

QUALITY-ASSURANCE DATA FOR ROUTINE WATER ANALYSIS IN THE NATIONAL WATER-QUALITY LABORATORY OF THE U.S. GEOLOGICAL SURVEY FOR WATER YEAR 1987

By Keith J. Lucey and Dale B. Peart

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ABSTRACT

The U.S. Geological Survey maintains a quality-assurance program based on the analysis of reference samples for its National Water-Quality Laboratory located in Denver, Colorado. Reference samples containing selected inorganic constituents are prepared at the Survey's Water Quality Services Unit in Ocala, Florida, disguised as routine samples, and sent daily or weekly, as appropriate, to the laboratory through other Survey offices. Nutrient samples and precipitation samples also were submitted as samples of unknown concentration. The results are stored permanently in the National Water Data Storage and Retrieval System (WATSTORE), the Survey's data base for all water data. These data are analyzed statistically for precision and bias. The results of these statistical analyses are discussed for data collected during water-year 1987.

An overall evaluation of the major and trace constituent data for water-year 1987 indicated a lack of precision in the National Water-Quality Laboratory for the determination of 6 out of 58 constituents: chloride; chromium; iron, total recoverable; zinc, dissolved (atomic absorption spectroscopy); zinc, (inductively coupled plasma emission spectroscopy); and zinc, total recoverable. There were fewer constituents having positive or negative bias during water-year 1987 than during water-year 1986.

A lack of precision was indicated in the determination of three of the six nutrient constituents: nitrate + nitrite nitrogen as N, orthophosphate as P, and phosphorus as P. A biased condition was indicated in the determination of ammonia + organic nitrogen as N.

There was acceptable precision in the determination of all 10 precipitation-level constituents. One precipitation-level constituent, sodium, indicated a biased condition.

INTRODUCTION

The National Water-Quality Laboratory (NWQL) of the U.S. Geological Survey, located in Denver, Colorado, routinely analyzes 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 at the NWQL are discussed in this report. Previous reports (Peart and Thomas, 1983a, 1983b, 1984; Peart and Sutphin, 1987; Lucey and Peart, 1988, 1989) document results from February 1981 through September 1986.

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. No effort was made to correct nonanalytical errors, even when it was obvious which corrective measures were appropriate; so the data are preserved as produced by the laboratory. These errors include any made in logging the sample into the laboratory, transcription errors by the analyst, and data entry errors. Therefore, if the data reviewer in the Survey's office that collected the sample, is capable of detecting errors of this type, the reviewer can increase the quality of the data, when compared to those data presented in this report. For example, two samples from different sites are submitted to the laboratory on the same day and are misidentified, in a way that the analytical data reported for one, would actually belong to the other. A data reviewer who was familiar with the site or its historical data usually could detect the problem and correct it.
2. No quality-assurance samples had any constituents redetermined except those requested by the laboratory internal quality-assurance groups. Survey data reviewers in the offices that collected the samples are expected to scrutinize incoming new data for discrepancies and make requests for reanalysis. These requests

may result in the detection of analytical and nonanalytical errors, and data quality would improve, when compared to data quality presented in this report.

3. Figures included in this report may be used to determine analytical conditions at any given time for water-year 1987. Where figures show that an analytical process has been in statistical control for most of the year, but the process also has been out of statistical control for a certain period, that period may be long enough that the statistical tests applied indicate lack of precision or significant bias for the year. The data from that period when the analytical process was in control can be considered to have acceptable precision and bias.
4. Several data points seemed to be in error because of an incorrectly applied dilution factor. Dilutions of the sample are made routinely in the laboratory to bring the sample concentration into analytical range. If the dilution factor is not applied or is applied incorrectly, the reported value will be in error by the amount of the dilution factor. For example, if several analyses of a solution result in reported values of 250 mg/L each and one analysis results in a reported value of 25 mg/L, a 10X dilution may have been used and not applied to the final results. These kinds of errors are difficult to confirm. Their detection and correction in the field offices will increase the reliability of the data above that stated in this report. Non-analytical errors for nutrient analyses can result when the samples are not maintained at the ideal temperature of 4°C during shipping and receiving.

During water-year 1987, the following sample categories, containing the indicated constituents in the dissolved phase were included in this quality-assurance program:

Inorganic constituents—alkalinity, aluminum, antimony, arsenic, barium, beryllium, boron, cadmium, calcium, chloride, chromium, cobalt, copper, dissolved solids (residue on evaporation at 180°C), fluoride, iron, lead, lithium, magnesium, manganese, molybdenum, nickel, potassium, selenium, silica, silver, sodium, strontium, sulfate, and zinc.

Nutrients—ammonia, as nitrogen; ammonia plus organic nitrogen as nitrogen; nitrite as nitrogen; nitrite plus nitrate as nitrogen; orthophosphate as phosphorus; and phosphorus.

Precipitation—minute concentrations of: ammonia, as nitrogen; calcium; chloride; fluoride; magnesium; nitrate, as nitrogen; orthophosphate, as phosphorus; potassium; sodium; and sulfate.

PROGRAM DESCRIPTION

Standard reference water samples (SRWS's) (Skougstad and Fishman, 1975; Schroder and others, 1980; Janzer, 1985) are used as the principal component of the reference samples used in this program. The SRWS's are diluted with deionized water, mixed in varying proportions with other SRWS's, 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 characteristics.

In addition to the SRWS's, synthetic samples made from reagent-grade chemicals are used in preparing reference samples. The reference samples are prepared in the Survey's Water Quality Service Unit in Ocala, Fla., and are made to appear as much like environmental samples as possible. When the samples are prepared and proper forms are completed to ensure that appropriate constituents have been requested for the sample, the samples and the forms are shipped to selected Survey offices across the country. These Survey offices then ship the quality-assurance samples to the NWQL on a daily or weekly basis, as appropriate, with their regular samples.

The number of quality-assurance determinations requested for inorganic constituents and nutrients are in direct proportion to the total number of requests for those determinations from all sources 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, to have an appropriate number of quality-assurance samples analyzed for those constituents determined less frequently. Natural precipitation samples were submitted once each week.

All constituents in the reference materials are in the dissolved phase because the reference materials themselves have been filtered in the preparation process. Therefore, those constituents in this report that are designated as "total recoverable" are from reference samples that have undergone a digestion process (Fishman and

Friedman, 1985, p 87–88) during analysis, rather than from unfiltered or whole–water samples. Differences that appear in this report between the dissolved analyses and the total recoverable analyses will be due largely or entirely to the digestion process rather than from any difference in the sampling techniques or sample source.

Quality–assurance samples are processed by the NWQL as routine samples, including the normal laboratory quality–control and quality–assurance procedures. The data then are stored in the Survey’s National Water Data Storage and Retrieval System (WATSTORE). After being processed by the laboratory, data from these quality–assurance samples will indicate the quality of the analytical data produced for environmental samples.

STATISTICAL EVALUATION

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

Standard deviations were determined by using linear least squares equations developed by regressing the means of each constituent obtained from all the SRWS’s analyzed during the last seven years against the corresponding standard deviations for those constituents. This method enabled an estimation of a most probable standard deviation (MPSD) for each constituent on a sample–by–sample basis to ascertain whether the determination in question was statistically in or out of control. An individual reported value was considered in statistical control if it was within two standard deviations of the MPV.

In certain situations, the resulting equation produced a MPSD too small for the standard deviation criterion to be met. This was true for barium, cadmium, chromium, copper, fluoride, lead, lithium, molybdenum, nickel, and selenium; and also beryllium, iron, manganese and zinc when determined by atomic absorption spectrometry or total recoverable digestion. 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 $\mu\text{g/L}$ (micrograms per liter) is set to 7.5 $\mu\text{g/L}$; the minimum standard deviation for cadmium, reported to the nearest 1 $\mu\text{g/L}$, is 0.75 $\mu\text{g/L}$. The equations for determining the most probable standard deviation (MPSD) for each constituent and the established minimum MPSD, if any, are listed in table 1.

The number of standard deviations each constituent differs 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 results for each laboratory and each constituent are shown on control charts in figures 1 through 74 in the “Supplemental Data” section of this report. Three symbols are used in figures 1 through 58 to indicate results from the lower (+), middle (x), and upper (o) one–thirds of the potential analytical range tested in this program for inorganic constituents. This range does not necessarily correspond with the analytical capabilities of the laboratory instrumentation or methods, but rather corresponds with the analytical range tested using the available SRWS’s or other reference samples. The three parts of this range are based on the MPV’s of the quality–assurance samples and not on the reporting policy; for example, available resources limit the maximum MPV for sulfate to be 377.0 mg/L (fig. 55) and still allow a correctly reported value of 380 mg/L, based on the policy to report sulfate to the nearest 10 mg/L at this concentration. Not all figures will show all three parts of the analytical range, because some flexibility is given to the Ocala, Fla., office in sample selection and because of limited concentration ranges in the available SRWS’s. Results for nutrient constituents are shown in figures 59 through 64 and results for precipitation sample results are shown in figures 65 through 74. Due to the low–level concentrations of these constituents, symbols on these plots represent the entire potential analytical range tested. Points outside the range of the plots are forced to appear at the limit (± 6 standard deviations), with the actual number of standard deviations indicated adjacent to the point (see figure 1, for example).

Table 1. Linear least-squared equations for determining the most probable standard deviation

[MPSD, most probable standard deviation; mg/L, milligrams per liter; MPV, most probable value; ‡, not applicable; µg/L, micrograms per liter; ICP, inductively coupled plasma emission spectrometry; AA, atomic absorption spectrometry; TOT, total recoverable; COL, colorimetry; N, nitrogen; P, phosphorus.]

Constituent (dissolved except as indicated)	Units	Equation to determine MPSD	Minimum MPSD
Inorganic constituents			
Alkalinity	mg/L	$(0.021 \times \text{MPV}) + 1.14$	‡
Aluminum	µg/L	$(0.17 \times \text{MPV}) + 30.4$	7.5
Antimony	µg/L	$(0.069 \times \text{MPV}) + 1.34$	‡
Arsenic	µg/L	$(0.11 \times \text{MPV}) + 1.27$	0.75
Barium (ICP)	µg/L	$(0.16 \times \text{MPV}) + 7.49$	0.75
Barium (AA)	µg/L	$(0.17 \times \text{MPV}) + 26.0$	75
Barium (TOT)	µg/L	$(0.17 \times \text{MPV}) + 26.0$	75
Beryllium	µg/L	$(0.043 \times \text{MPV}) + 1.45$	‡
Beryllium (TOT)	µg/L	$(0.043 \times \text{MPV}) + 1.45$	7.5
Boron	µg/L	$(0.042 \times \text{MPV}) + 33.2$	‡
Cadmium (ICP)	µg/L	$(0.106 \times \text{MPV}) + 0.72$	0.75
Cadmium (AA)	µg/L	$(0.106 \times \text{MPV}) + 0.72$	0.75
Cadmium (TOT)	µg/L	$(0.106 \times \text{MPV}) + 0.72$	0.75
Calcium (ICP)	mg/L	$(0.040 \times \text{MPV}) + 0.54$	‡
Calcium (AA)	mg/L	$(0.040 \times \text{MPV}) + 0.54$	‡
Chloride	mg/L	$(0.026 \times \text{MPV}) + 0.62$	‡
Chromium	µg/L	$(0.16 \times \text{MPV}) + 1.49$	7.5
Chromium (TOT)	µg/L	$(0.16 \times \text{MPV}) + 1.49$	7.5
Cobalt (ICP)	µg/L	$(0.075 \times \text{MPV}) + 2.09$	‡
Cobalt (AA)	µg/L	$(0.075 \times \text{MPV}) + 2.09$	‡
Cobalt (TOT)	µg/L	$(0.075 \times \text{MPV}) + 2.09$	‡
Copper (ICP)	µg/L	$(0.046 \times \text{MPV}) + 3.25$	7.5
Copper (AA)	µg/L	$(0.046 \times \text{MPV}) + 3.25$	0.75
Copper (TOT)	µg/L	$(0.046 \times \text{MPV}) + 3.25$	0.75
Dissolved solids	mg/L	$(0.022 \times \text{MPV}) + 7.2$	‡
Fluoride	mg/L	$(0.071 \times \text{MPV}) + 0.01$	0.05
Iron (ICP)	µg/L	$(0.042 \times \text{MPV}) + 8.60$	‡
Iron (AA)	µg/L	$(0.042 \times \text{MPV}) + 8.60$	7.5
Iron (TOT)	µg/L	$(0.042 \times \text{MPV}) + 8.60$	7.5
Lead (ICP)	µg/L	$(0.531 \times \text{MPV}) - 0.16$	7.5
Lead (AA)	µg/L	$(0.531 \times \text{MPV}) - 0.16$	3.75
Lead (TOT)	µg/L	$(0.531 \times \text{MPV}) - 0.16$	3.75
Lithium	µg/L	$(0.11 \times \text{MPV}) + 1.73$	7.5
Lithium (TOT)	µg/L	$(0.11 \times \text{MPV}) + 1.73$	7.5
Magnesium (ICP)	mg/L	$(0.035 \times \text{MPV}) + 0.26$	‡
Magnesium (AA)	mg/L	$(0.035 \times \text{MPV}) + 0.26$	‡
Manganese (ICP)	µg/L	$(0.044 \times \text{MPV}) + 2.52$	‡
Manganese (AA)	µg/L	$(0.044 \times \text{MPV}) + 2.52$	7.5
Manganese (TOT)	µg/L	$(0.044 \times \text{MPV}) + 2.52$	7.5
Molybdenum (ICP)	µg/L	$(0.081 \times \text{MPV}) + 4.21$	7.5
Molybdenum (AA)	µg/L	$(0.081 \times \text{MPV}) + 4.21$	0.75

Table 1. Linear least-squared equations for determining the most probable standard deviation.
—continued

Constituent (dissolved except as indicated)	Units	Equation to determine MPVD	Minimum MPVD
Inorganic constituents			
Nickel (ICP)	µg/L	$(0.109 \times \text{MPV}) + 4.52$	7.5
Nickel (AA)	µg/L	$(0.109 \times \text{MPV}) + 4.52$	‡
Nickel (TOT)	µg/L	$(0.109 \times \text{MPV}) + 4.52$	7.5
Potassium	mg/L	$(0.075 \times \text{MPV}) + 0.07$	‡
Selenium	µg/L	$(0.347 \times \text{MPV}) - 0.30$	0.75
Silica (ICP)	mg/L	$(0.038 \times \text{MPV}) + 0.53$	‡
Silica (COL)	mg/L	$(0.038 \times \text{MPV}) + 0.53$	‡
Silver (ICP)	µg/L	$(0.260 \times \text{MPV}) + 1.06$	0.75
Silver (AA)	µg/L	$(0.260 \times \text{MPV}) + 1.06$	0.75
Silver (TOT)	µg/L	$(0.260 \times \text{MPV}) + 1.06$	0.75
Sodium (ICP)	mg/L	$(0.032 \times \text{MPV}) + 0.23$	‡
Sodium (AA)	mg/L	$(0.032 \times \text{MPV}) + 0.23$	‡
Strontium	µg/L	$(0.039 \times \text{MPV}) + 9.30$	‡
Sulfate	mg/L	$(0.045 \times \text{MPV}) + 1.20$	‡
Zinc (ICP)	µg/L	$(0.039 \times \text{MPV}) + 4.39$	‡
Zinc (AA)	µg/L	$(0.039 \times \text{MPV}) + 4.39$	7.5
Zinc (TOT)	µg/L	$(0.039 \times \text{MPV}) + 4.39$	7.5
Nutrient constituents			
Ammonia nitrogen, as N	mg/L	$(0.10 \times \text{MPV}) + 0.035$	‡
Ammonia plus organic nitrogen, as N	mg/L	$(0.601 \times \text{MPV}) - 0.06$	‡
Nitrate plus nitrite nitrogen, as N	mg/L	$(0.038 \times \text{MPV}) + 0.034$	‡
Nitrate nitrogen, as N	mg/L	$(0.07 \times \text{MPV}) + 0.003$	‡
Orthophosphate phosphorus, as P	mg/L	$(0.057 \times \text{MPV}) + 0.009$	‡
Phosphorus, as P	mg/L	$(0.076 \times \text{MPV}) + 0.007$	‡
Constituents in precipitation samples			
Calcium	mg/L	$(0.065 \times \text{MPV}) + 0.05$	‡
Chloride	mg/L	$(0.073 \times \text{MPV}) + 0.20$	‡
Fluoride	mg/L	$(-0.08 \times \text{MPV}) + 0.031$	‡
Magnesium	mg/L	$(0.038 \times \text{MPV}) + 0.014$	‡
Ammonia nitrogen, as N	mg/L	$(0.32 \times \text{MPV}) + 0.008$	‡
Nitrate nitrogen, as N	mg/L	$(0.23 \times \text{MPV}) + 0.018$	‡
Orthophosphate phosphorus, as P	mg/L	$(0.064 \times \text{MPV}) + 0.008$	‡
Potassium	mg/L	$(0.10 \times \text{MPV}) + 0.02$	‡
Sodium	mg/L	$(0.044 \times \text{MPV}) + 0.04$	‡
Sulfate	mg/L	$(0.037 \times \text{MPV}) + 0.035$	‡

Precision and bias are determined by applying binomial-probability-distribution equations to the data using procedures described by Friedman, Bradford, and Peart, (1983); and by Peart and Thomas, (1983a). When precision is determined using these procedures, it contains an element of bias because MPV's, rather than analyzed

means, are used as the basis for determining the number of standard deviations each constituent deviates from that value. Therefore, in this analysis, precision, or lack of it, is based on whether or not the analytical process was statistically in or out of control (± 2 standard deviations from the theoretical value).

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 proportionally as constituent concentration in chemical analyses varies, these calculations were done separately for individual sample mixtures; therefore, they do not result in overall evaluations of the analytical processes. Relative standard deviations for inorganic, nutrient, and precipitation constituents were calculated and plotted as a percent against their mean concentrations (figs. 75 through 148 in the "Supplemental data" section of this report). These plots allow a data reviewer to estimate the error at any concentration shown for all constituents. For example, the precision of the alkalinity values from the NWQL are estimated to be ± 2 percent from figure 75. To allow the precision charts to be used to estimate an expected error from the analytical results, outliers were deleted from the data set. An outlier was defined as being greater than 6 or less than -6 standard deviations from the MPV. The total number of analyses for each constituent processed during the water-year, the number of analyses with standard deviations greater than 2 or less than -2 from the MPV, and the number of analyses with standard deviations greater than 6 or less than -6 from the MPV are listed in table 2. If the relative standard deviation for a given mix has a value of zero, the data point will plot on the horizontal axis, as in figure 80.

Because of an insufficient supply of SRWS's for nutrients, most of the reference materials were made from reagent-grade chemicals in the Ocala, Fla., office. Preparation methods used for these samples were virtually the same as those used for preparing samples for the SRWS program. Precipitation samples were SRWS's initially prepared from natural matrix materials (Janzer, 1985).

Table 2. *Total number of analyses from quality-assurance samples during water-year 1987*

[> 2SD, number of analyses greater than 2 or less than -2 standard deviations from the most probable value; > 6SD, number of analyses greater than 6 or less than -6 standard deviations from the most probable value; ICP, inductively coupled plasma emission spectrometry; AA, atomic absorption spectrometry; TOT, total recoverable; COL, colorimetry; N, nitrogen; P, phosphorus.]

Constituent (dissolved except as indicated)	Number of analyses			Constituent (dissolved except as indicated)	Number of analyses		
	Total	>2SD	>6SD		Total	>2SD	>6SD
Inorganic constituents							
Alkalinity	279	3	3	Chloride	300	44	4
Aluminum	173	1	1	Chromium	216	20	3
Antimony	9	0	0	Chromium (TOT)	36	5	1
Arsenic	211	1	0	Cobalt (ICP)	246	5	1
Barium (ICP)	240	0	0	Cobalt (AA)	19	0	0
Barium (AA)	19	0	0	Cobalt (TOT)	36	1	0
Barium (TOT)	36	0	0	Copper (ICP)	246	0	0
Beryllium	128	4	0	Copper (AA)	52	5	2
Beryllium (TOT)	17	0	0	Copper (TOT)	36	5	2
Boron	156	0	0	Dissolved solids	272	18	1
Cadmium (ICP)	246	1	0	Fluoride	299	10	8
Cadmium (AA)	52	1	0	Iron (ICP)	240	18	0
Cadmium (TOT)	36	1	0	Iron (AA)	52	7	1
Calcium (ICP)	220	11	0	Iron (TOT)	31	10	1
Calcium (AA)	61	6	3	Lead (ICP)	246	1	0

**Table 2. Total number of analyses from quality-assurance samples during water-year 1987
—continued**

Constituent (dissolved except as indicated)	Number of analyses			Constituent (dissolved except as indicated)	Number of analyses		
	Total	>2SD	>6SD		Total	>2SD	>6SD
Lead (AA)	53	1	0	Potassium	280	9	4
Lead (TOT)	36	1	0	Selenium	177	8	0
Lithium	240	1	0	Silica (ICP)	220	3	2
Lithium (TOT)	17	1	1	Silica (COL)	80	4	2
Magnesium (ICP)	220	7	0	Silver (ICP)	163	1	0
Magnesium (AA)	61	2	2	Silver (AA)	20	0	0
Manganese (ICP)	240	4	0	Silver (TOT)	36	2	2
Manganese (AA)	52	1	1	Sodium (ICP)	220	2	0
Manganese (TOT)	36	4	1	Sodium (AA)	63	3	1
Molybdenum (ICP)	240	1	0	Strontium	240	1	0
Molybdenum (AA)	33	1	0	Sulfate	300	17	2
Nickel (ICP)	163	0	0	Zinc (ICP)	240	79	17
Nickel (AA)	52	0	0	Zinc (AA)	52	8	1
Nickel (TOT)	36	2	1	Zinc (TOT)	36	6	4
Nutrient constituents							
Ammonia nitrogen, as N	706	37	5	Nitrite nitrogen, as N	327	21	4
Ammonia + organic nitrogen, as N	702	17	7	Orthophosphate, as P	358	79	35
Nitrate + nitrite nitrogen, as N	766	90	7	Phosphorus, as P	745	160	82
Constituents in precipitation samples							
Calcium	39	2	0	Nitrate nitrogen, as N	34	0	0
Chloride	35	0	0	Phosphorus, as P	8	0	0
Fluoride	35	4	1	Potassium	39	0	0
Magnesium	39	2	0	Sodium	39	3	2
Ammonia nitrogen, as N	16	0	0	Sulfate	36	4	1

QUALITY-ASSURANCE DATA FOR INORGANIC-CONSTITUENT SAMPLES

Precision

The results of statistical testing for lack of precision for each inorganic constituent are presented in table 3. For each constituent, this table indicates significant lack of precision at the 95 percent confidence level (indicated by "LOP") as well as all acceptable results (indicated by "+").

Evaluating the data for the year, chloride; chromium; iron, total recoverable; zinc (ICP); zinc (AA); and zinc, total recoverable, indicated LOP in the NWQL. Chloride; iron, total recoverable; zinc (ICP); zinc (AA); and zinc, total recoverable, all failed the precision criteria in the NWQL during water-year 1986 (Lucey and Peart, 1989) and again in 1987. Only iron, total recoverable, and zinc (ICP) have failed the precision criteria at the NWQL during each of the last three years (Lucey and Peart, 1988, 1989).

In the NWQL during water-year 1987, iron (ICP), selenium, and sodium (AA) had acceptable results after failing the precision tests during water-year 1986 (Lucey and Peart, 1989).

Table 3. Results of statistical testing for lack of precision in inorganic constituent data

[+, acceptable results; ICP, inductively coupled plasma emission spectrometry; AA, atomic absorption spectrometry; TOT, total recoverable; LOP, significant lack of precision; COL, colorimetry]

Constituent (dissolved, except as indicated)	Results from Oct. 1986– Sept. 1987	Constituent (dissolved, except as indicated)	Results from Oct. 1986– Sept. 1987	Constituent (dissolved, except as indicated)	Results from Oct. 1986– Sept. 1987
Alkalinity	+	Cobalt (TOT)	+	Molybdenum (AA)	+
Aluminum	+	Copper (ICP)	+	Nickel (ICP)	+
Antimony	+	Copper (AA)	+	Nickel (AA)	+
Arsenic	+	Copper (TOT)	+	Nickel (TOT)	+
Barium (ICP)	+	Dissolved solids	+	Potassium	+
Barium (AA)	+	Fluoride	+	Selenium	+
Barium, (TOT)	+	Iron (ICP)	+	Silica (ICP)	+
Beryllium	+	Iron (AA)	+	Silica (COL)	+
Beryllium (TOT)	+	Iron (TOT)	LOP	Silver (ICP)	+
Boron	+	Lead (ICP)	+	Silver (AA)	+
Cadmium (ICP)	+	Lead (AA)	+	Silver (TOT)	+
Cadmium (AA)	+	Lead (TOT)	+	Sodium (ICP)	+
Cadmium, (TOT)	+	Lithium	+	Sodium (AA)	+
Calcium (ICP)	+	Lithium (TOT)	+	Strontium	+
Calcium (AA)	+	Magnesium (ICP)	+	Sulfate	+
Chloride	LOP	Magnesium (AA)	+	Zinc (ICP)	LOP
Chromium	LOP	Manganese (ICP)	+	Zinc (AA)	LOP
Chromium (TOT)	+	Manganese (AA)	+	Zinc (TOT)	LOP
Cobalt (ICP)	+	Manganese (TOT)	+		
Cobalt (AA)	+	Molybdenum (ICP)	+		

Bias

Results of the statistical tests for bias are shown in table 4. There were fewer constituents indicating bias for water-year 1987 than for water-year 1986 at the NWQL (Lucey and Peart, 1989). Constituents that showed negative bias for water-years 1987 and 1986 were: antimony, barium (ICP), beryllium, boron, dissolved solids, potassium, and strontium. In addition, aluminum; magnesium (AA); nickel (AA); nickel, total recoverable; and silver (ICP) had negative bias during water-year 1987.

