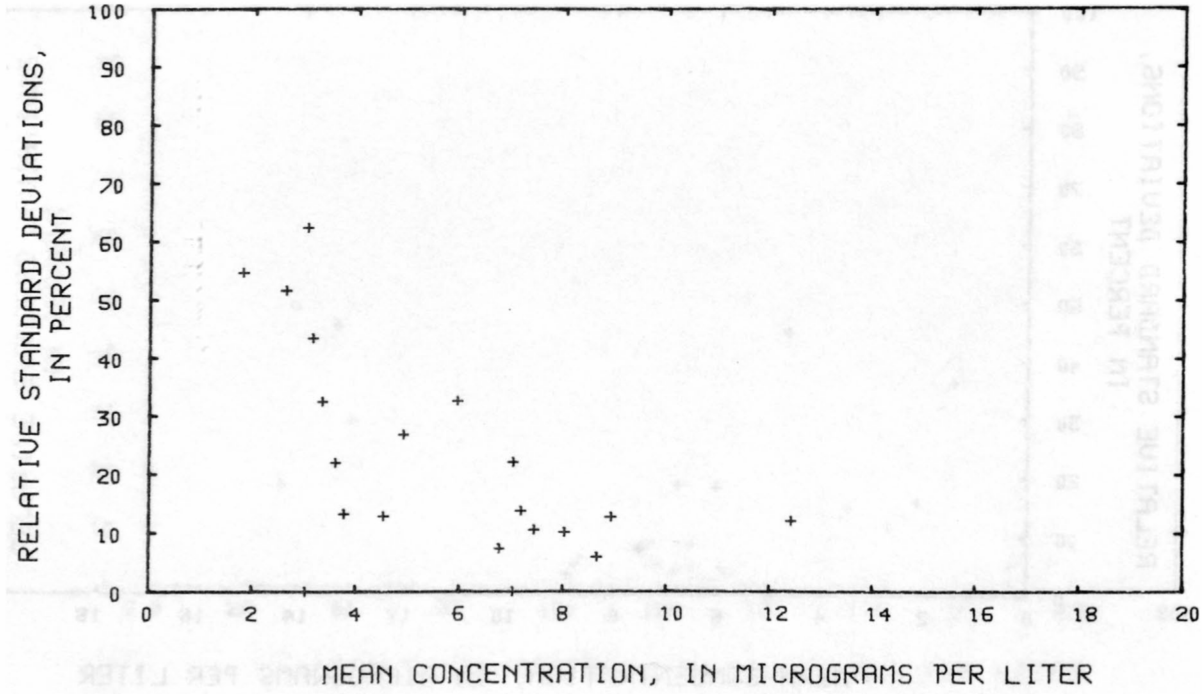

Figure 127--Precision data for cadmium, dissolved, (atomic absorption spectrometry) at the Atlanta laboratory.

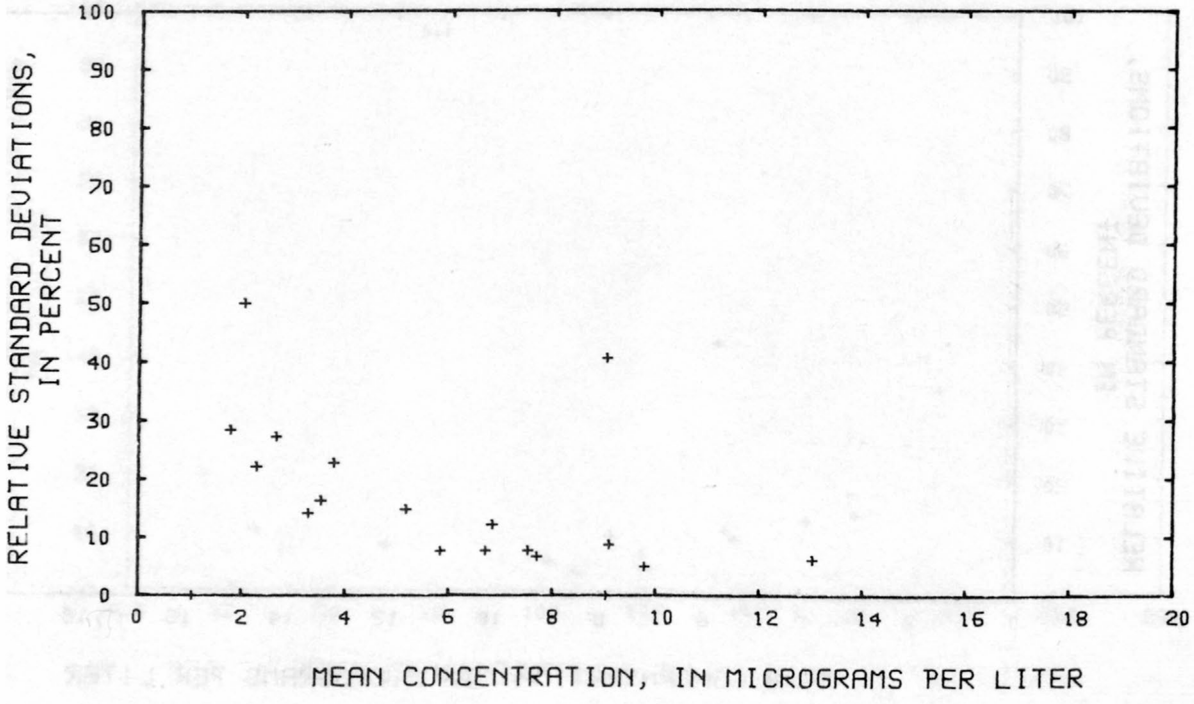

Figure 128--Precision data for cadmium, dissolved, (atomic absorption spectrometry) at the Denver laboratory.

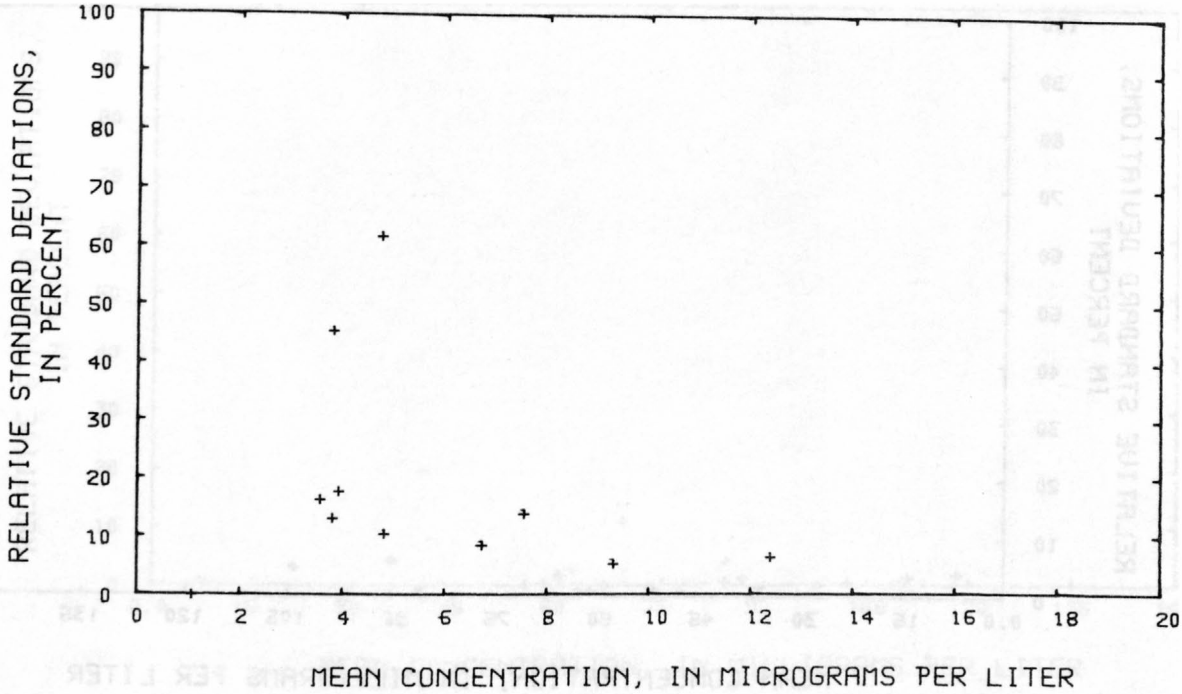

Figure 129--Precision data for cadmium, total recoverable, at the Atlanta laboratory.

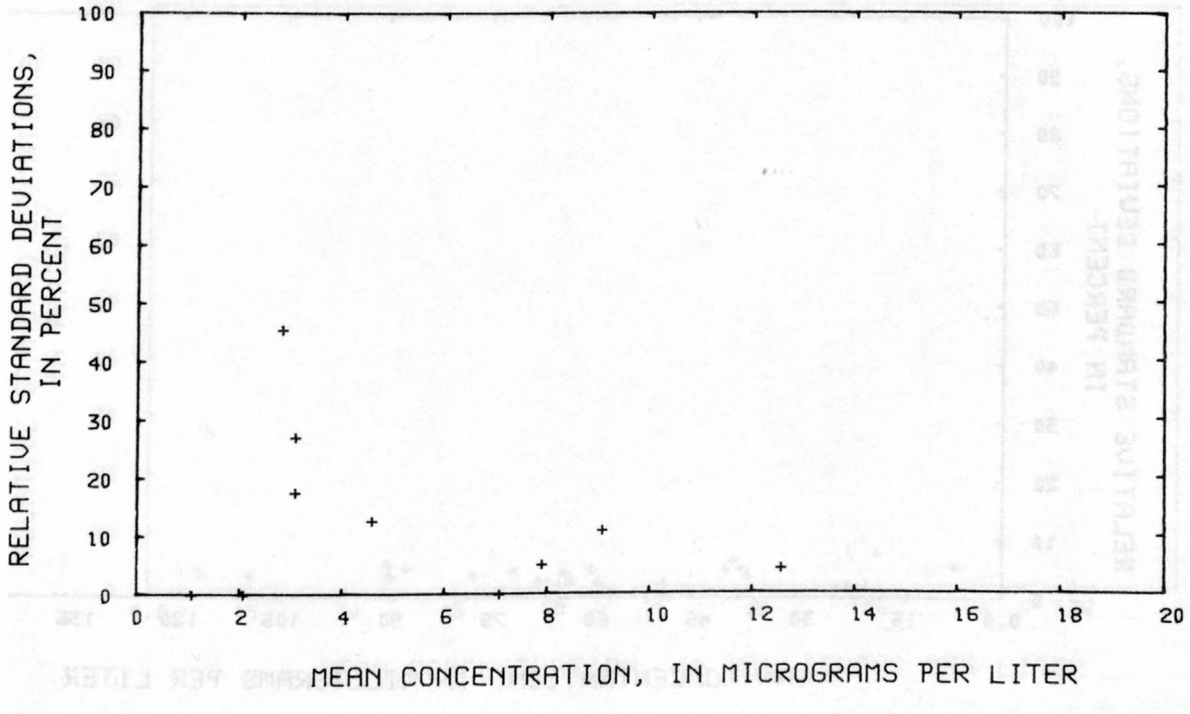

Figure 130--Precision data for cadmium, total recoverable, at the Denver laboratory.

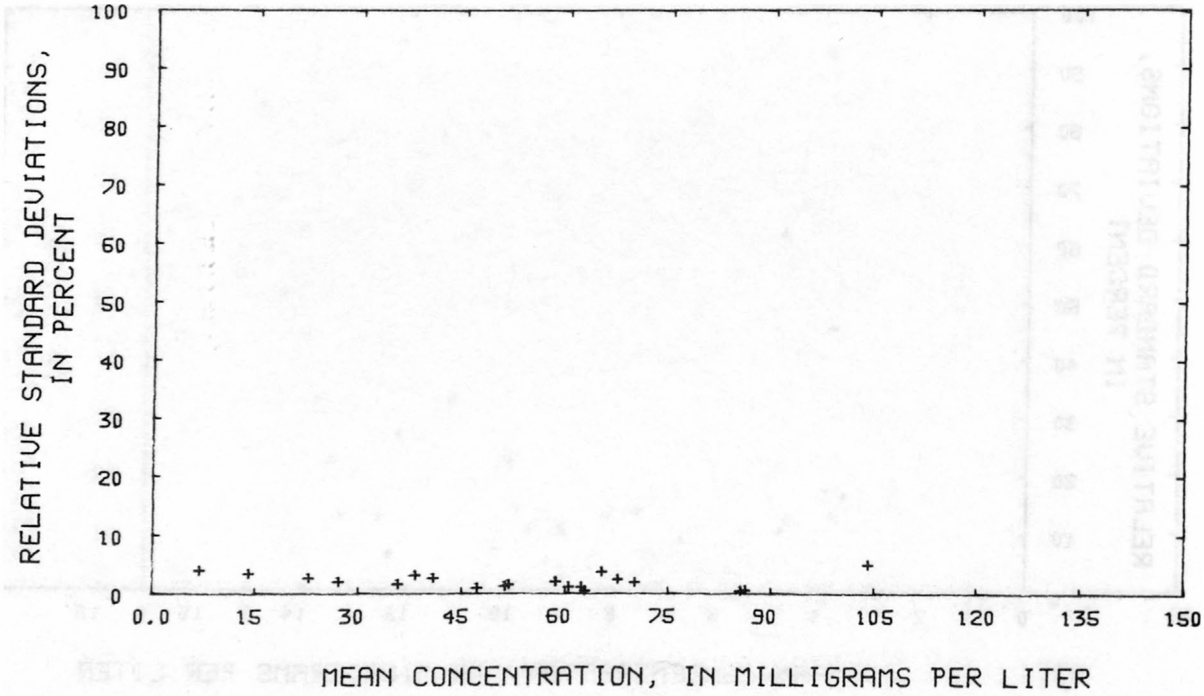

Figure 131--Precision data for calcium, dissolved, (inductively coupled plasma emission spectrometry) at the Atlanta laboratory.

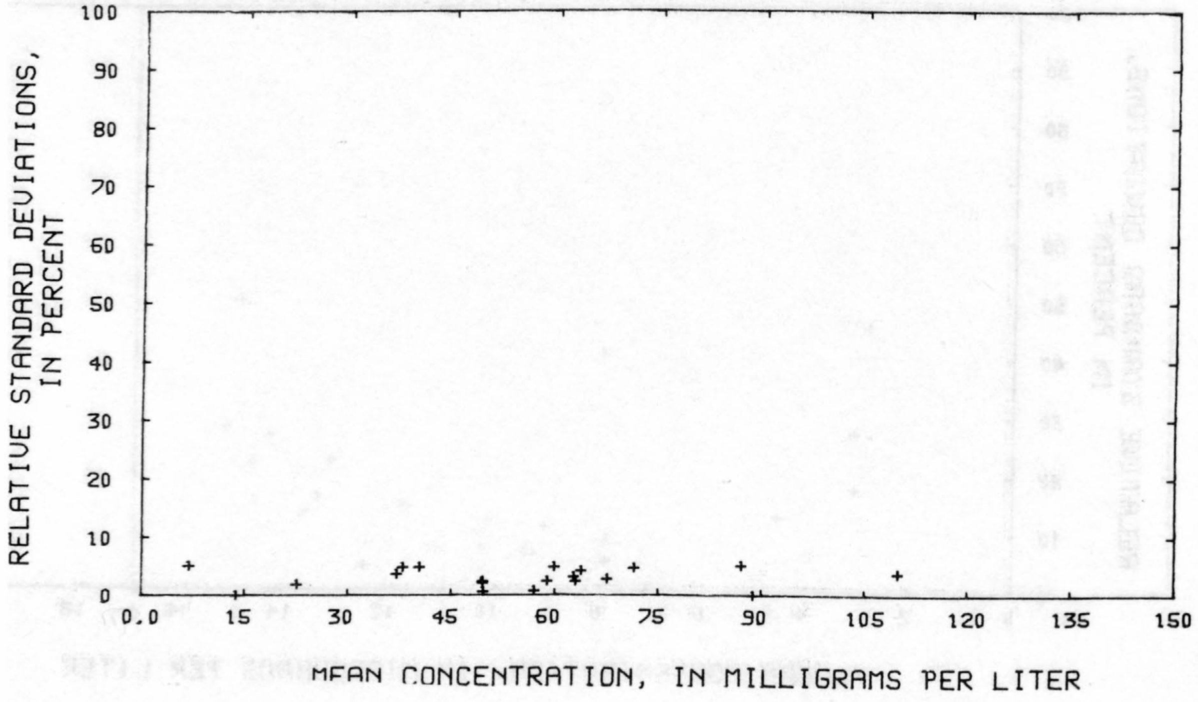

Figure 132--Precision data for calcium, dissolved, (inductively coupled plasma emission spectrometry), at the Denver laboratory.

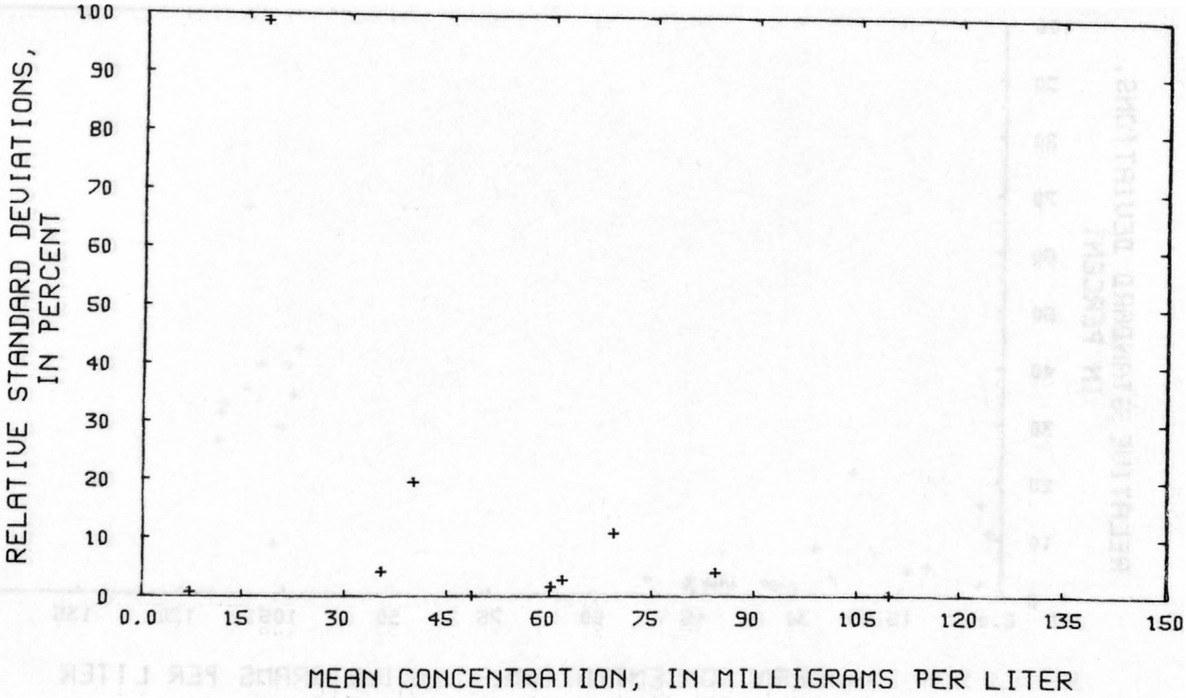

Figure 133--Precision data for calcium, dissolved, (atomic absorption spectrometry) at the Atlanta laboratory.

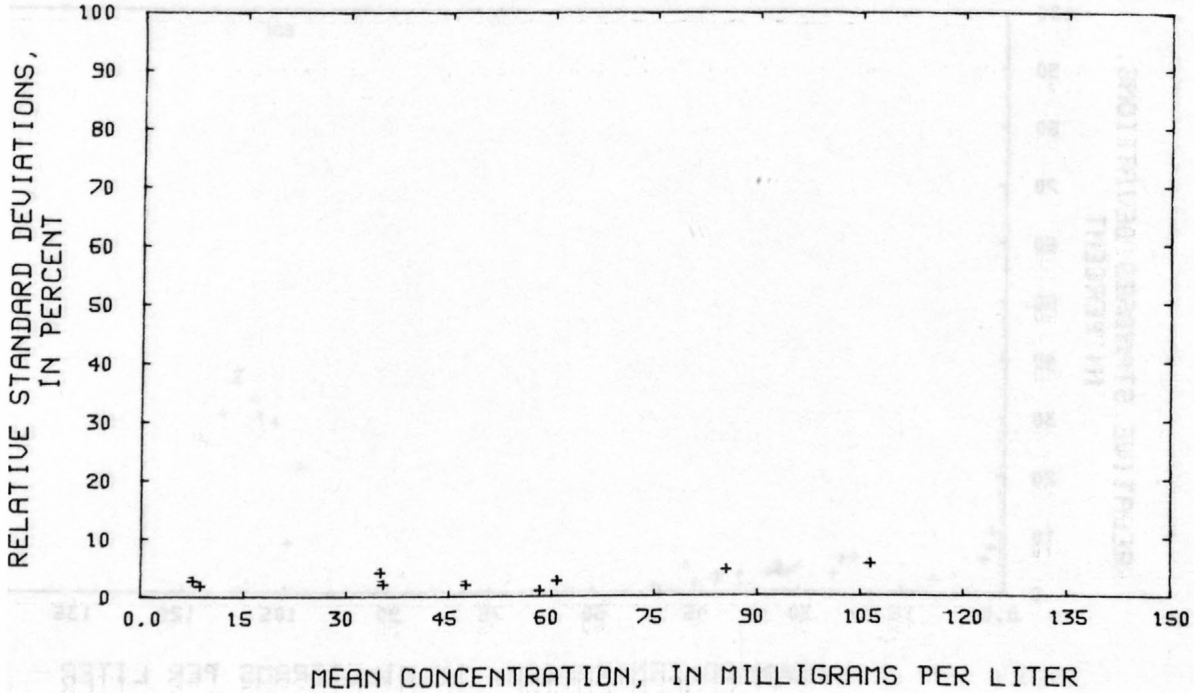

Figure 134--Precision data for calcium, dissolved, (atomic absorption spectrometry) at the Denver laboratory.

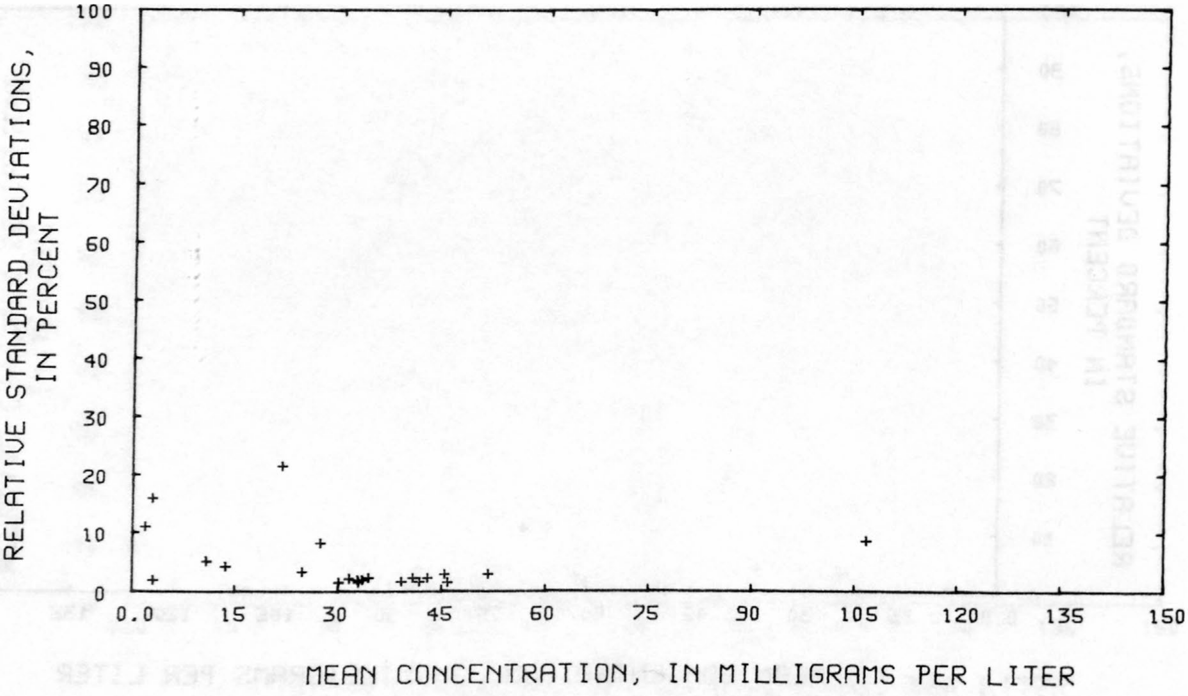

Figure 135--Precision data for chloride, dissolved, at the Atlanta laboratory.

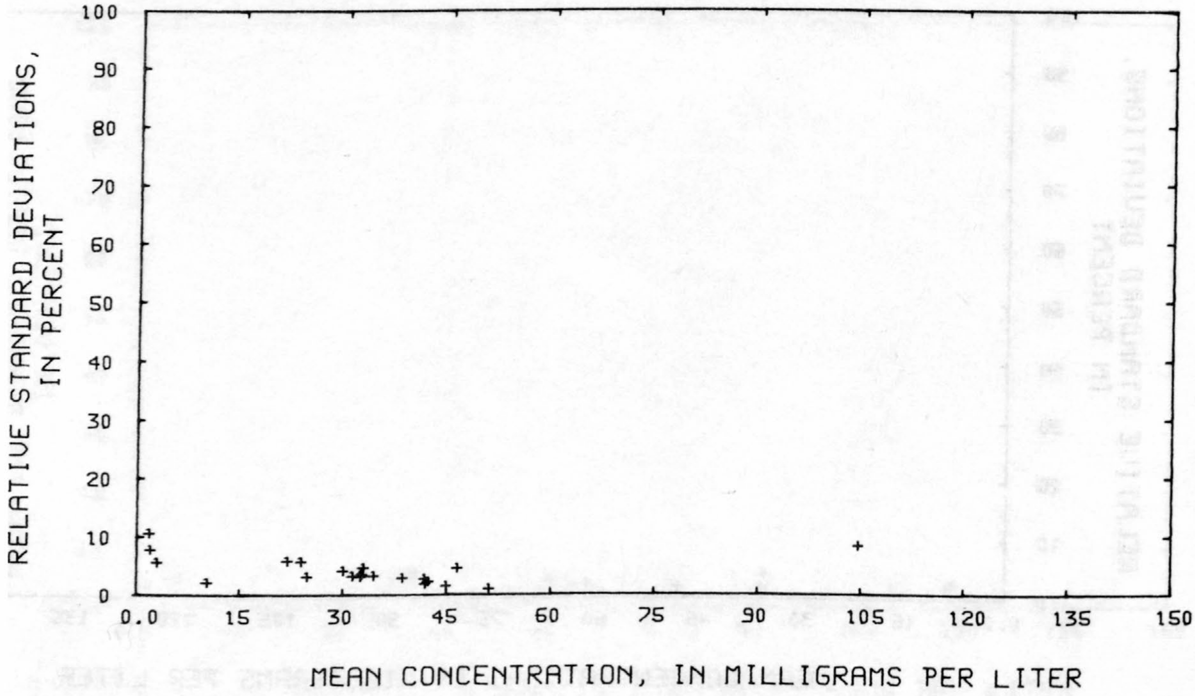

Figure 136--Precision data for chloride, dissolved, at the Denver laboratory.

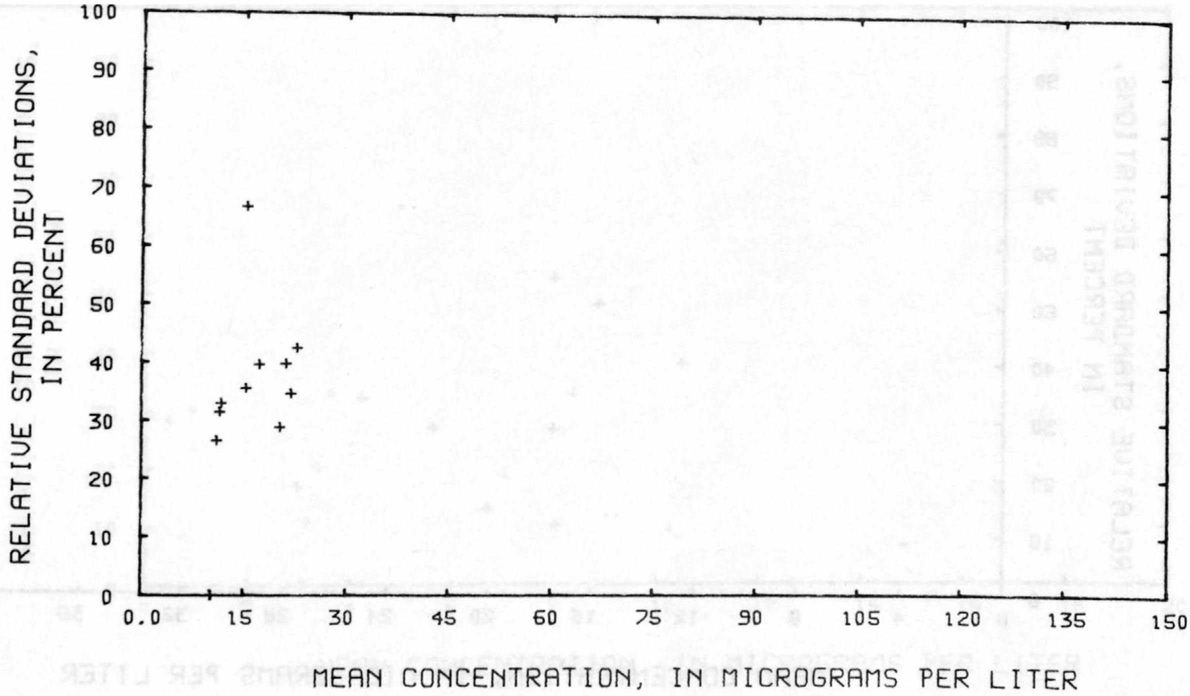

Figure 137--Precision data for chromium, dissolved, at the Atlanta laboratory.