Positively biased constituents for water-years 1987 and 1986 were: arsenic; barium (AA); barium, total recoverable; chromium; iron (ICP); magnesium (ICP); molybdenum (ICP); selenium; silica (ICP); sodium (ICP); sulfate; and zinc (ICP). Additional positively biased constituents that did not have a positive bias during water-year 1986 were: alkalinity; cadmium (AA); lead (ICP); lithium; silver, total recoverable; and zinc (AA).

There were no predominant patterns for bias between dissolved versus total recoverable analyses or between ICP and AA determinations. For barium (AA); barium, total recoverable; chromium; lead (ICP); and lead (AA) an apparent biased condition occurred because the minimum reporting levels (barium, 100 µg/L; chromium, 10 µg/L; lead (ICP) 10 µg/L; and lead (AA), 5 µg/L) were greater than the MPV's.

Results for barium (ICP), boron, and potassium indicated a negative bias for each of the last three water-years (1985, 1986, and 1987). During this same period, barium (AA); barium, total recoverable; chromium; magnesium (ICP); selenium; silica (ICP); sodium (ICP); sulfate; and zinc (ICP) have all had positively biased results (Lucey and Peart, 1988, 1989).

Table 4. Results of statistical testing for bias in inorganic constituent data

[P, positive bias; N, negative bias; ICP, inductively coupled plasma emission spectrometry; AA, atomic absorption spectrometry; TOT, total recoverable; +, acceptable results; COL, colorimetry]

Constituent (dissolved, except as indicated)	Results from Oct. 1986– Sept. 1987	Constituent (dissolved, except as indicated)	Results from Oct. 1986– Sept. 1987	Constituent (dissolved, except as indicated)	Results from Oct. 1986– Sept. 1987
Alkalinity	P	Cobalt (TOT)	+	Molybdenum (AA)	+
Aluminum	N	Copper (ICP)	+	Nickel (ICP)	+
Antimony	N	Copper (AA)	+	Nickel (AA)	N
Arsenic	P	Copper (TOT)	+	Nickel (TOT)	N
Barium (ICP)	N	Dissolved solids	N	Potassium	N
Barium (AA)	P ¹	Fluoride	P	Selenium	P
Barium (TOT)	P ¹	Iron (ICP)	P	Silica (ICP)	P
Beryllium	N	Iron (AA)	+	Silica (COL)	+
Beryllium (TOT)	+	Iron (TOT)	+	Silver (ICP)	N
Boron	N	Lead (ICP)	P ¹	Silver (AA)	+
Cadmium (ICP)	+	Lead (AA)	P ¹	Silver (TOT)	P
Cadmium (AA)	P	Lead (TOT)	+	Sodium (ICP)	P
Cadmium (TOT)	+	Lithium	P	Sodium (AA)	+
Calcium (ICP)	+	Lithium (TOT)	+	Strontium	N
Calcium (AA)	+	Magnesium (ICP)	P	Sulfate	P
Chloride	+	Magnesium (AA)	N	Zinc (ICP)	P
Chromium	P ¹	Manganese (ICP)	+	Zinc (AA)	P
Chromium (TOT)	+	Manganese (AA)	+	Zinc (TOT)	+
Cobalt (ICP)	+	Manganese (TOT)	+		
Cobalt (AA)	+	Molybdenum (ICP)	P		

¹Bias occurs because some most probable values are less than the lowest reporting limit.

The control chart for dissolved solids for the NWQL (fig. 25) shows a definite positive bias in the first month of the water-year with several data points greater than plus two standard deviations from the MPV. These results are a continuation of a trend that began in the last month of water-year 1986 (Lucey and Peart, 1989). However, the results returned to an unbiased condition after the first month of the 1987 water-year.

There are several analyses clustered between three and four standard deviations from the MPV for iron (ICP) during the month of October (fig. 27). This could be due to contamination of the samples during preparation prior to analysis at the NWQL. This uncertainty could be resolved if comparable data had been available from two laboratories instead of only one.

The control chart for lithium (fig. 33) indicates an abrupt change from a positive to a negative bias in the last three months of water-year 1987. This likely is due to an error in the preparation of standards in the laboratory or an error in calibration of the instruments.

The lack of data for March and April on the control charts for boron (fig. 10), calcium (AA) (fig. 15), magnesium (AA) (fig. 36), silica (COL) (fig. 48), and sodium (AA) (fig. 53) indicates that the reference samples were not analyzed at the NWQL during those months. These samples were misplaced in transit between the Ocala office and the NWQL.

The patterns of clustered points on the control charts for chromium (fig. 17), lead (ICP) (fig. 30), molybdenum (ICP) (fig. 40), and silver (AA) (fig. 50) are due to variations in concentrations of the constituent in the SRWS

mixes and the minimum standard deviation that was established in certain situations (such as low concentrations) equal to three-fourths of the value of the reporting level.

Several factors may have affected the results for other constituents that indicated occasional bias; the factors may include 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's, reporting levels being higher than the MPV's, or undetected contamination. When bias is indicated statistically but precision is good, the bias may have minimal effect on data interpretation and minimal practical significance.

QUALITY-ASSURANCE DATA FOR NUTRIENT-CONSTITUENT SAMPLES

Precision

The results of statistical testing for lack of precision for each nutrient constituent are presented in table 5. Results for nitrate + nitrite nitrogen as N, orthophosphate as phosphorus, and phosphorus failed the precision test at the NWQL in water-year 1987. All nutrient constituents had passed the precision test during water-year 1986 (Lucey and Peart, 1989).

Table 5. *Results of statistical testing for lack of precision in nutrient constituent data*

[N, nitrogen; +, acceptable results; LOP, lack of precision; P, phosphorus]

Constituent (dissolved)	Results from Oct. 1986– Sept. 1987	Constituent (dissolved)	Results from Oct. 1986– Sept. 1987	Constituent (dissolved)	Results from Oct. 1986– Sept. 1987
Ammonia nitrogen, as N .. + Ammonia + organic + nitrogen, as N		Nitrite + nitrate LOP nitrogen, as N Nitrite nitrogen, as N +		Orthophosphate, as P ... LOP Phosphorus, as P LOP	

Bias

Results of the statistical tests for bias are presented in table 6. Only results for ammonia + organic nitrogen as nitrogen indicated a positive bias, while the results for the other nutrient constituents did not indicate bias. During water-year 1986, ammonia as nitrogen indicated a negative bias, while nitrate plus nitrite as nitrogen and nitrite as nitrogen indicated a positive bias (Lucey and Peart, 1989).

Table 6. *Results of statistical testing for bias in nutrient constituent data*

[N, nitrogen; +, acceptable results; p, positive bias; P, phosphorus]

Constituent (dissolved)	Results from Oct. 1986– Sept. 1987	Constituent (dissolved)	Results from Oct. 1986– Sept. 1987	Constituent (dissolved)	Results from Oct. 1986– Sept. 1987
Ammonia nitrogen, as N .. + Ammonia + organic p nitrogen, as N		Nitrite + nitrate + nitrogen, as N Nitrite nitrogen, as N +		Orthophosphate, as P + Phosphorus, as P +	

QUALITY-ASSURANCE DATA FOR PRECIPITATION SAMPLES

The results for statistical testing for lack of precision and bias for each constituent in the precipitation and simulated-precipitation samples are presented in tables 7 and 8, respectively. Results for all of the constituents in

the precipitation samples indicated acceptable precision for water-year 1987, as they did in water-year 1986. Results for sodium indicate a positive bias. In water-year 1986, results for ammonia as nitrogen, magnesium, and potassium indicated negative bias and results for fluoride indicated a positive bias (Lucey and Peart, 1989).

Table 7. Results of statistical testing for lack of precision in precipitation constituent data

[N, nitrogen; +, acceptable results; P, phosphorus]

Constituent (dissolved)	Results from Oct. 1986– Sept. 1987	Constituent (dissolved)	Results from Oct. 1986– Sept. 1987	Constituent (dissolved)	Results from Oct. 1986– Sept. 1987
Ammonia nitrogen, as N .. +		Magnesium +		Potassium +	
Calcium +		nitrogen, as N		Sodium +	
Chloride +		Nitrite nitrogen, as N +		Sulfate +	
Fluoride +		Phosphorus, as P +			

Table 8. Results of statistical testing for bias in precipitation constituent data

[N, nitrogen; +, acceptable results; P, phosphorus; p, positive bias]

Constituent (dissolved)	Results from Oct. 1986– Sept. 1987	Constituent (dissolved)	Results from Oct. 1986– Sept. 1987	Constituent (dissolved)	Results from Oct. 1986– Sept. 1987
Ammonia nitrogen, as N .. +		Magnesium +		Potassium +	
Calcium +		nitrogen, as N		Sodium p	
Chloride +		Nitrite nitrogen, as N +		Sulfate +	
Fluoride +		Phosphorus, as P +			

SUMMARY AND CONCLUSIONS

Reference water samples that had known MPV's were disguised as regular samples and submitted with environmental water samples by selected offices of the Survey to the National Water-Quality Laboratory in Denver, Colo. The resulting data were stored in WATSTORE. Data for inorganic constituents, nutrient constituents, and constituents in precipitation samples then were analyzed statistically for precision and bias by using a binomial-probability-distribution equation.

An overall evaluation of the data for water-year 1987 indicates a lack of precision in results from the NWQL for chloride; chromium; iron, total recoverable; zinc (ICP); zinc (AA); and zinc, total recoverable.

Chloride; iron, total recoverable; zinc (ICP); zinc (AA); and zinc, total recoverable, failed the precision criteria in the NWQL for water-years 1987 and 1986. Only iron, total recoverable, and zinc (ICP) have failed the precision criteria during each of the last three years (Lucey and Peart, 1988, 1989).

An overall evaluation of the data for water-year 1987 indicates a significant bias in results from the NWQL for alkalinity; antimony; arsenic; barium (ICP); barium (AA); barium, total recoverable; beryllium; boron; cadmium (AA); chromium; dissolved solids; fluoride; iron (ICP); lead (ICP); lead (AA); lithium; magnesium (ICP);

magnesium (AA); molybdenum (ICP); nickel (AA); nickel, total recoverable; potassium; selenium; silica (ICP); silver, total recoverable; sodium (ICP); strontium; sulfate; zinc (ICP); and zinc (AA).

Fewer constituents had biased results in water-year 1987 than in water-year 1986 at the NWQL. Constituents having negative bias for water-years 1986 and 1987 were: antimony, barium (ICP), beryllium, boron, dissolved solids, potassium, and strontium. Constituents having positively biased results for water-years 1986 and 1987 were: arsenic; barium (AA); barium, total recoverable; chromium; iron (ICP); magnesium (ICP); molybdenum (ICP); selenium; silica; sodium (ICP); sulfate; and zinc (ICP).

Results for barium (ICP), boron, and potassium have indicated a negative bias for each of the last three years, while barium (AA); barium, total recoverable; chromium; magnesium (ICP); selenium; silica (ICP); sodium (ICP); sulfate; and zinc (ICP) have indicated positive bias during the same period (Lucey and Peart, 1988, 1989).

For nutrient constituents, results for nitrate + nitrite nitrogen as N, orthophosphate as P, and phosphorus failed the precision test at the NWQL during water-year 1987. Results for ammonia + organic nitrogen as N indicate a positive bias.

Results for all constituents in precipitation samples indicate acceptable precision. Results for sodium indicate a positive bias.

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SUPPLEMENTAL DATA

(pg 17 follows)

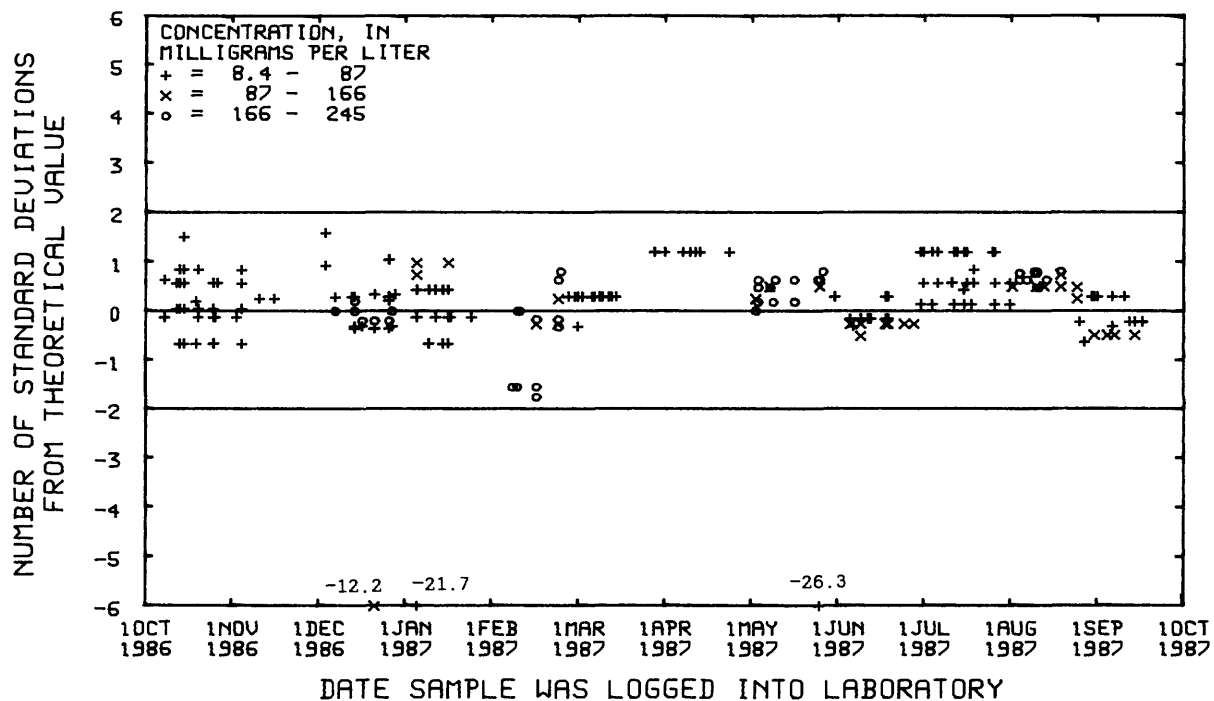


Figure 1.--Alkalinity, dissolved,
data from the National Water Quality Laboratory.

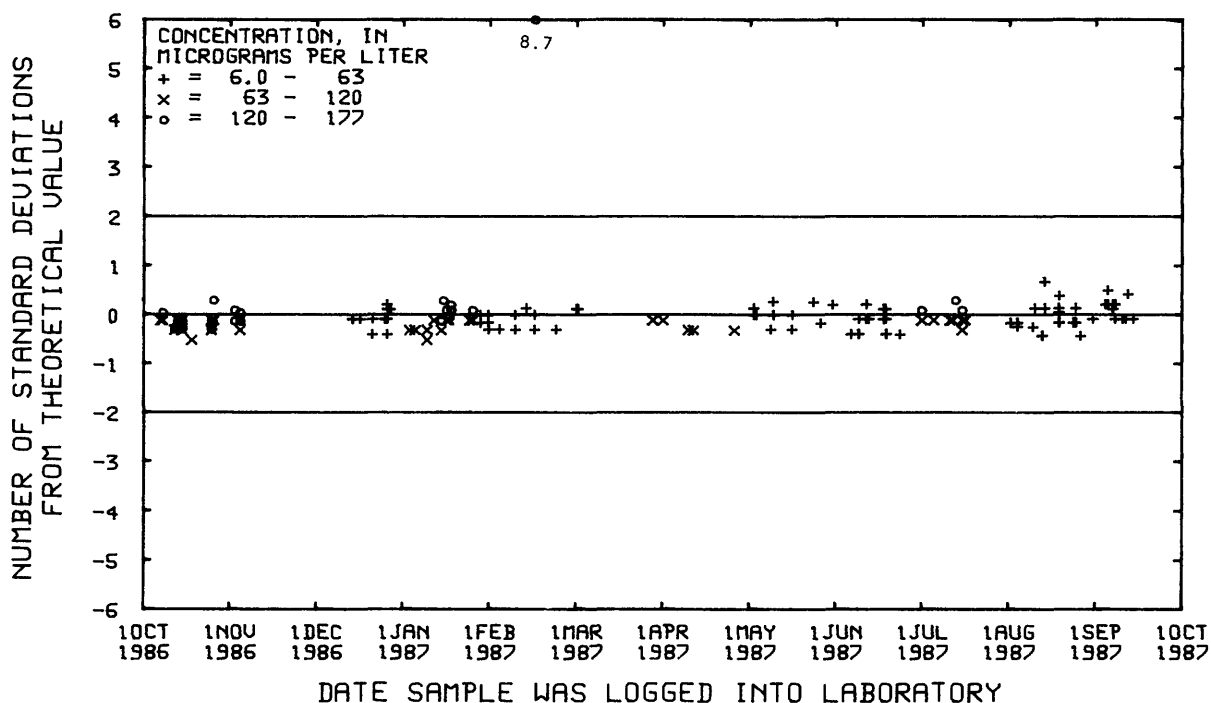


Figure 2.--Aluminum, dissolved,
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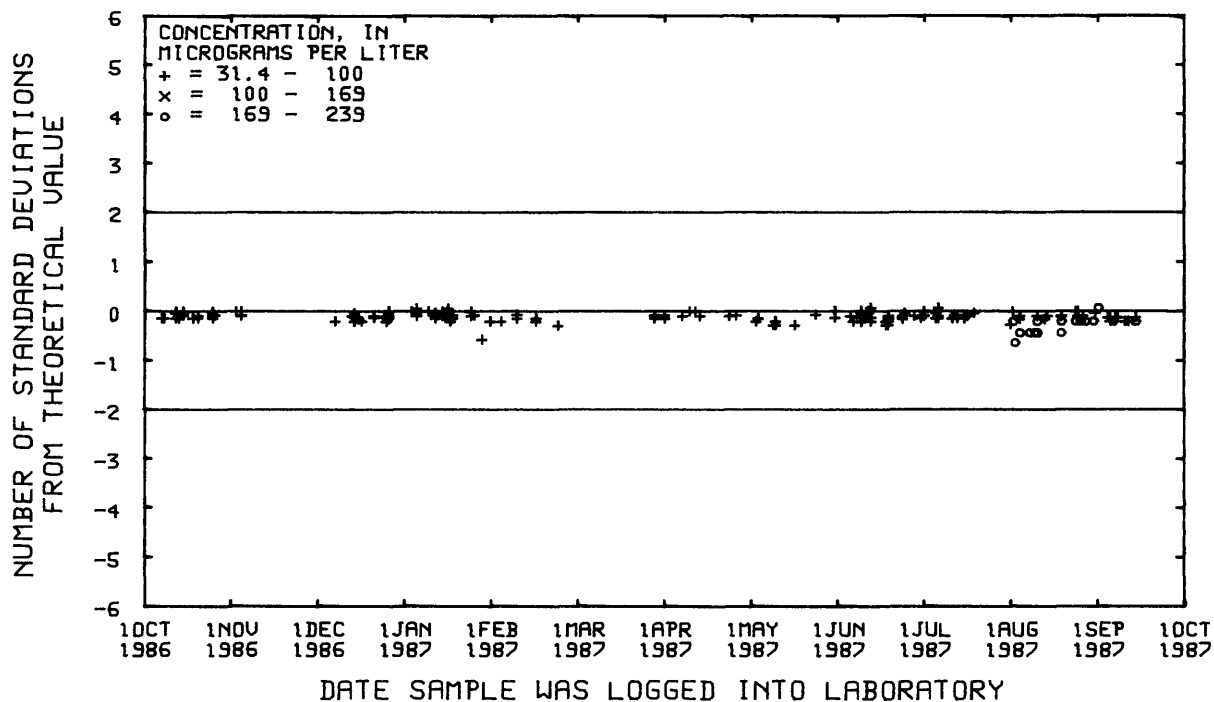


Figure 5.--Barium, dissolved,
(inductively coupled plasma emission spectrometry)
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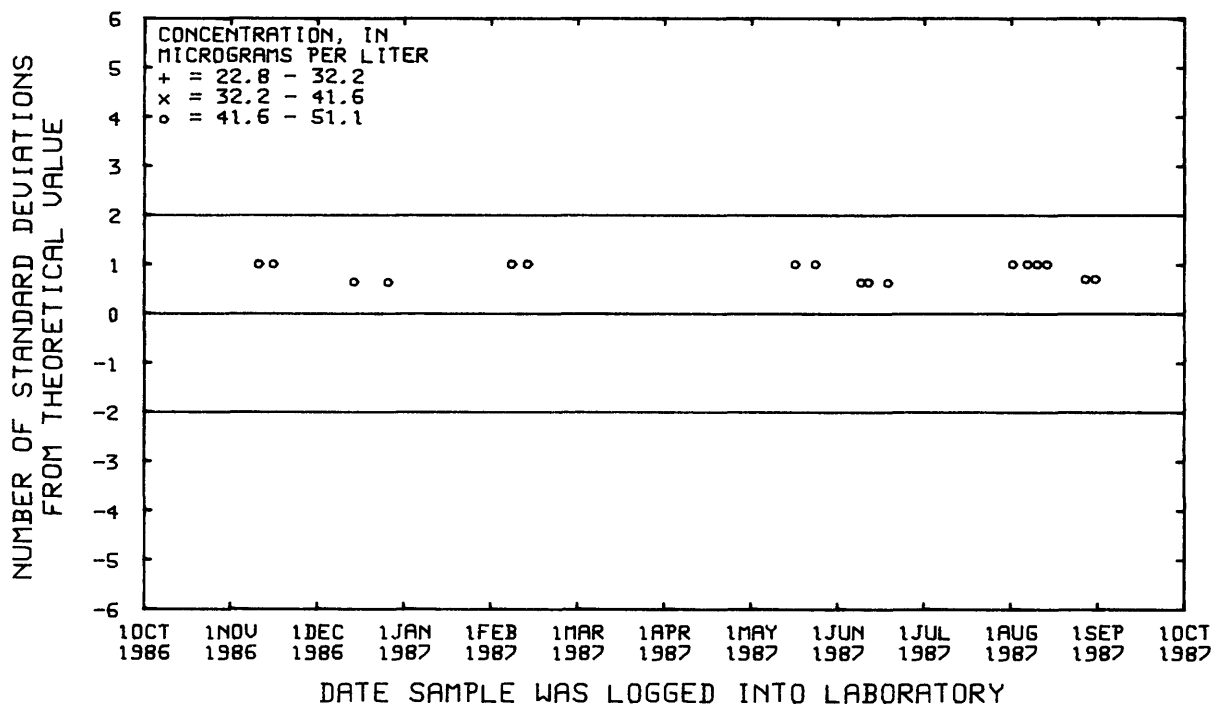


Figure 6.--Barium, dissolved,
(atomic absorption spectrometry)
data from the National Water Quality Laboratory.

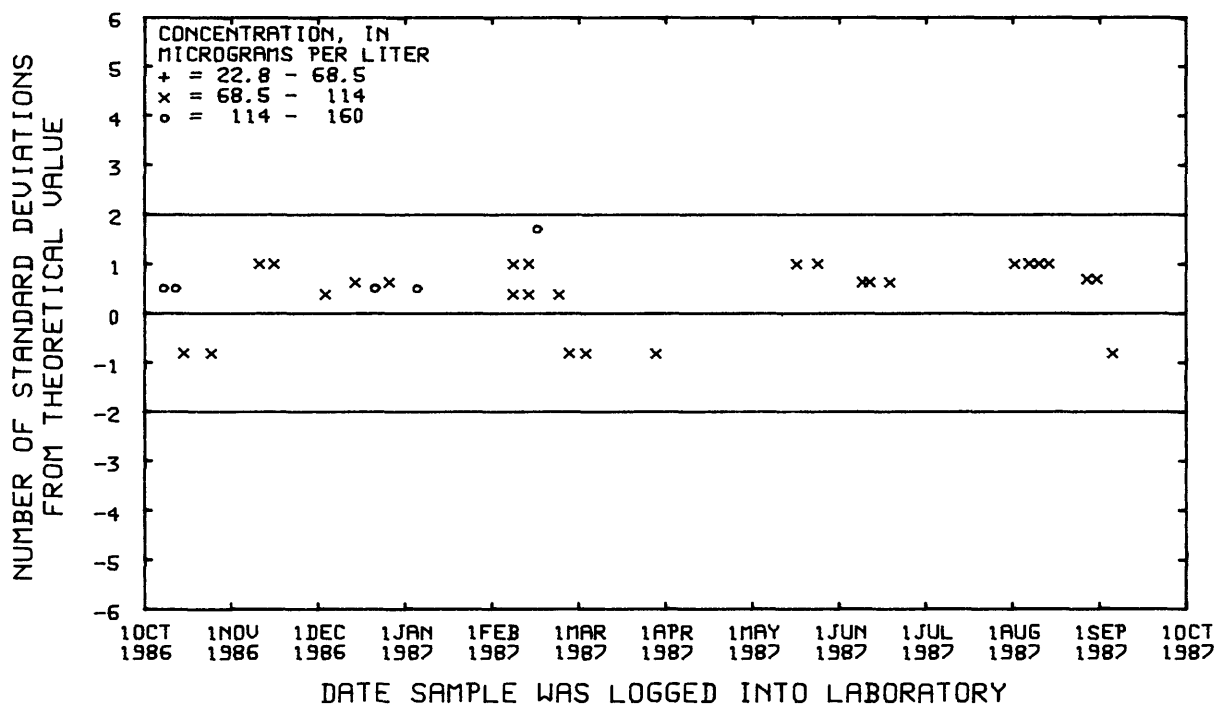


Figure 7.--Barium, total recoverable,
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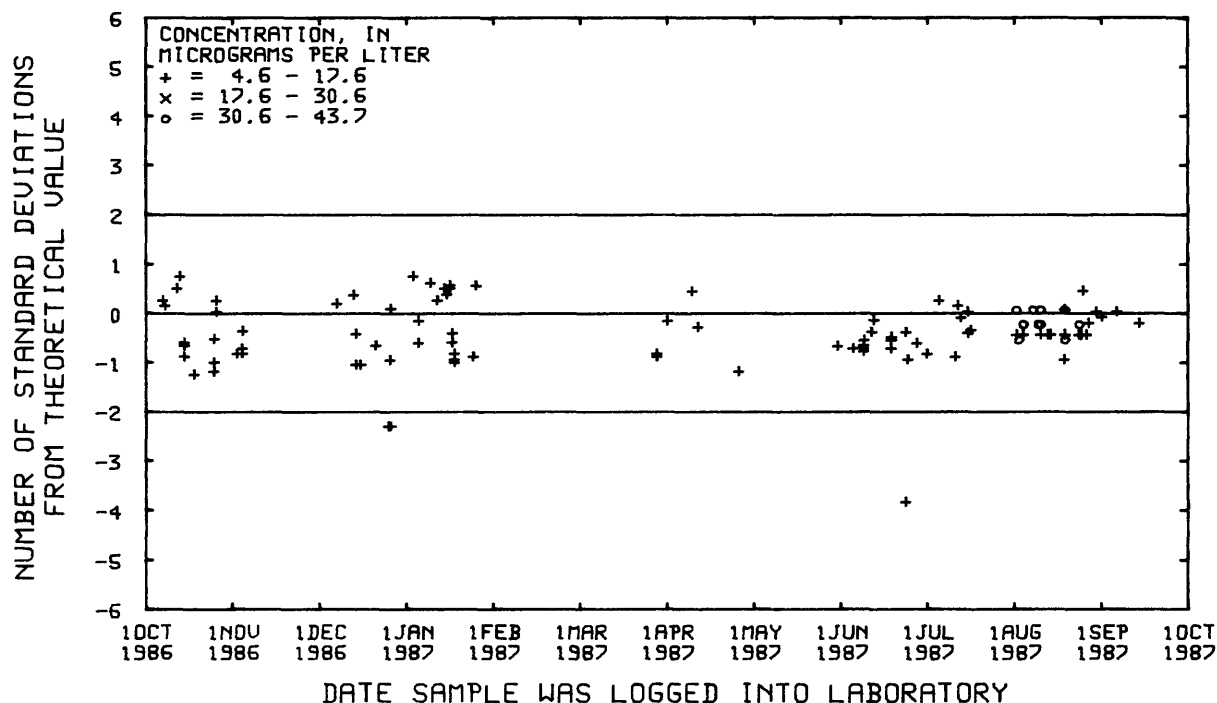
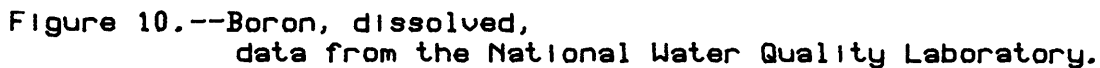
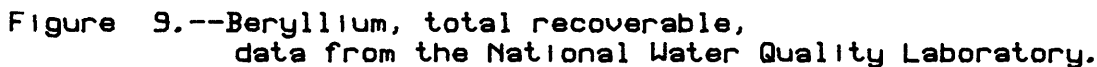


Figure 8.--Beryllium, dissolved,
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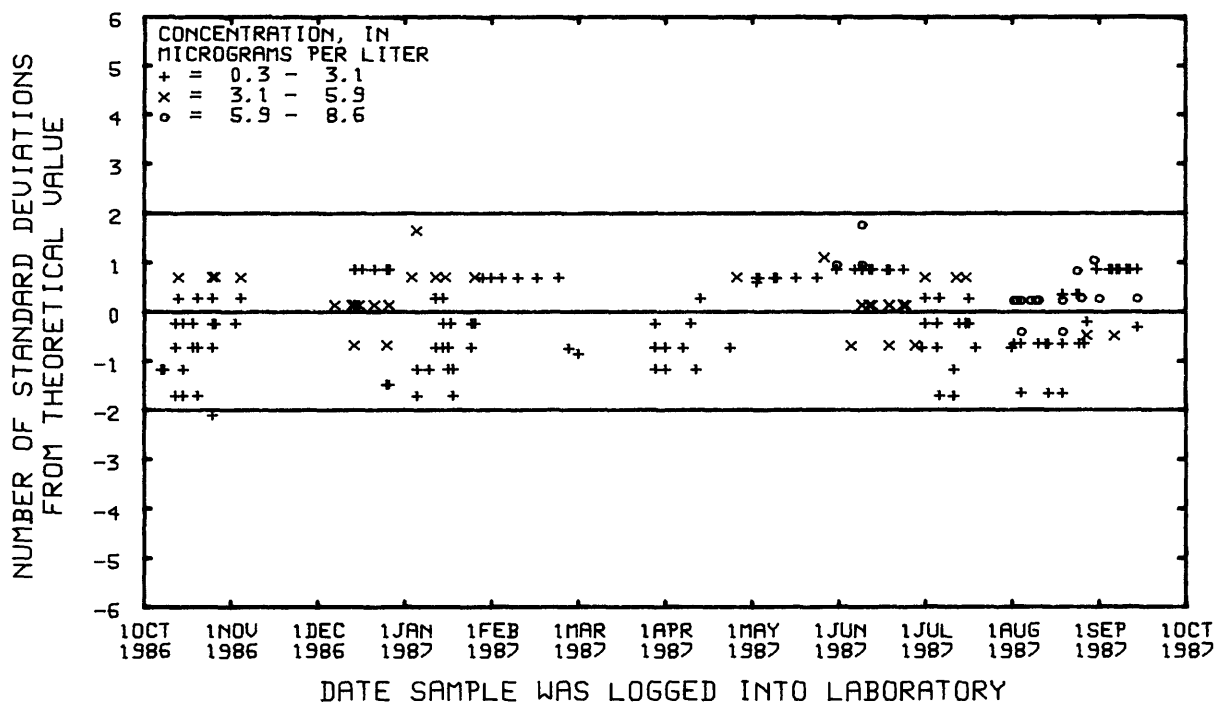


Figure 11.--Cadmium, dissolved,
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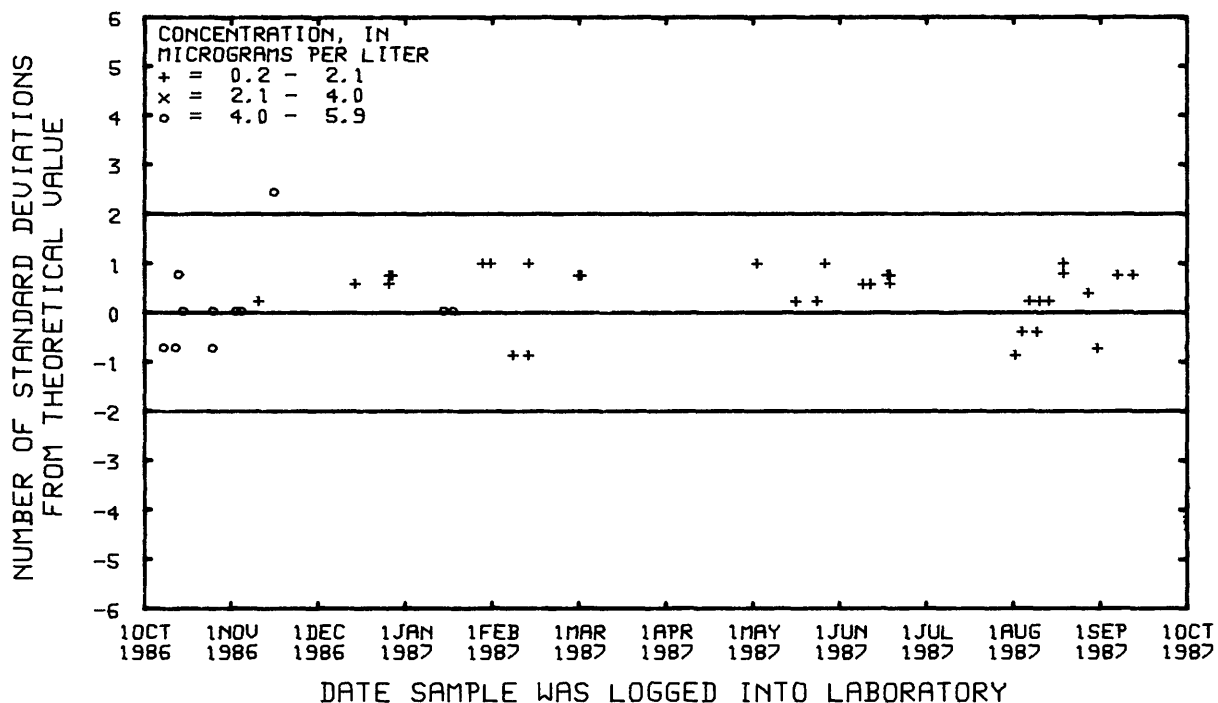


Figure 12.--Cadmium, dissolved,
(atomic absorption spectrometry)
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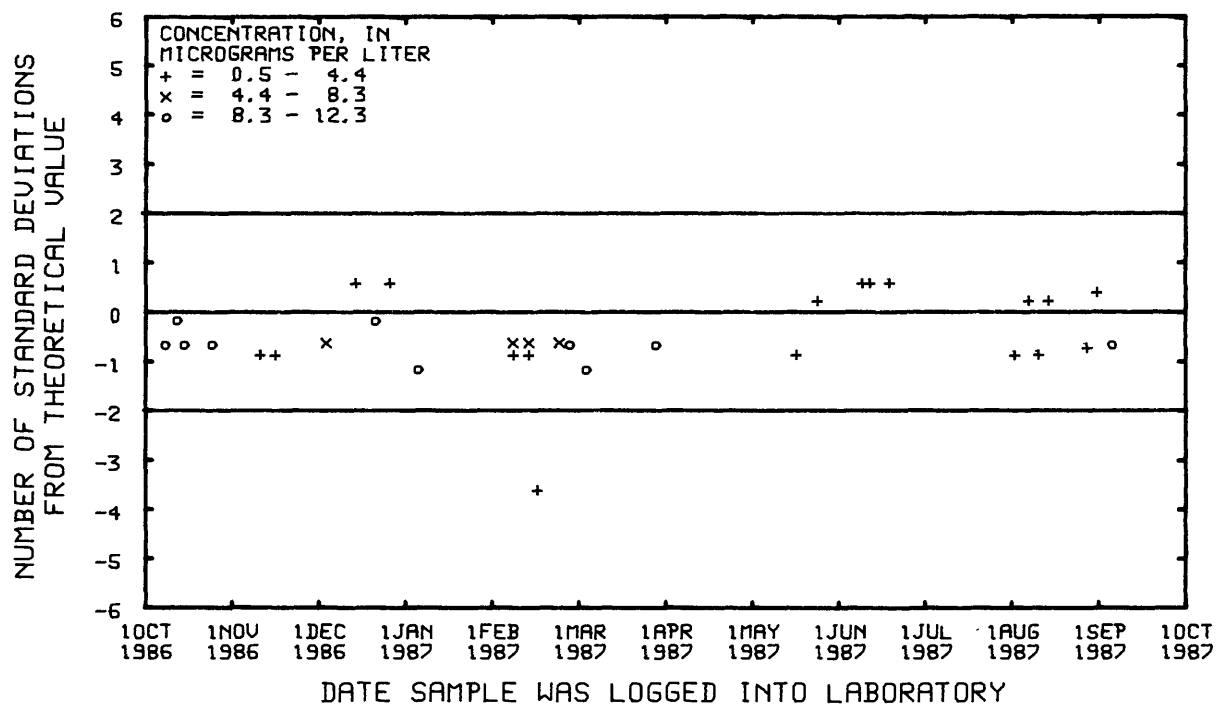


Figure 13.--Cadmium, total recoverable,
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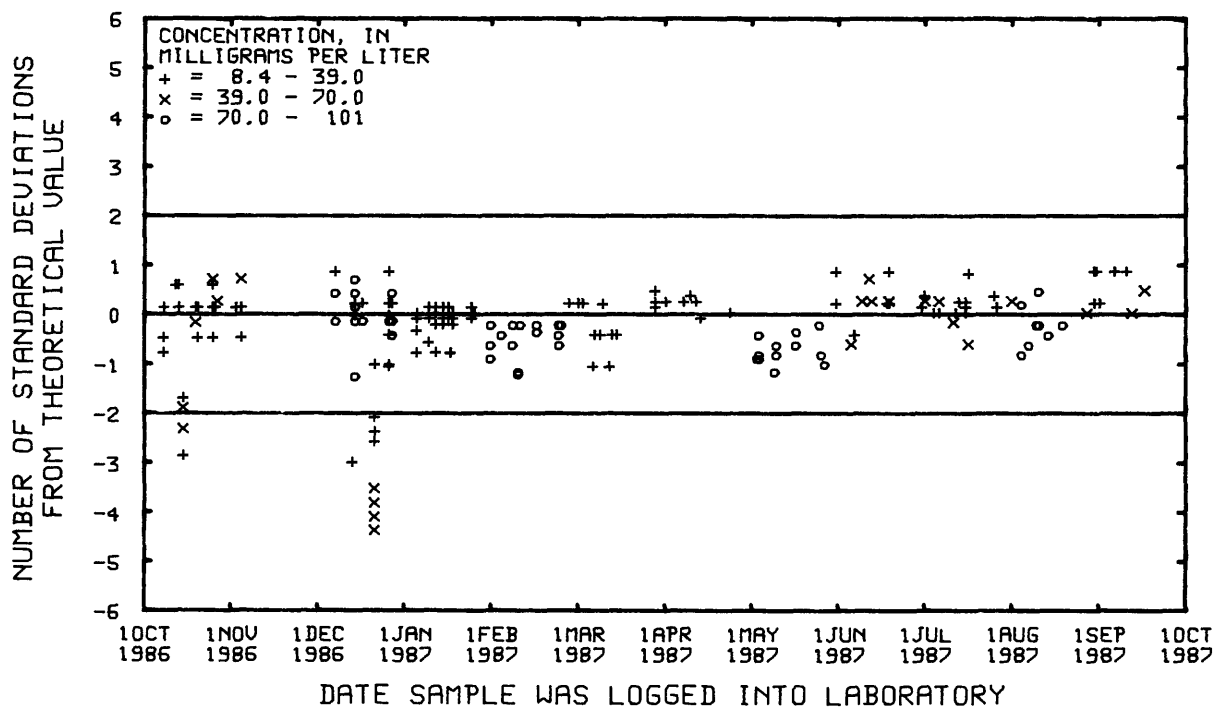


Figure 14.--Calcium, dissolved,
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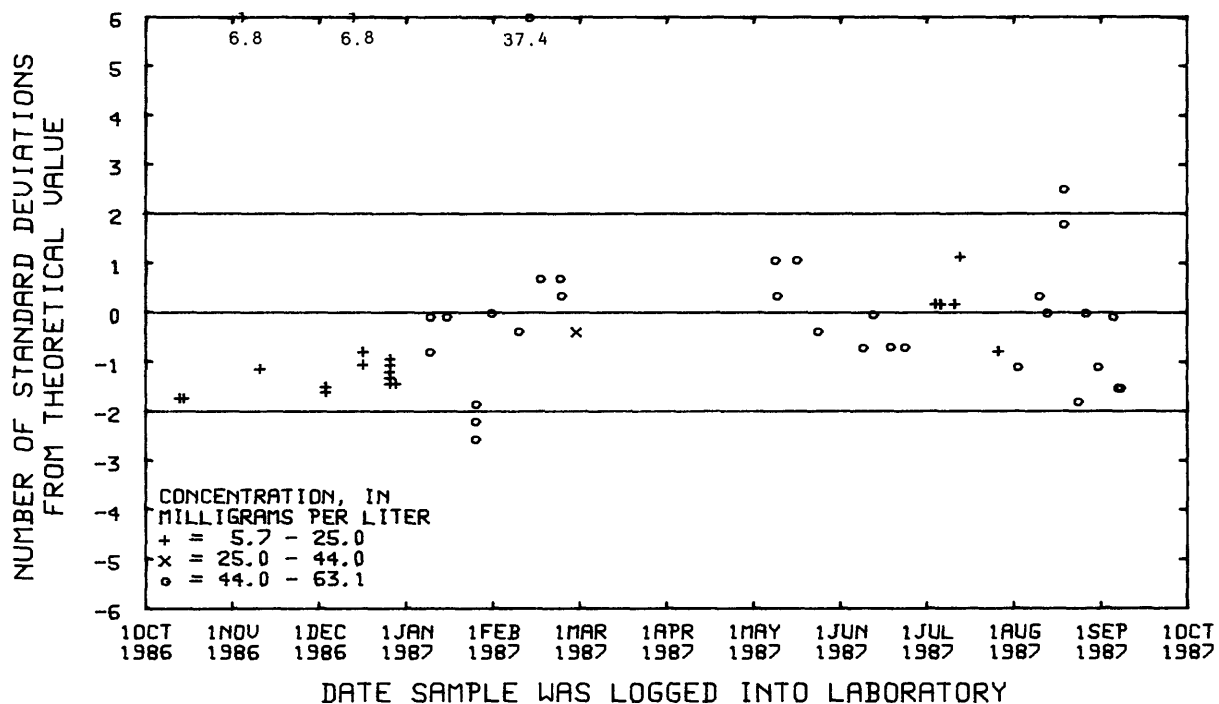


Figure 15.--Calcium, dissolved,
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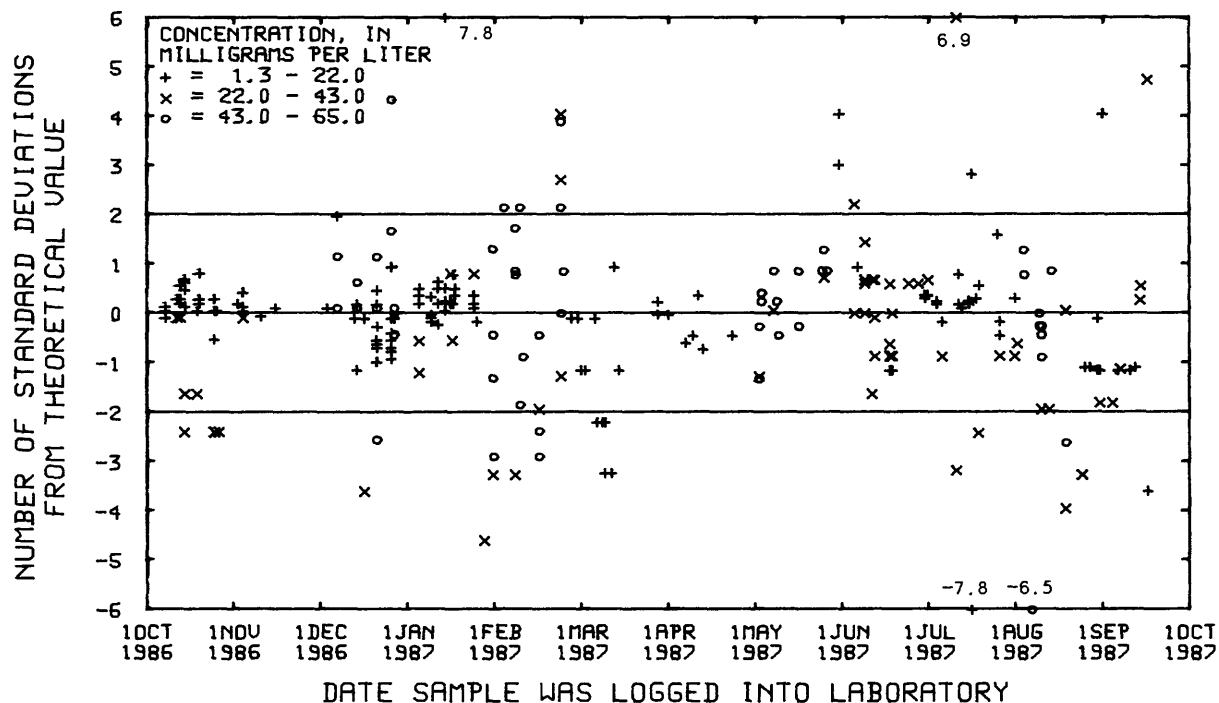


Figure 16.--Chloride, dissolved,
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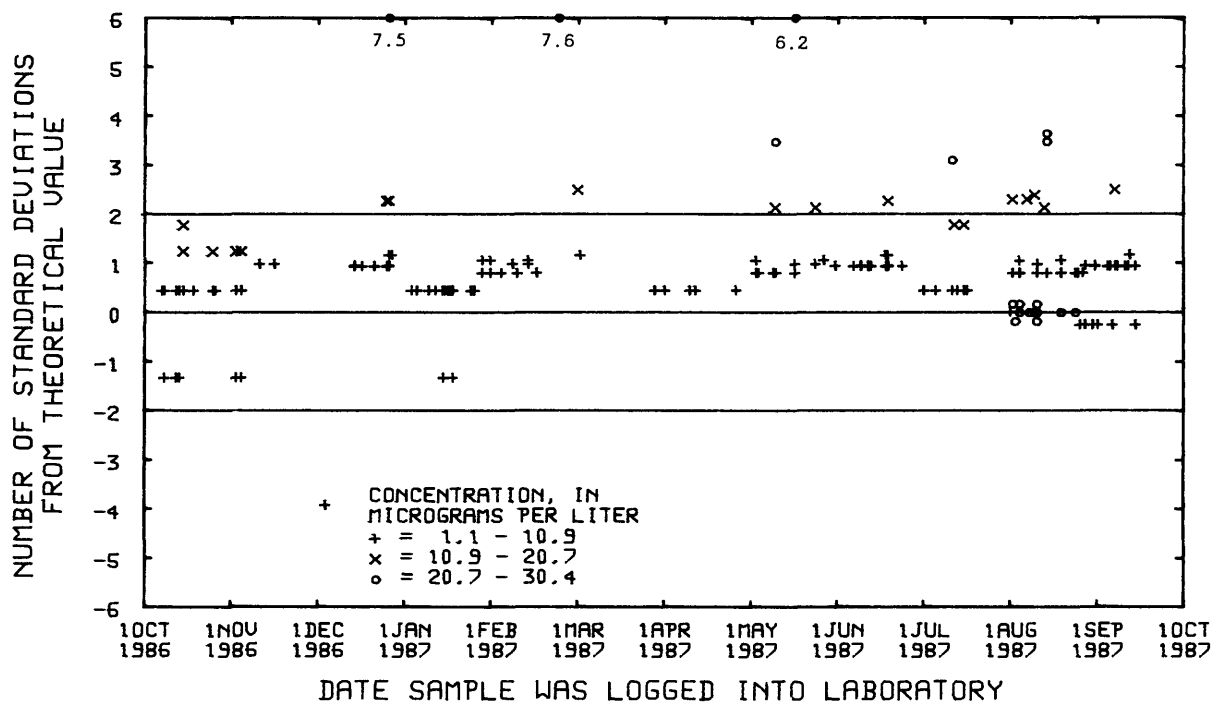