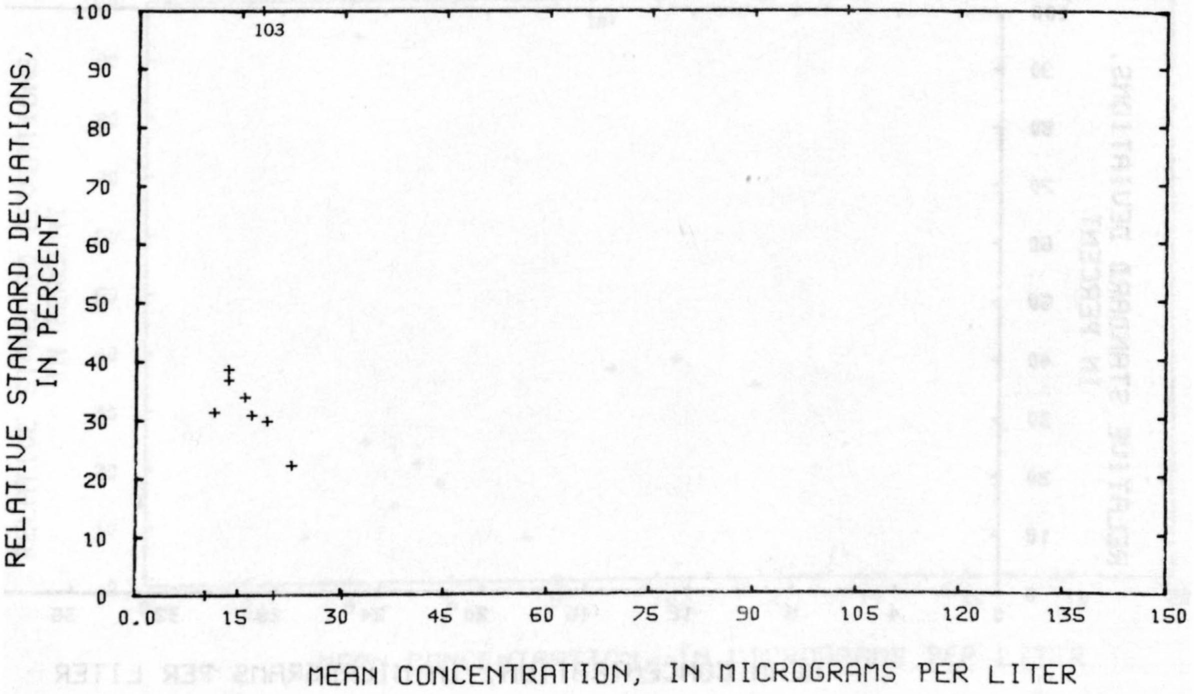

Figure 138--Precision data for chromium, dissolved, at the Denver laboratory.

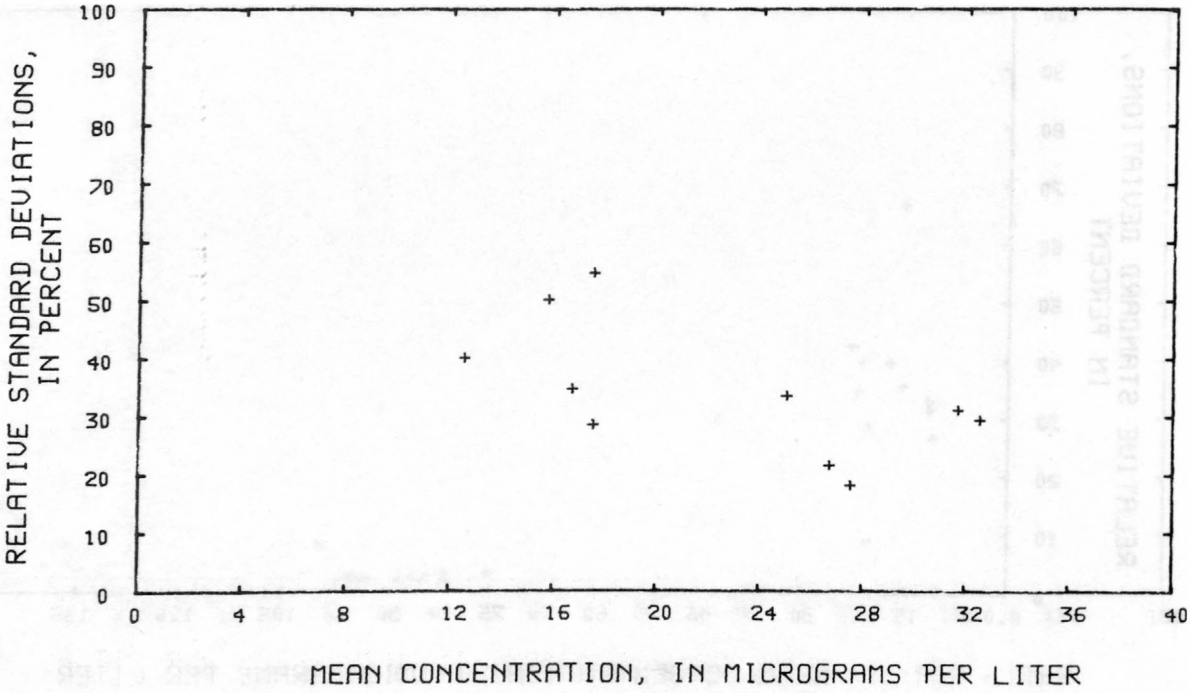

Figure 139--Precision data for chromium, total recoverable, at the Atlanta laboratory.

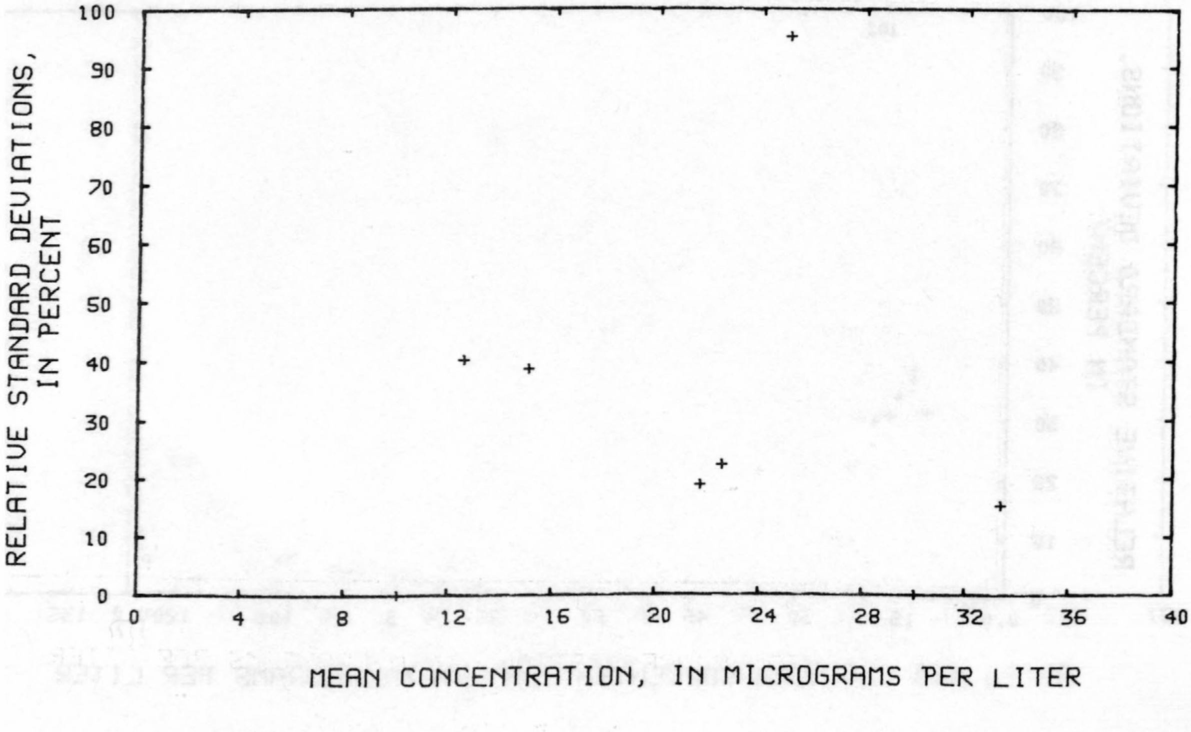

Figure 140--Precision data for chromium, total recoverable, at the Denver laboratory.

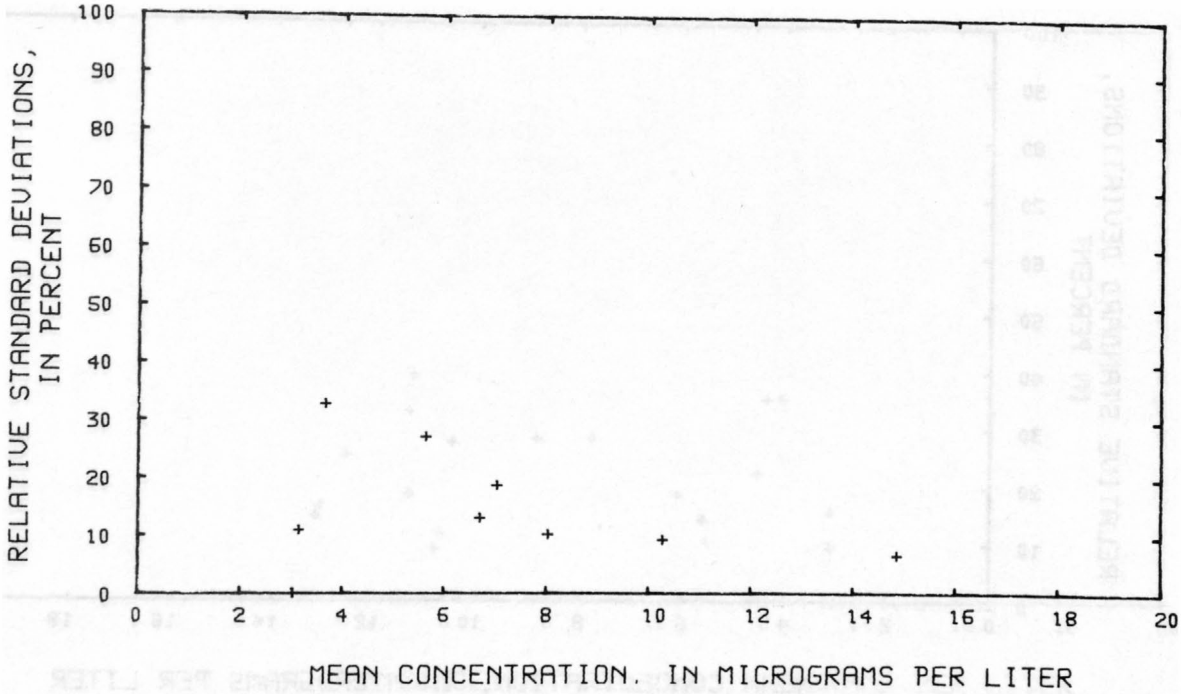

Figure 141--Precision data for cobalt, dissolved, (inductively coupled plasma emission spectrometry) at the Atlanta laboratory.

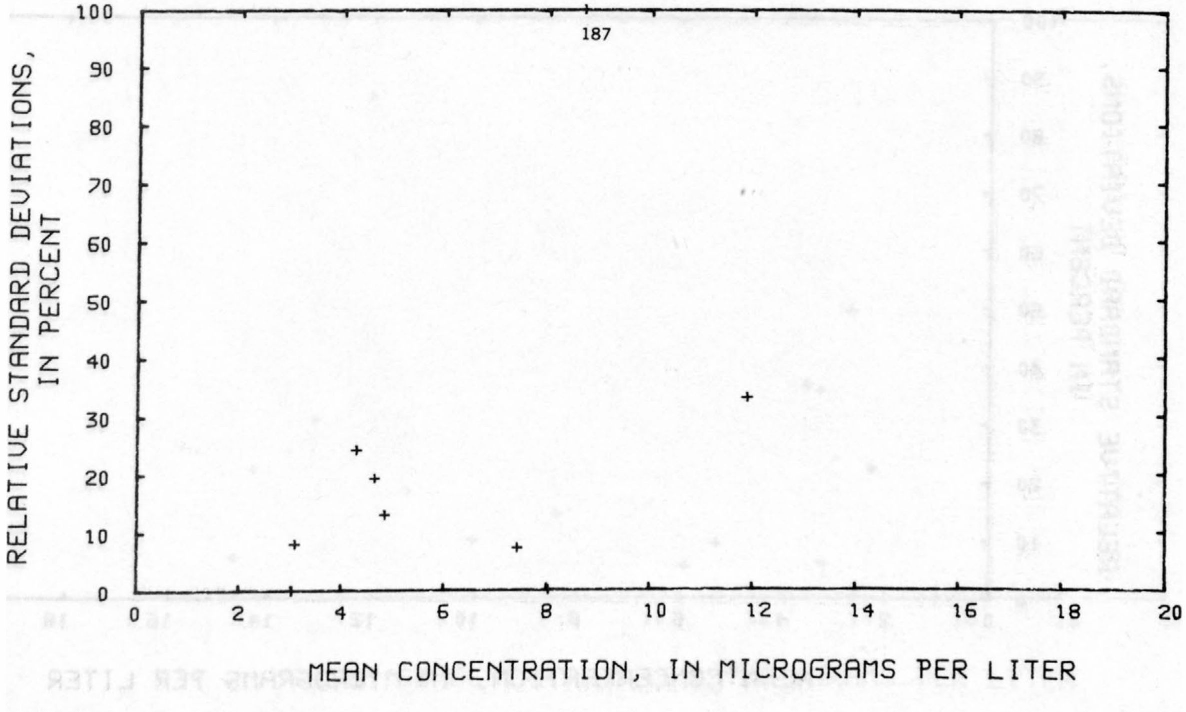

Figure 142--Precision data for cobalt, dissolved, (inductively coupled plasma emission spectrometry) at the Denver laboratory.

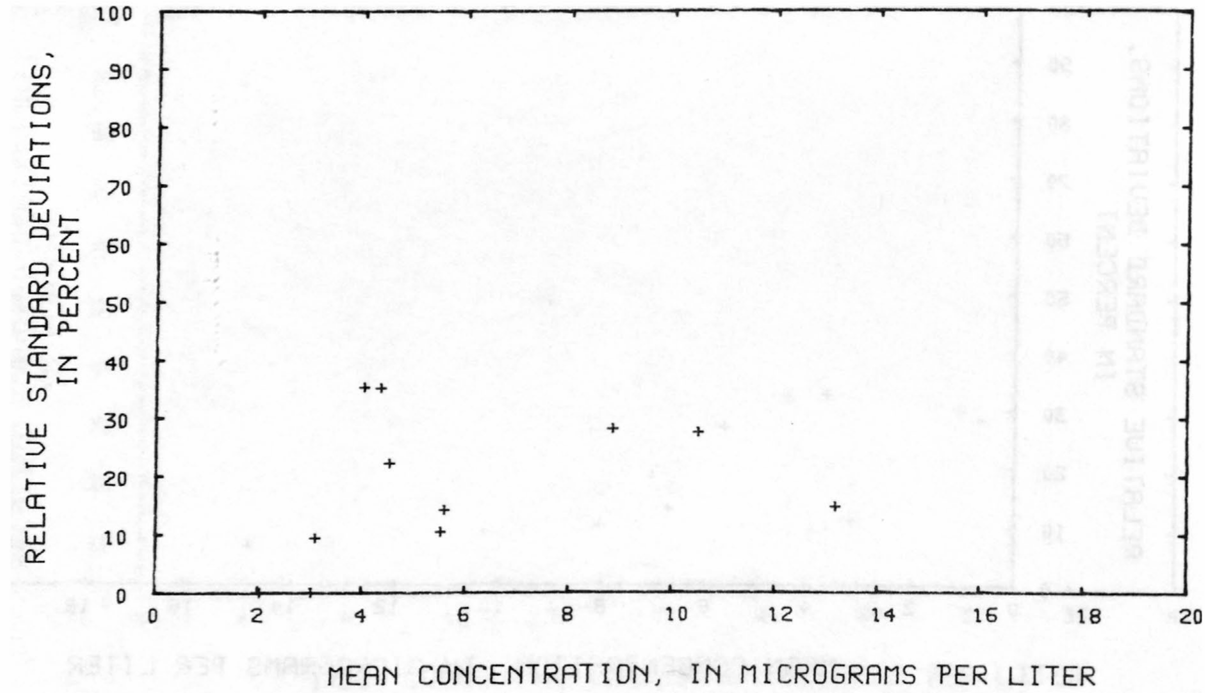

Figure 143--Precision data for cobalt, dissolved, (atomic absorption spectrometry) at the Atlanta laboratory.

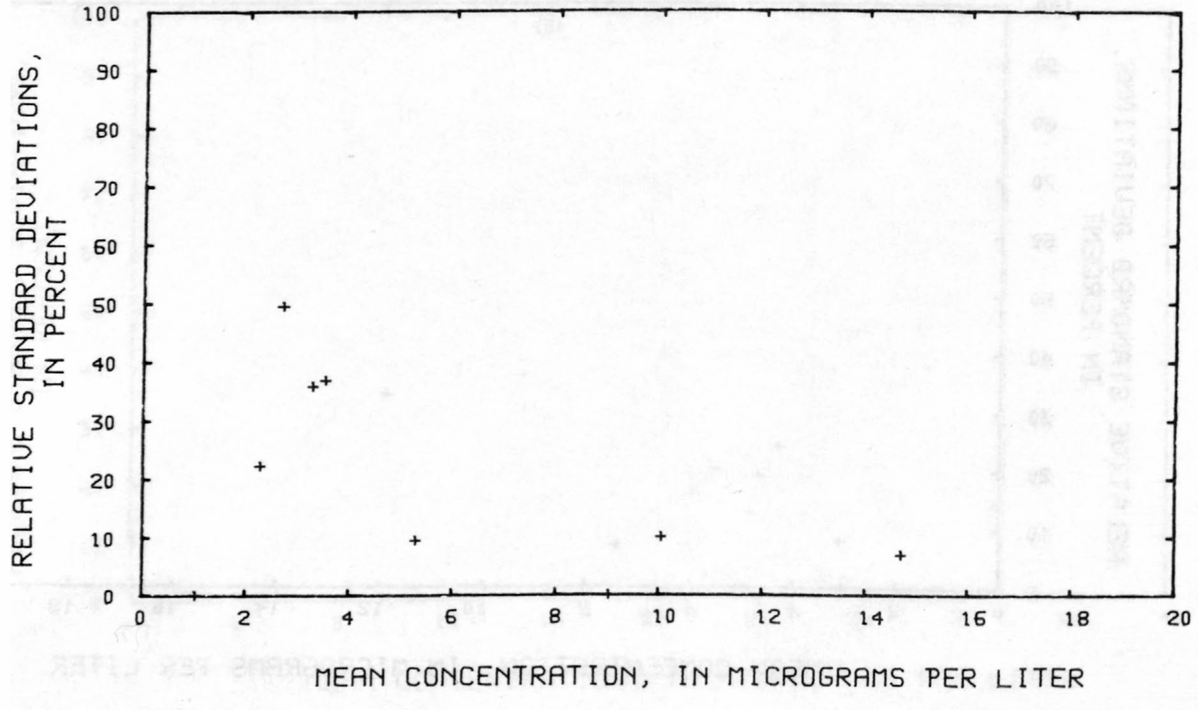

Figure 144--Precision data for cobalt, dissolved, (atomic absorption spectrometry) at the Denver laboratory.

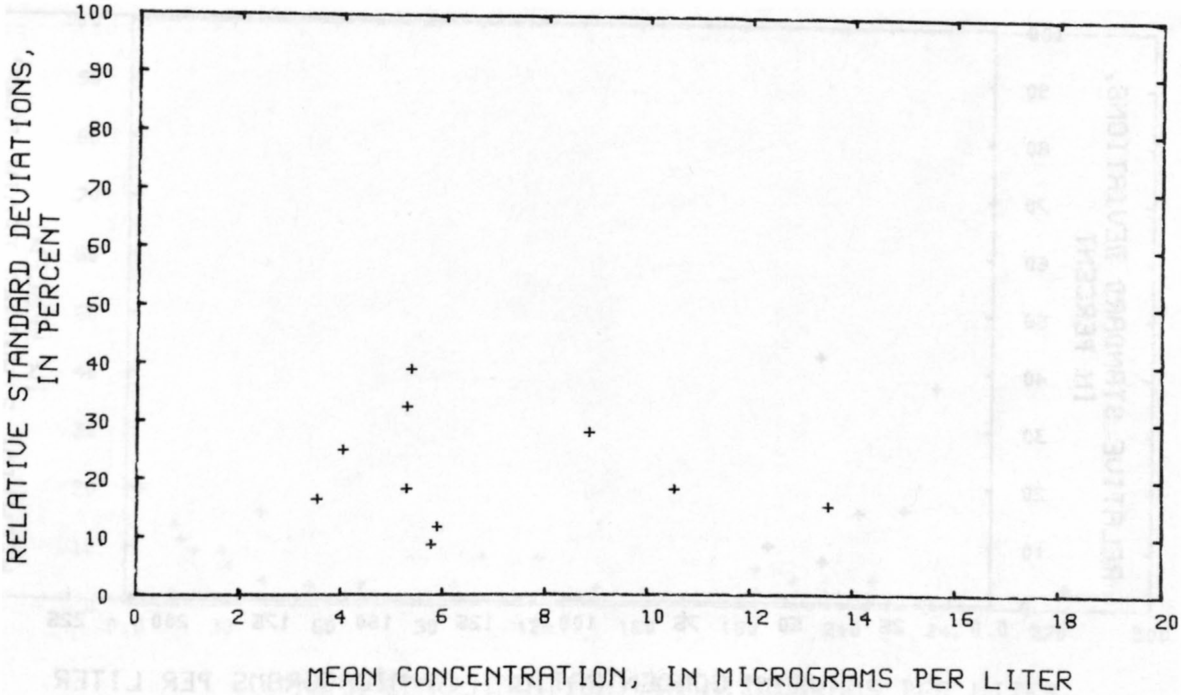

Figure 145--Precision data for cobalt, total recoverable, at the Atlanta laboratory.

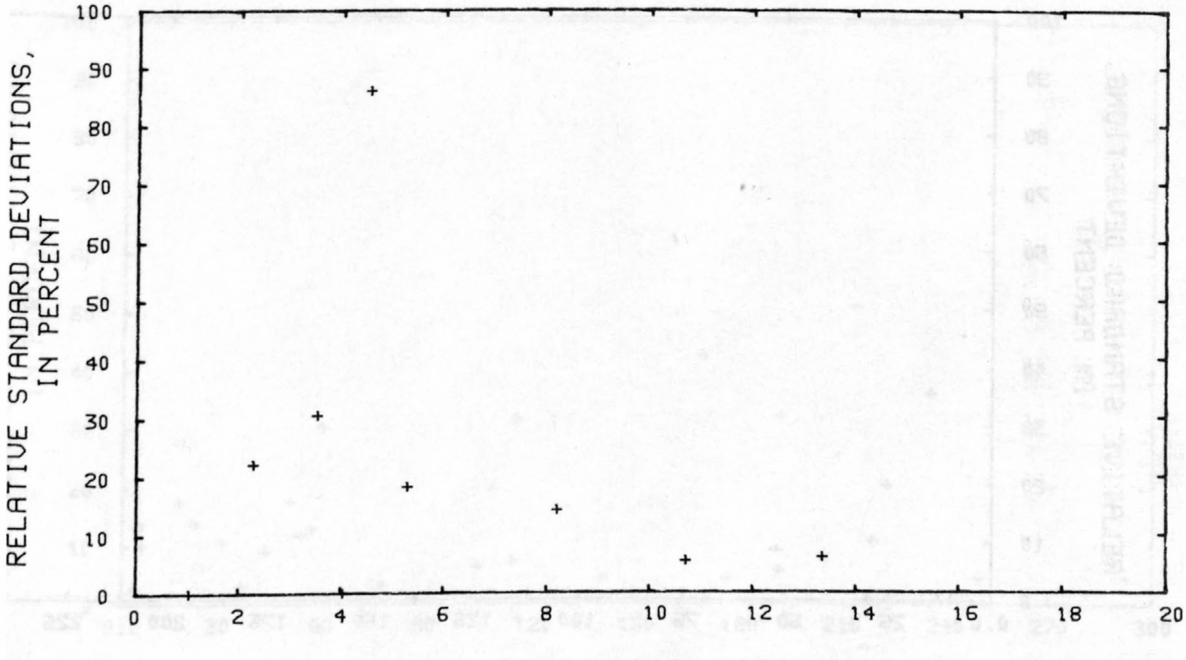

Figure 146--Precision data for cobalt, total recoverable, at the Denver laboratory.

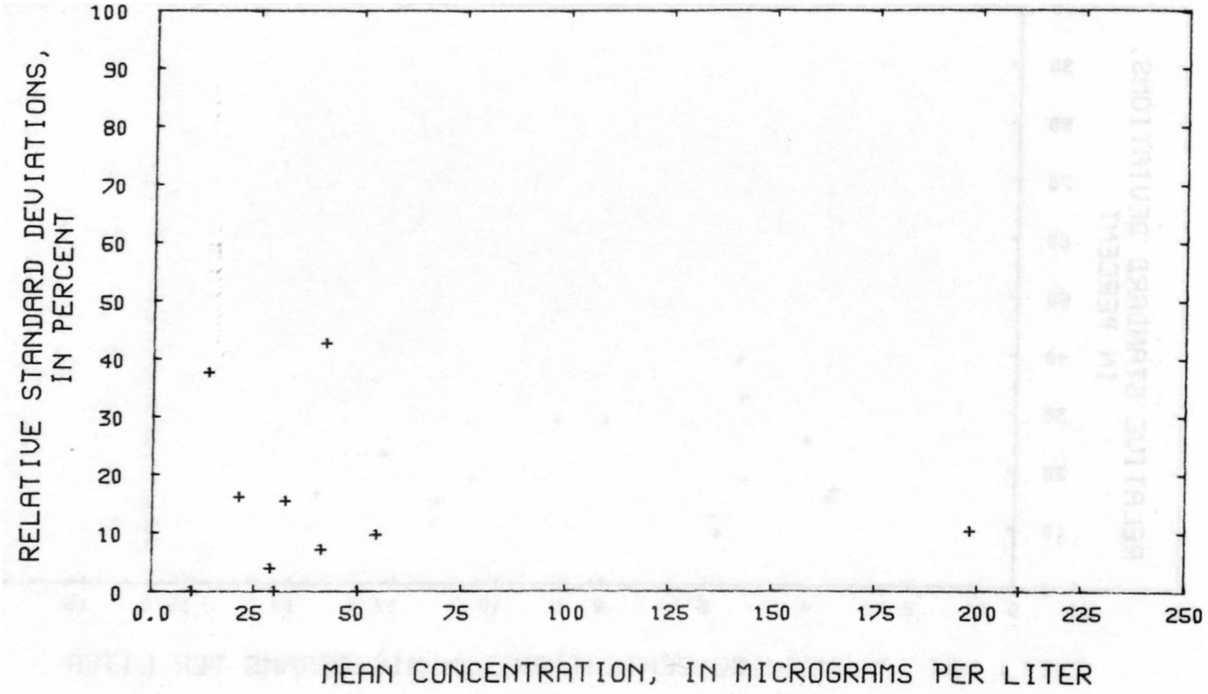

Figure 147--Precision data for copper, dissolved, (inductively coupled plasma emission spectrometry) at the Atlanta laboratory.

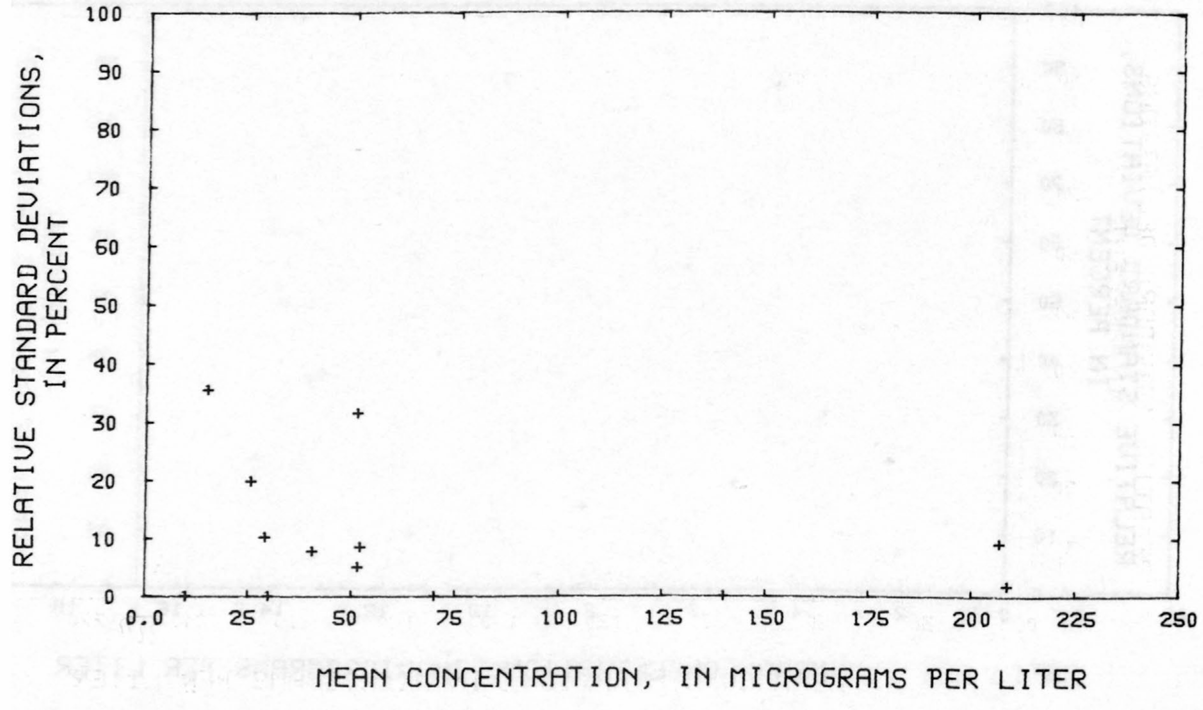

Figure 148--Precision data for copper, dissolved, (inductively coupled plasma emission spectrometry) at the Denver laboratory.

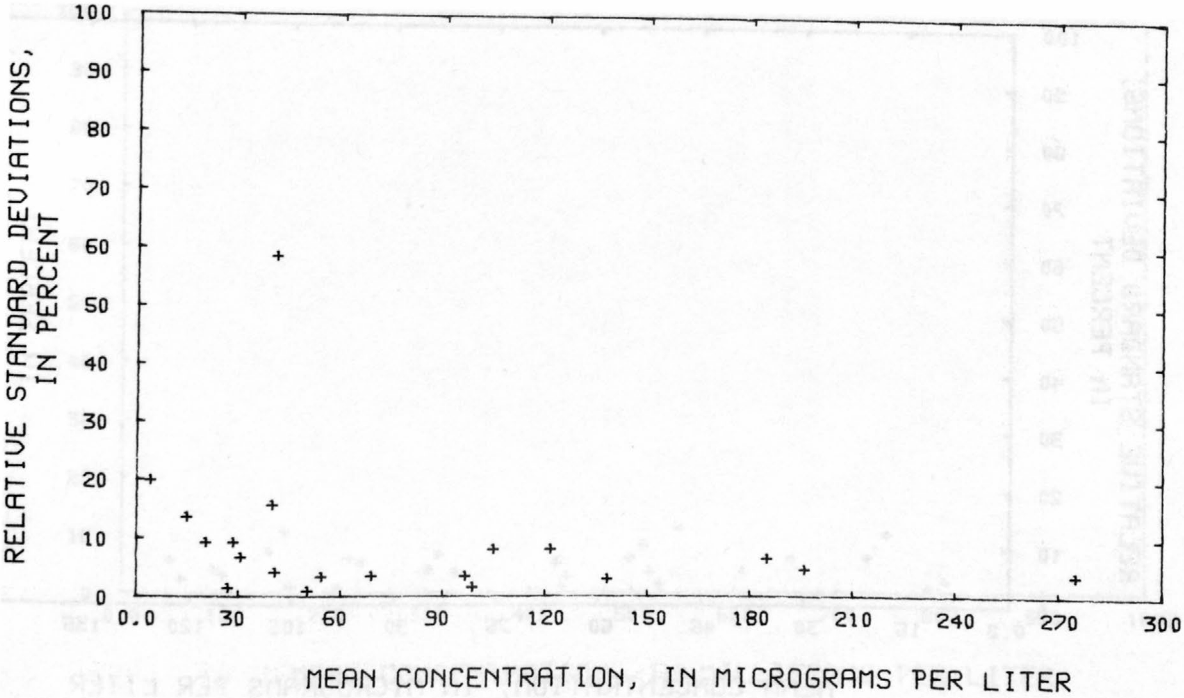

Figure 149--Precision data for copper, dissolved, (atomic absorption spectrometry) at the Atlanta laboratory.

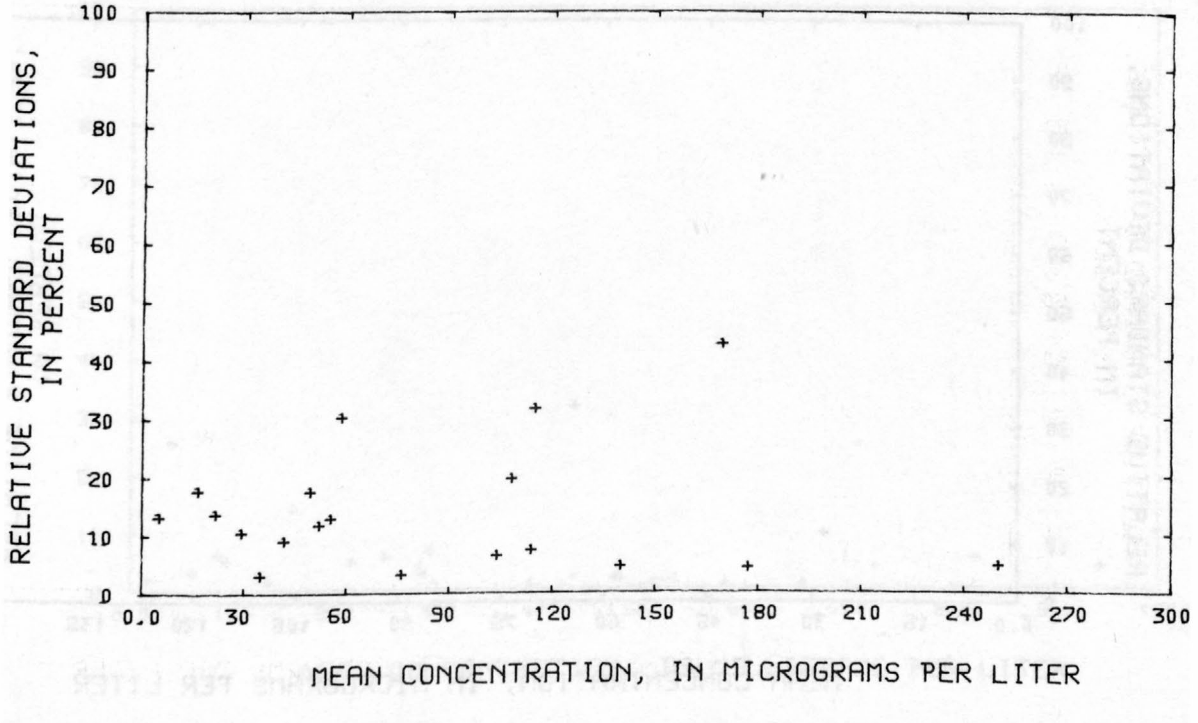

Figure 150--Precision data for copper, dissolved, (atomic absorption spectrometry) at the Denver laboratory.

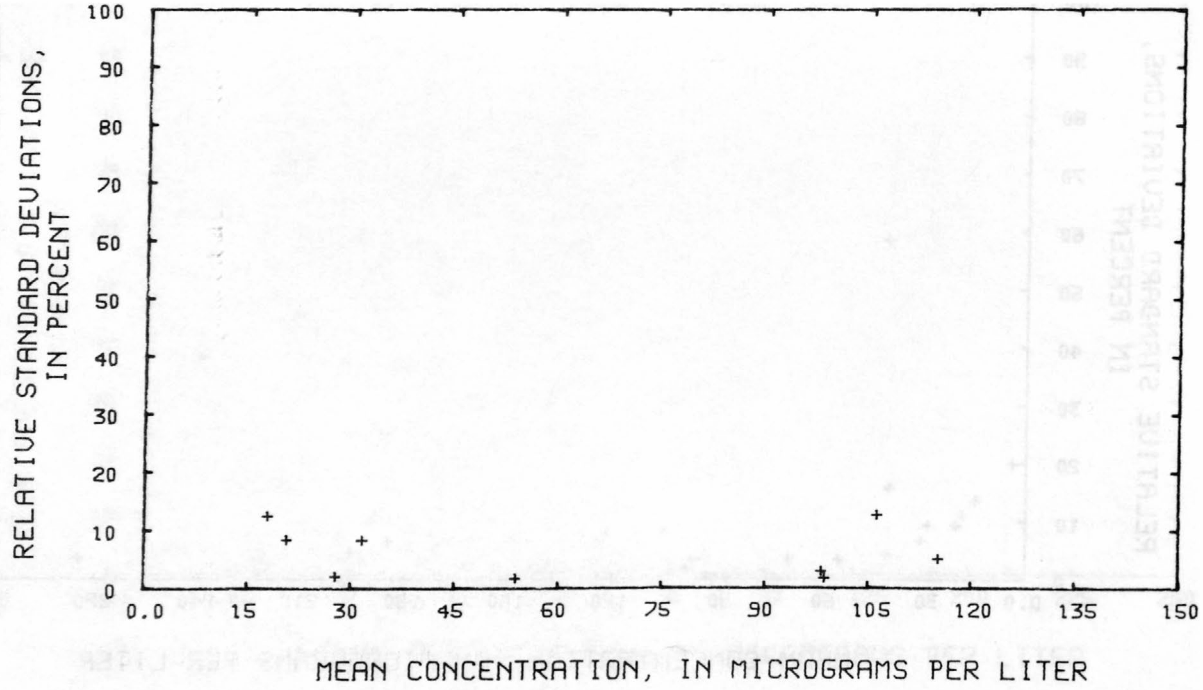

Figure 151--Precision data for copper, total recoverable, at the Atlanta laboratory.

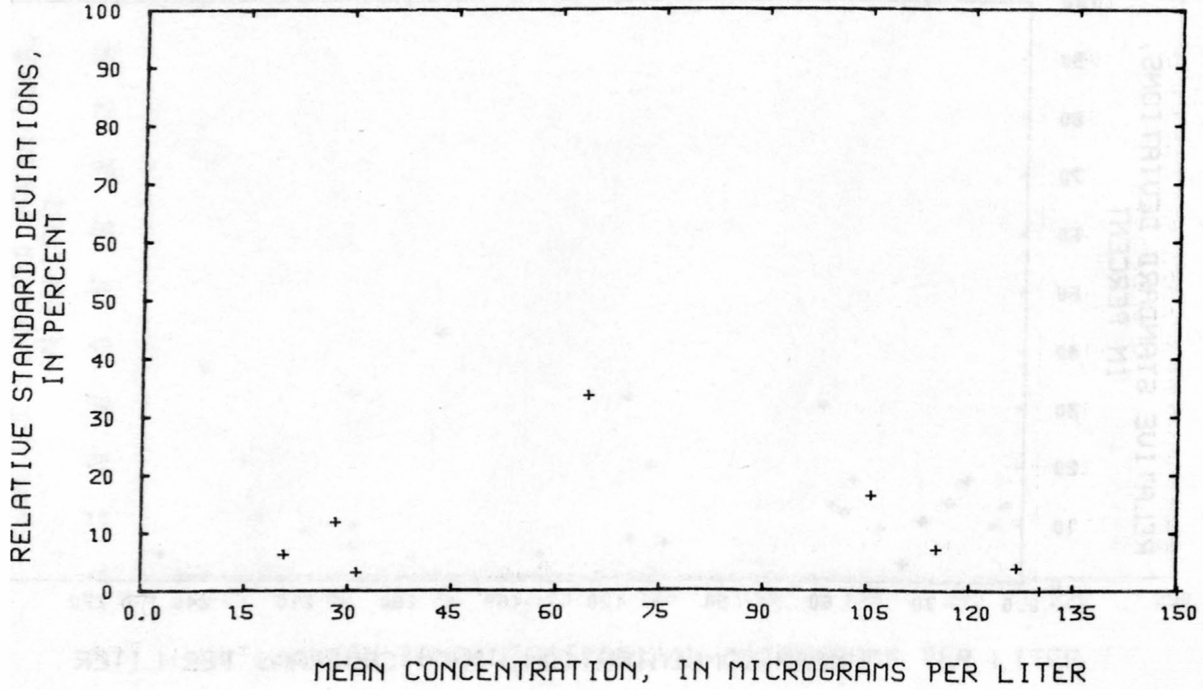

Figure 152--Precision data for copper, total recoverable, at the Denver laboratory.

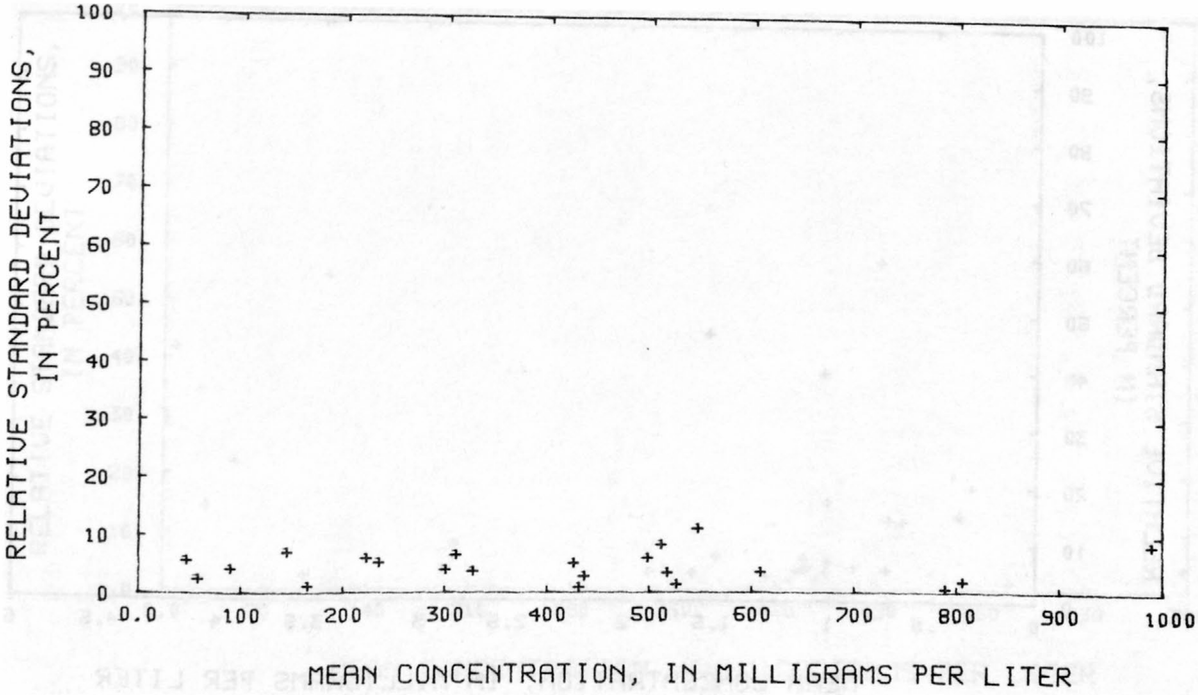

Figure 153--Precision data for dissolved solids at the Atlanta laboratory.

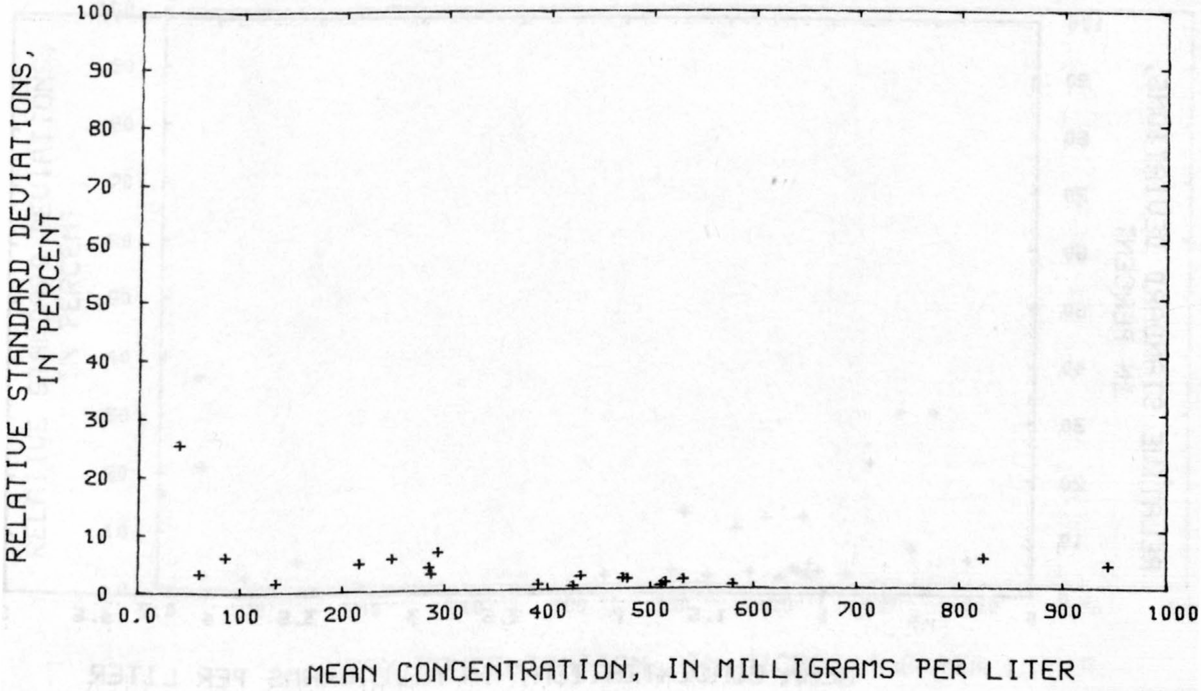

Figure 154--Precision data for dissolved solids at the Denver laboratory.

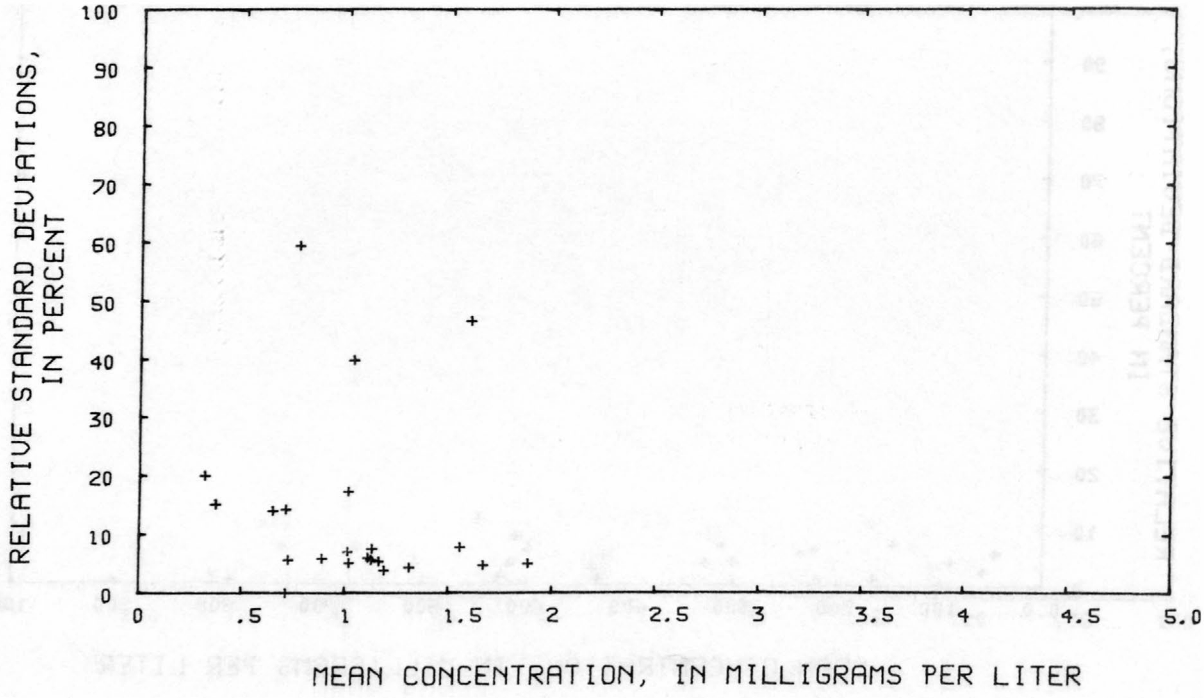

Figure 155--Precision data for flouride, dissolved, at the Atlanta laboratory.

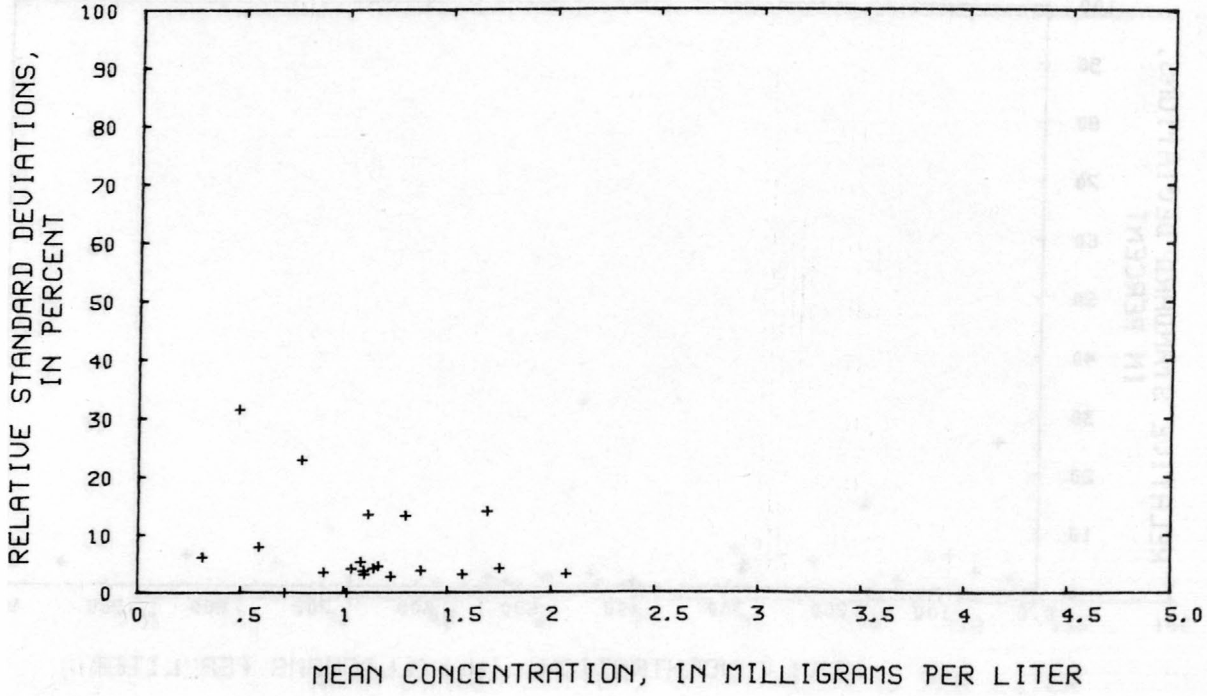

Figure 156--Precision data for flouride, dissolved, at the Denver laboratory.

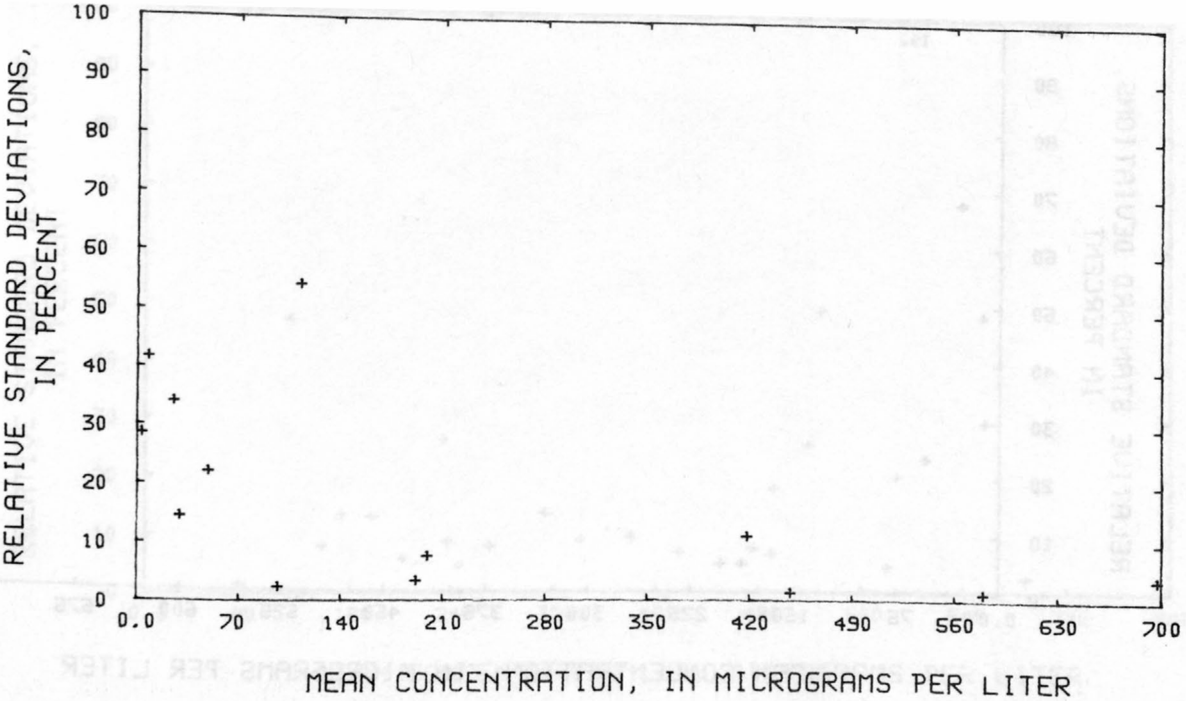

Figure 157--Precision data for iron, dissolved, (inductively coupled plasma emission spectrometry) at the Atlanta laboratory.

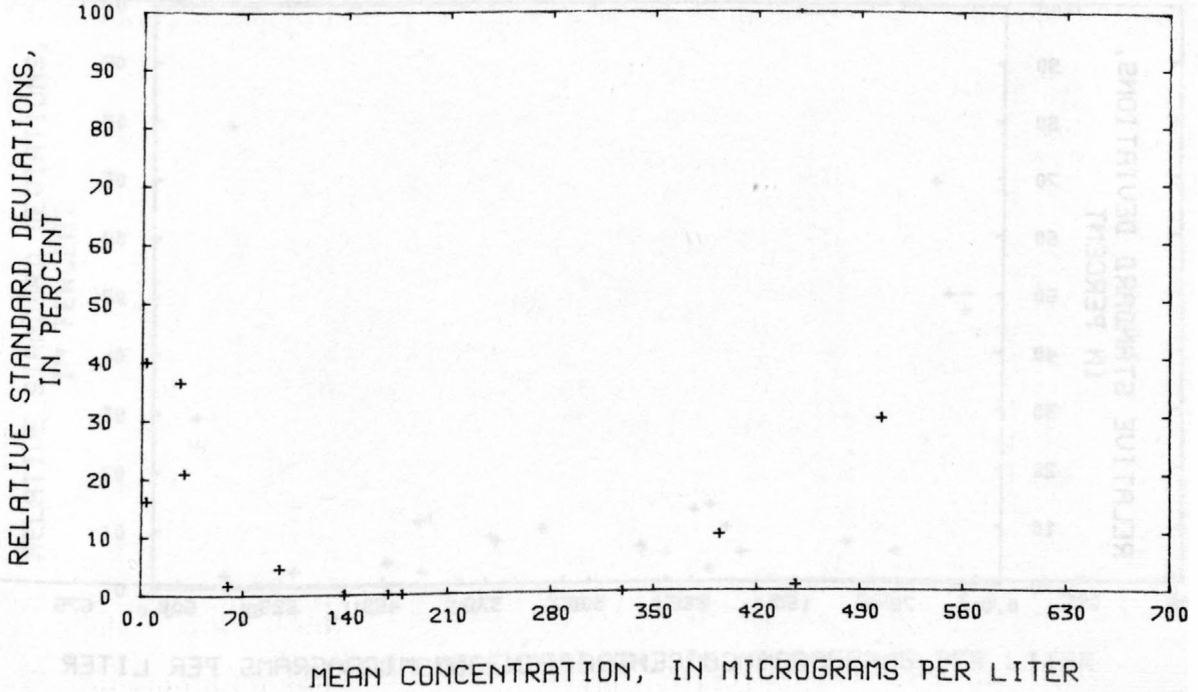

Figure 158--Precision data for iron, dissolved, (inductively coupled plasma emission spectrometry) at the Denver laboratory.

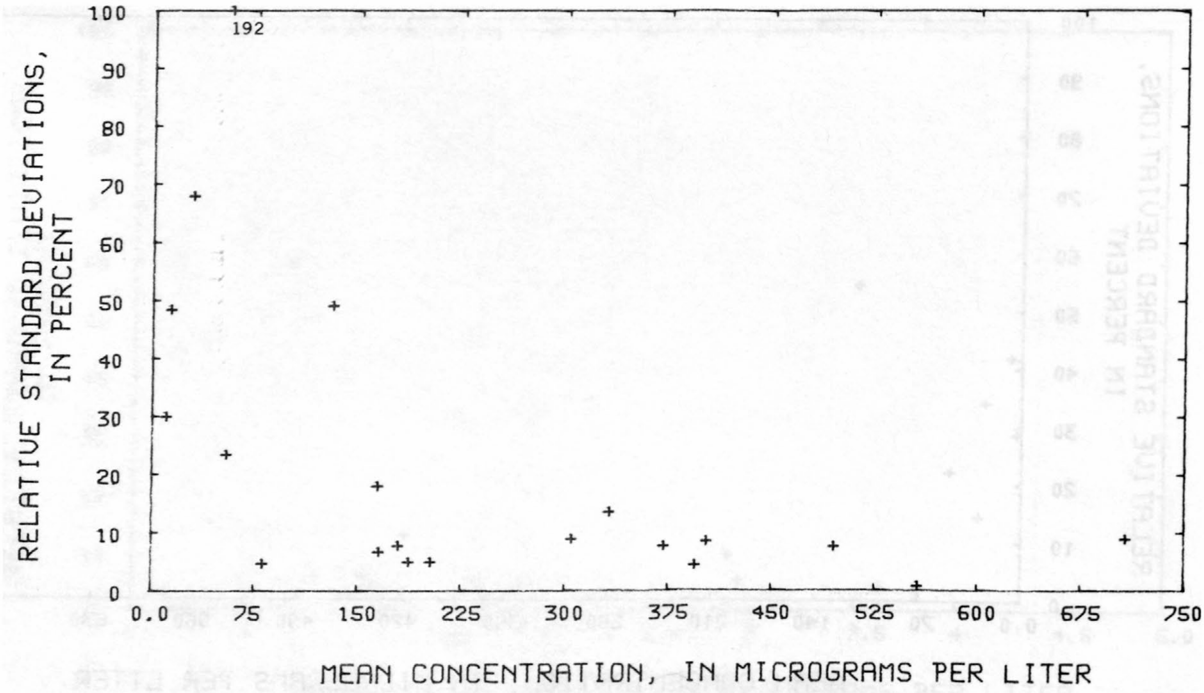

Figure 159--Precision data for iron, dissolved, (atomic absorption spectrometry) at the Atlanta laboratory.