Figure 17.--Chromium, dissolved,
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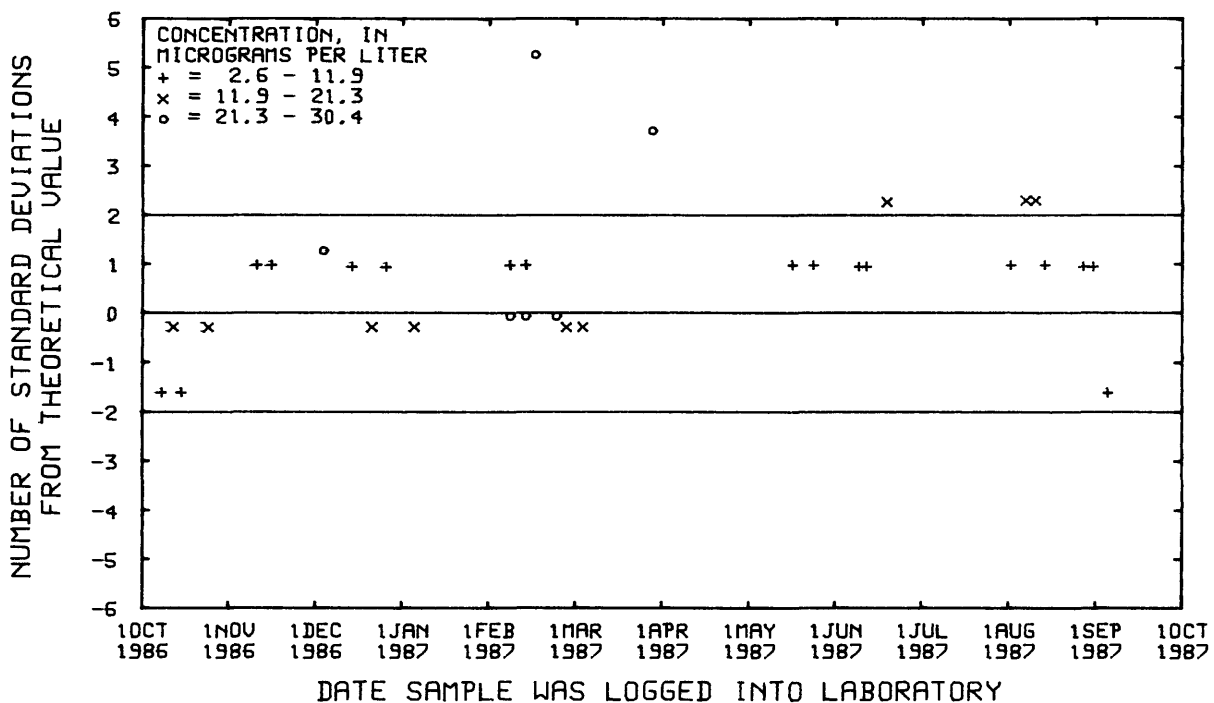


Figure 18.--Chromium, total recoverable,
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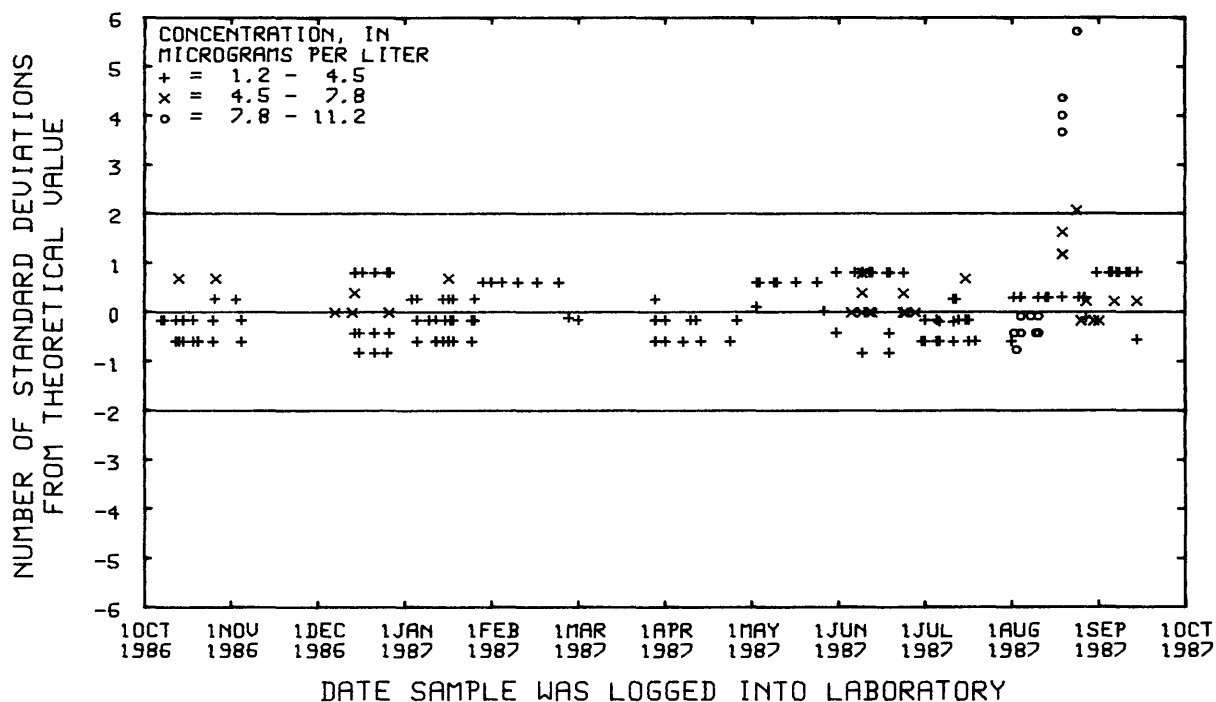


Figure 19.--Cobalt, dissolved,
 (inductively coupled plasma emission spectrometry)
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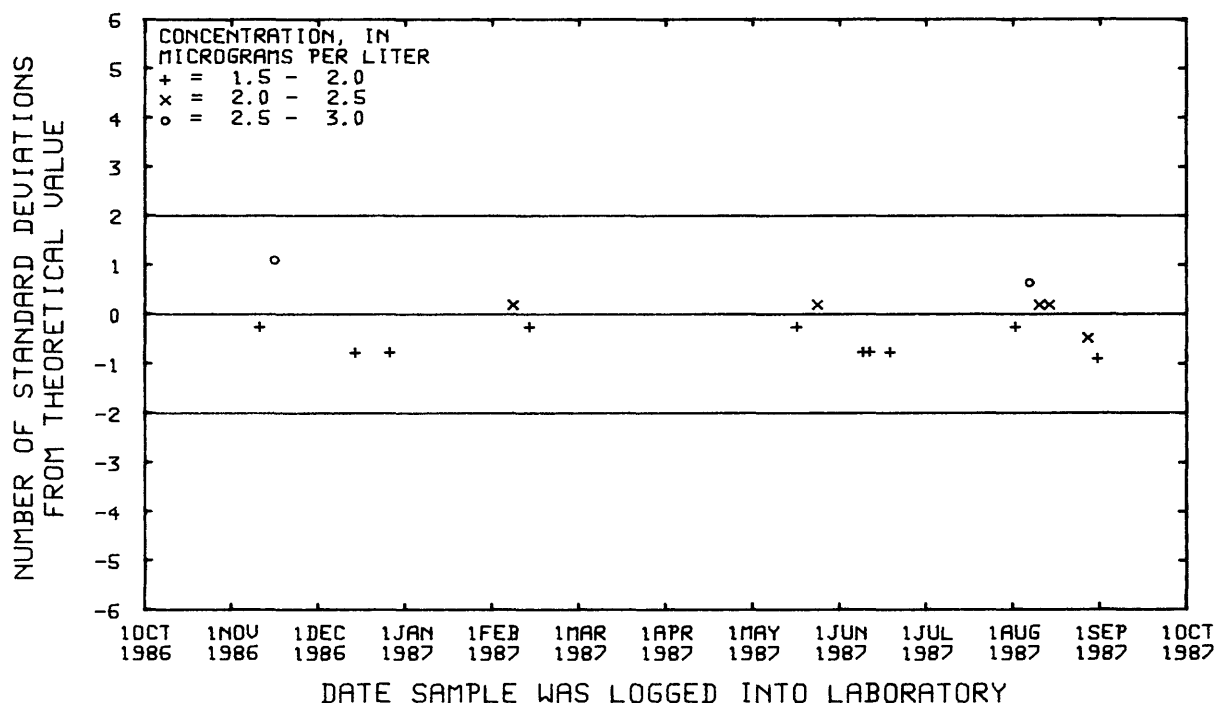


Figure 20.--Cobalt, dissolved,
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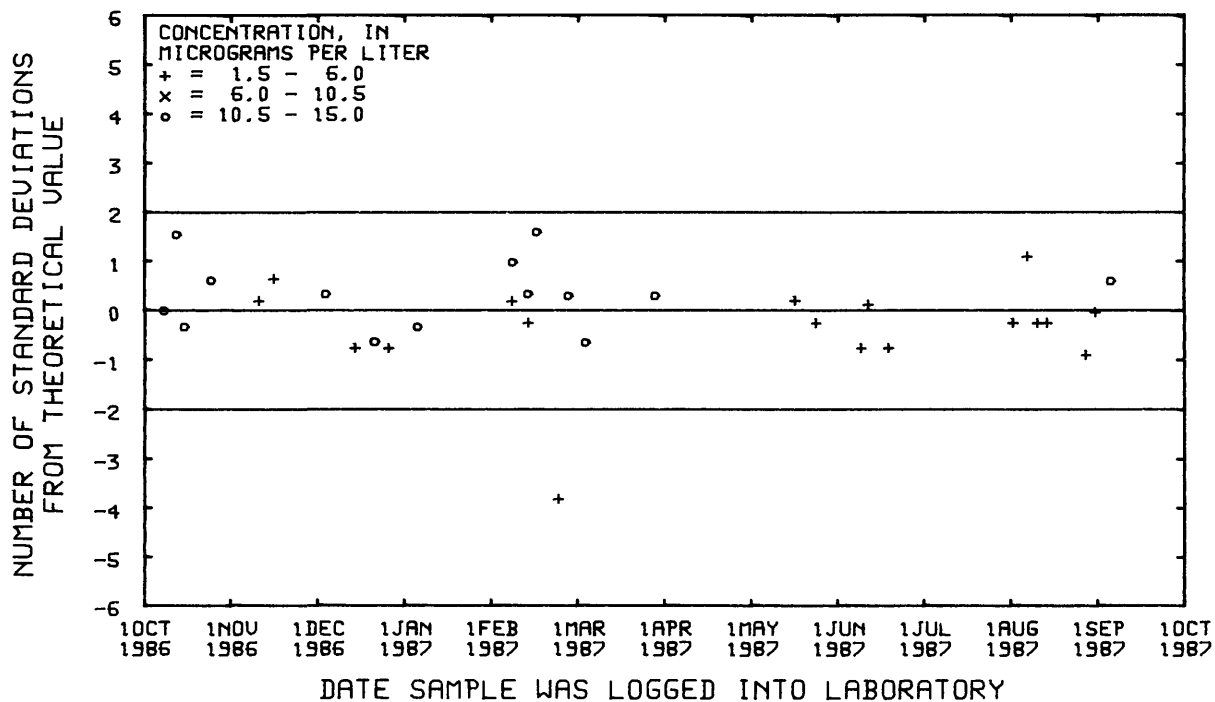


Figure 21.--Cobalt, total recoverable,
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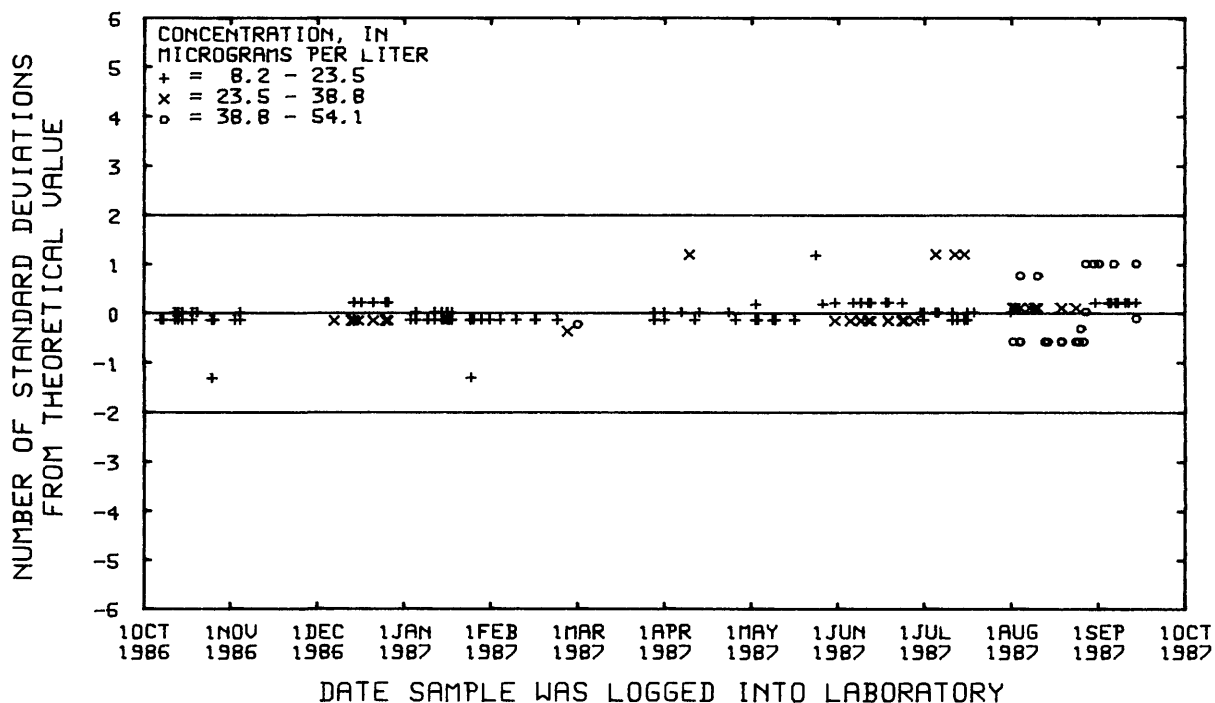


Figure 22.--Copper, dissolved,
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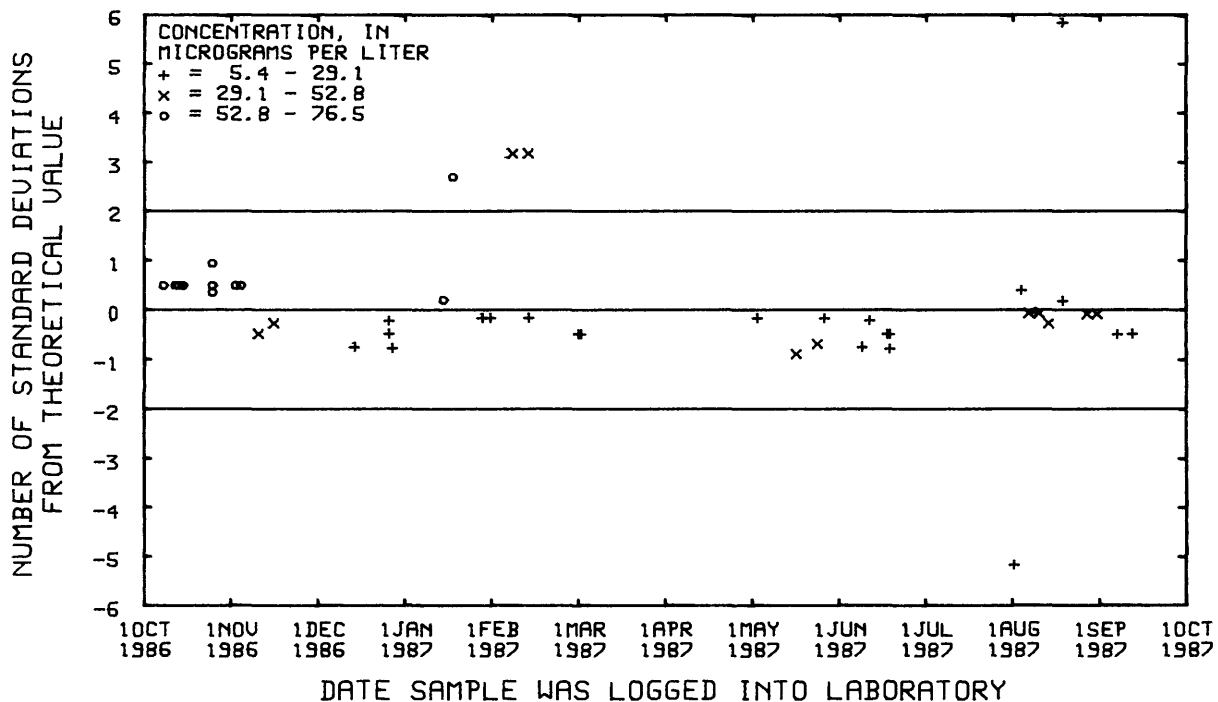


Figure 23.--Copper, dissolved,
 (atomic absorption spectrometry)
 data from the National Water Quality Laboratory.

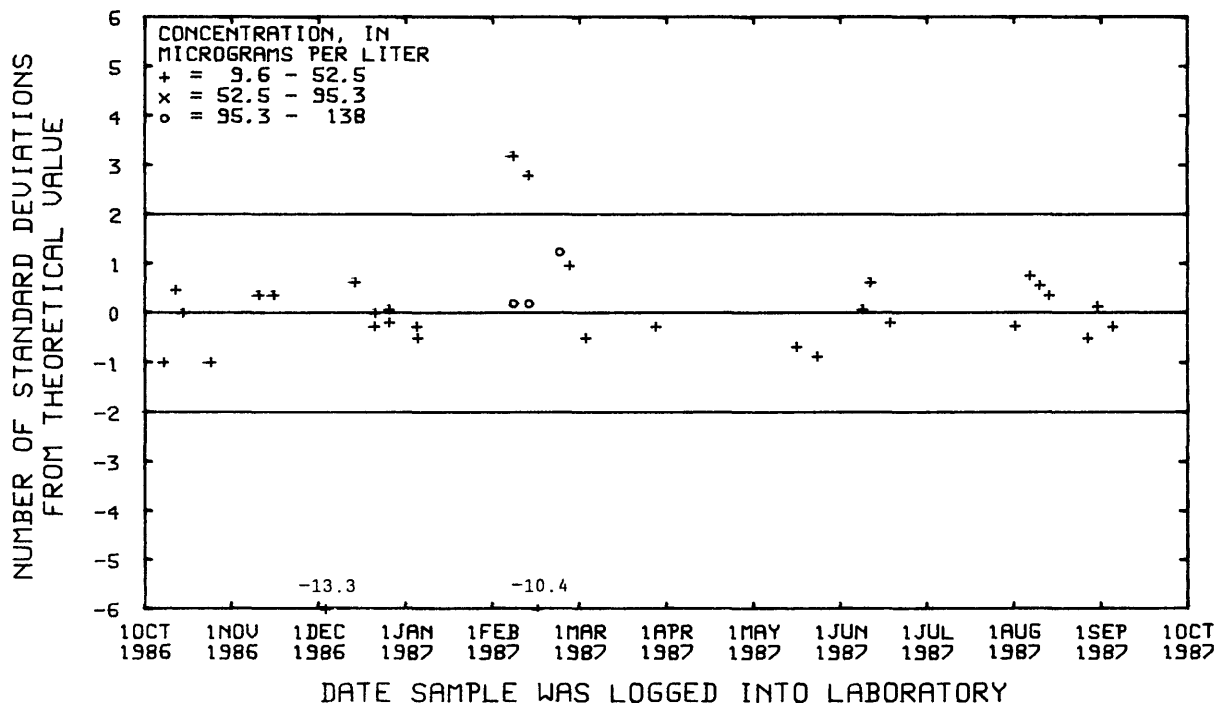


Figure 24.--Copper, total recoverable,
 data from the National Water Quality Laboratory.

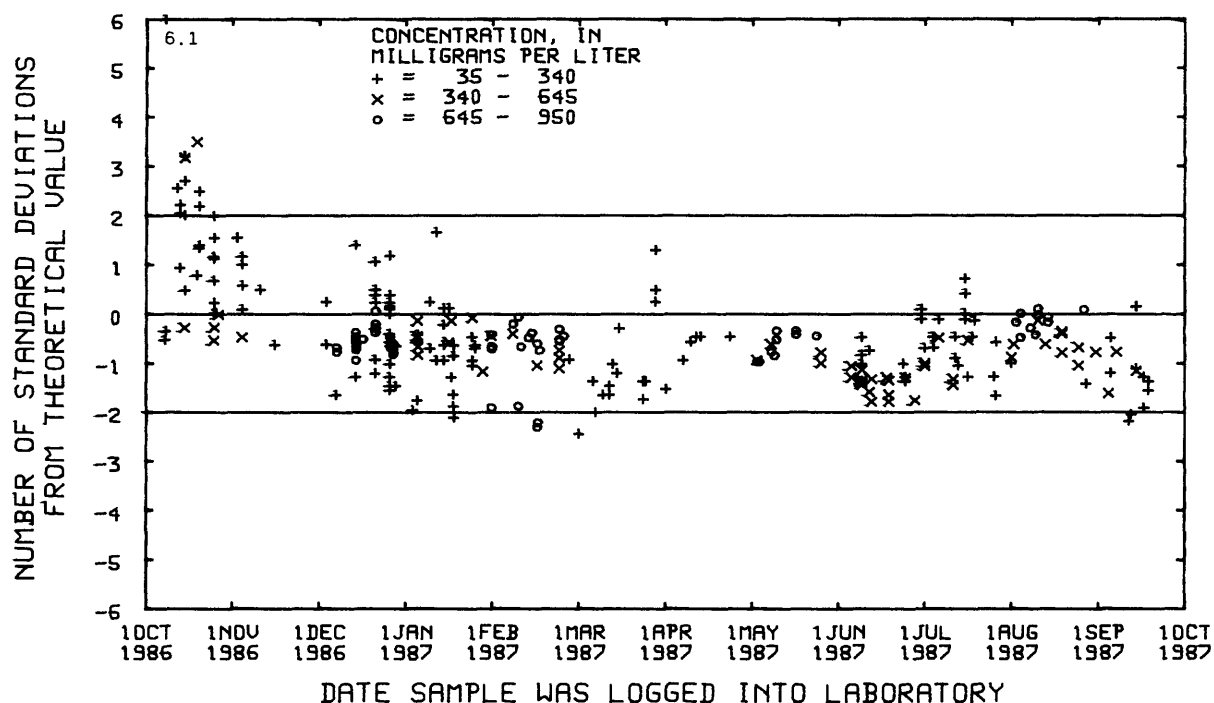


Figure 25.--Dissolved solids
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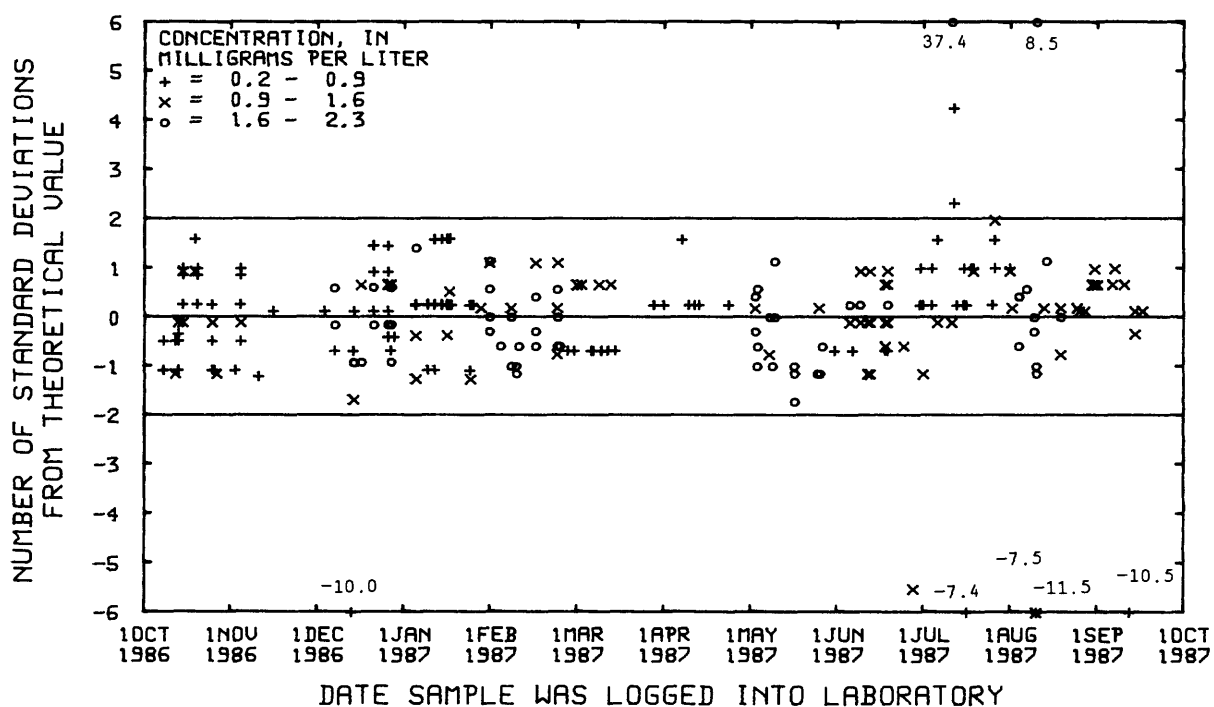