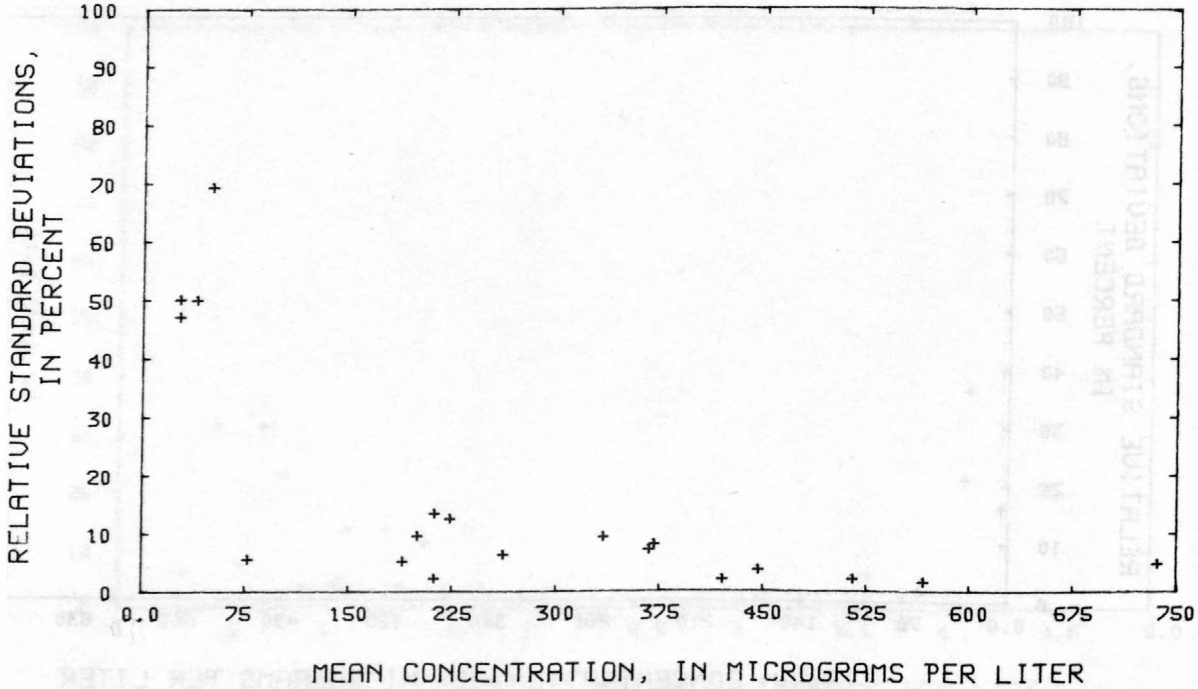

Figure 160--Precision data for iron, dissolved, (atomic absorption spectrometry) at the Denver laboratory.

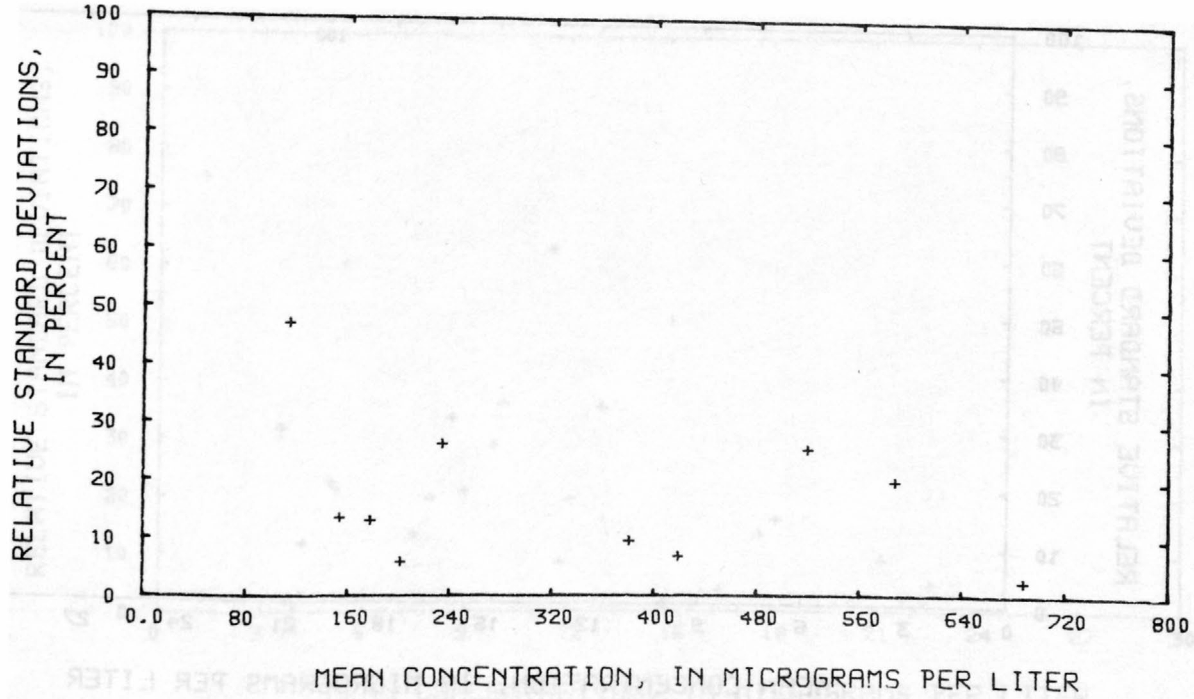

Figure 161--Precision data for iron, total recoverable, at the Atlanta laboratory.

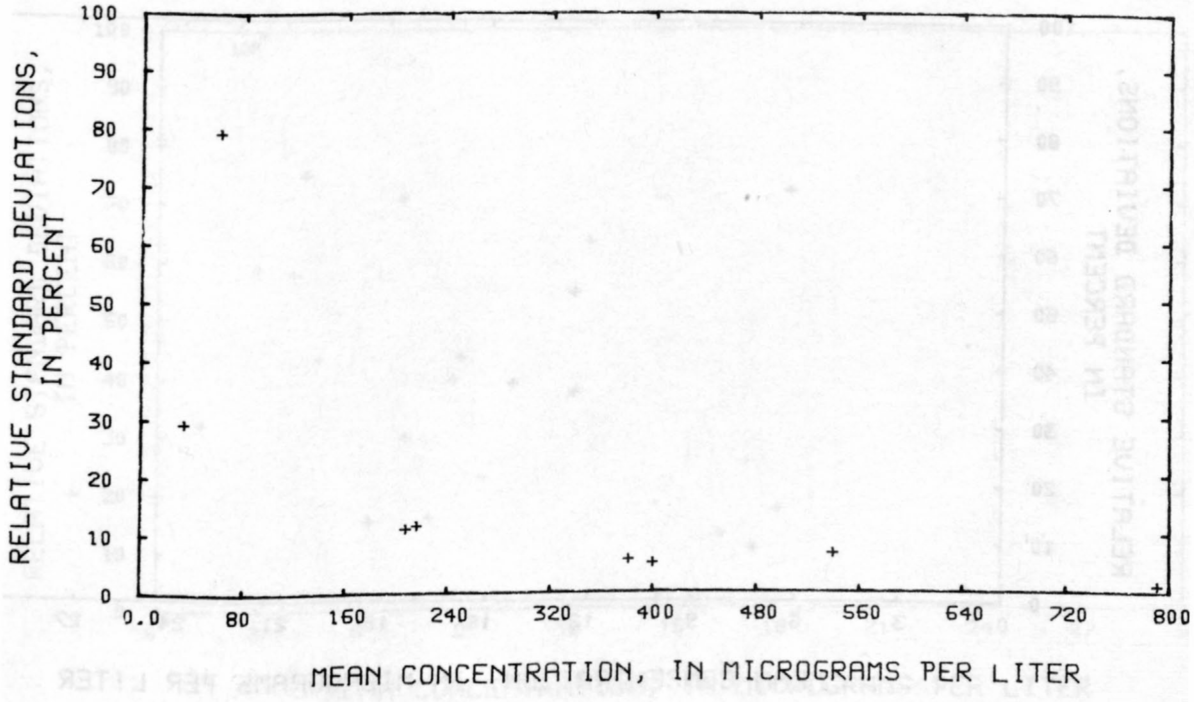

Figure 162--Precision data for iron, total recoverable, at the Denver laboratory.

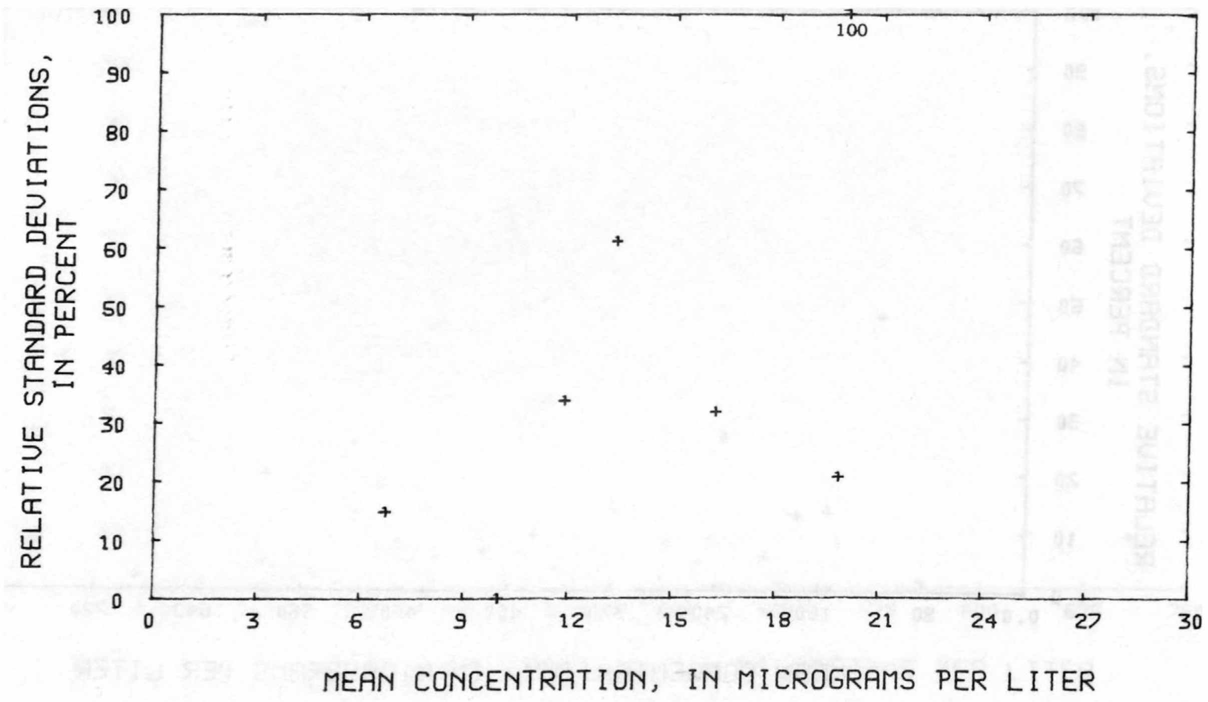

Figure 163--Precision data for lead, dissolved, (inductively coupled plasma emission spectrometry) at the Atlanta laboratory.

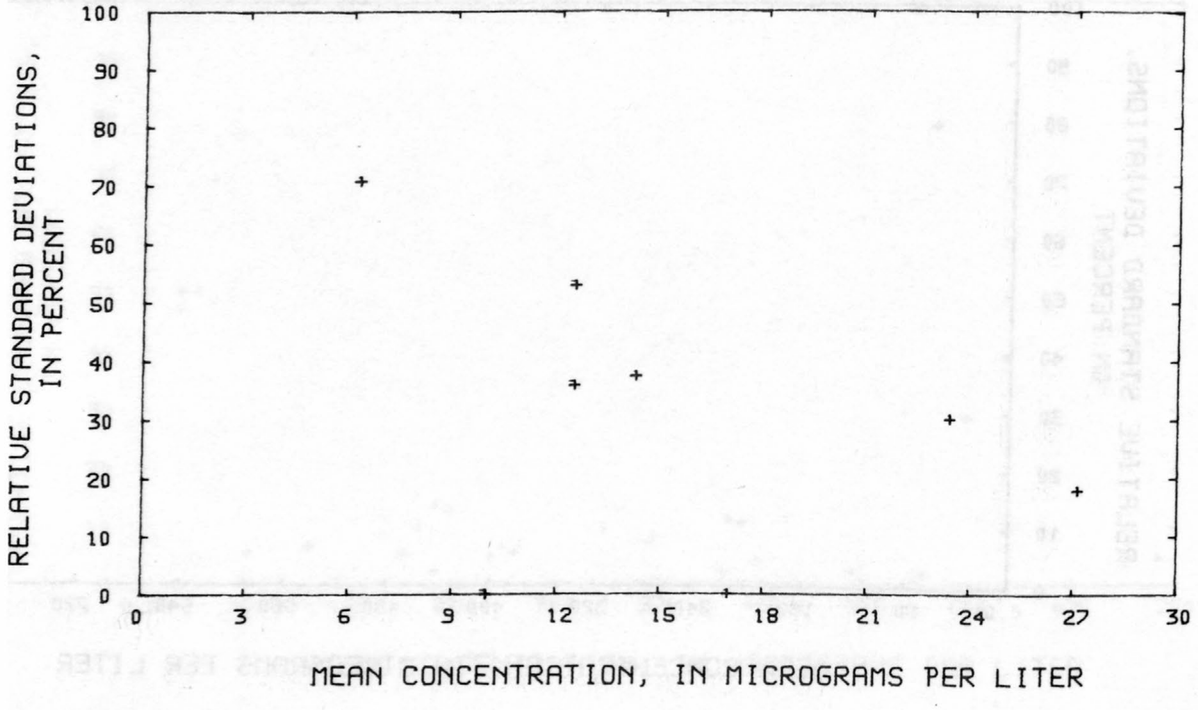

Figure 164--Precision data for lead, dissolved, (inductively coupled plasma emission spectrometry) at the Denver laboratory.

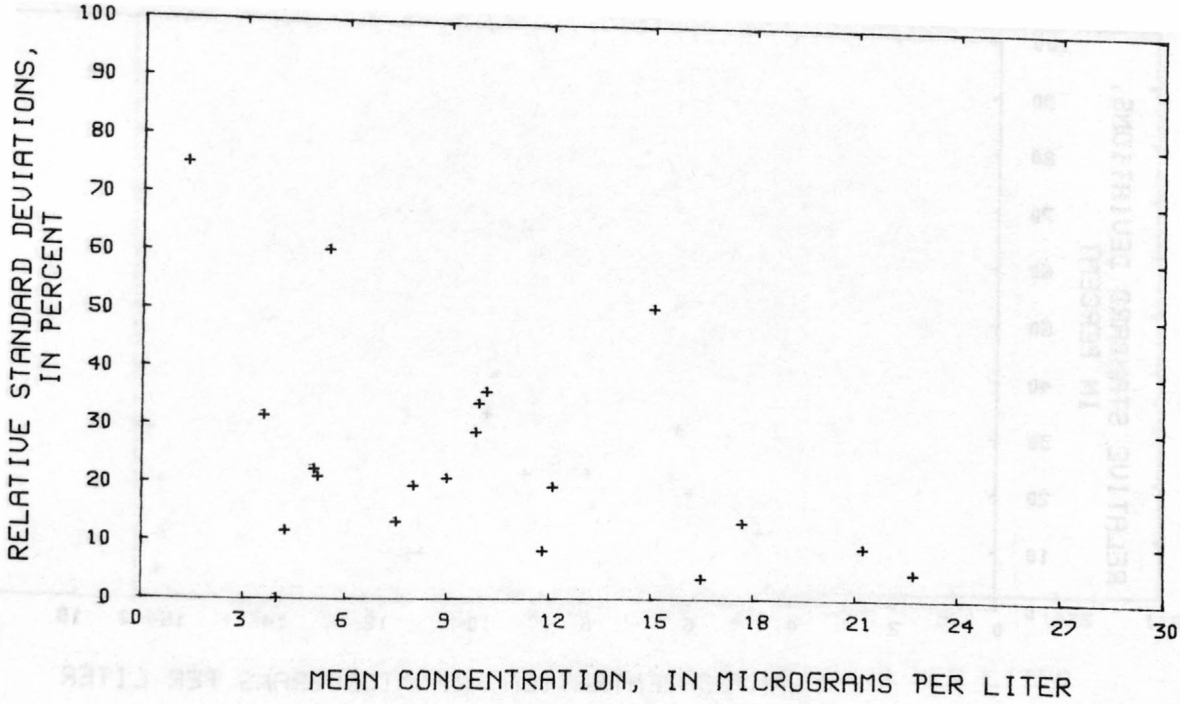

Figure 165--Precision data for lead, dissolved, (atomic absorption spectrometry) at the Atlanta laboratory.

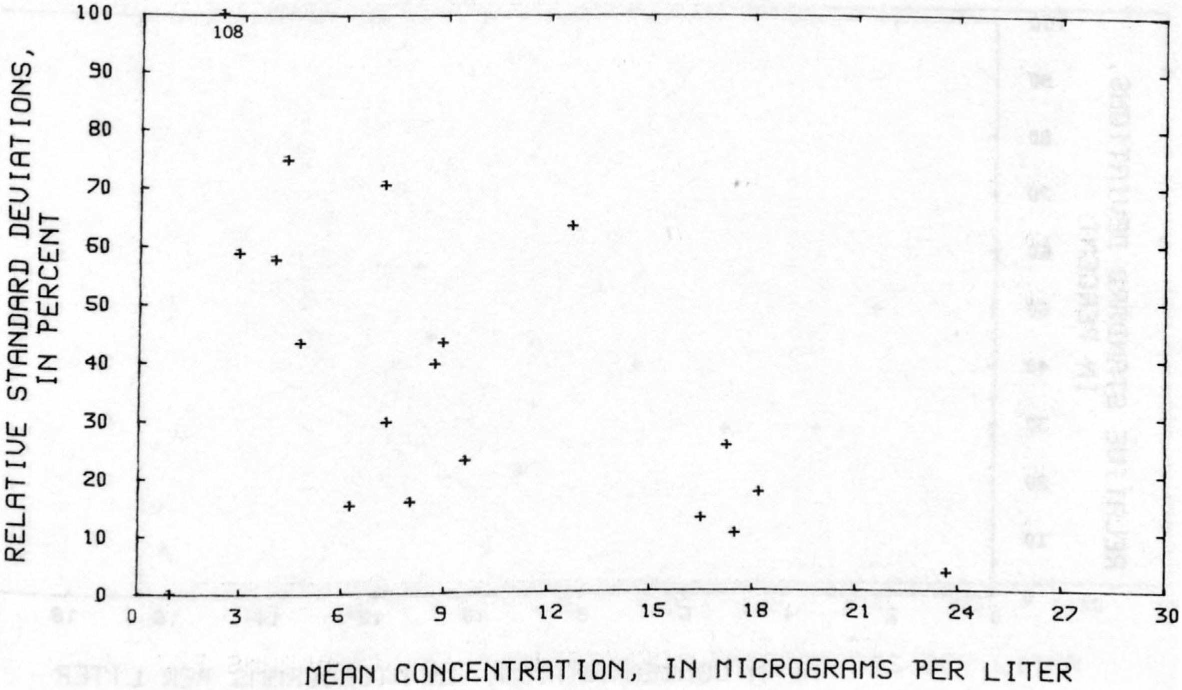

Figure 166--Precision data for lead, dissolved, (atomic absorption spectrometry) at the Denver laboratory.

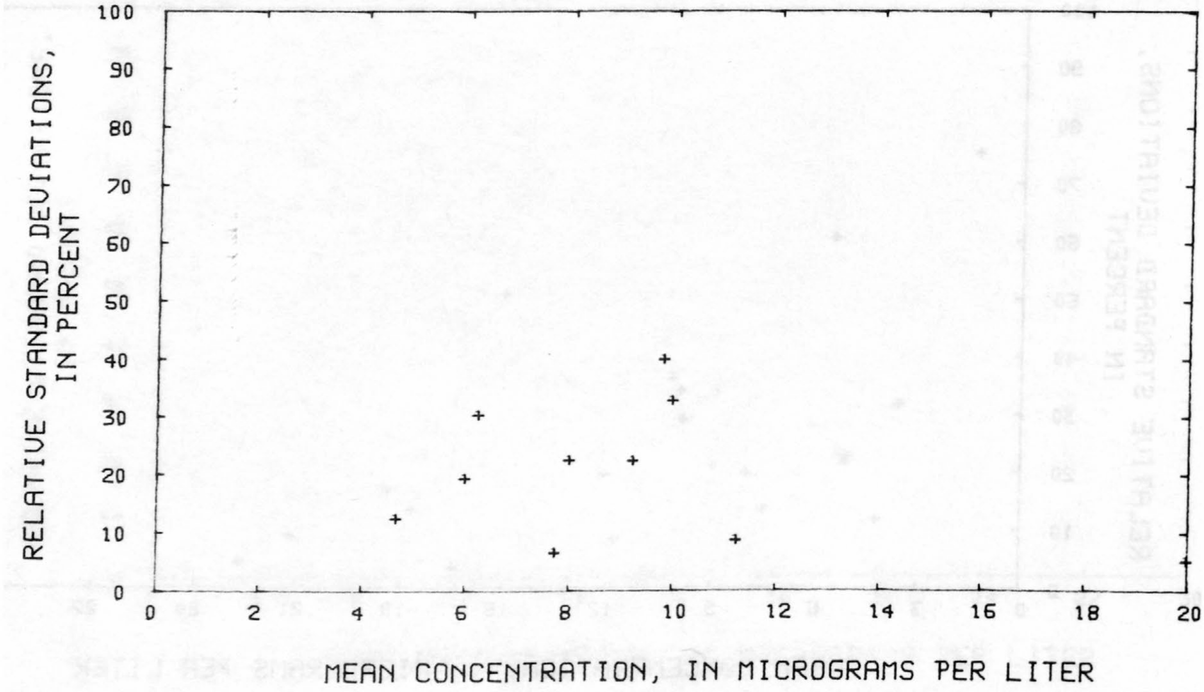

Figure 167--Precision data for lead, total recoverable, at the Atlanta laboratory.

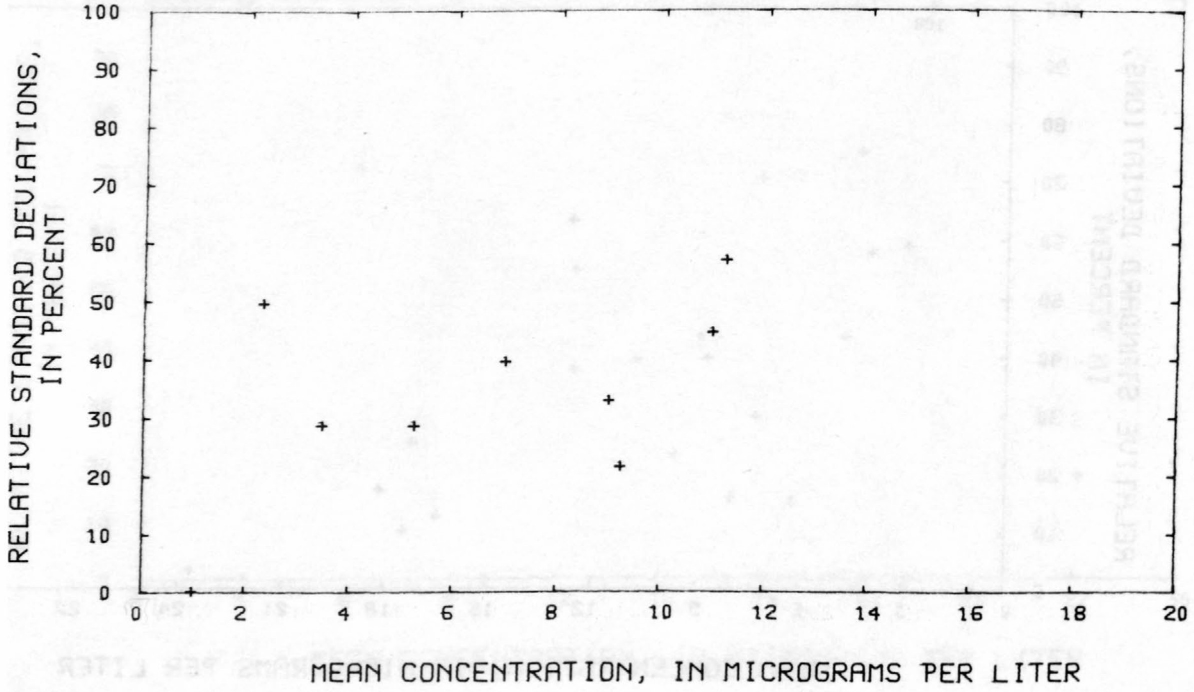

Figure 168--Precision data for lead, total recoverable, at the Denver laboratory.

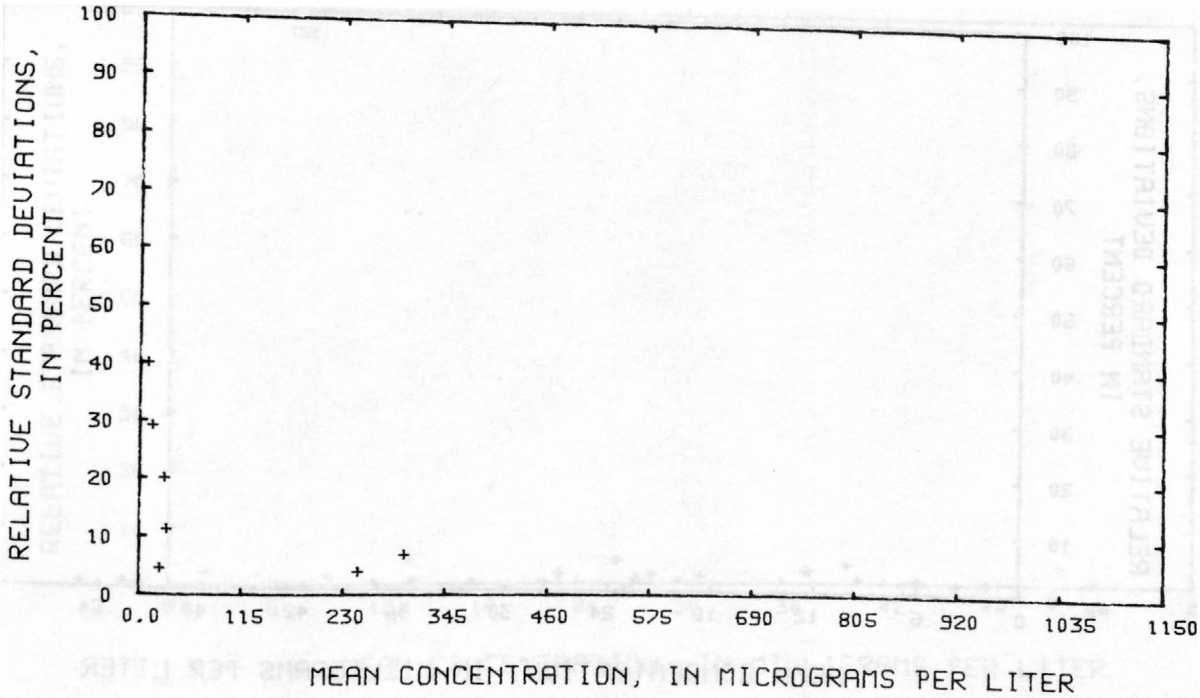

Figure 169--Precision data for lithium, dissolved, at the Atlanta laboratory.

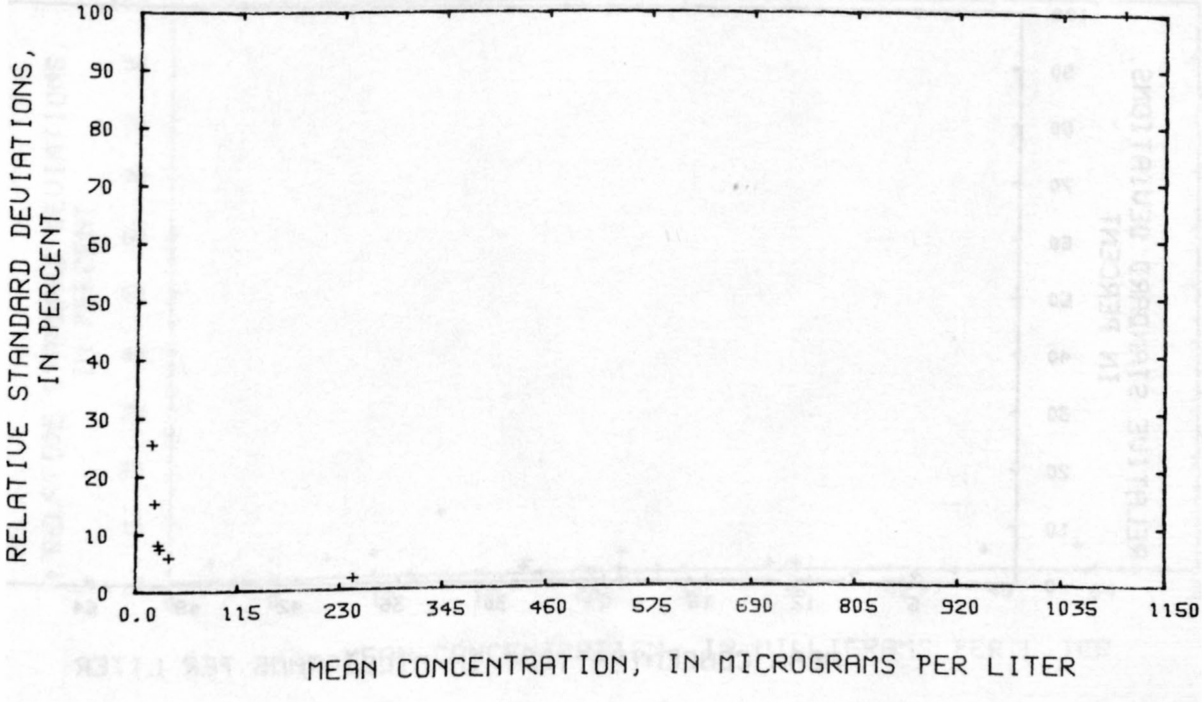

Figure 170--Precision data for lithium, dissolved, at the Denver laboratory.