Figure 26.--Fluoride, dissolved,
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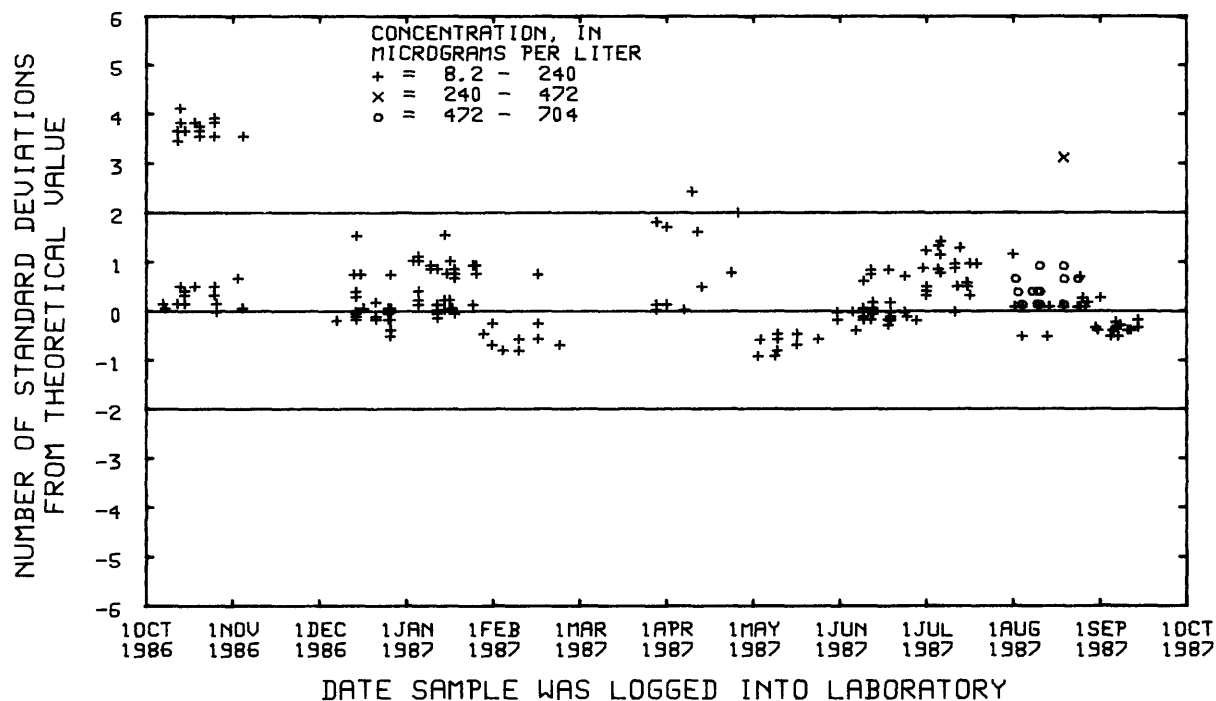


Figure 27.--Iron, dissolved,
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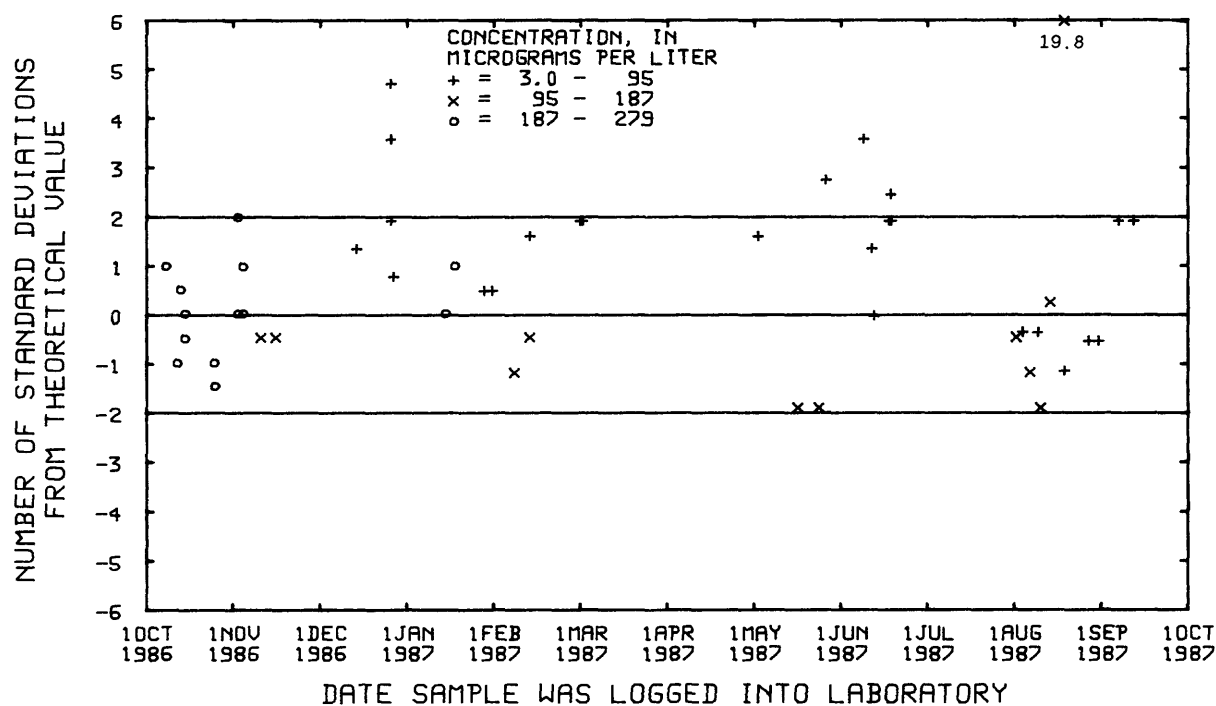


Figure 28.--Iron, dissolved,
 (atomic absorption spectrometry)
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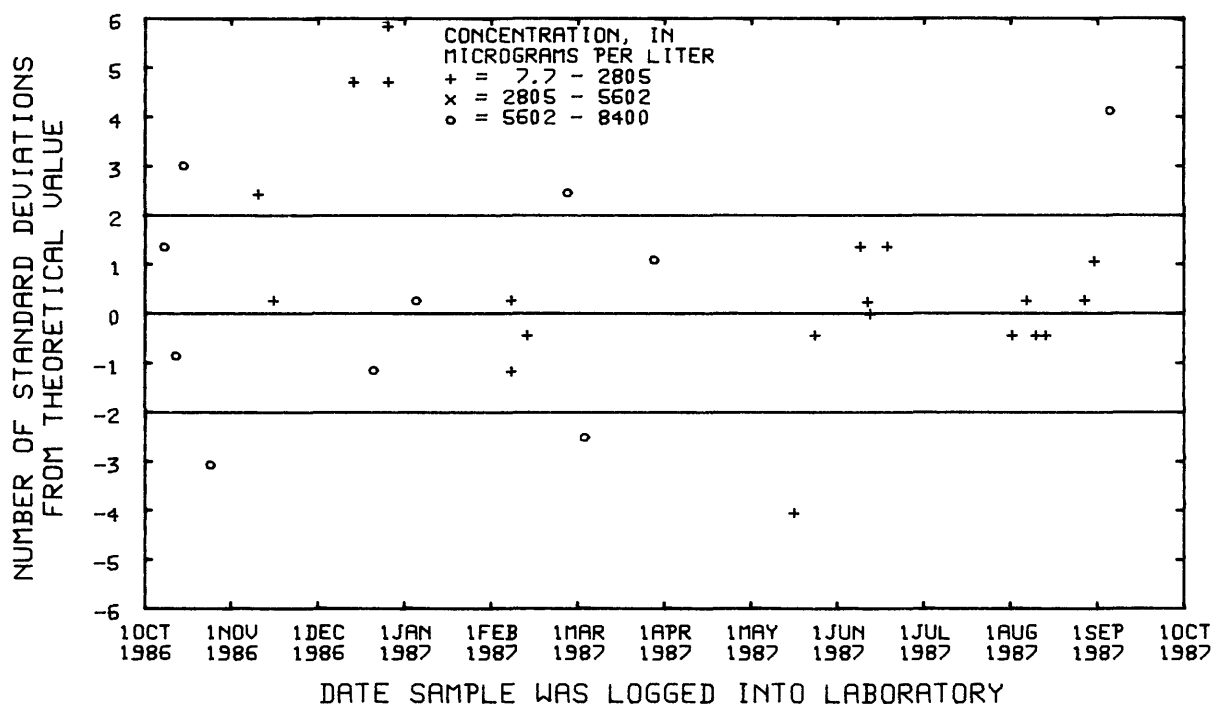


Figure 29.--Iron, total recoverable,
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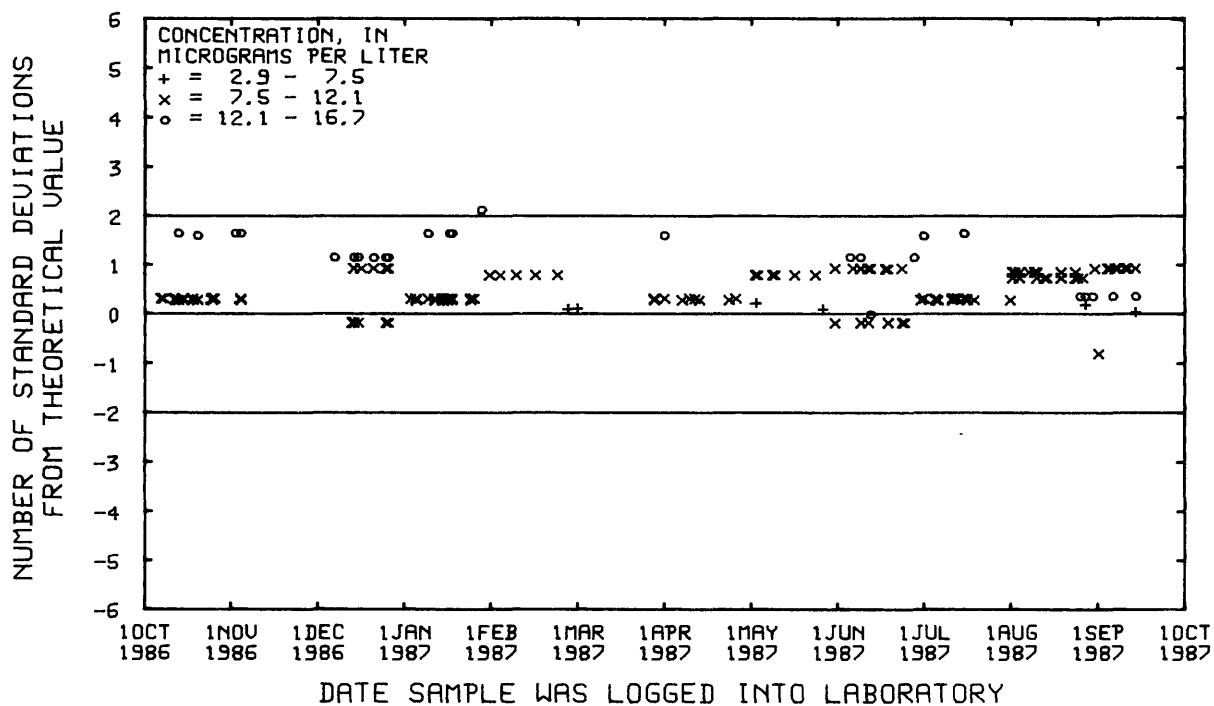


Figure 30.--Lead, dissolved,
 (inductively coupled plasma emission spectrometry)
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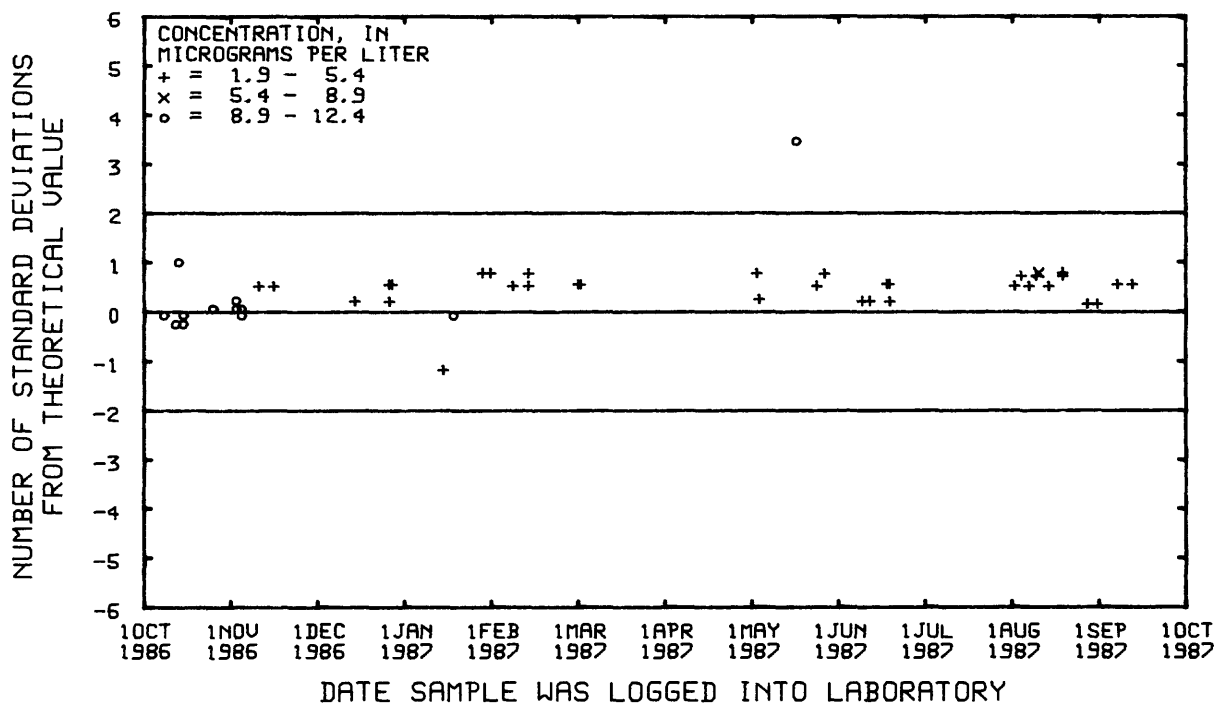


Figure 31.--Lead, dissolved,
(atomic absorption spectrometry)
data from the National Water Quality Laboratory.

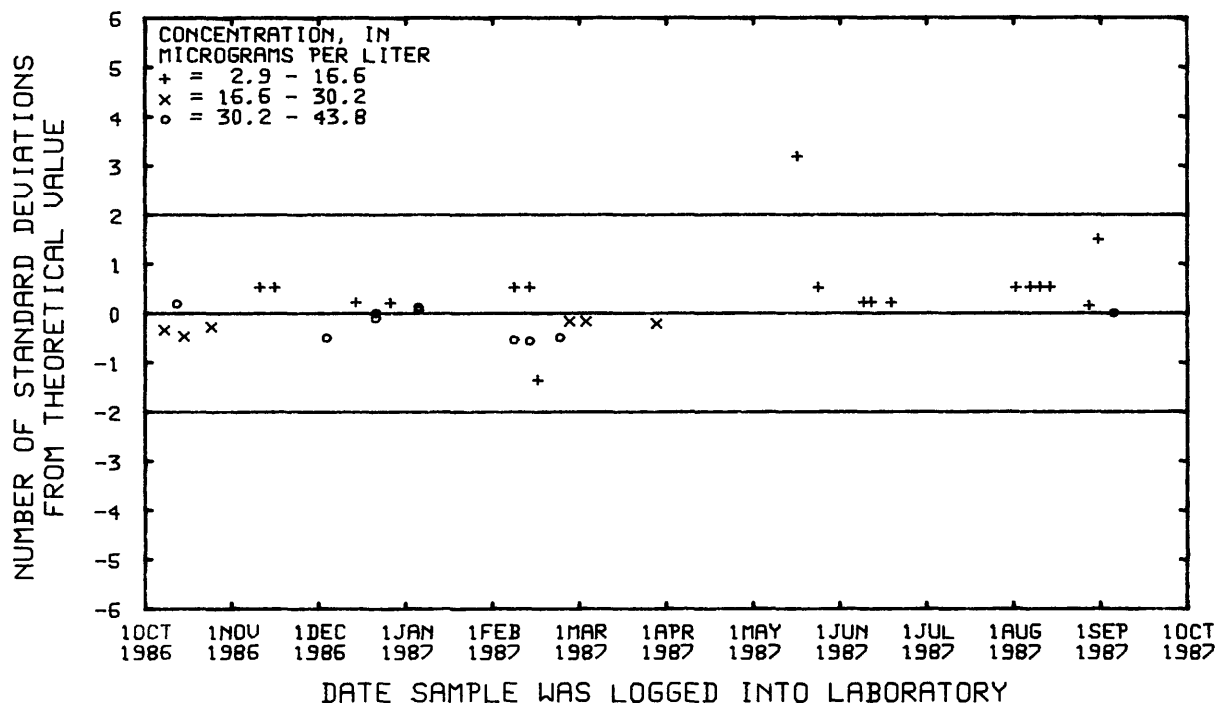


Figure 32.--Lead, total recoverable,
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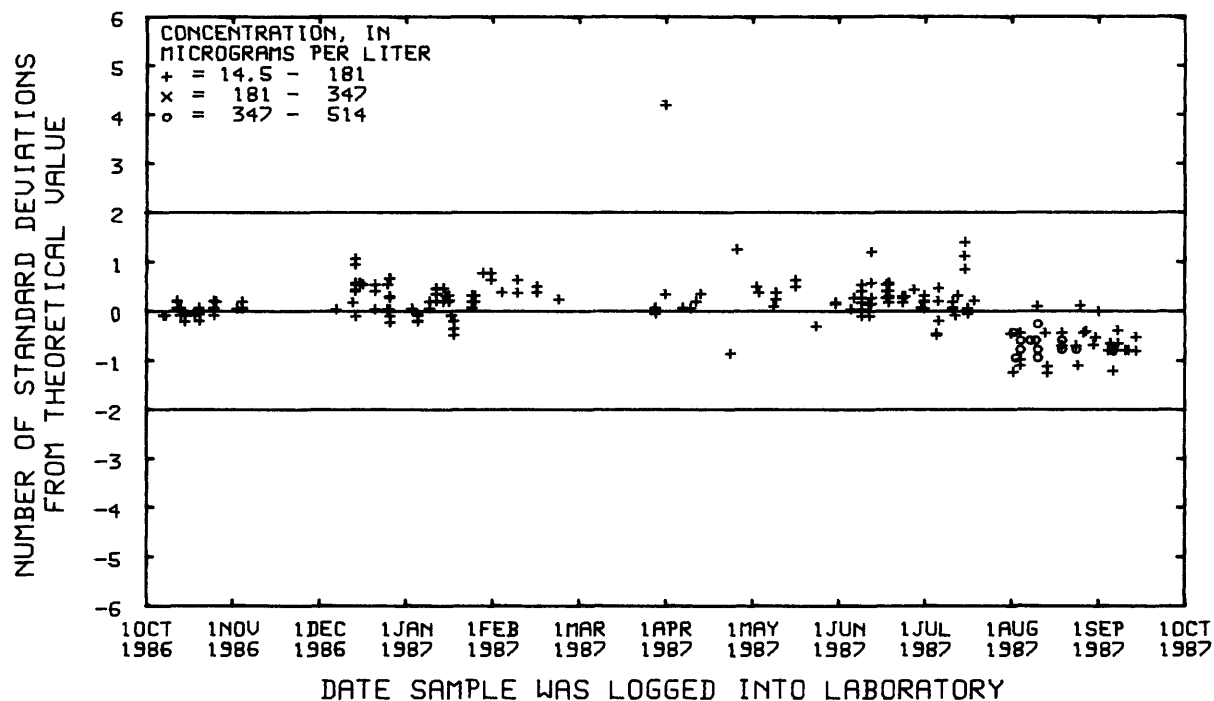


Figure 33.--Lithium, dissolved,
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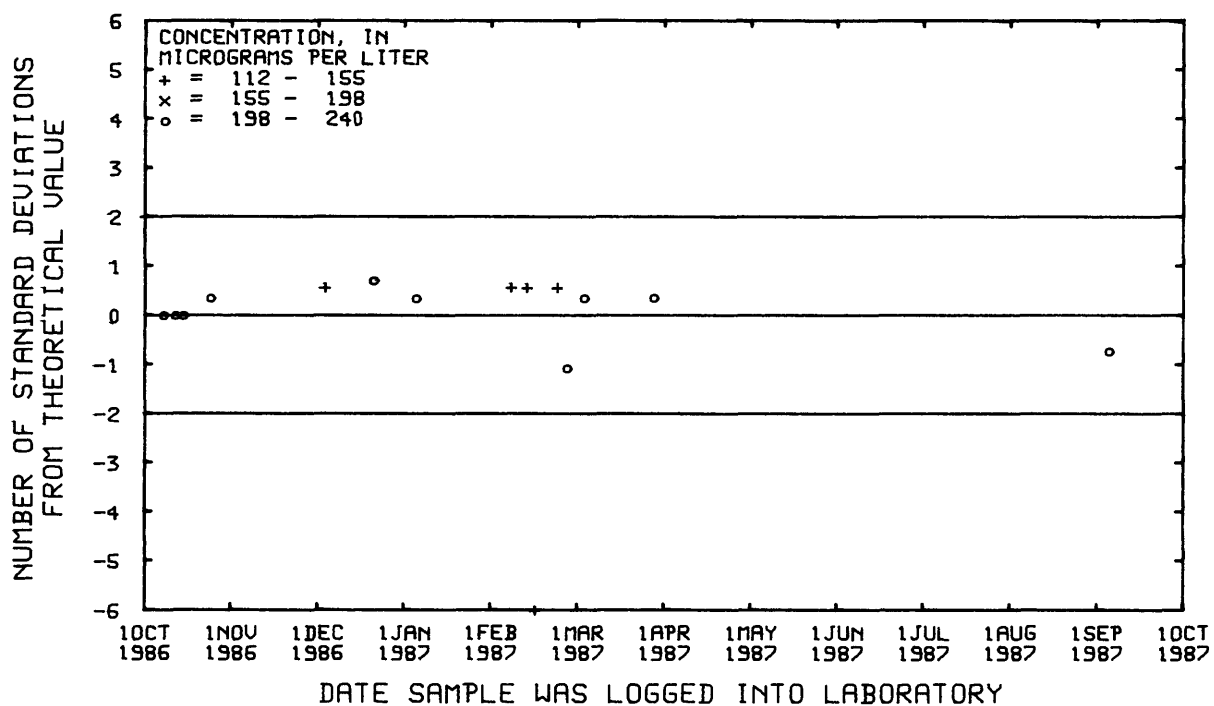


Figure 34.--Lithium, total recoverable,
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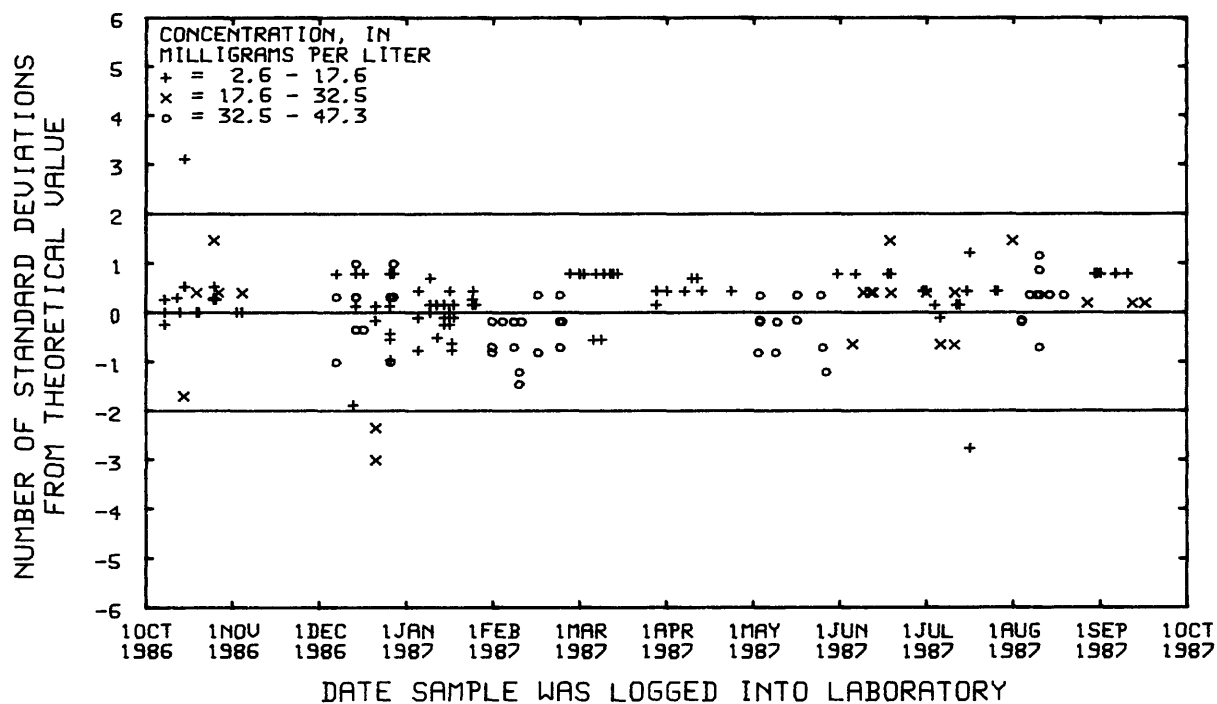