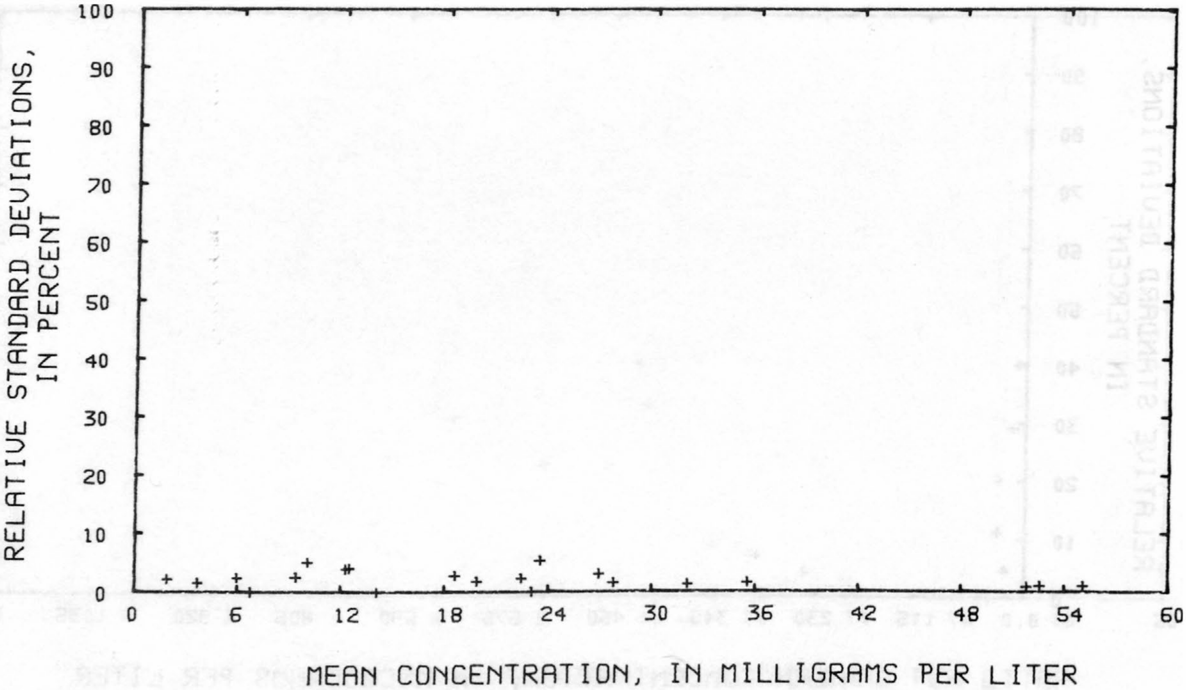

Figure 171--Precision data for magnesium, dissolved, (inductively coupled plasma emission spectrometry) at the Atlanta laboratory.

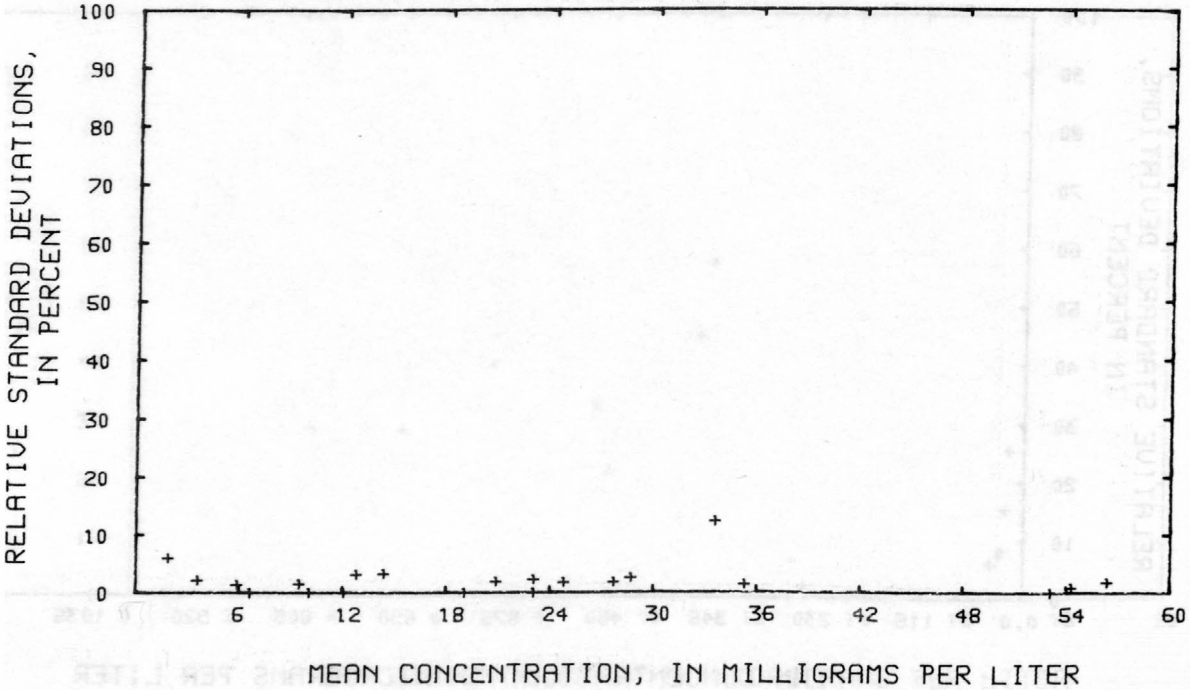

Figure 172--Precision data for magnesium, dissolved, (inductively coupled plasma emission spectrometry) at the Denver laboratory.

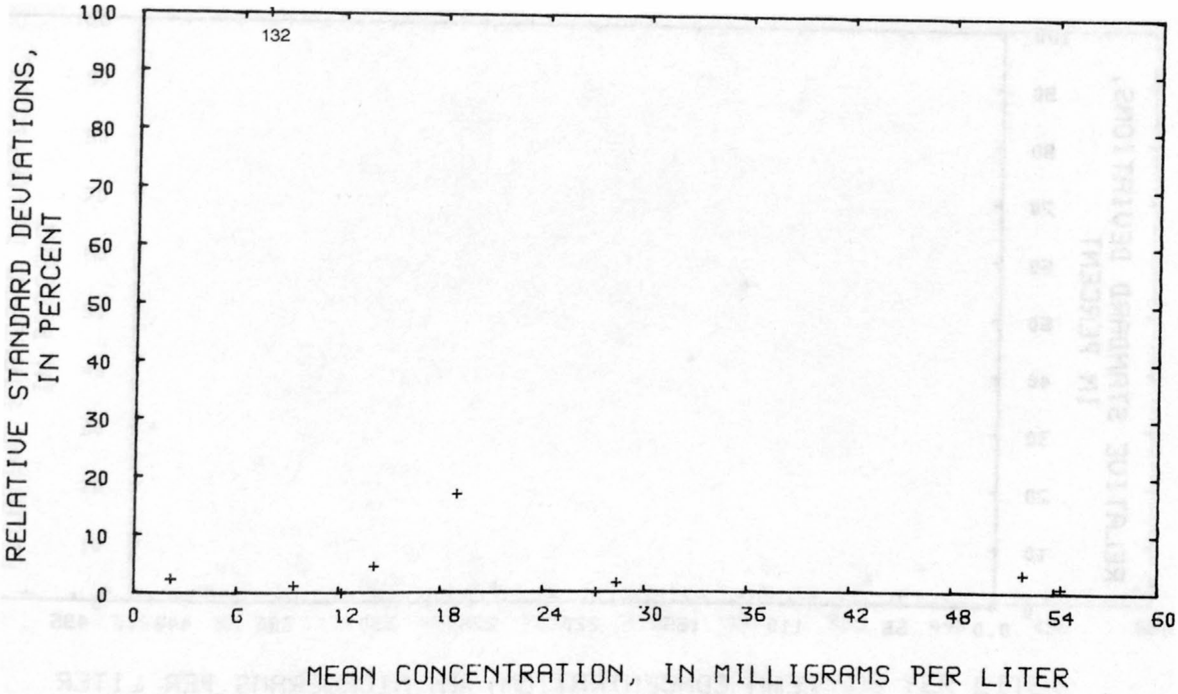

Figure 173--Precision data for magnesium, dissolved, (atomic absorption spectrometry) at the Atlanta laboratory.

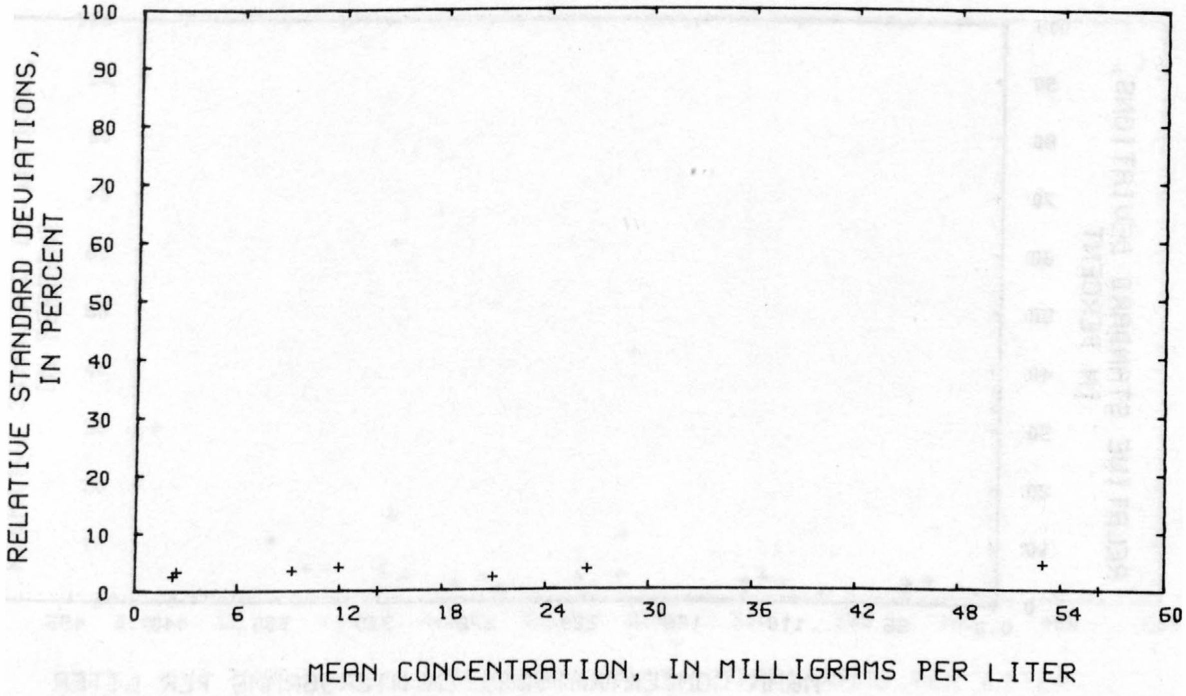

Figure 174--Precision data for magnesium, dissolved, (atomic absorption spectrometry) at the Denver laboratory.

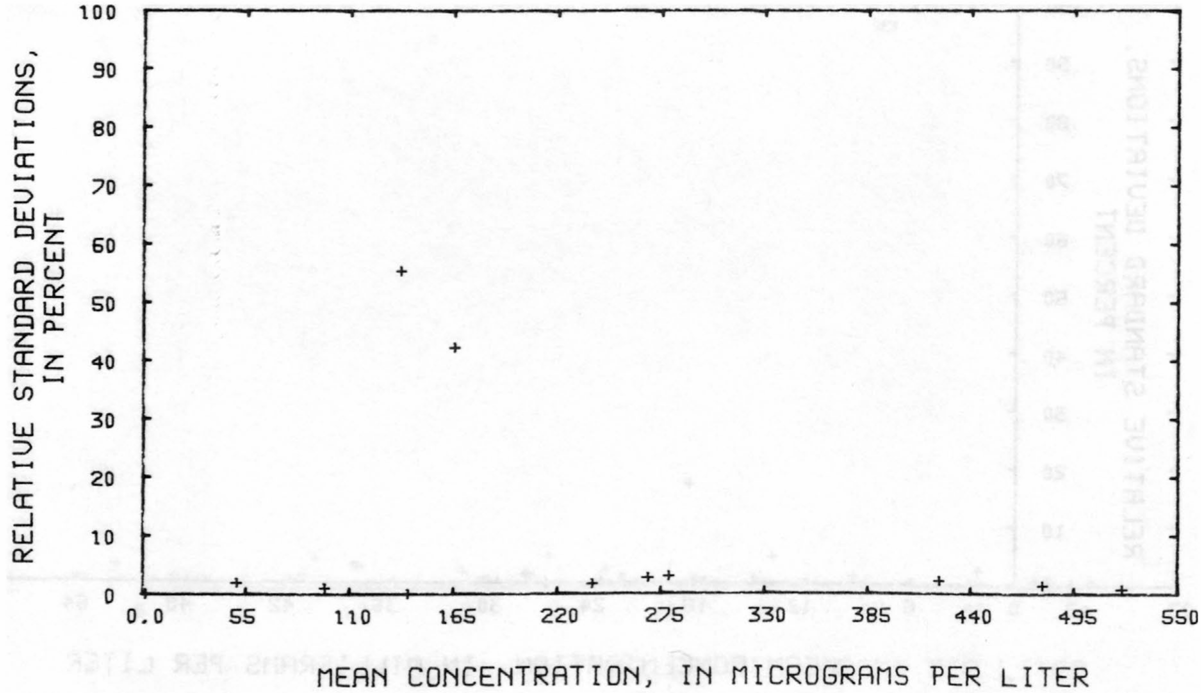

Figure 175--Precision data for manganese, dissolved, (inductively coupled plasma emission spectrometry) at the Atlanta laboratory.

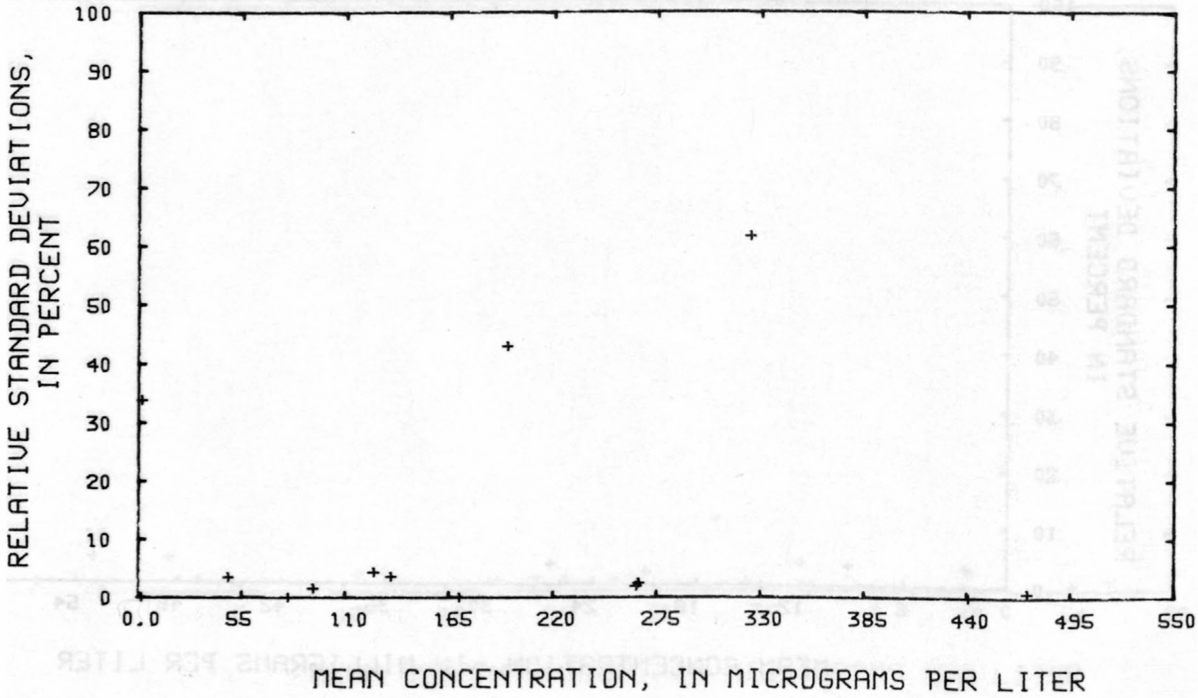

Figure 176--Precision data for manganese, dissolved, (inductively coupled plasma emission spectrometry) at the Denver laboratory.

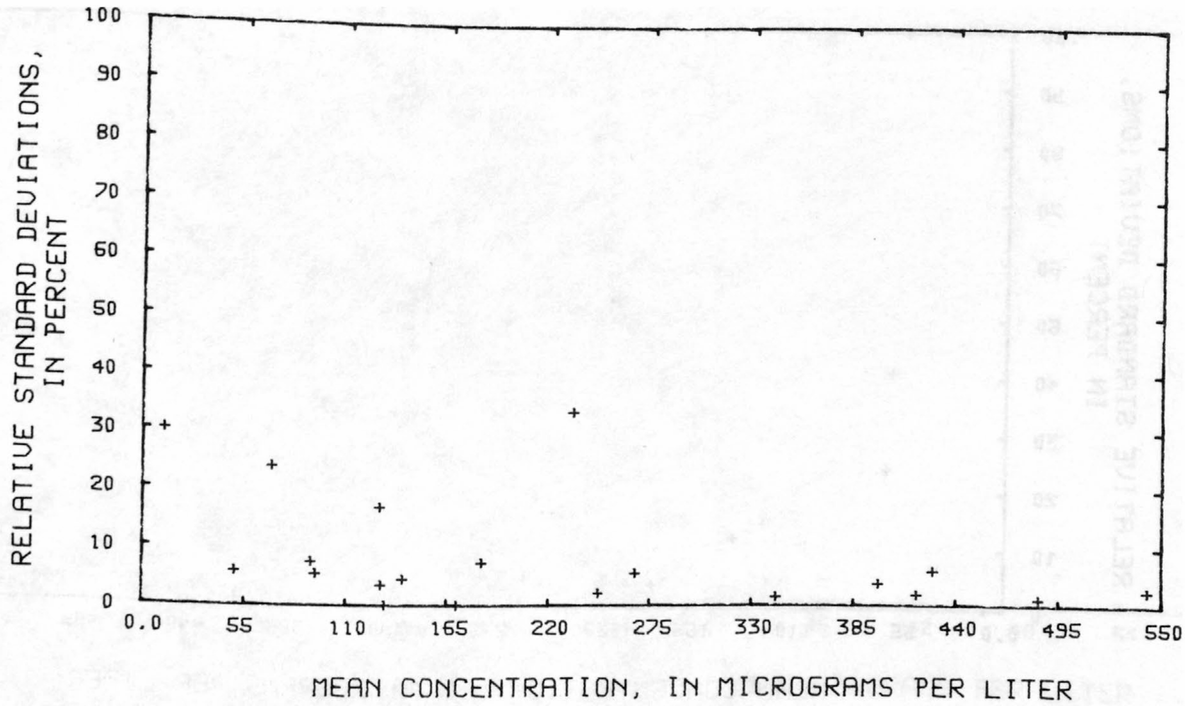

Figure 177--Precision data for manganese, dissolved, (atomic absorption spectrometry) at the Atlanta laboratory.

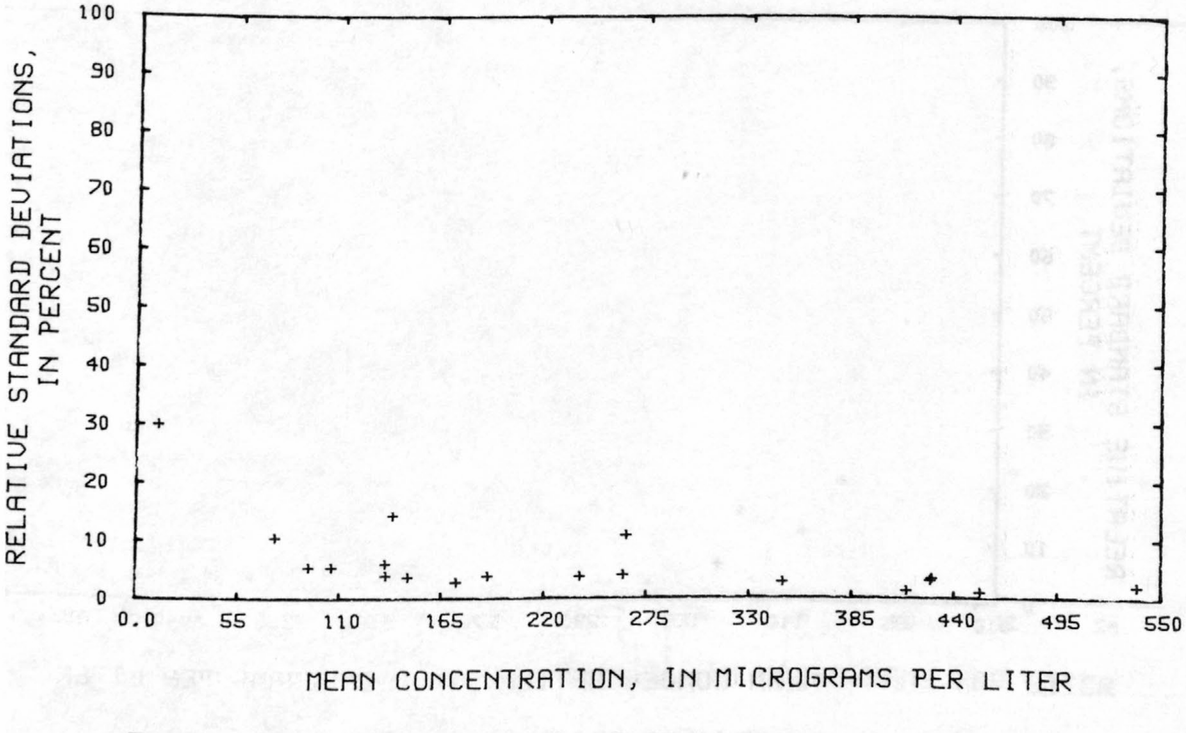

Figure 178--Precision data for manganese, dissolved, (atomic absorption spectrometry) at the Denver laboratory.

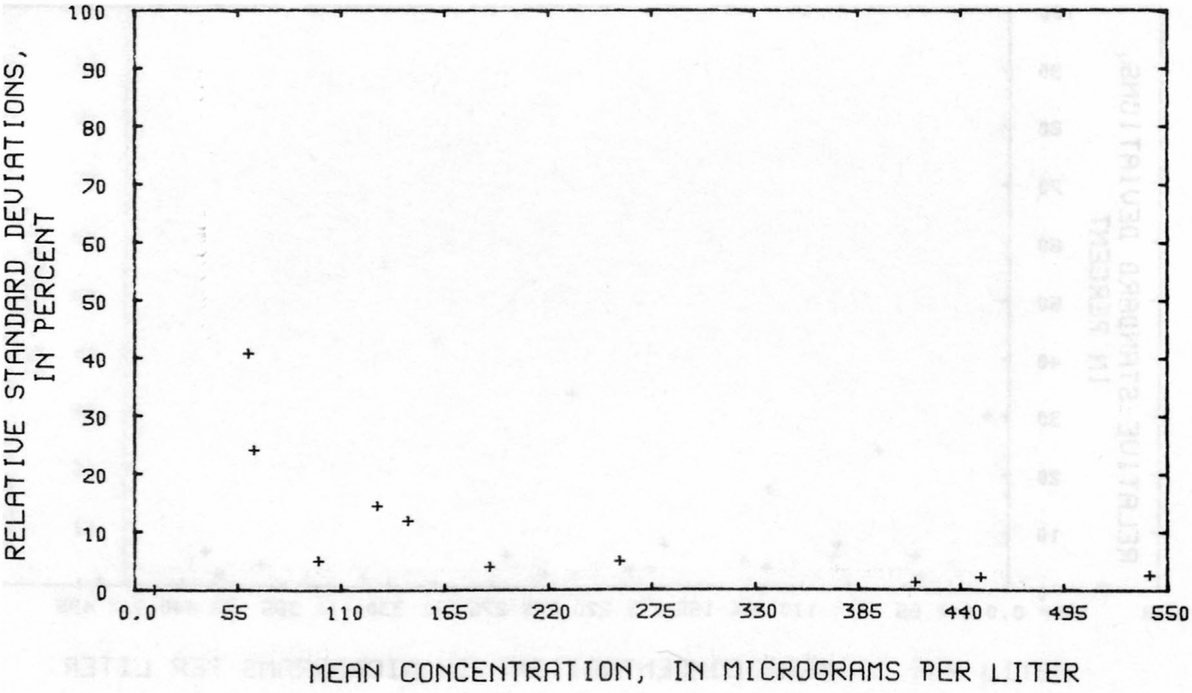

Figure 179--Precision data for manganese, total recoverable, at the Atlanta laboratory.

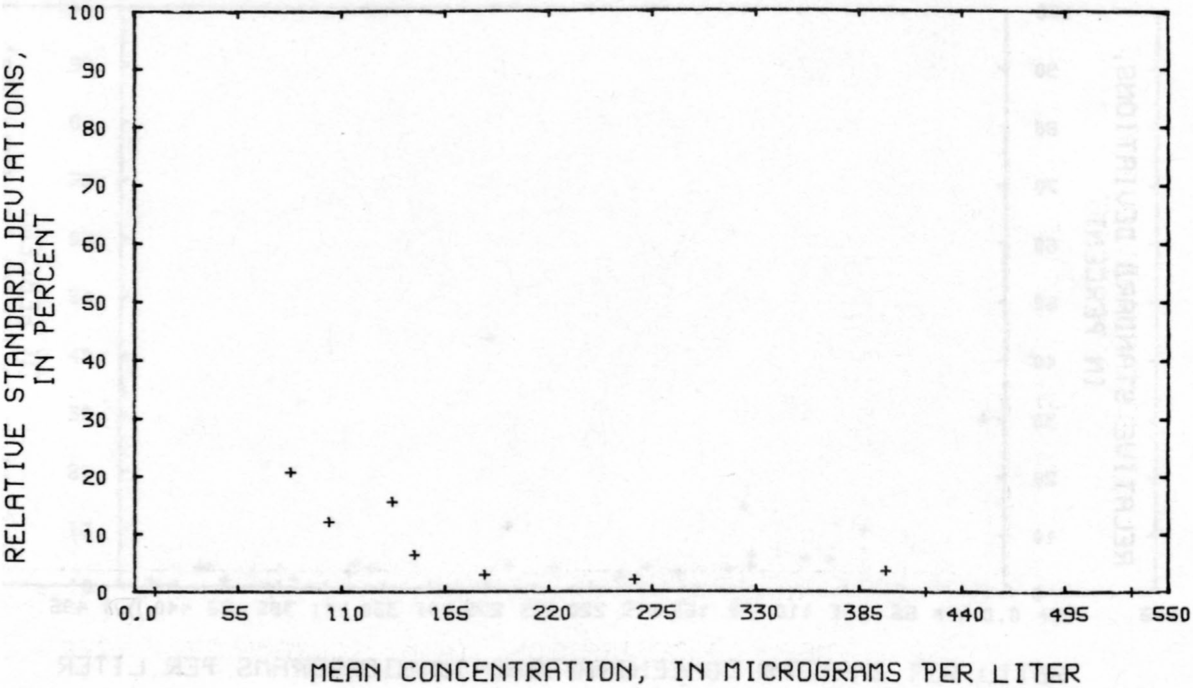

Figure 180--Precision data for manganese, total recoverable, at the Denver laboratory.

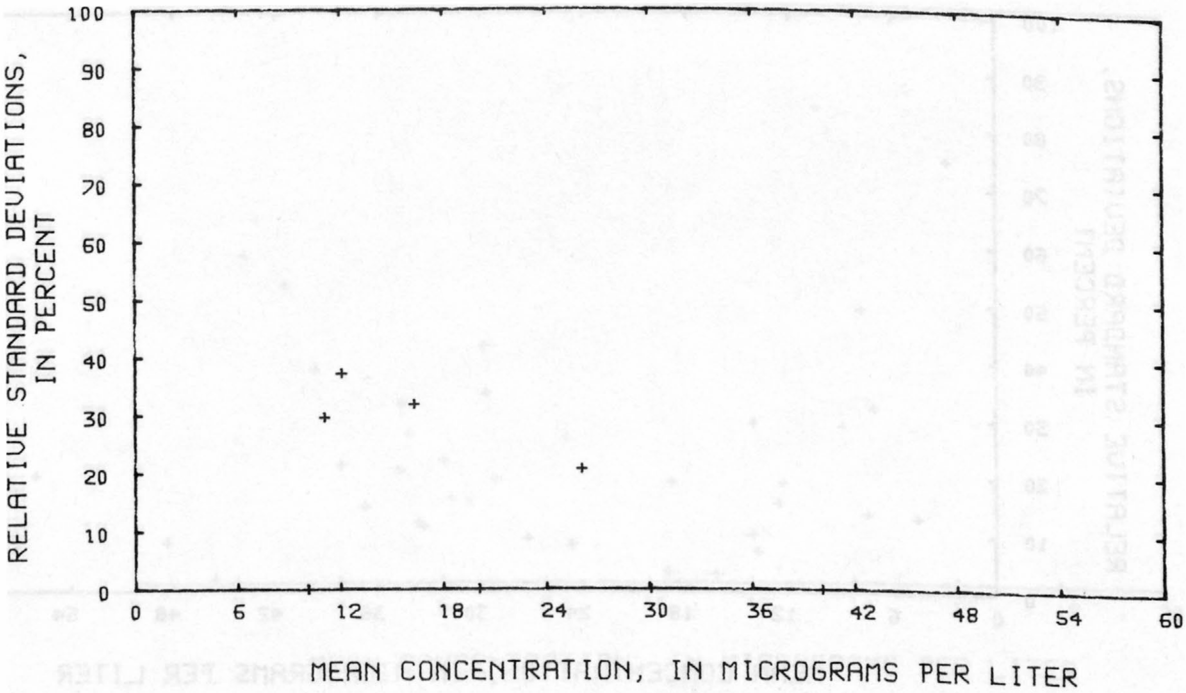

Figure 181--Precision data for molybdenum, dissolved, (inductively coupled plasma emission spectrometry) at the Atlanta laboratory.