Figure 35.--Magnesium, dissolved,
(inductively coupled plasma emission spectrometry)
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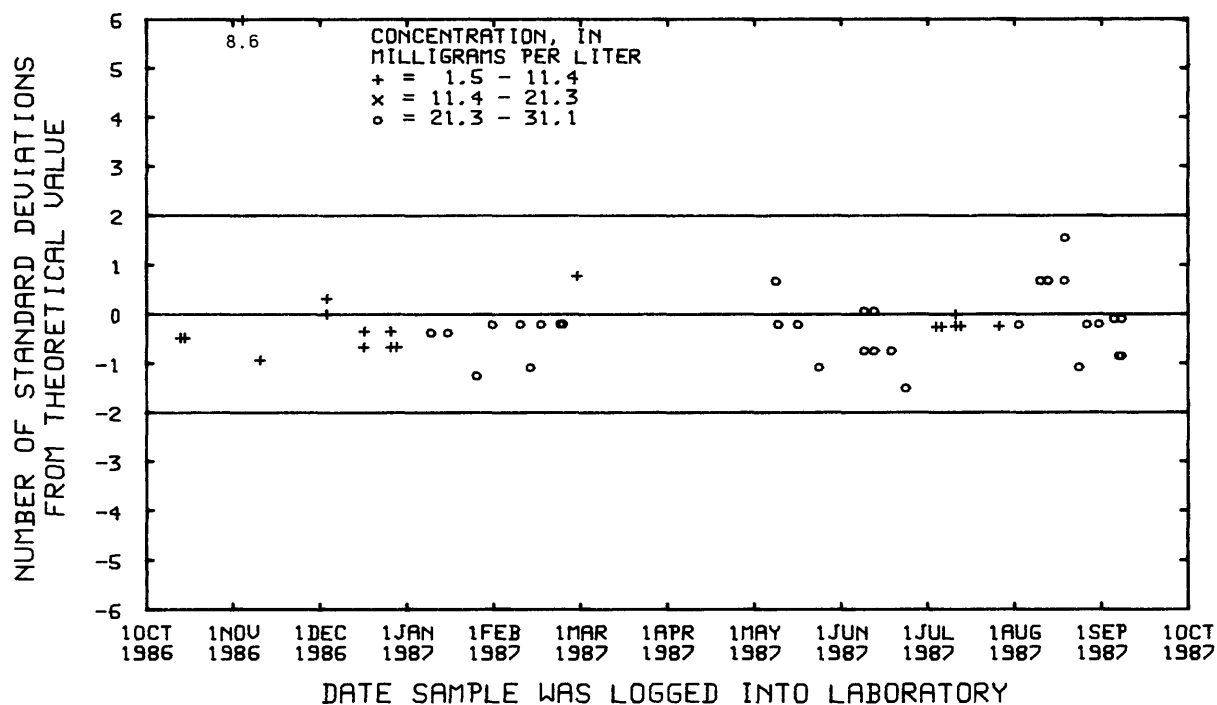


Figure 36.--Magnesium, dissolved,
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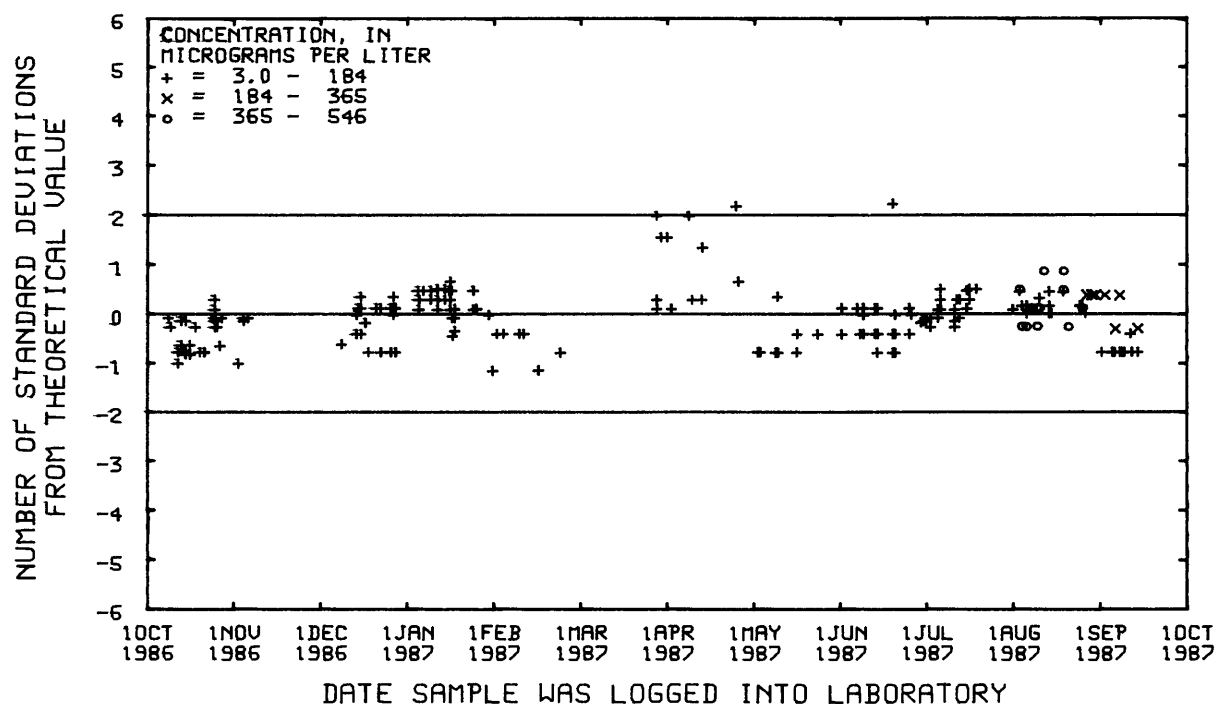


Figure 37.--Manganese, dissolved,
(inductively coupled plasma emission spectrometry)
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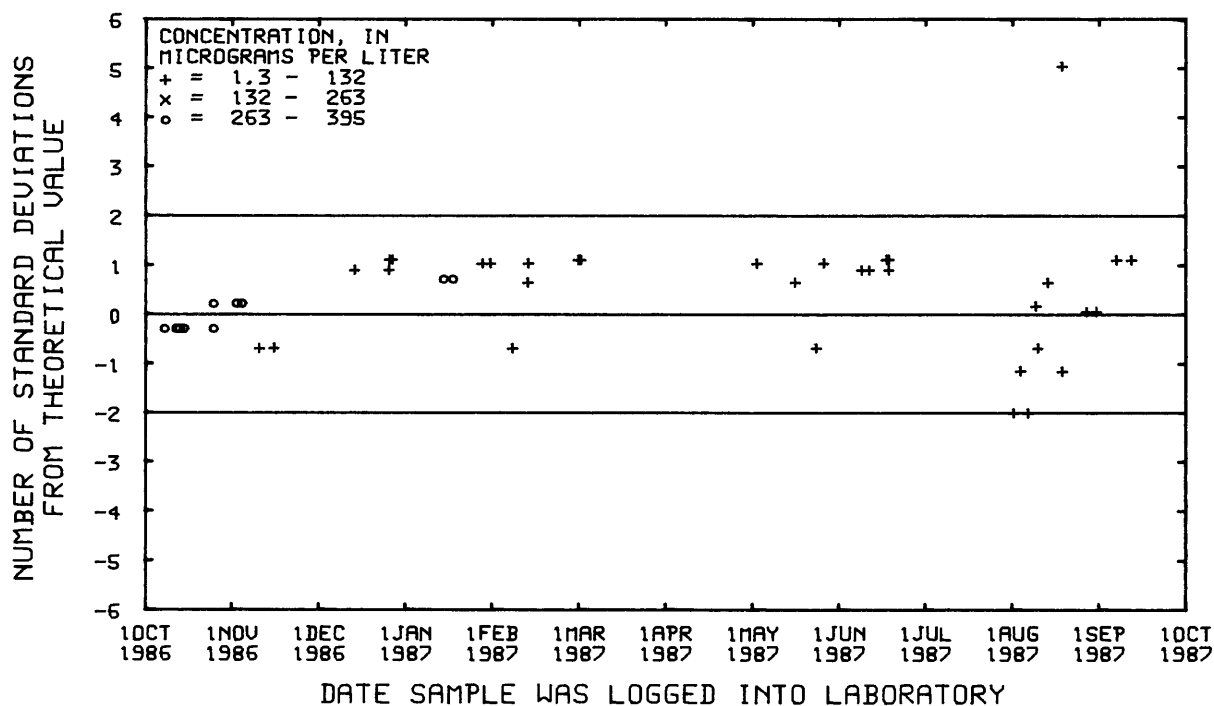


Figure 38.--Manganese, dissolved,
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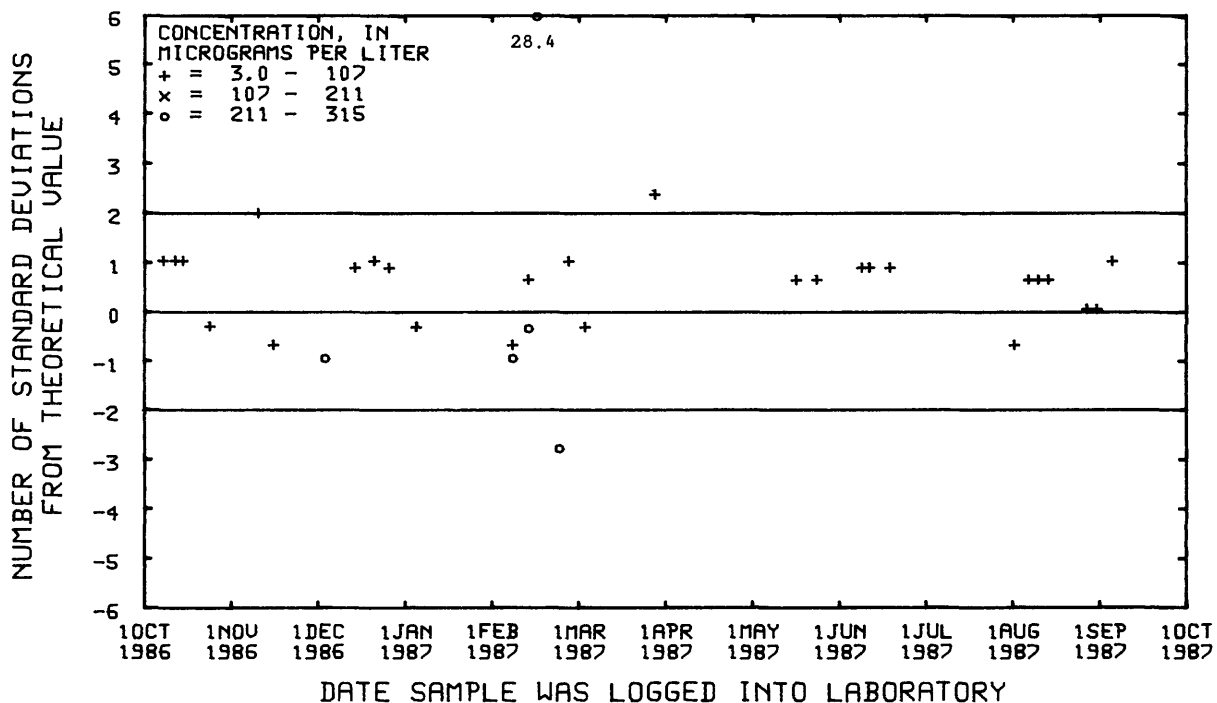


Figure 39.--Manganese, total recoverable,
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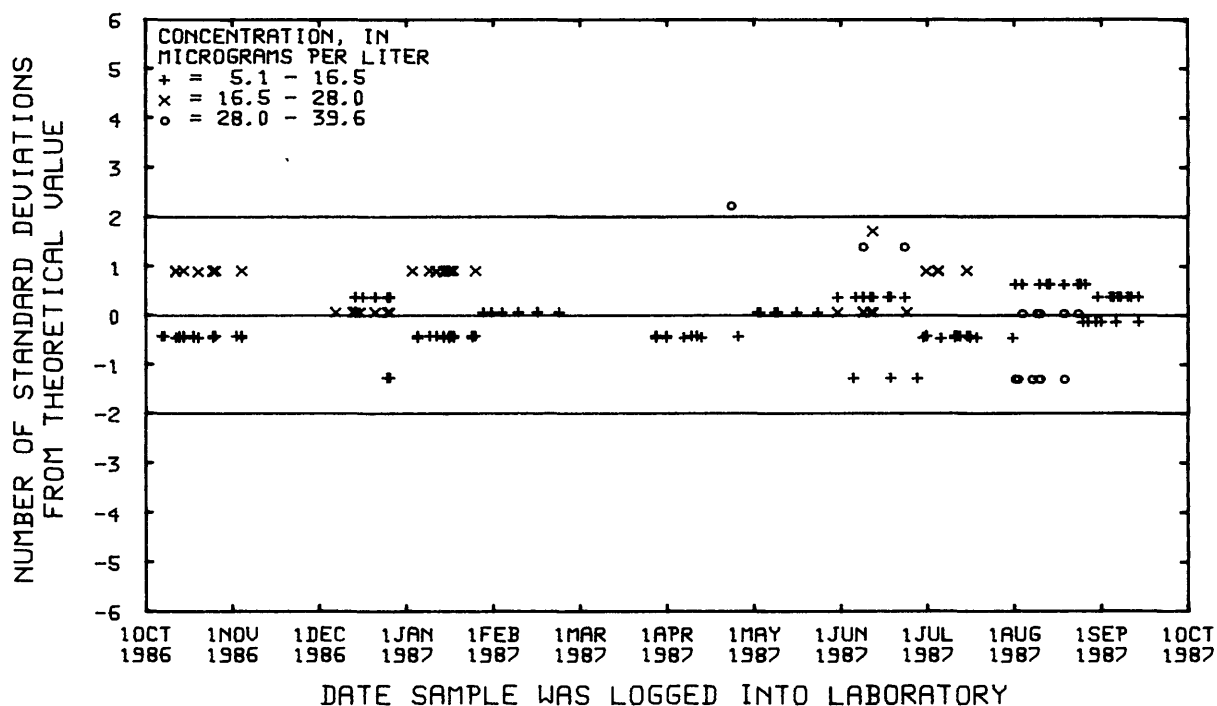


Figure 40.--Molybdenum, dissolved,
(inductively coupled plasma emission spectrometry)
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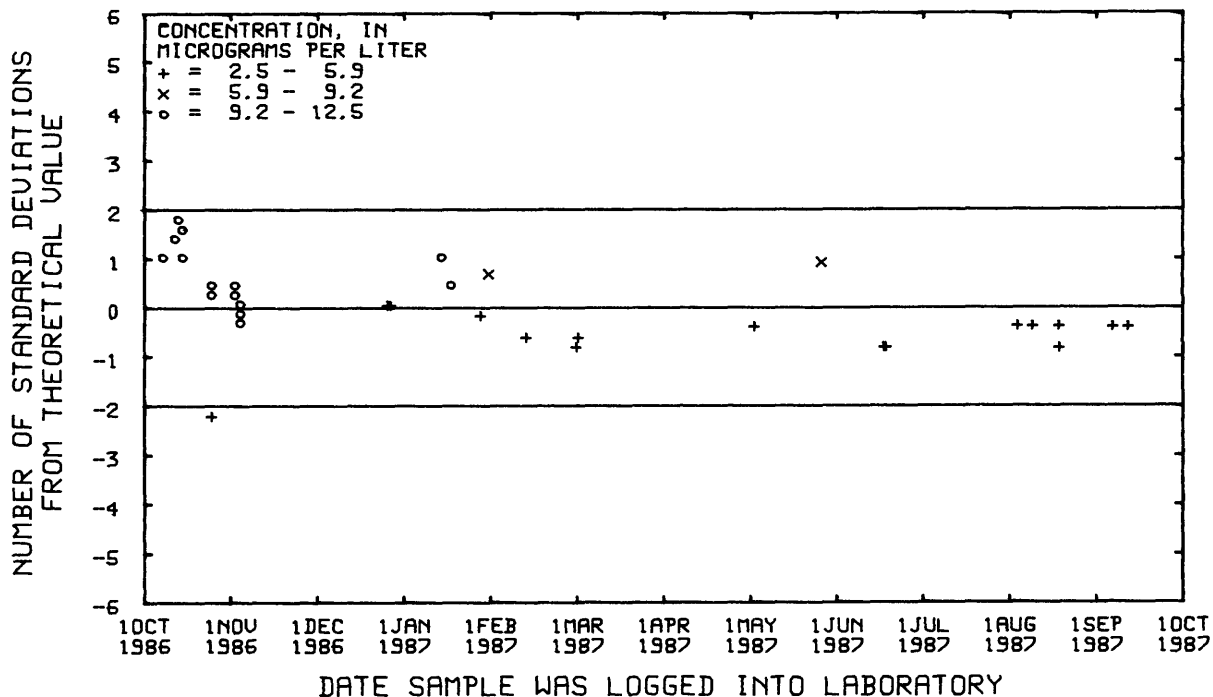


Figure 41.--Molybdenum, dissolved,
(atomic absorption spectrometry)
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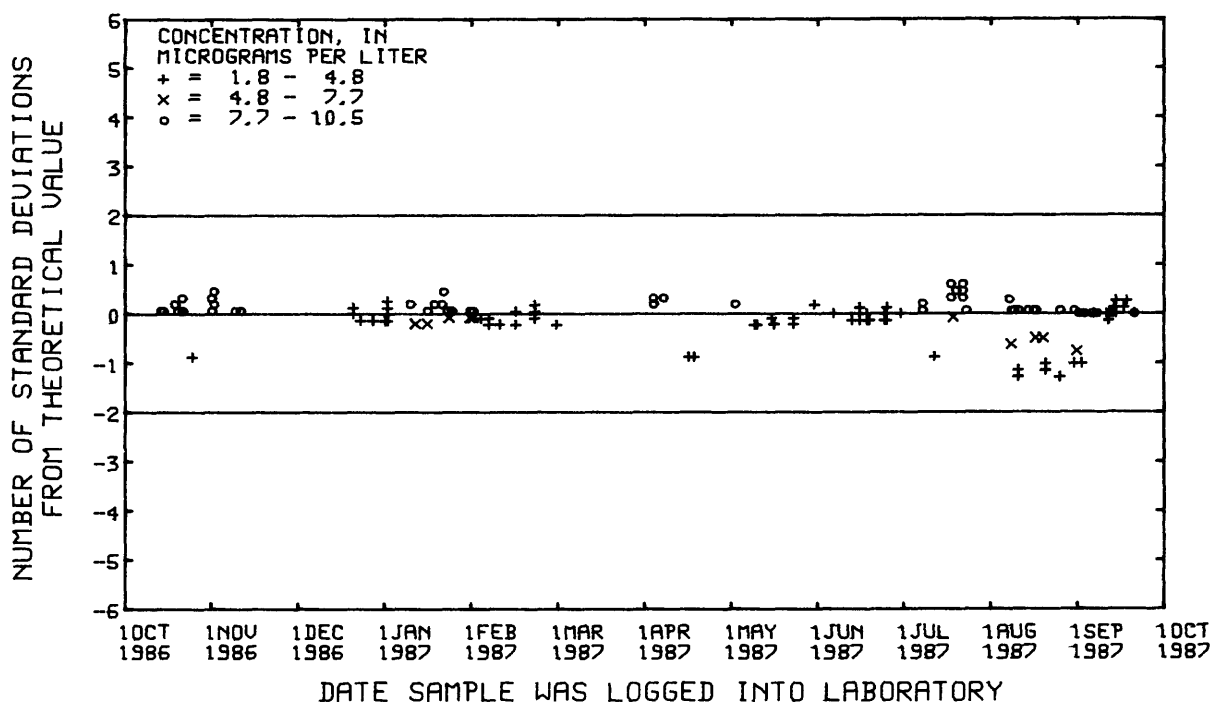
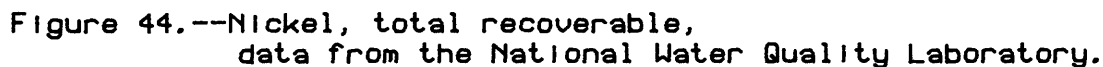
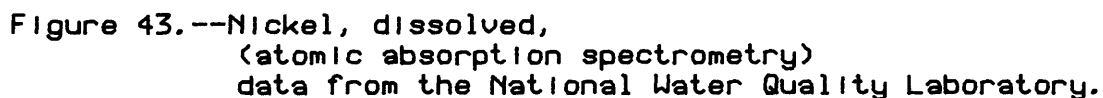


Figure 42.--Nickel, dissolved,
(inductively coupled plasma emission spectrometry)
data from the National Water Quality Laboratory.



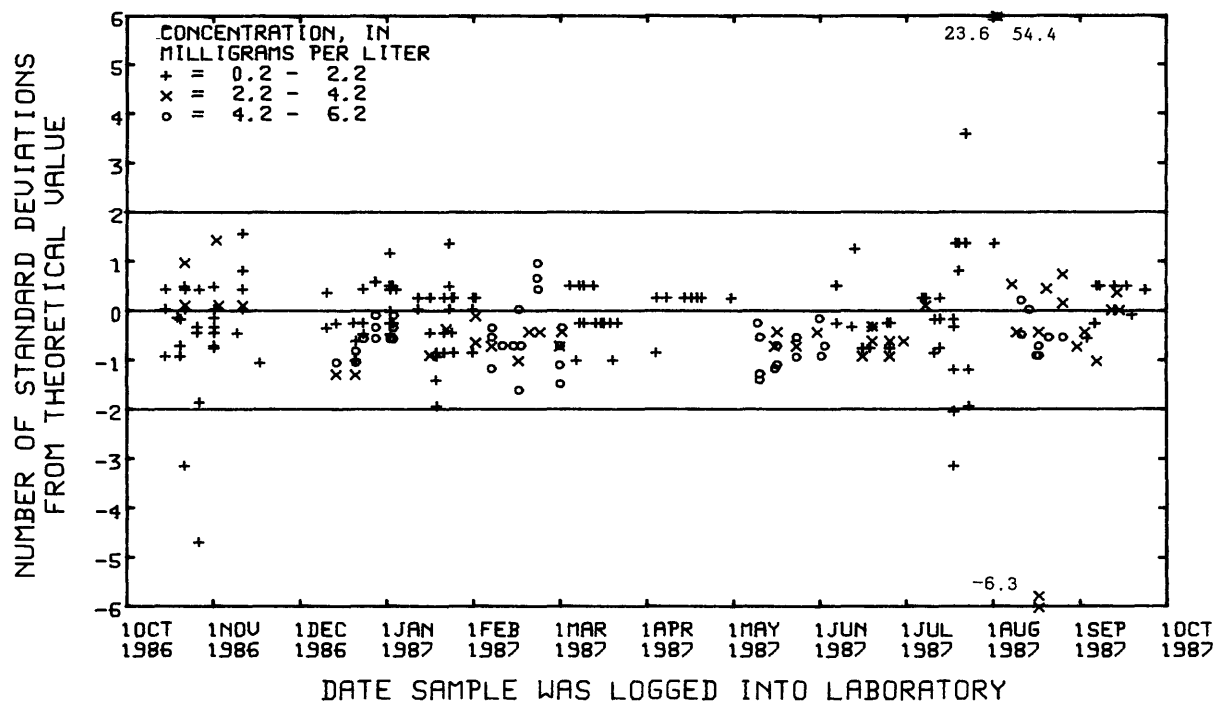


Figure 45.--Potassium, dissolved,
data from the National Water Quality Laboratory.