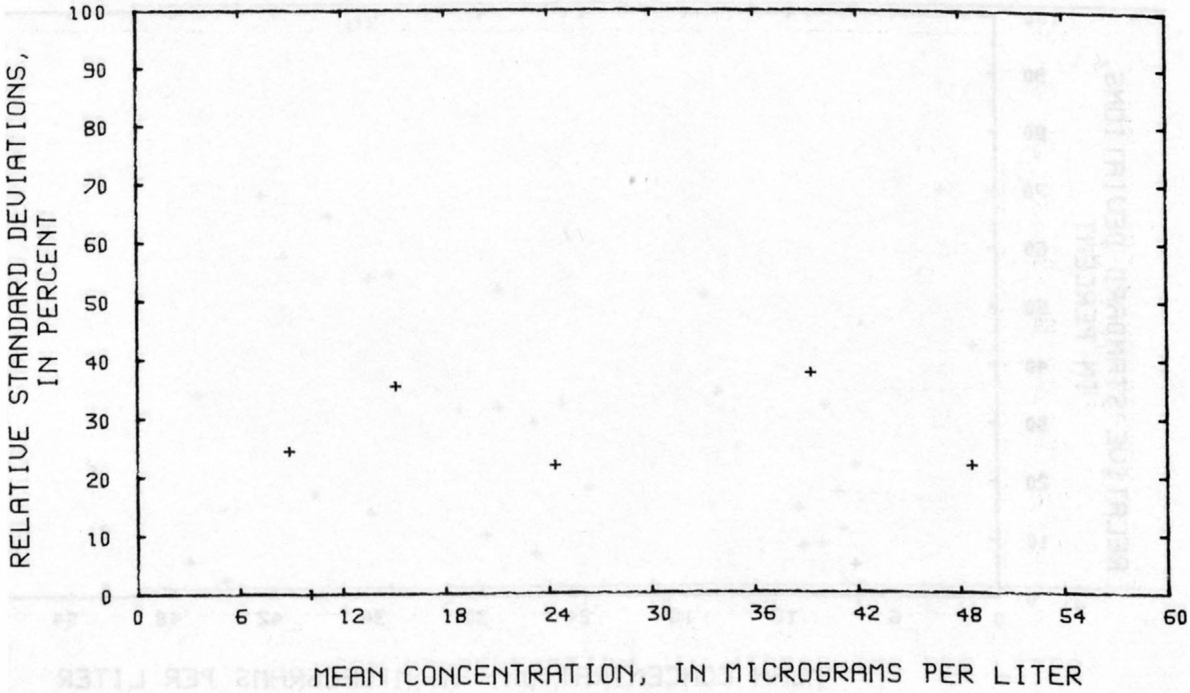

Figure 182--Precision data for molybdenum, dissolved, (inductively coupled plasma emission spectrometry) at the Denver laboratory.

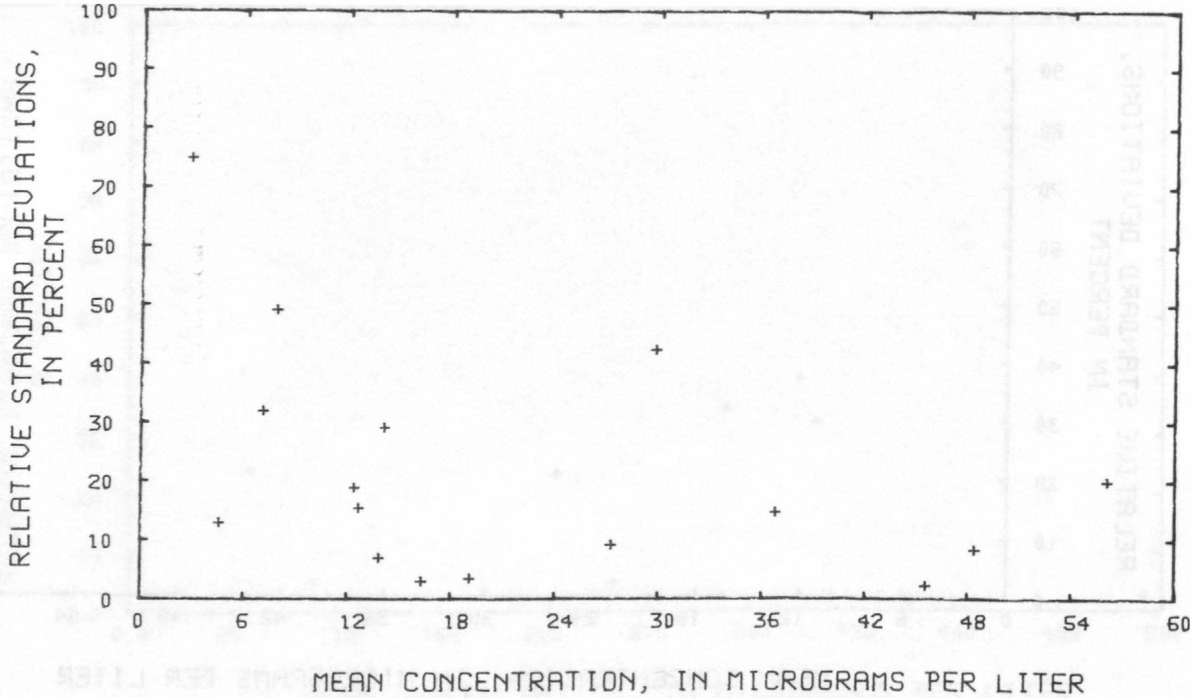

Figure 183--Precision data for molybdenum, dissolved, (atomic absorption spectrometry) at the Atlanta laboratory.

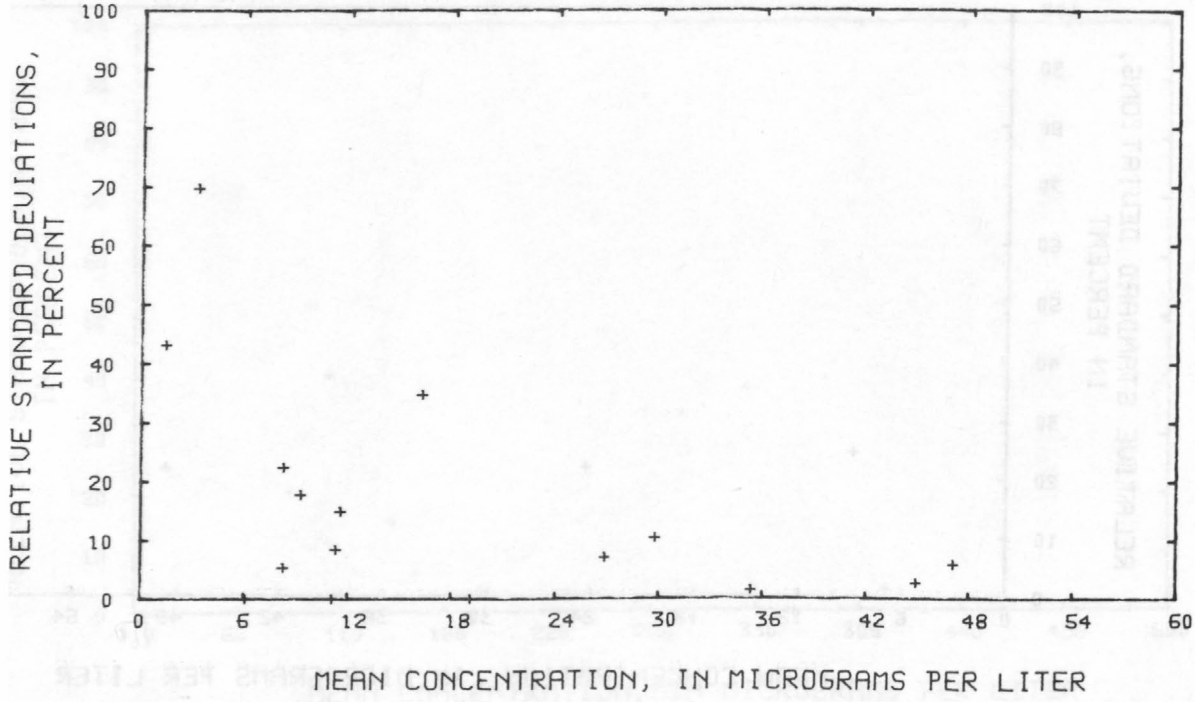

Figure 184--Precision data for molybdenum, dissolved, (atomic absorption spectrometry) at the Denver laboratory.

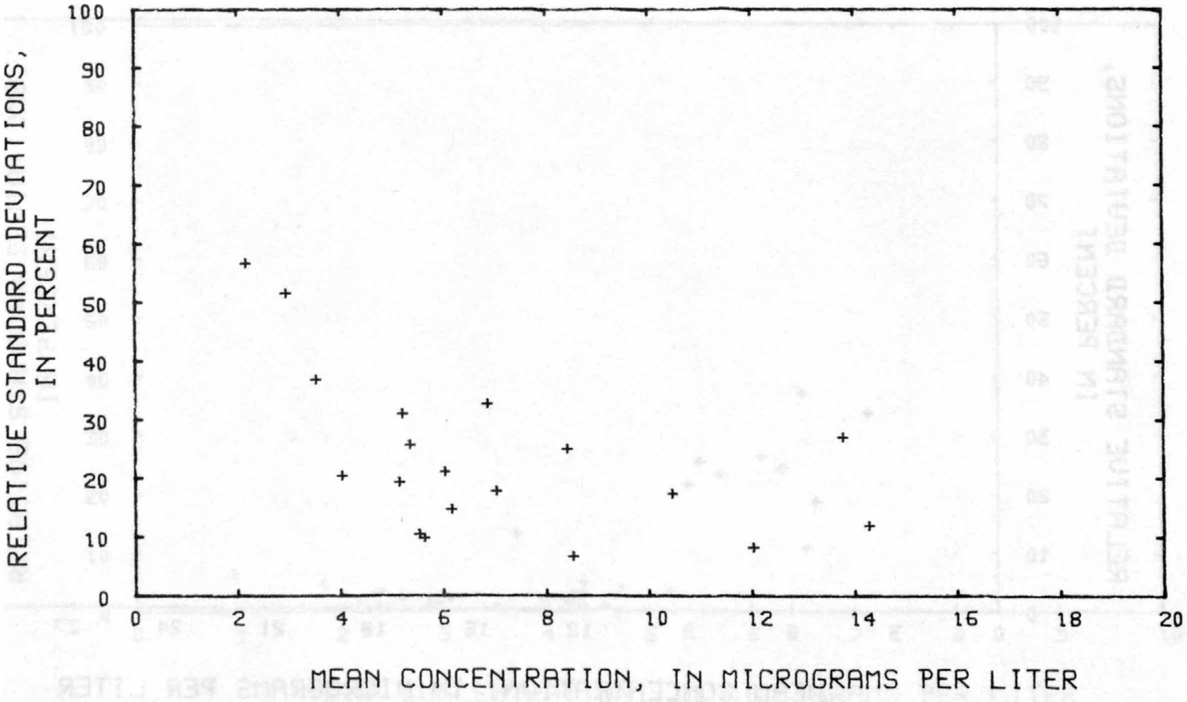

Figure 185--Precision data for nickel, dissolved, at the Atlanta laboratory.

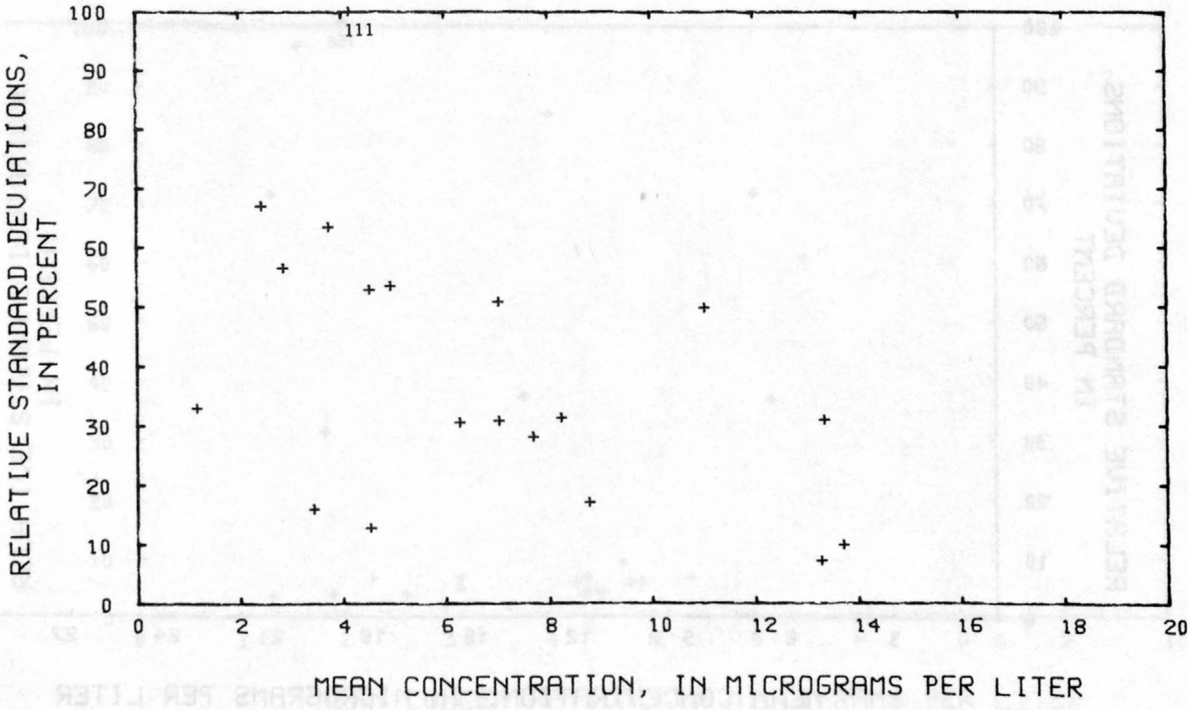

Figure 186--Precision data for nickel, dissolved, at the Denver laboratory.

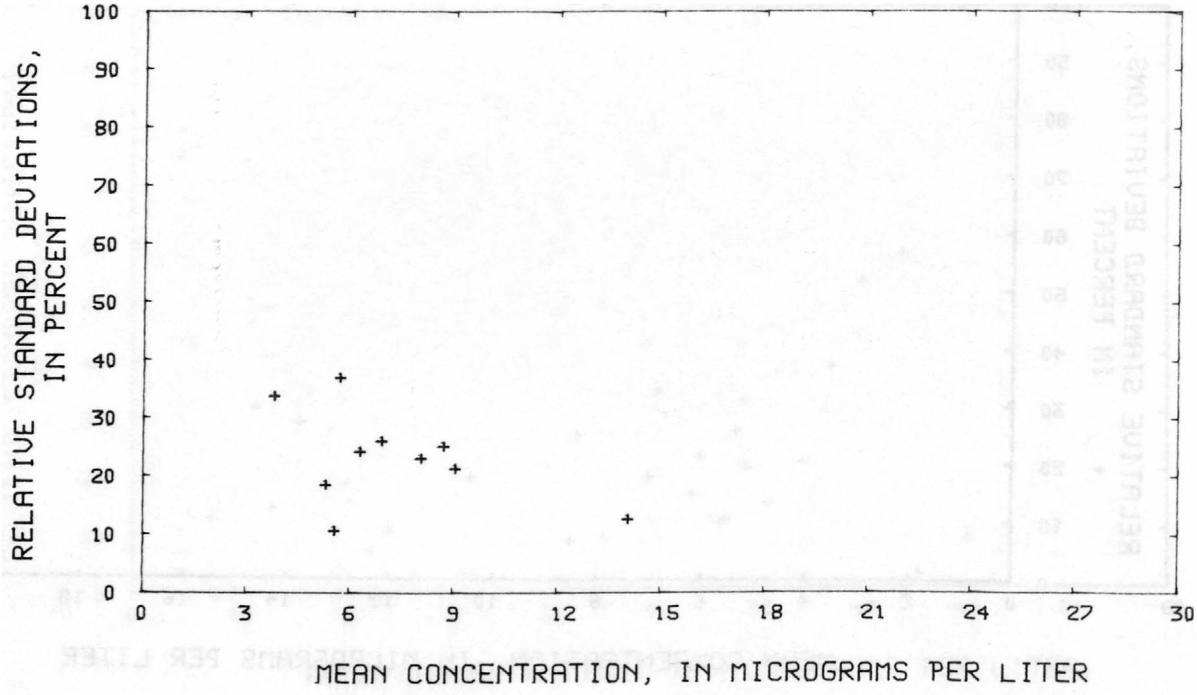

Figure 187--Precision data for nickel, total recoverable, at the Atlanta laboratory.

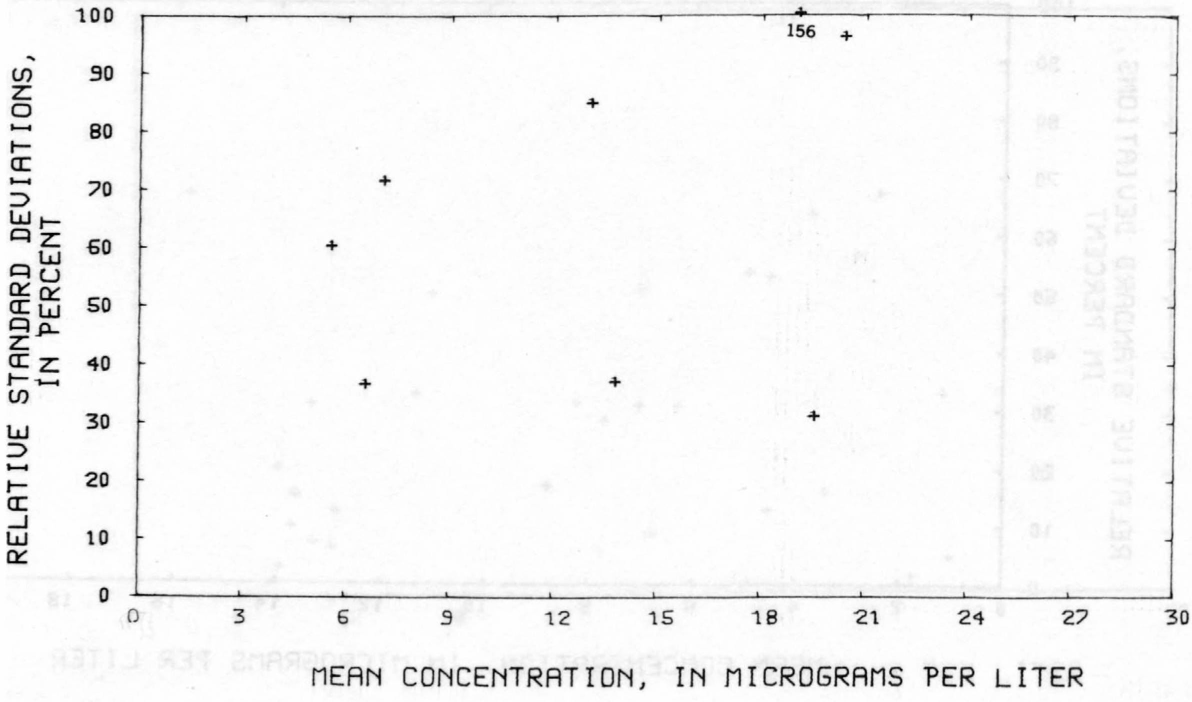

Figure 188--Precision data for nickel, total recoverable, at the Denver laboratory.

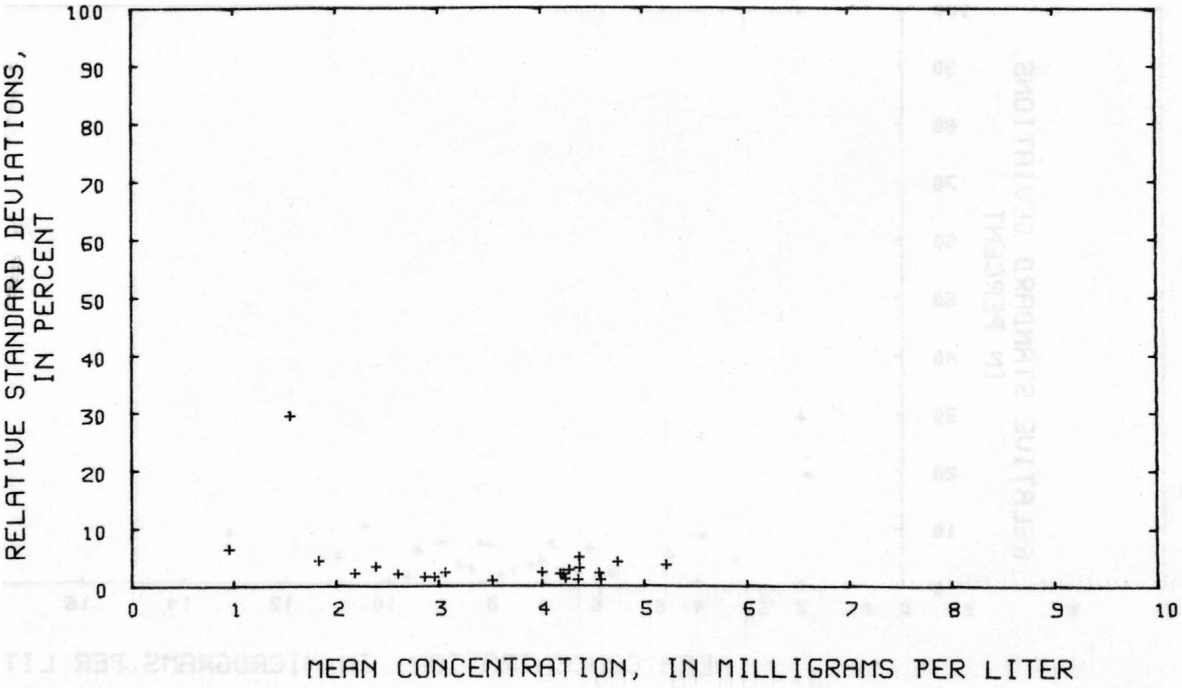

Figure 189--Precision data for potassium, dissolved, at the Atlanta laboratory.

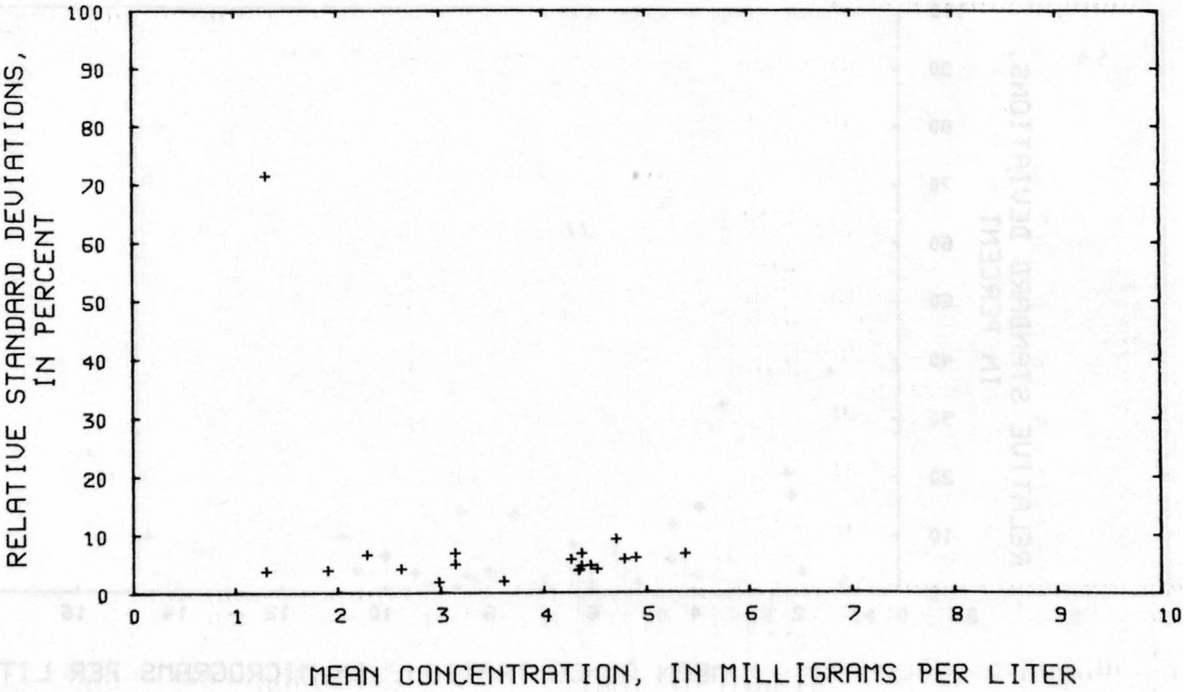

Figure 190--Precision data for potassium, dissolved, at the Denver laboratory.

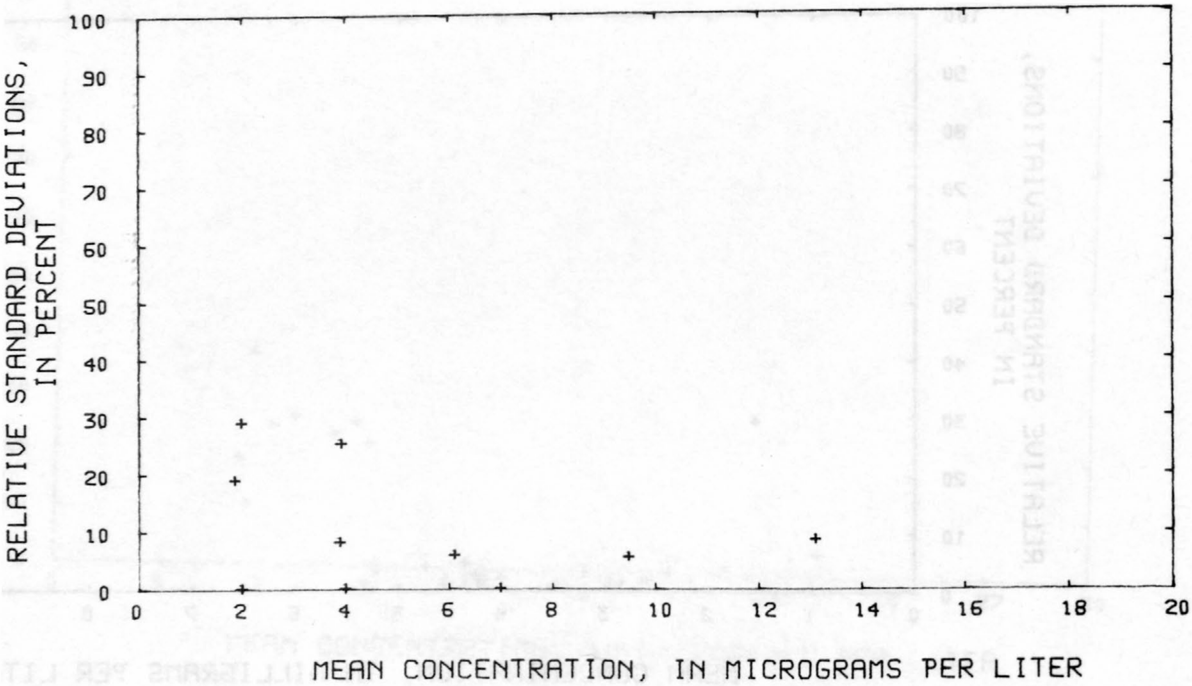

Figure 191--Precision data for selenium, dissolved, at the Atlanta laboratory.

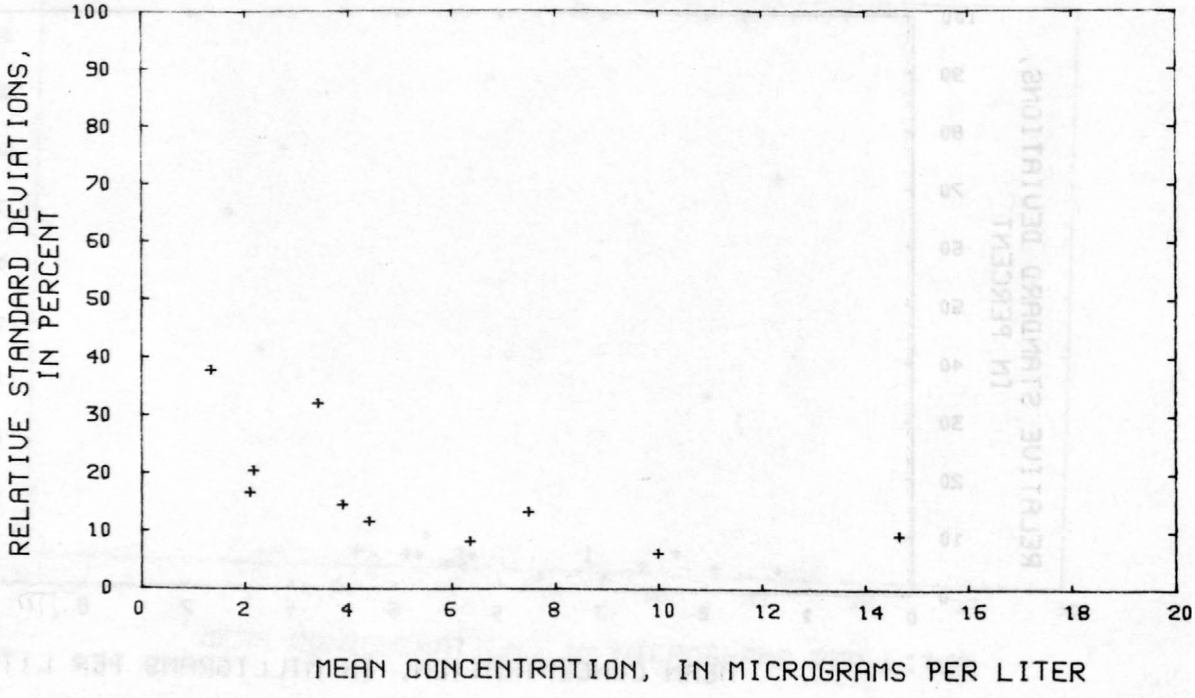

Figure 192--Precision data for selenium, dissolved, at the Denver laboratory.