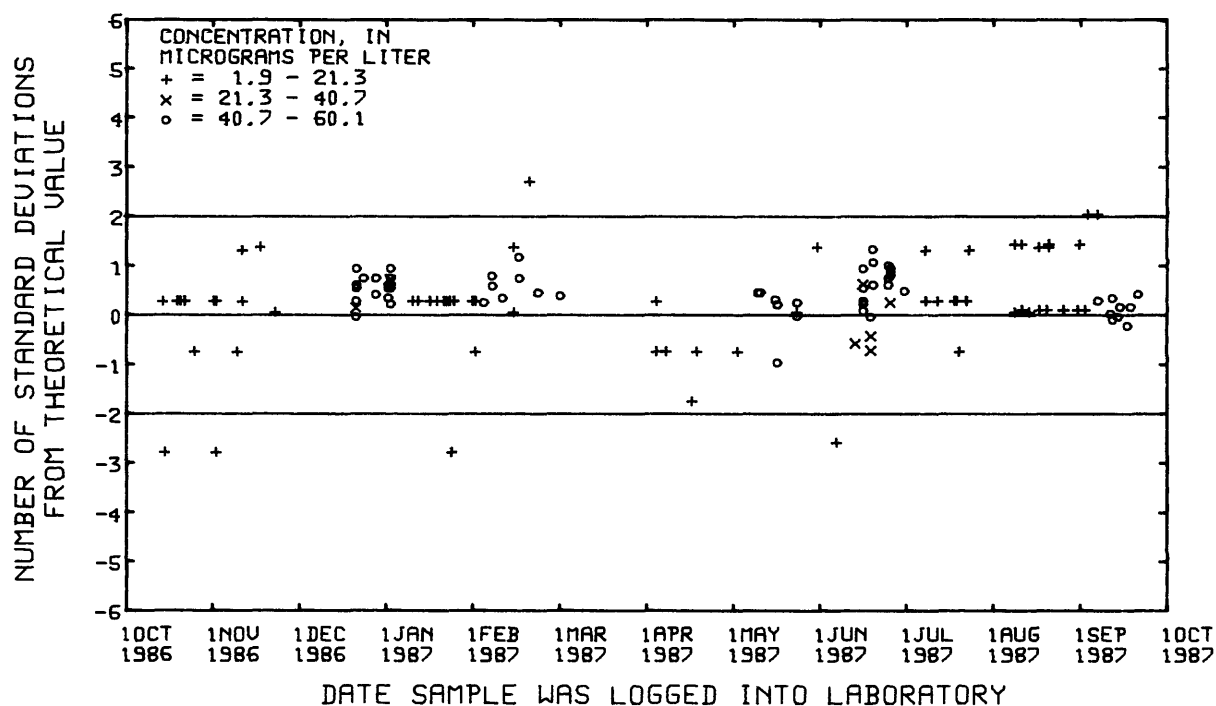


Figure 46.--Selenium, dissolved,
data from the National Water Quality Laboratory.

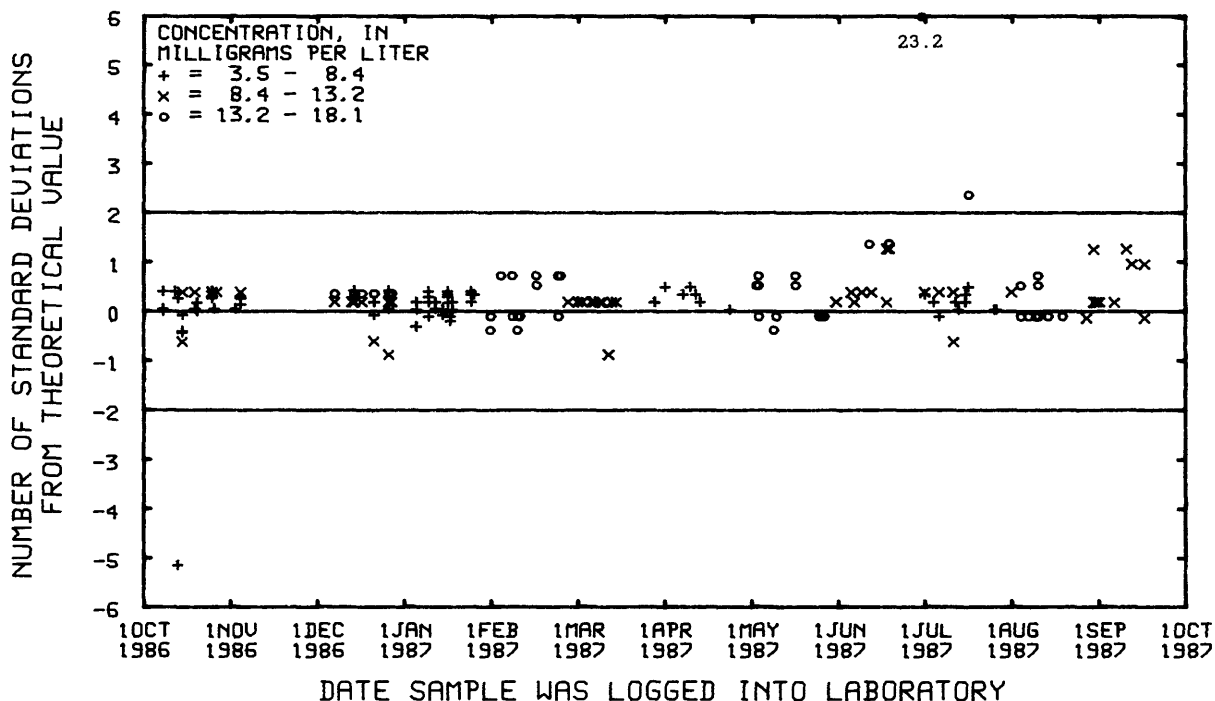


Figure 47.--Silica, dissolved,
 (inductively coupled plasma emission spectrometry)
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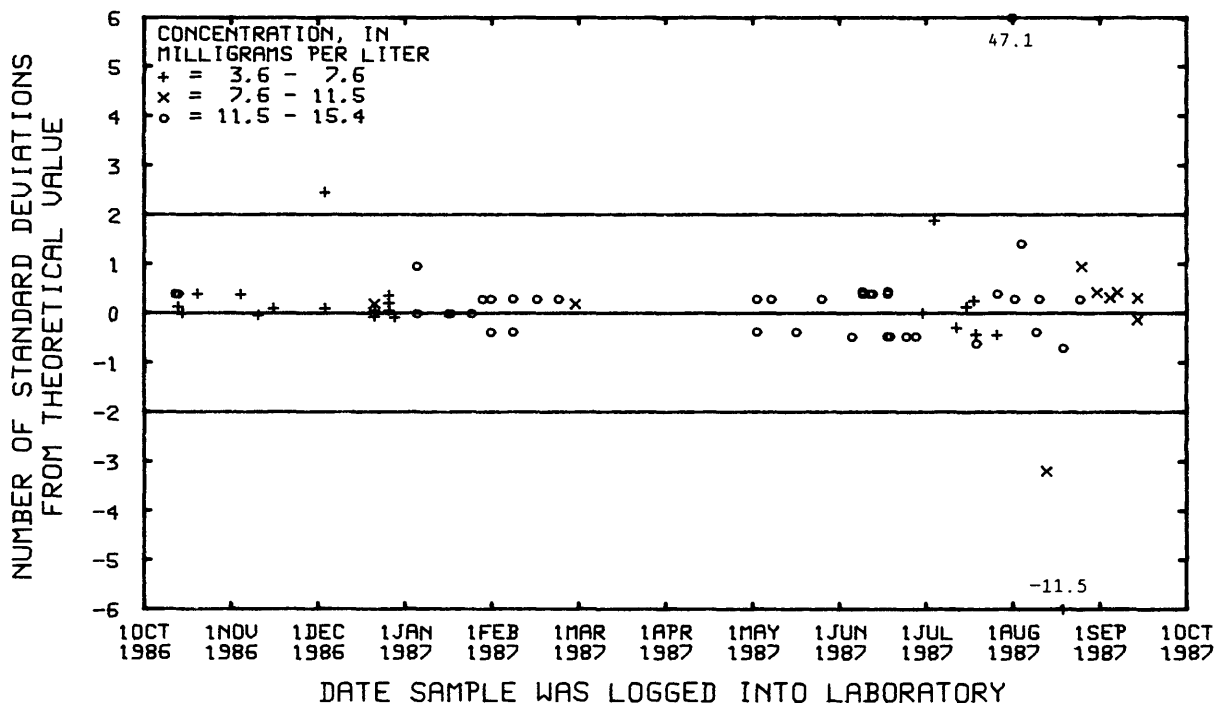


Figure 48.--Silica, dissolved, (colorimetry)
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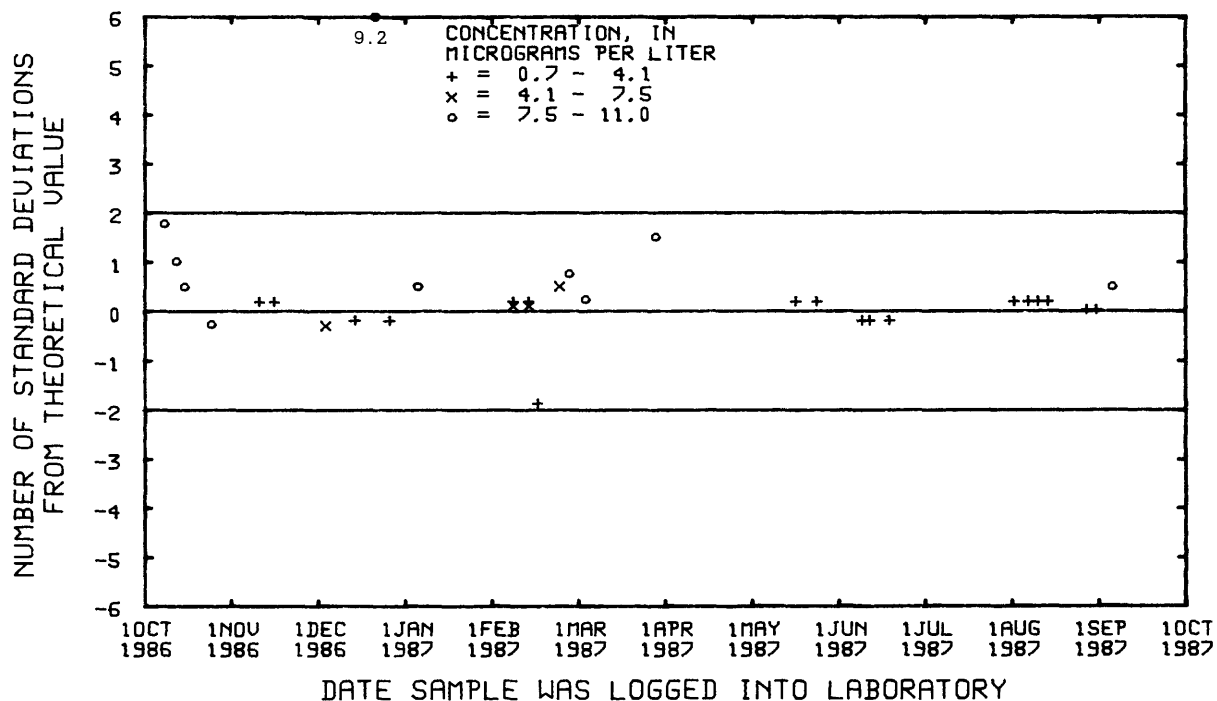


Figure 51.--Silver, total recoverable,
data from the National Water Quality Laboratory.

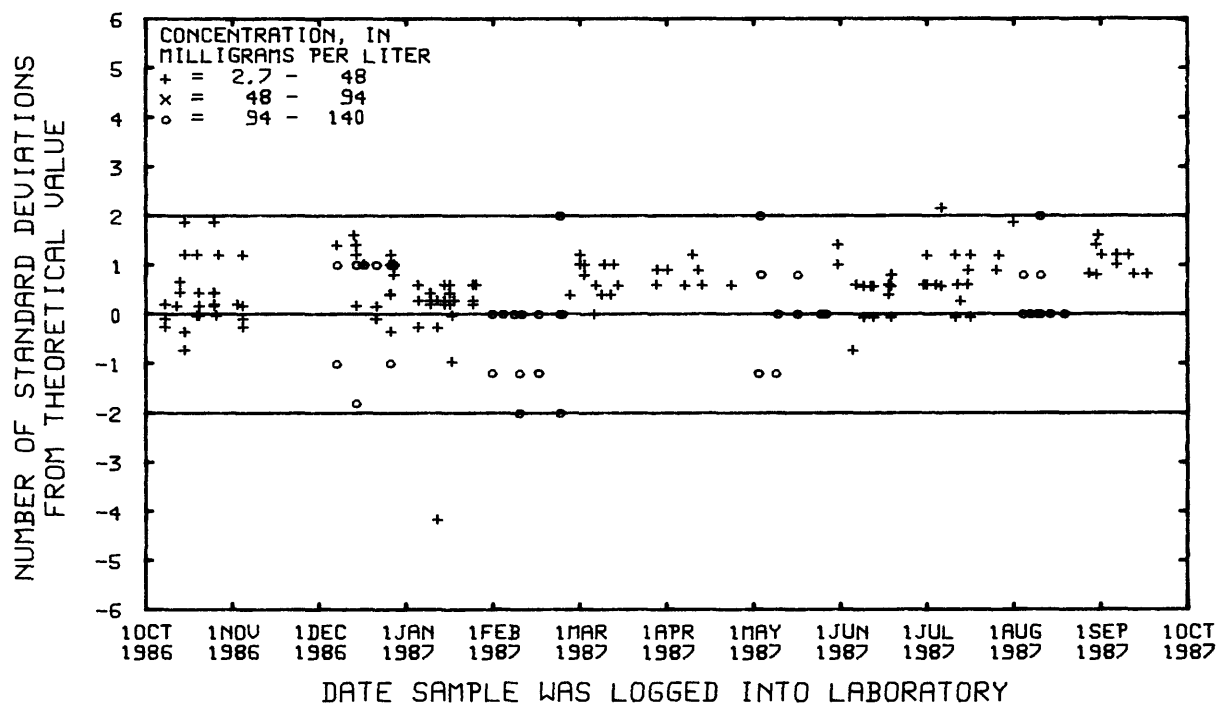


Figure 52.--Sodium, dissolved,
(inductively coupled plasma emission spectrometry)
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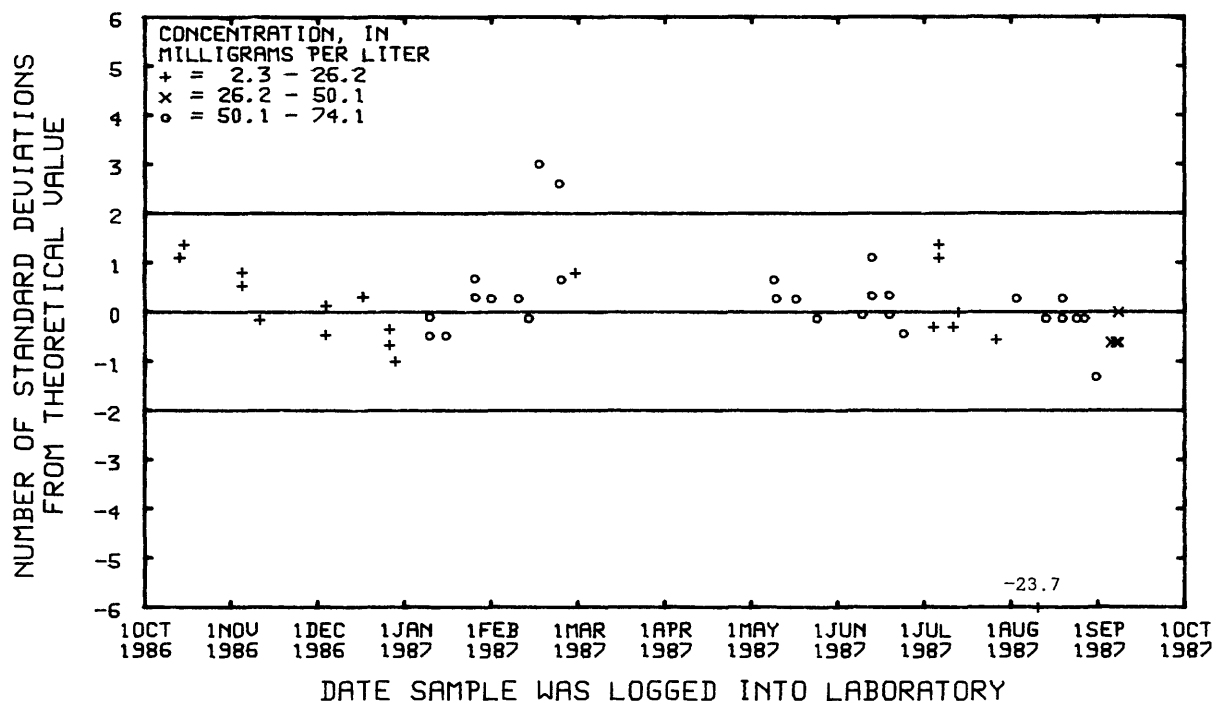


Figure 53.--Sodium, dissolved,
(atomic absorption spectrometry)
data from the National Water Quality Laboratory.

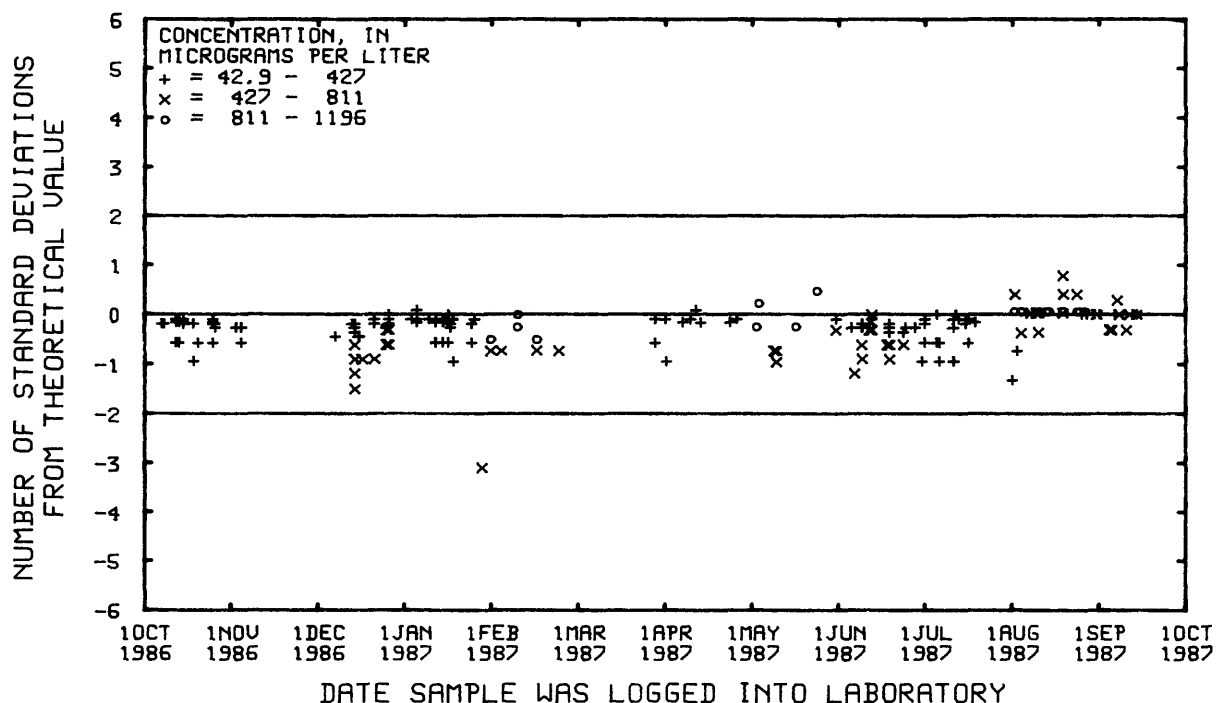


Figure 54.--Strontium, dissolved,
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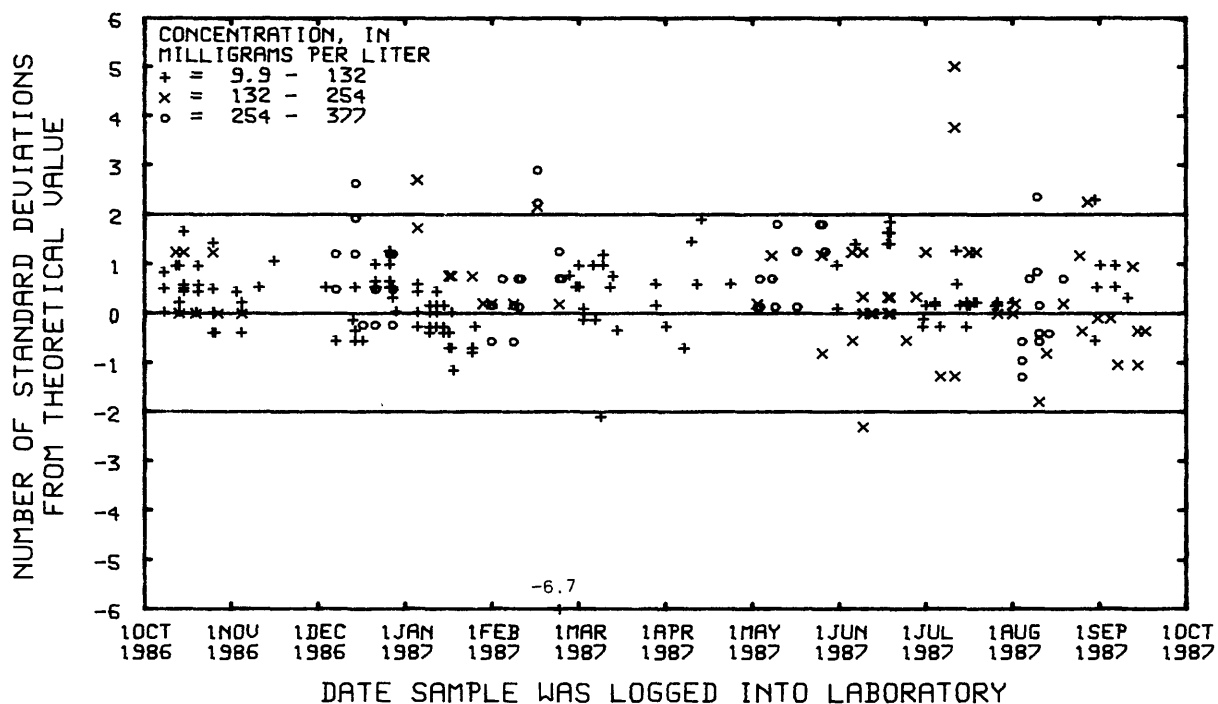


Figure 55.--Sulfate, dissolved,
data from the National Water Quality Laboratory.