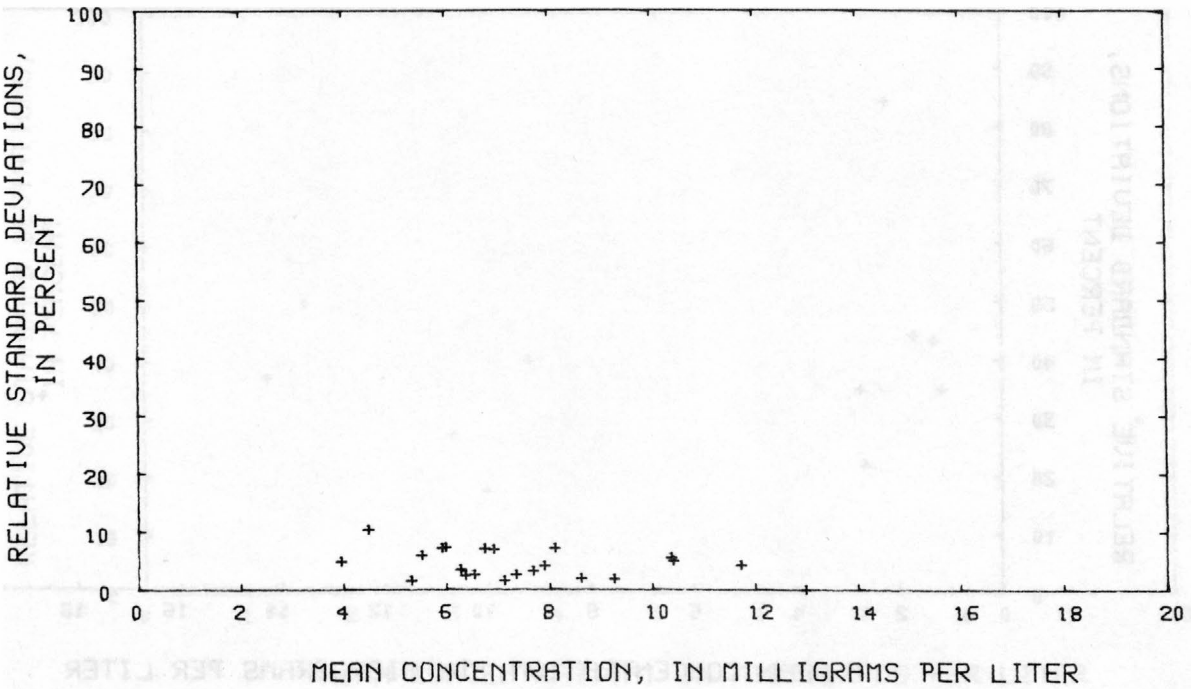

Figure 193--Precision data for silica, dissolved, at the Atlanta laboratory.

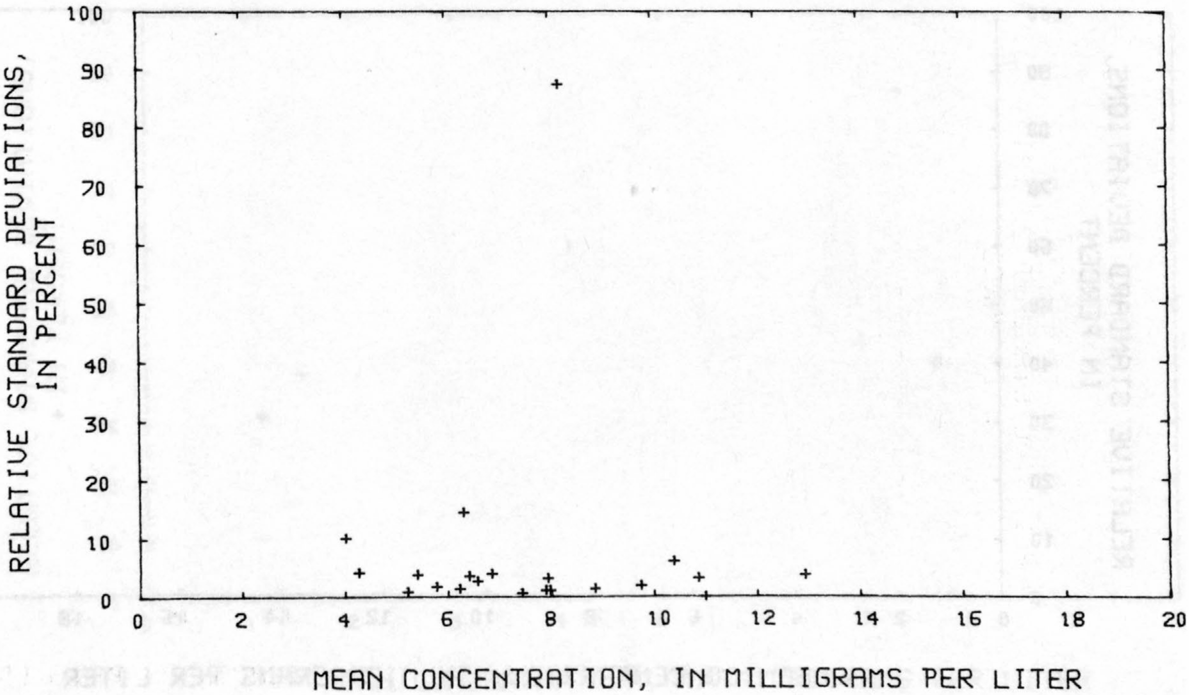

Figure 194--Precision data for silica, dissolved, at the Denver laboratory.

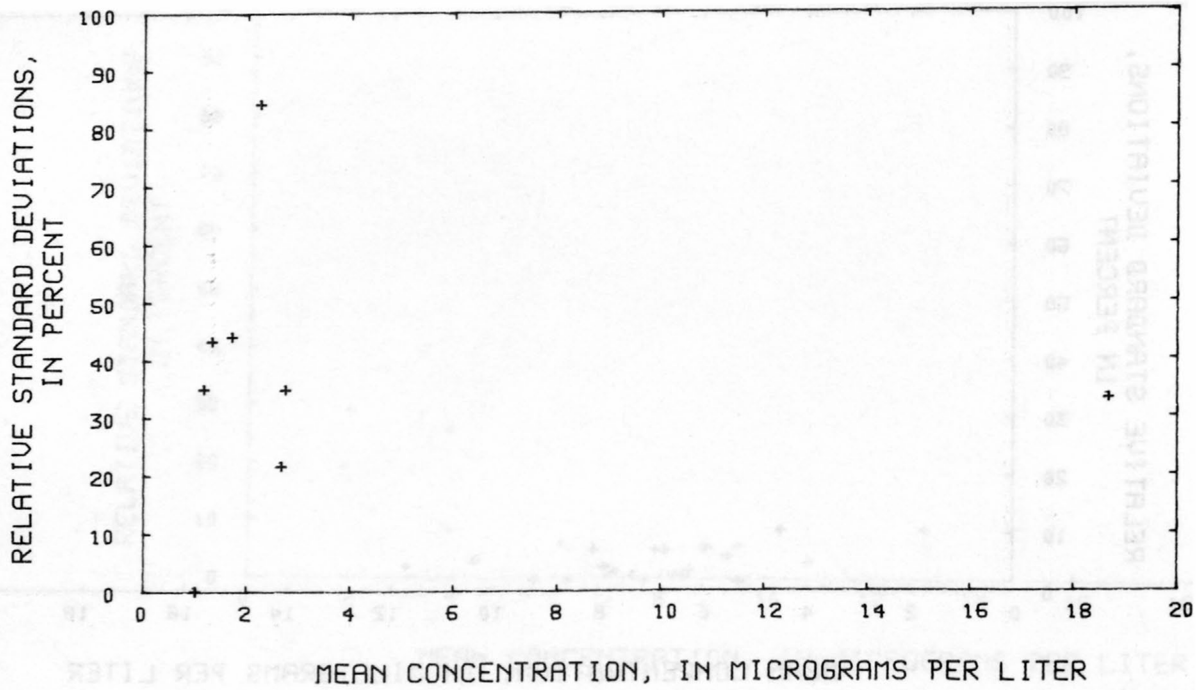

Figure 195--Precision data for silver, dissolved, at the Atlanta laboratory.

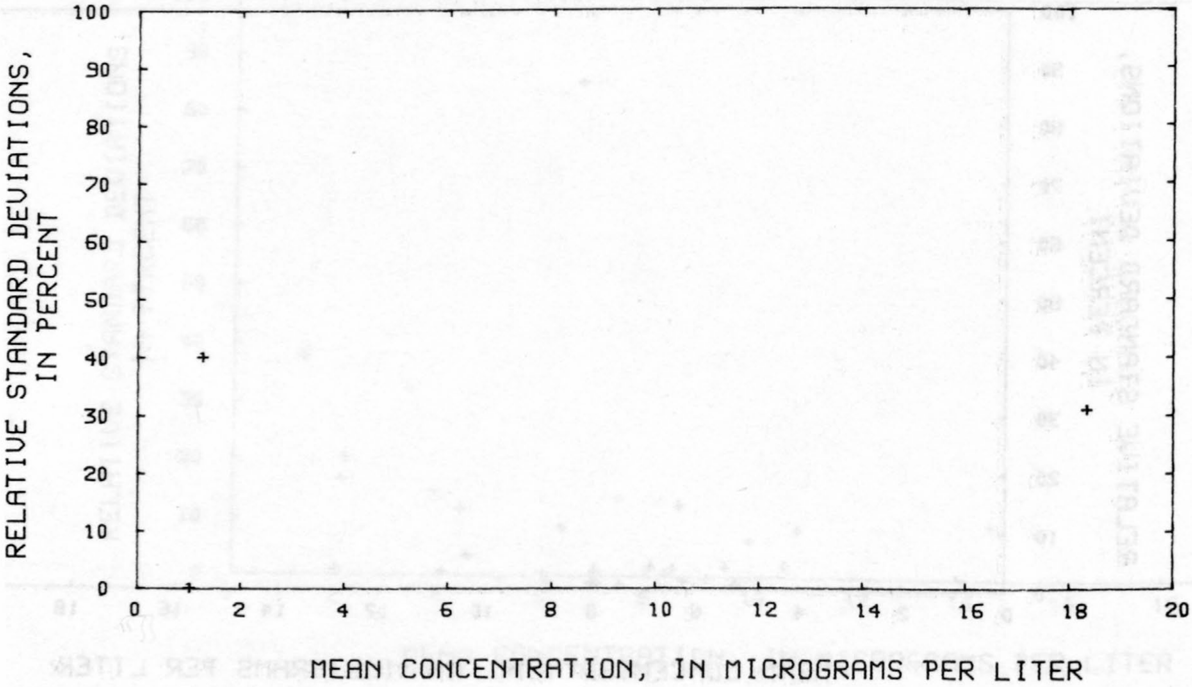

Figure 196--Precision data for silver, dissolved, at the Denver laboratory.

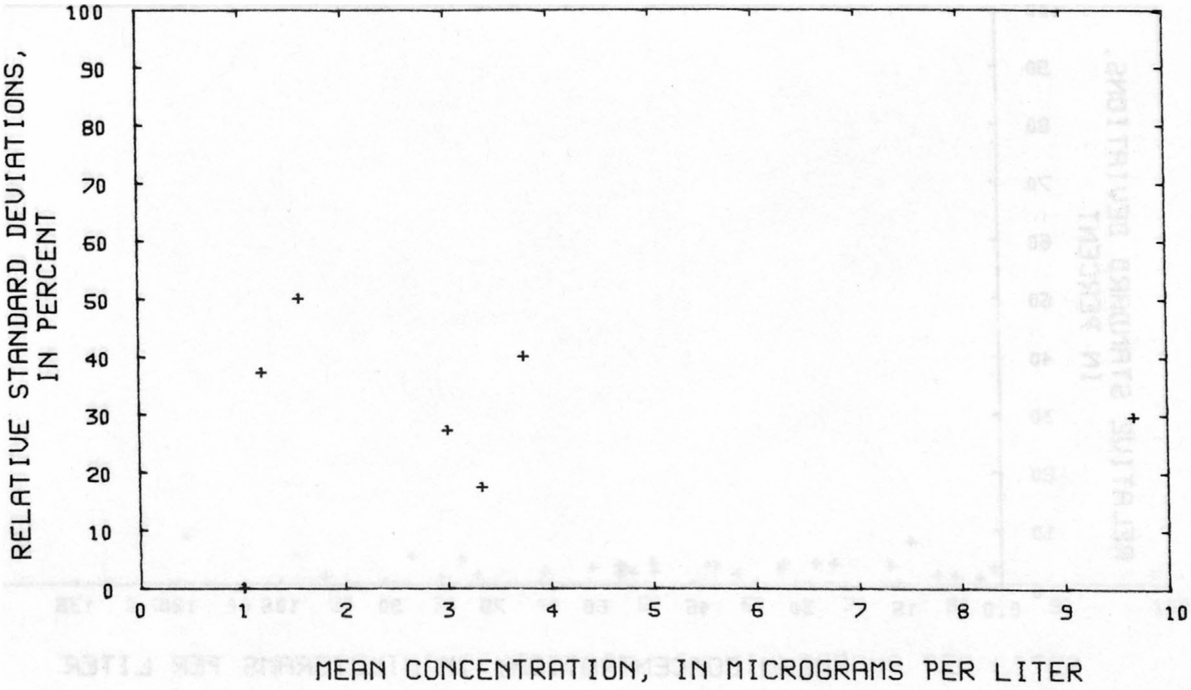

Figure 197--Precision data for silver, total recoverable, at the Atlanta laboratory.

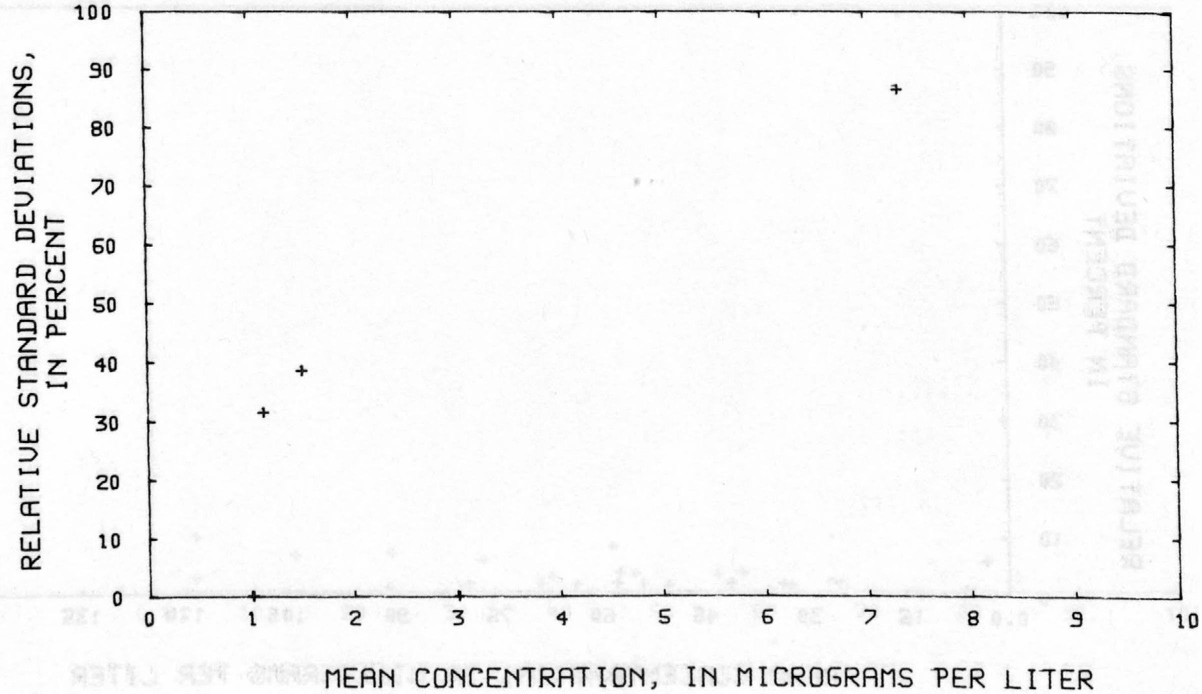

Figure 198--Precision data for silver, total recoverable, at the Denver laboratory.

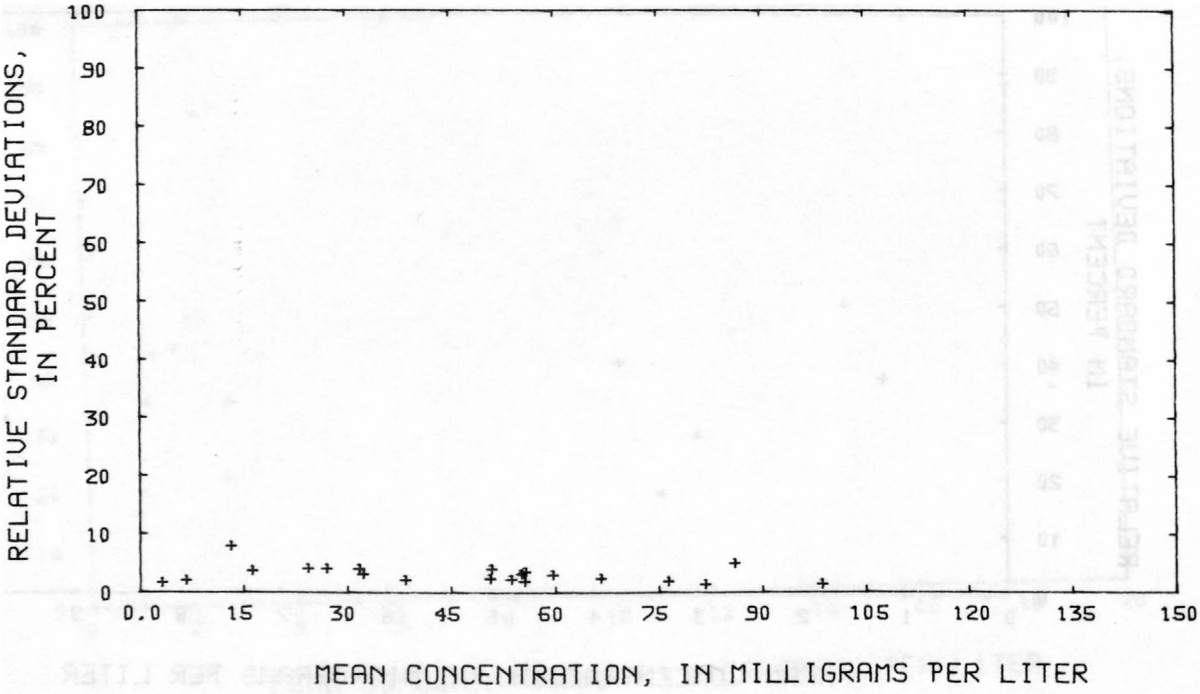

Figure 199--Precision data for sodium, dissolved, (inductively coupled plasma emission spectrometry) at the Atlanta laboratory.

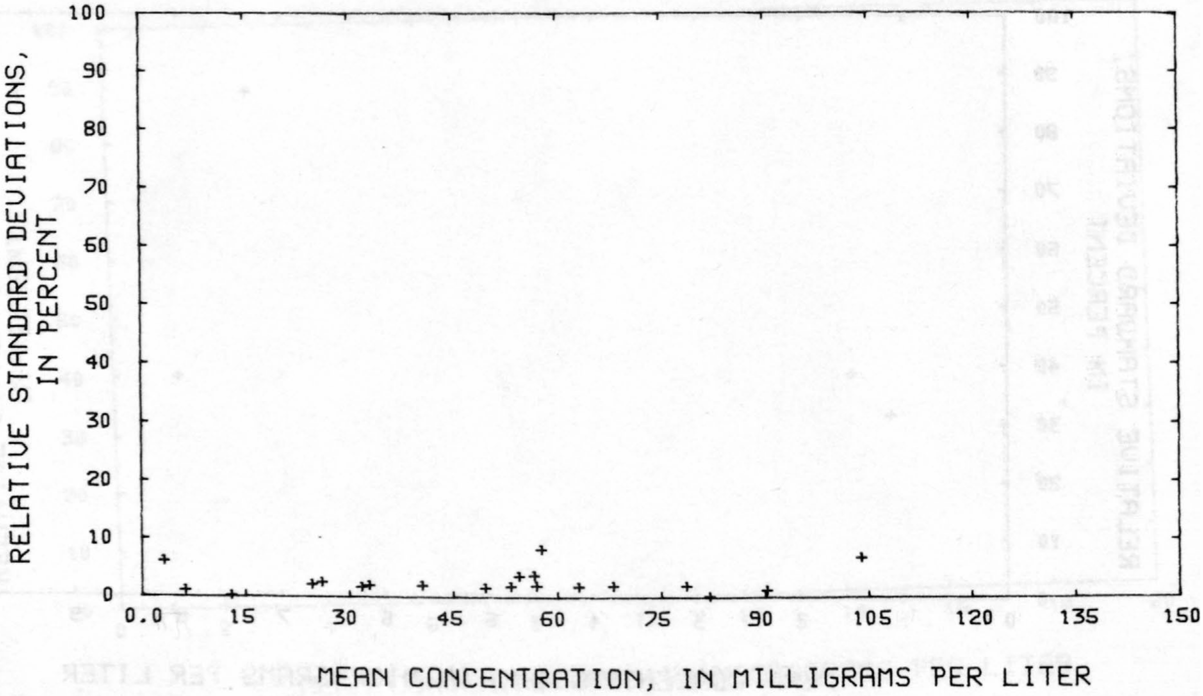

Figure 200--Precision data for sodium, dissolved, (inductively coupled plasma emission spectrometry) at the Denver laboratory.

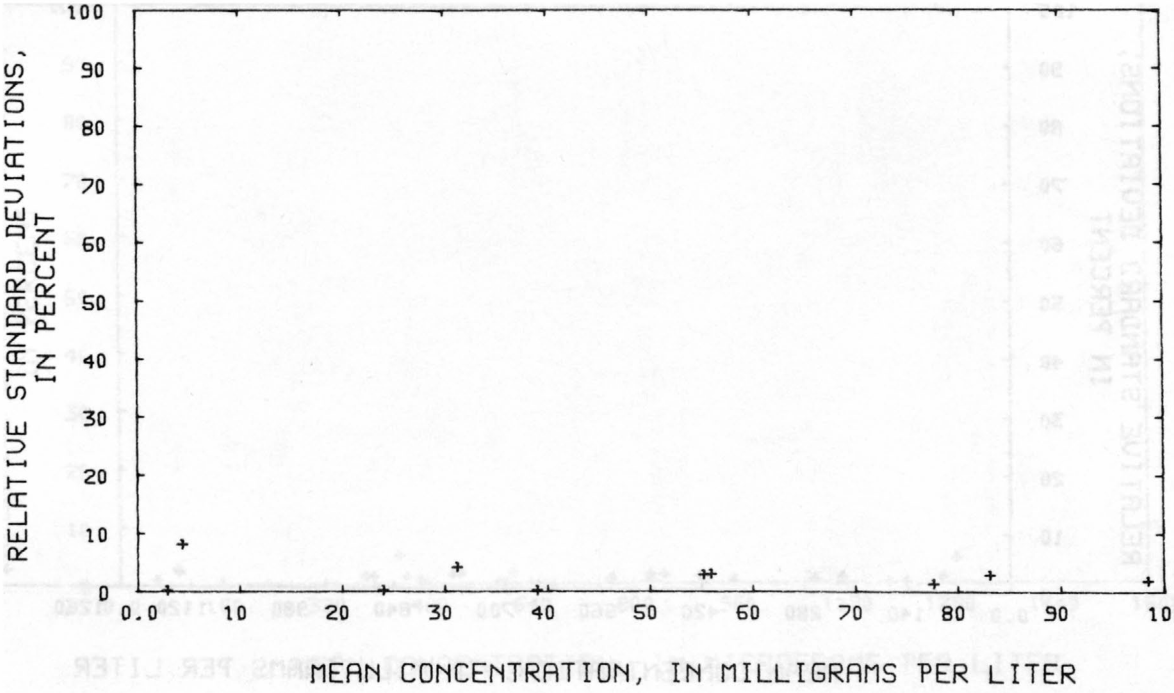

Figure 201--Precision data for sodium, dissolved, (atomic absorption spectrometry), at the Atlanta laboratory.

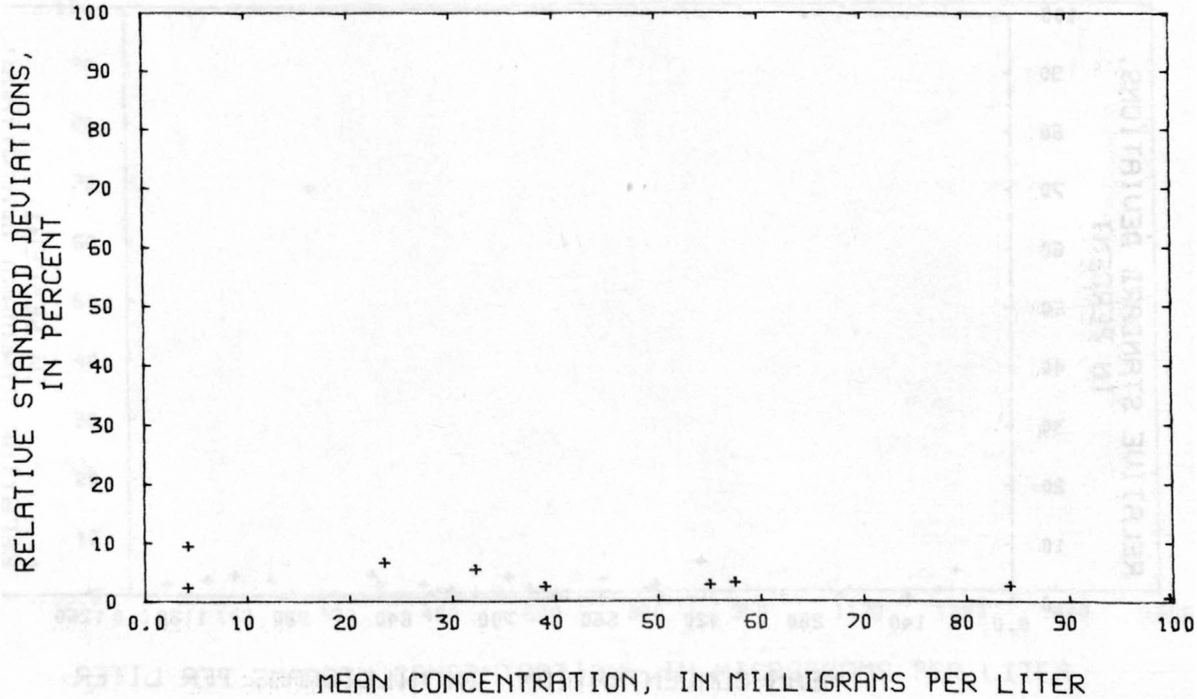

Figure 202--Precision data for sodium, dissolved, (atomic absorption spectrometry) at the Denver laboratory.

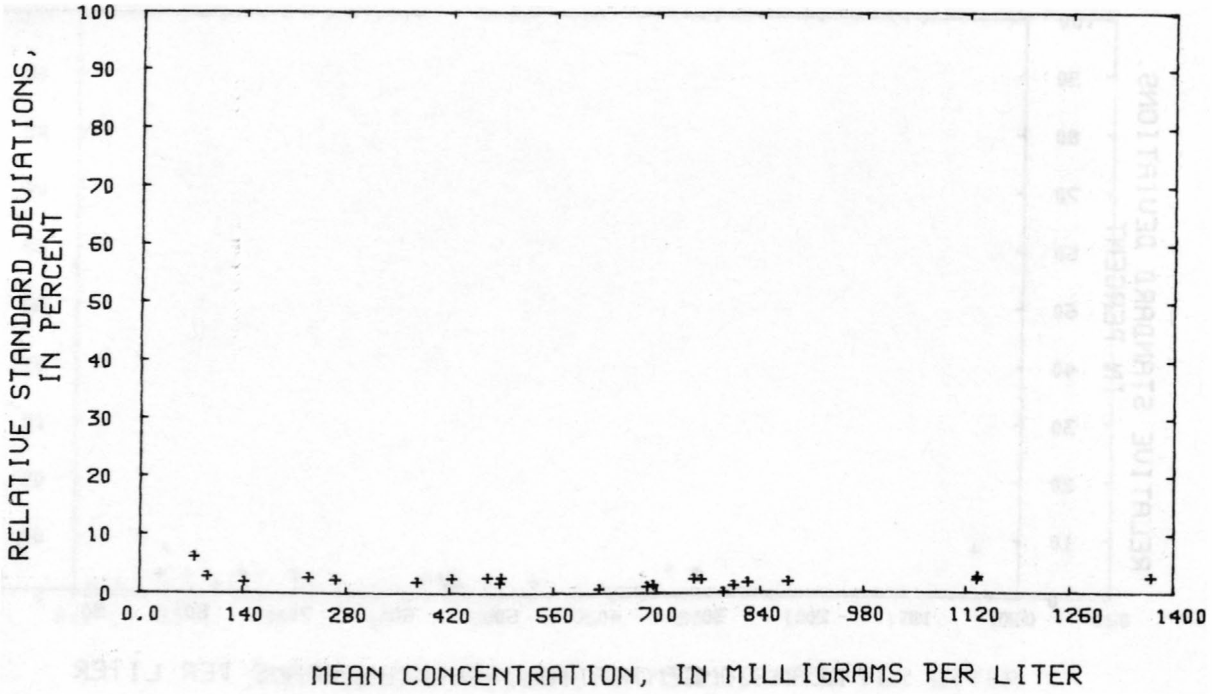

Figure 203--Precision data for specific conductance at the Atlanta laboratory.

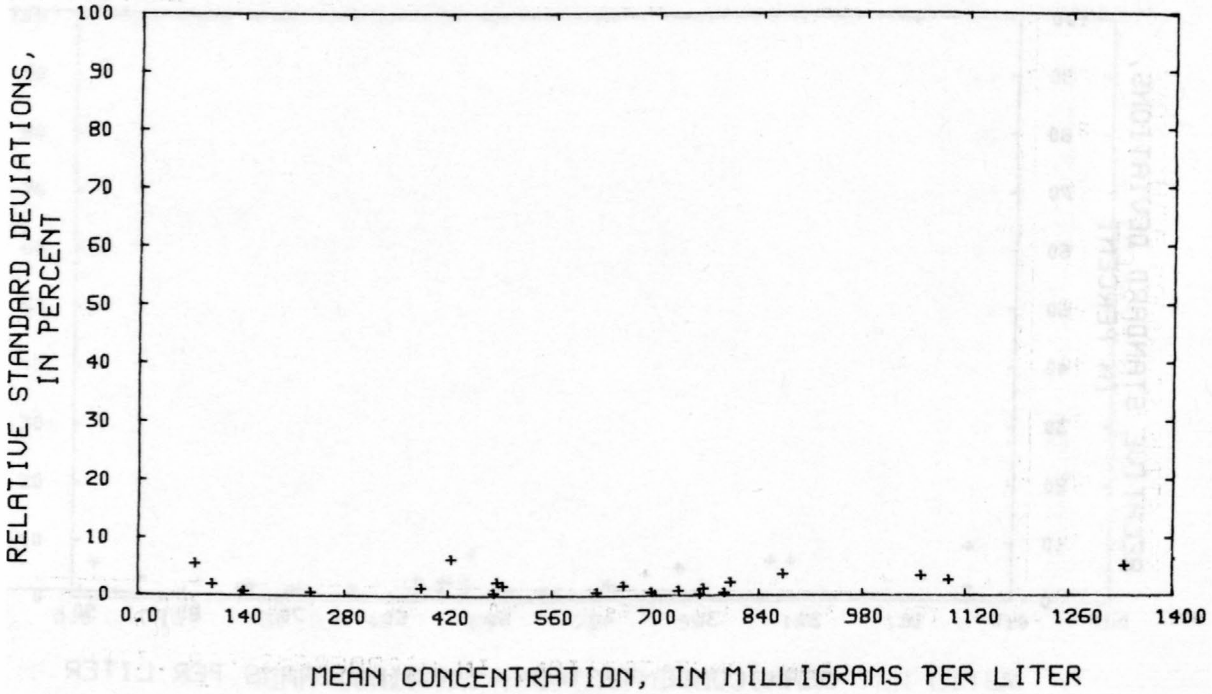

Figure 204--Precision data for specific conductance at the Denver laboratory.

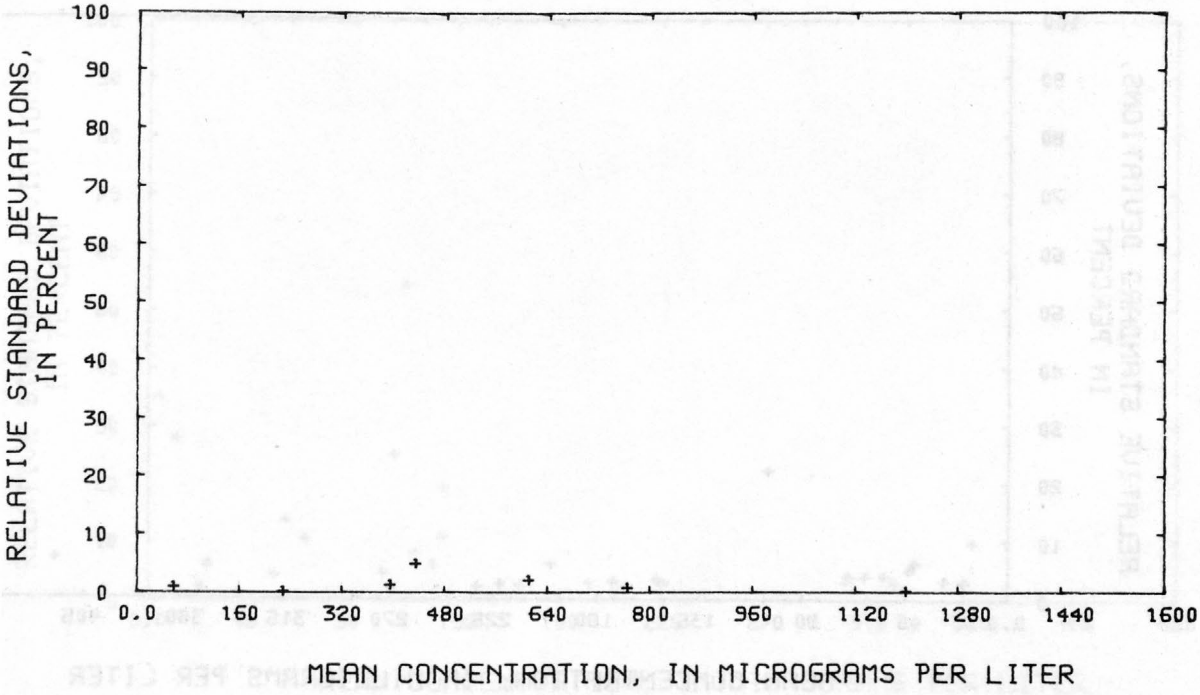

Figure 205--Precision data for strontium, dissolved, at the Atlanta laboratory.

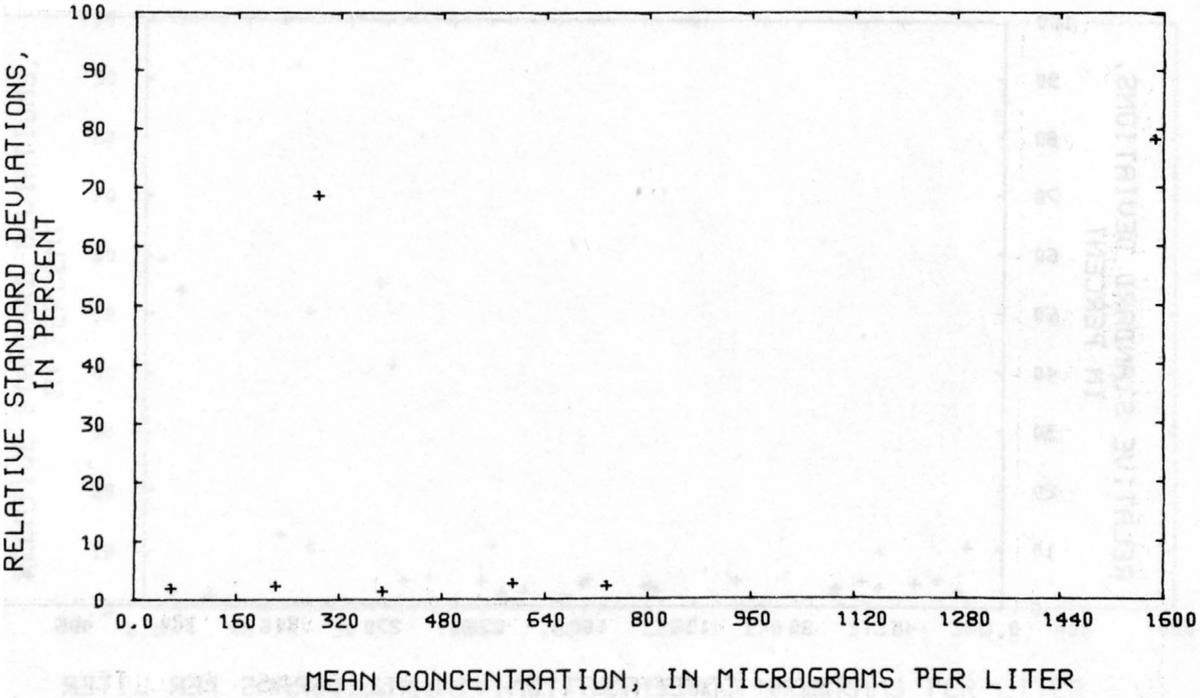

Figure 206--Precision data for strontium, dissolved, at the Denver laboratory.

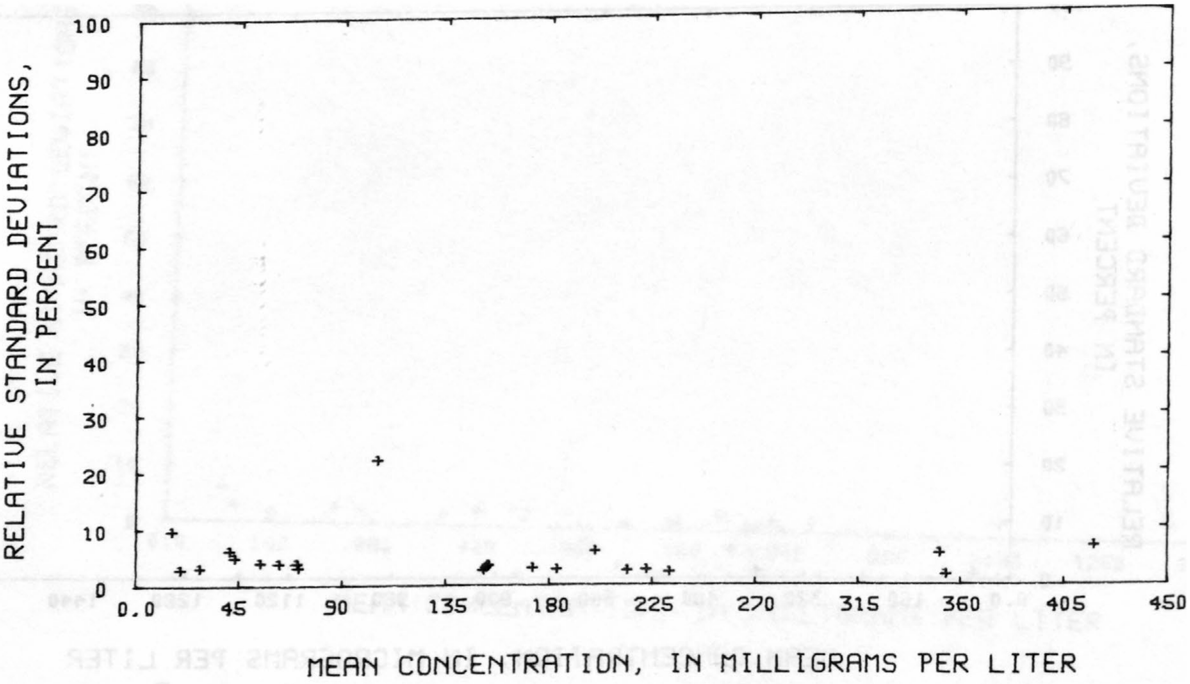

Figure 207--Precision data for sulfate, dissolved, at the Atlanta laboratory.

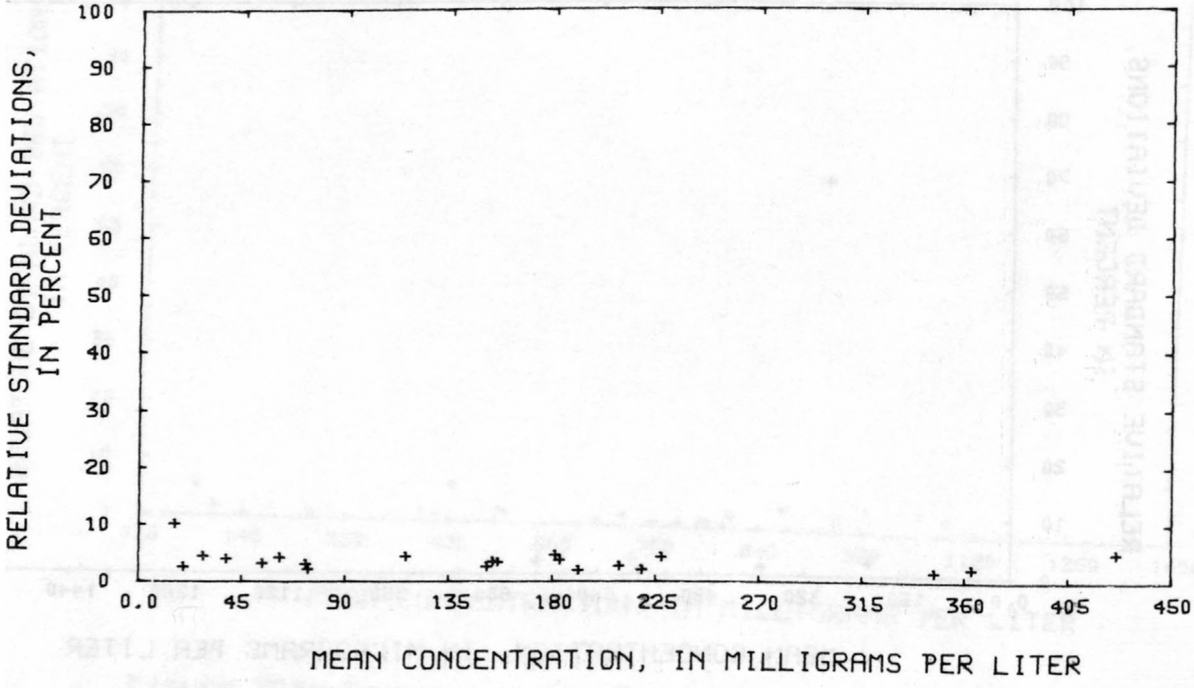

Figure 208--Precision data for sulfate, dissolved, at the Denver laboratory.

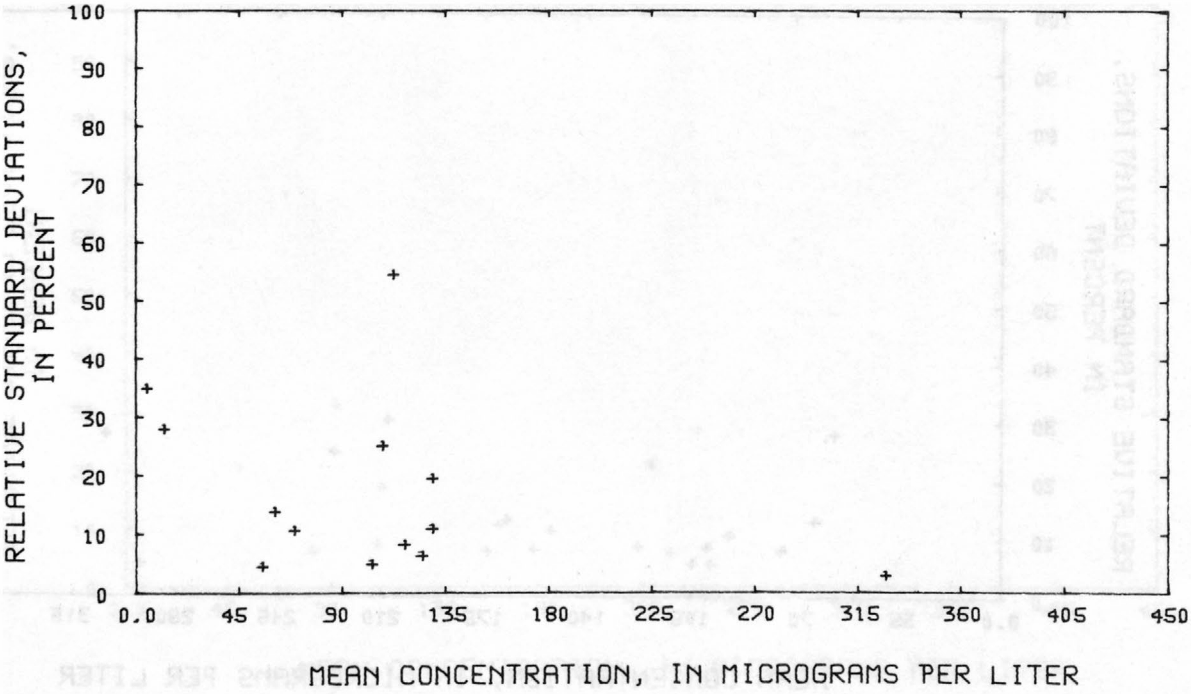

Figure 209--Precision data for zinc, dissolved, (inductively coupled plasma emission spectrometry) at the Atlanta laboratory.

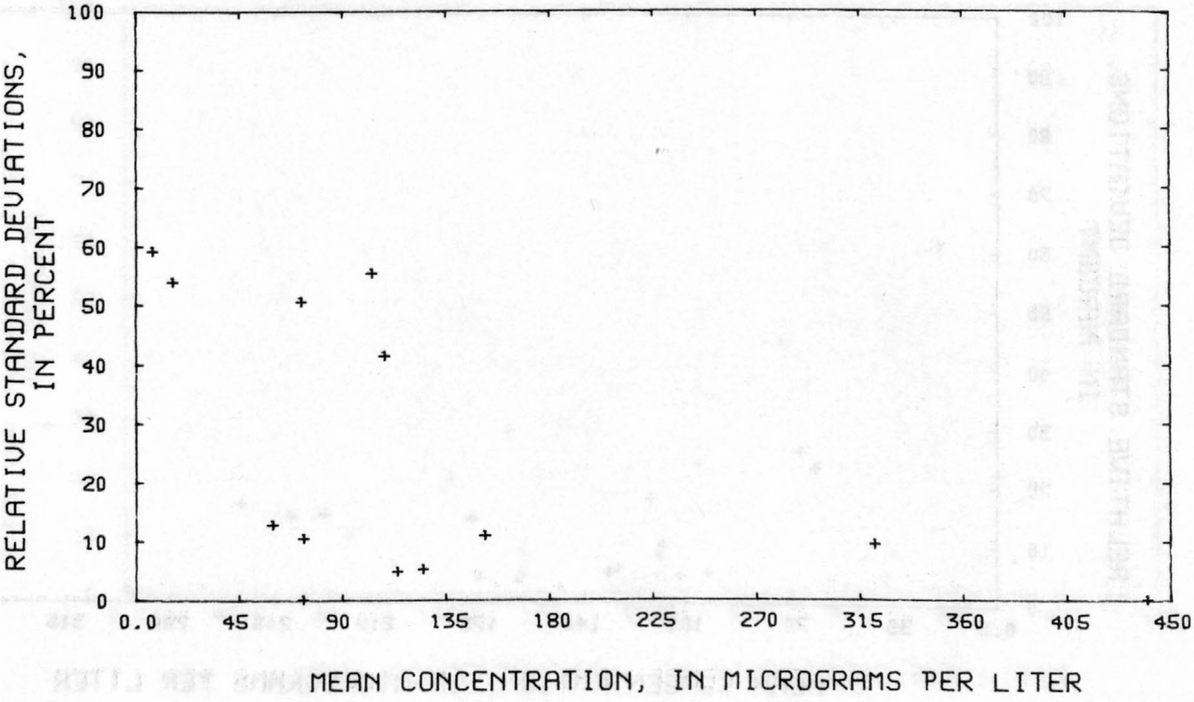

Figure 210--Precision data for zinc, dissolved, (inductively coupled plasma emission spectrometry), at the Denver laboratory.

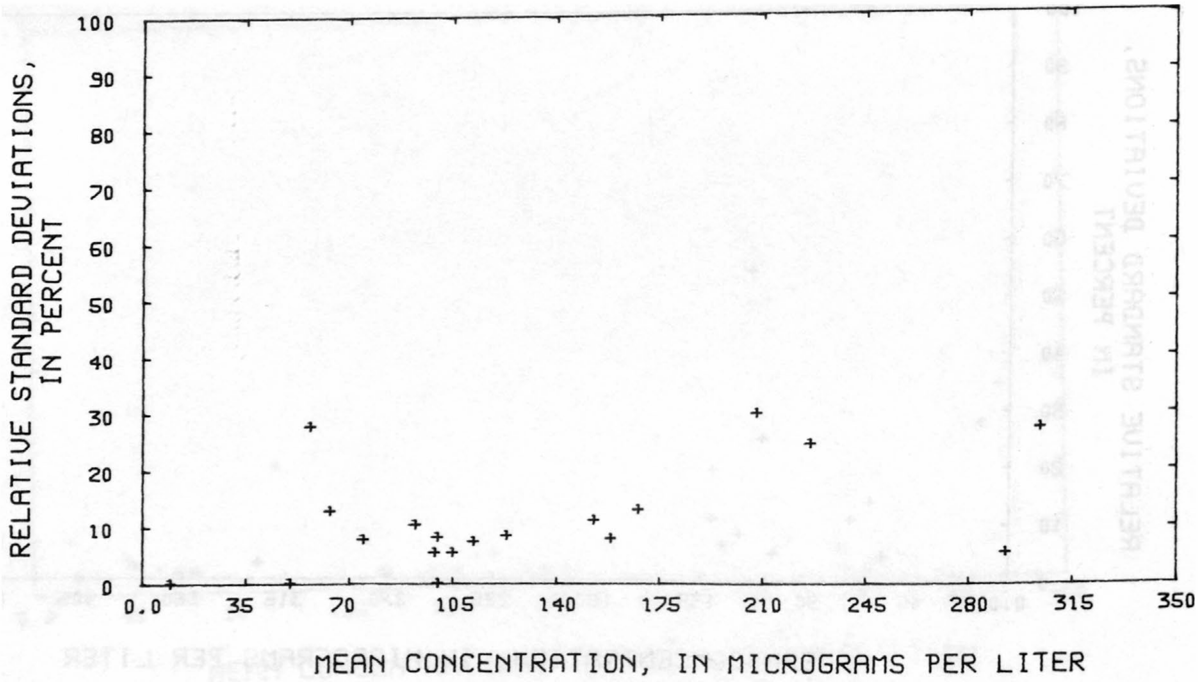

Figure 211--Precision data for zinc, dissolved, (atomic absorption spectrometry) at the Atlanta laboratory.

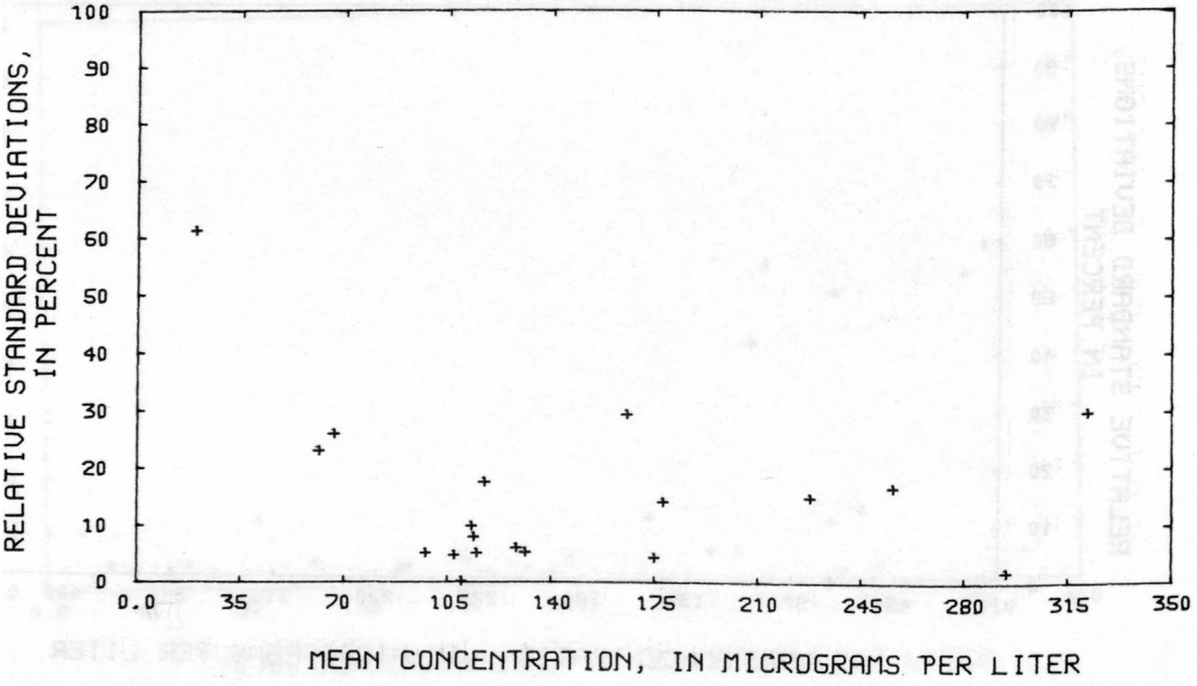

Figure 212--Precision data for zinc, dissolved, (atomic absorption spectrometry) at the Denver laboratory.

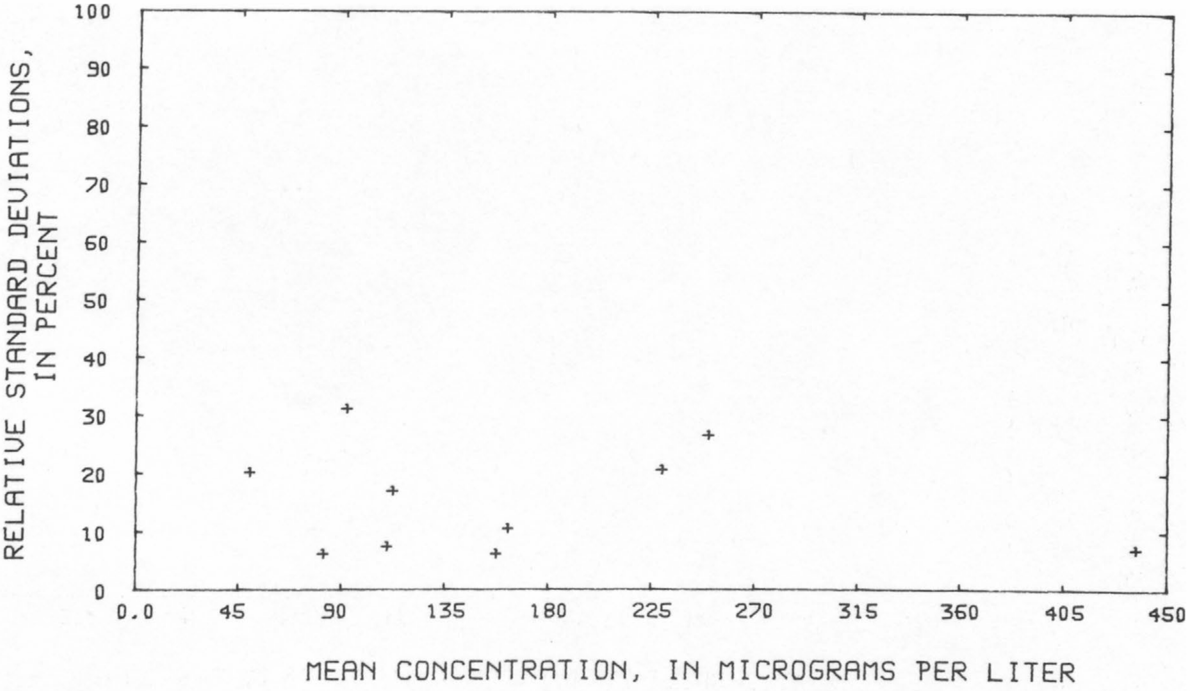

Figure 213--Precision data for zinc, total recoverable, at the Atlanta laboratory.

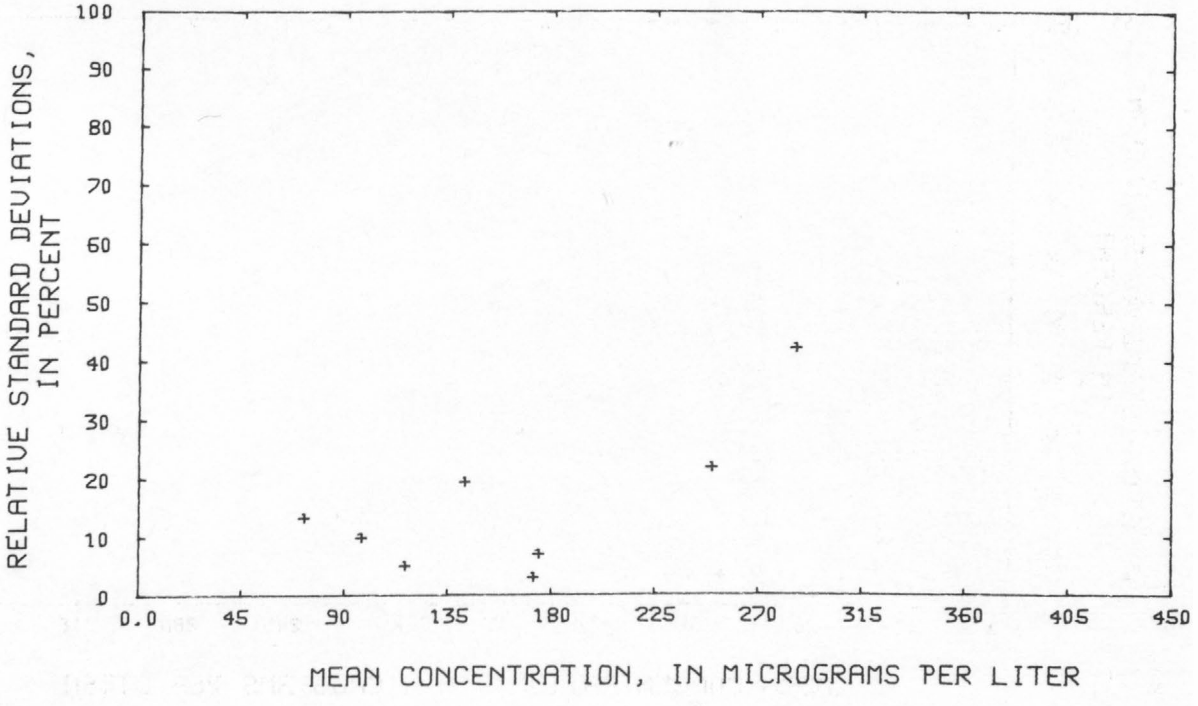

Figure 214--Precision data for zinc, total recoverable, at the Denver laboratory.

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