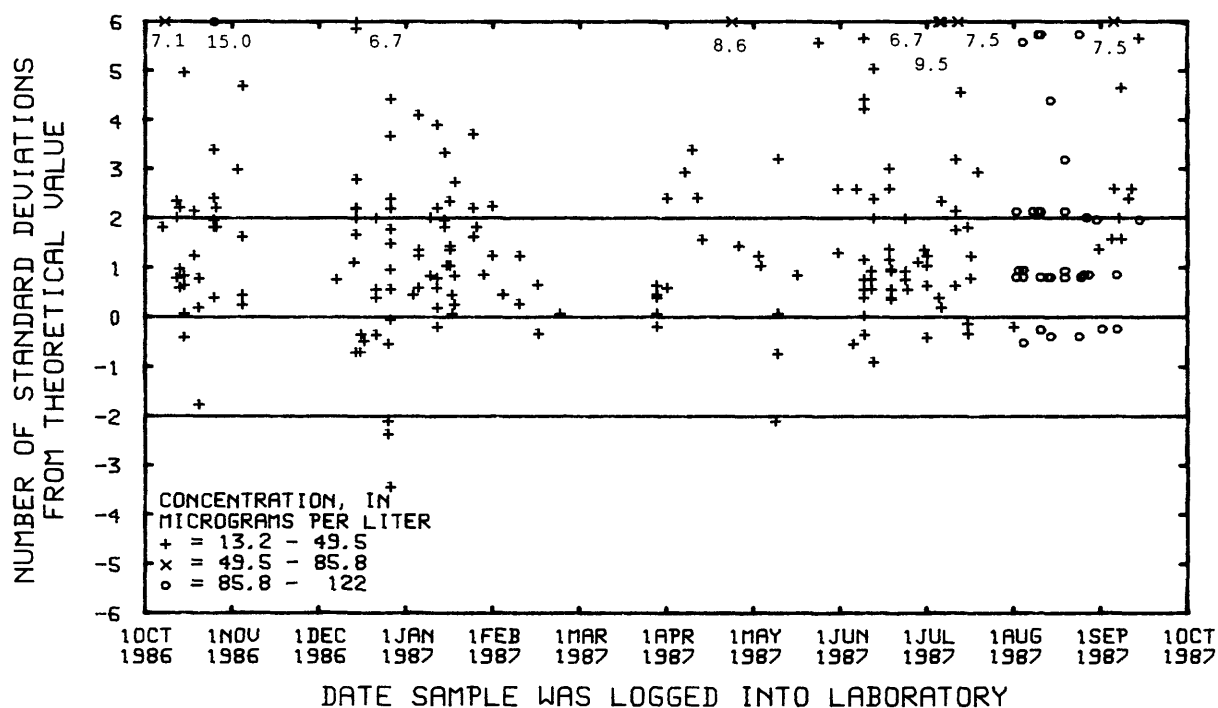


Figure 56.--Zinc, dissolved,
(inductively coupled plasma emission spectrometry)
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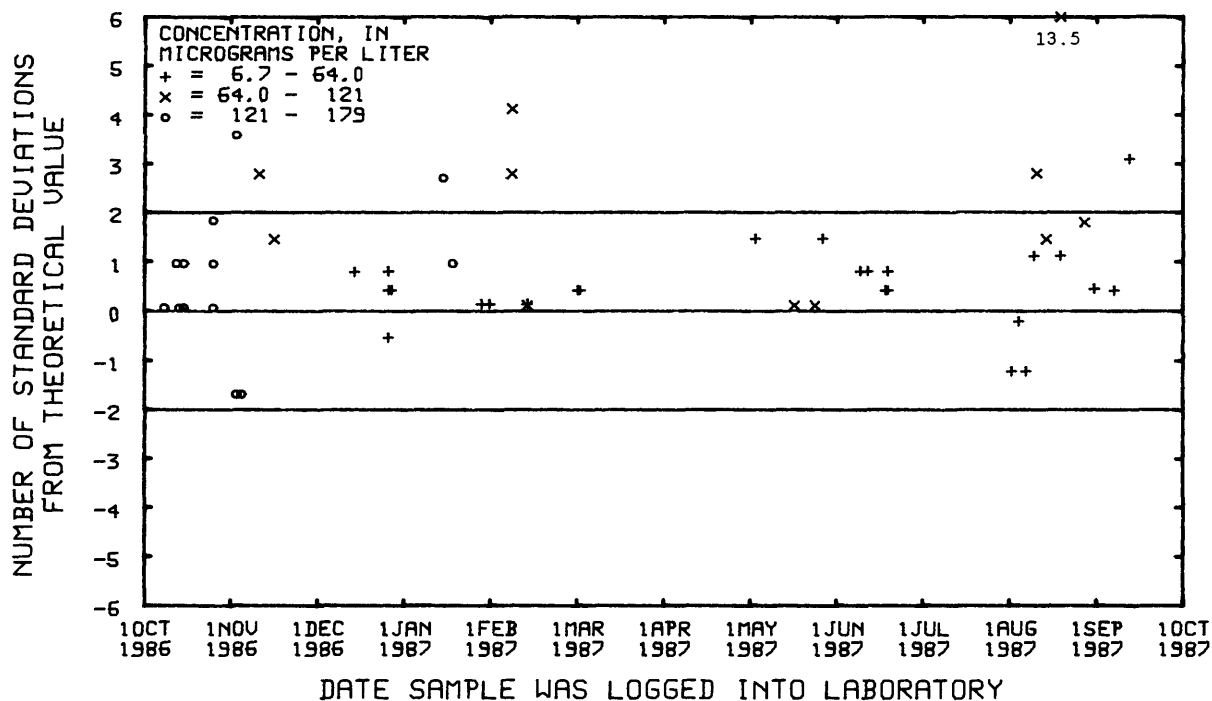


Figure 57.--Zinc, dissolved,
 (atomic absorption spectrometry)
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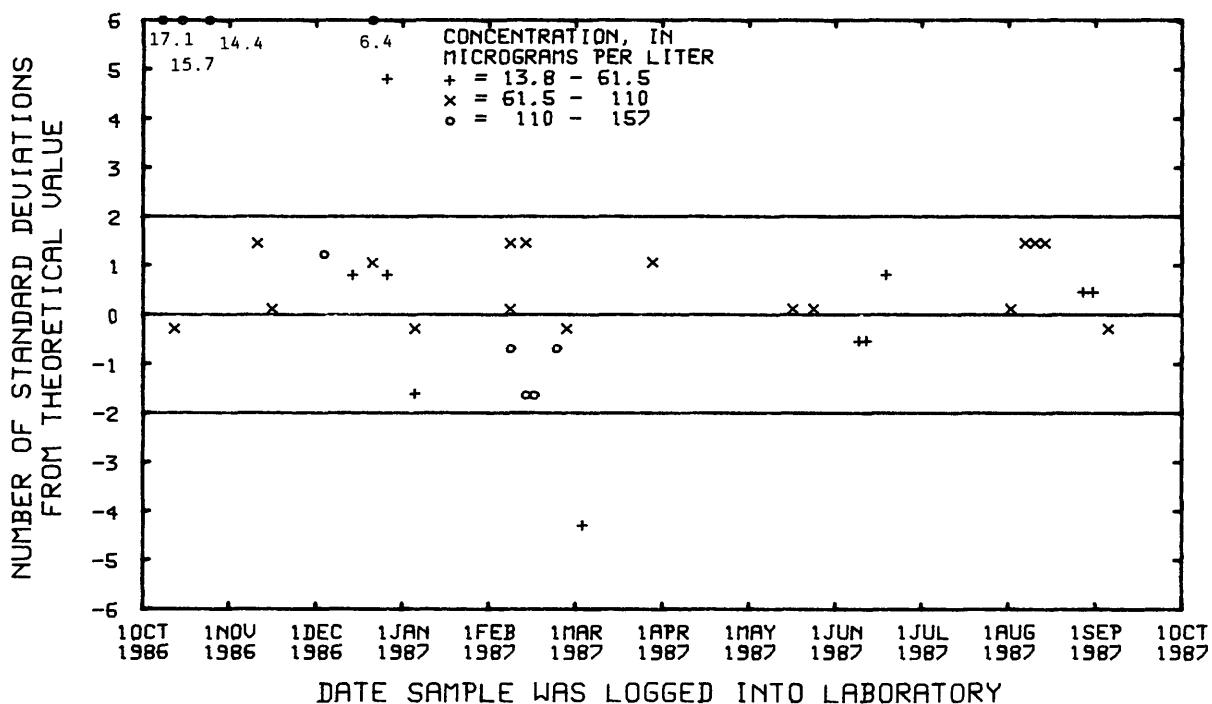


Figure 58.--Zinc, total recoverable,
 data from the National Water Quality Laboratory.

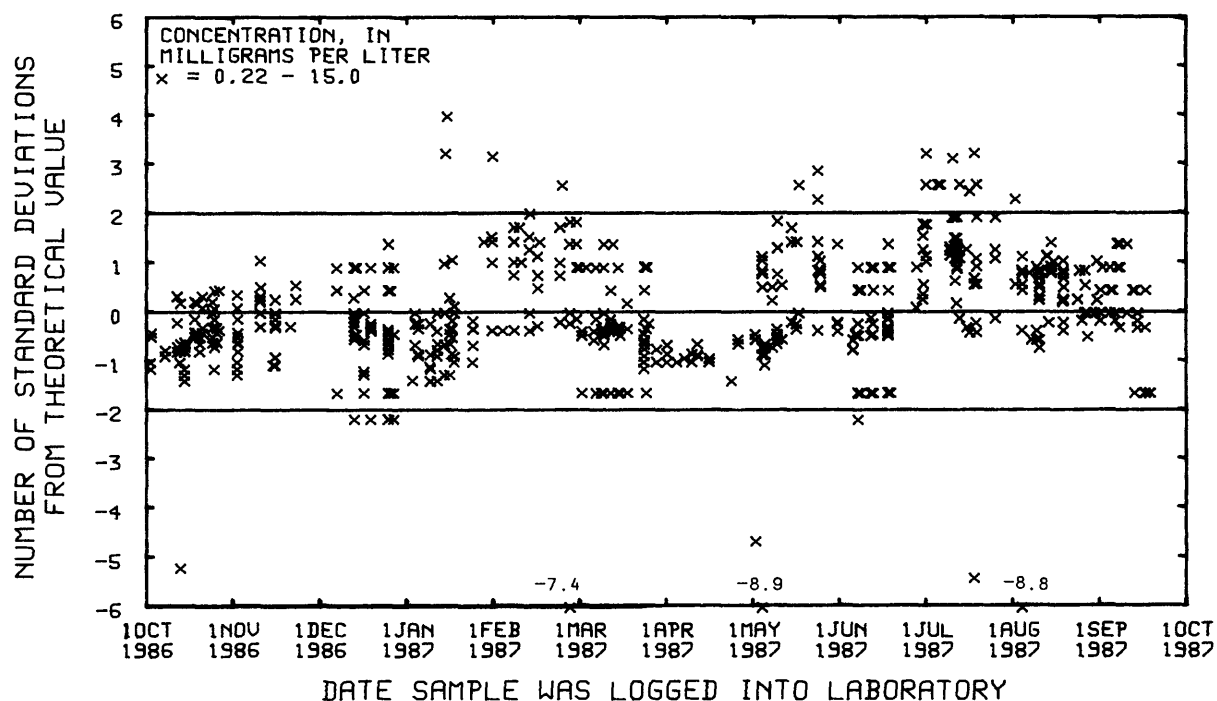


Figure 59.--Ammonia nitrogen as N, dissolved,
data from the National Water Quality Laboratory.

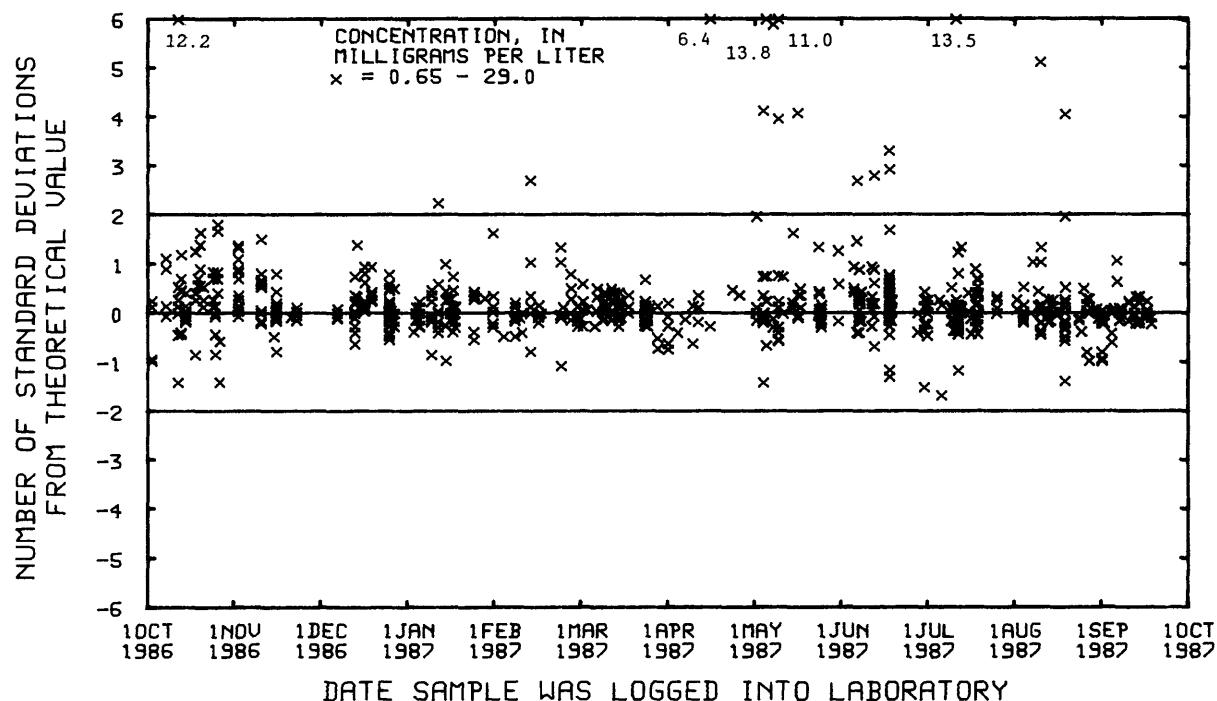


Figure 60.--Ammonia + organic nitrogen as N, dissolved,
data from the National Water Quality Laboratory.

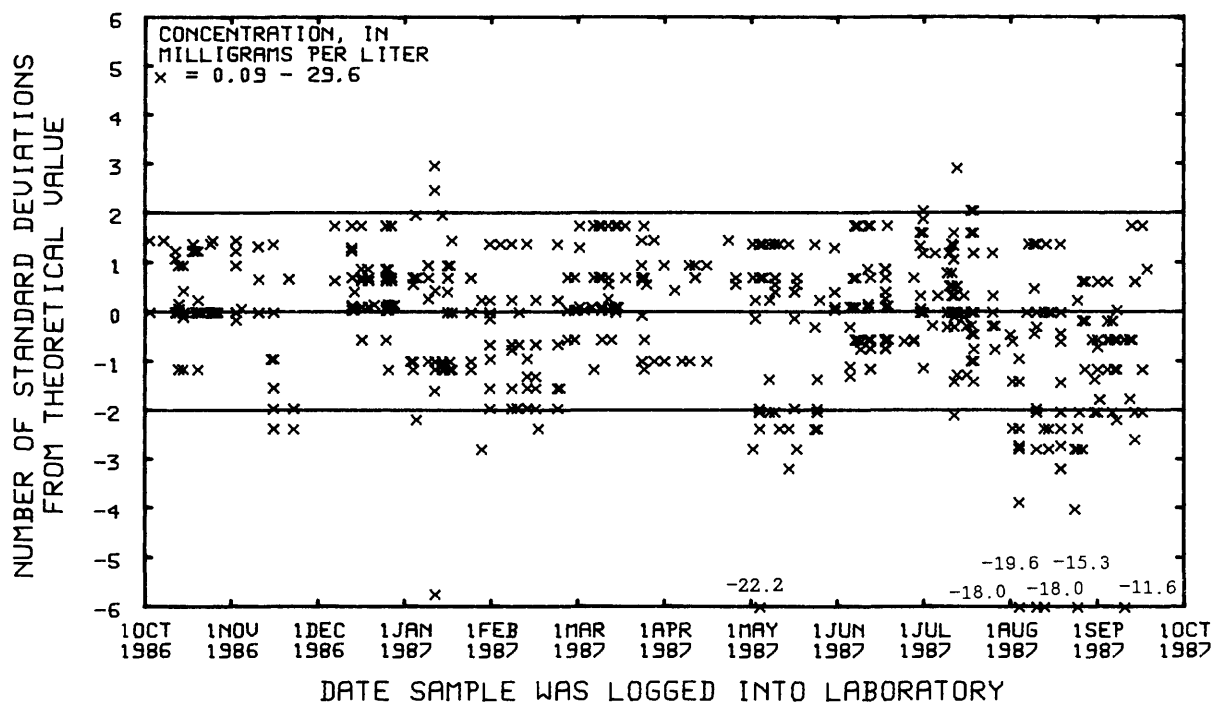


Figure 61.--Nitrite + nitrate nitrogen as N, dissolved, data from the National Water Quality Laboratory.

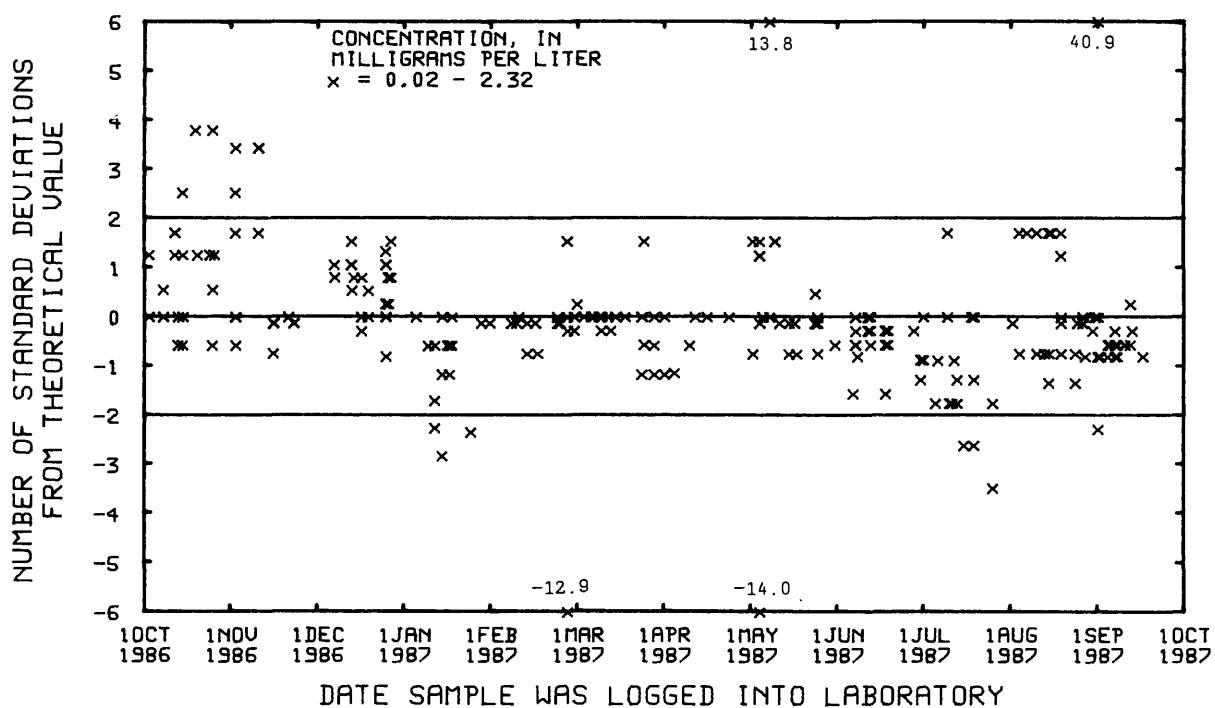


Figure 62.--Nitrite nitrogen as N, dissolved, data from the National Water Quality Laboratory.

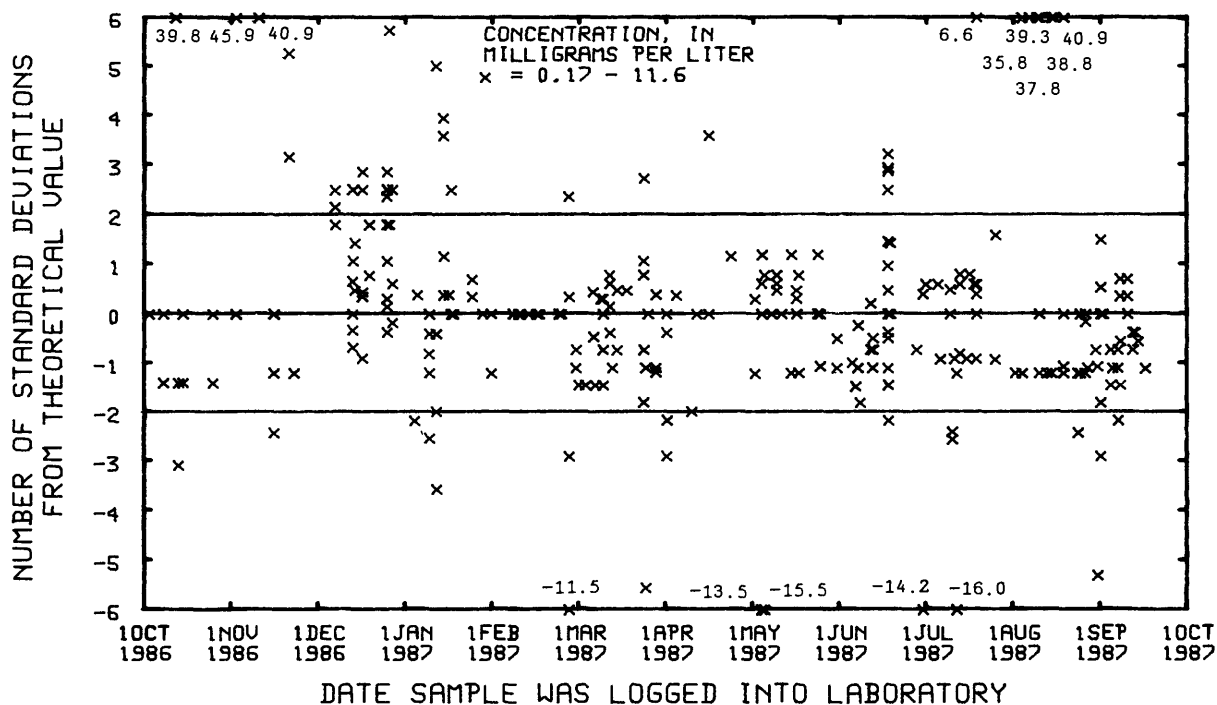


Figure 63.--Orthophosphate phosphorus as P, dissolved, data from the National Water Quality Laboratory.

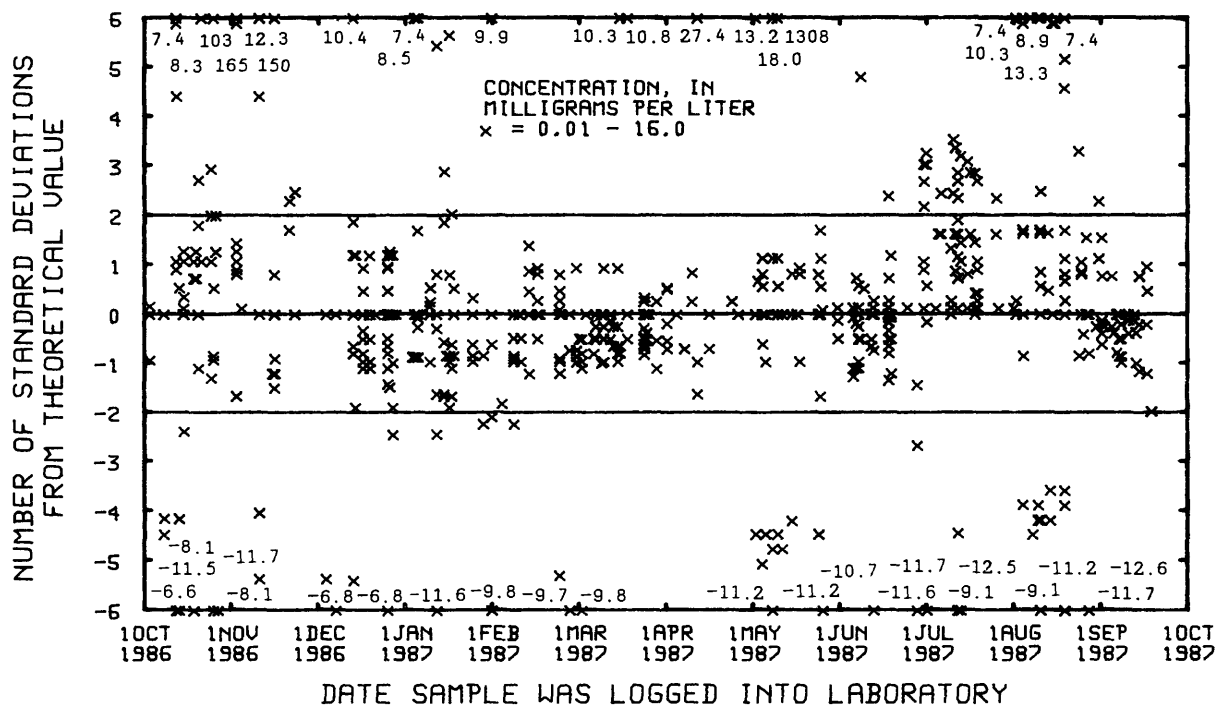


Figure 64.--Phosphorus as P, dissolved, data from the National Water Quality Laboratory.

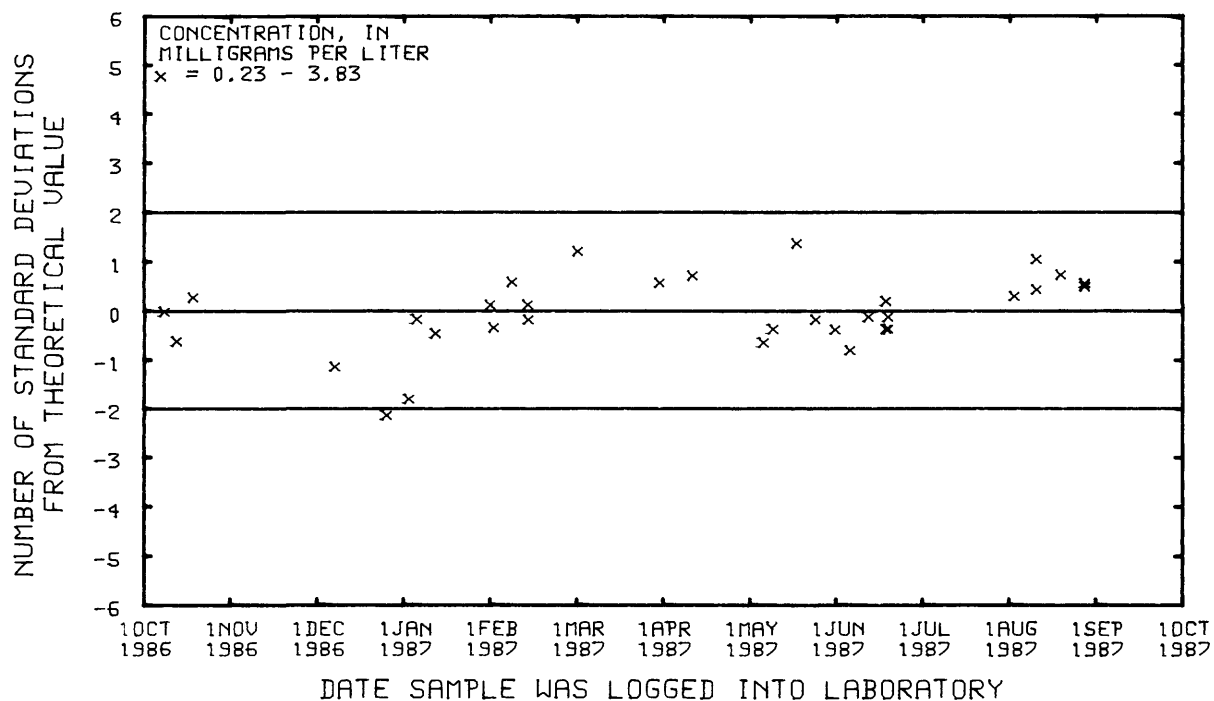


Figure 65.--Calcium, dissolved, (precipitation)
data from the National Water Quality Laboratory.

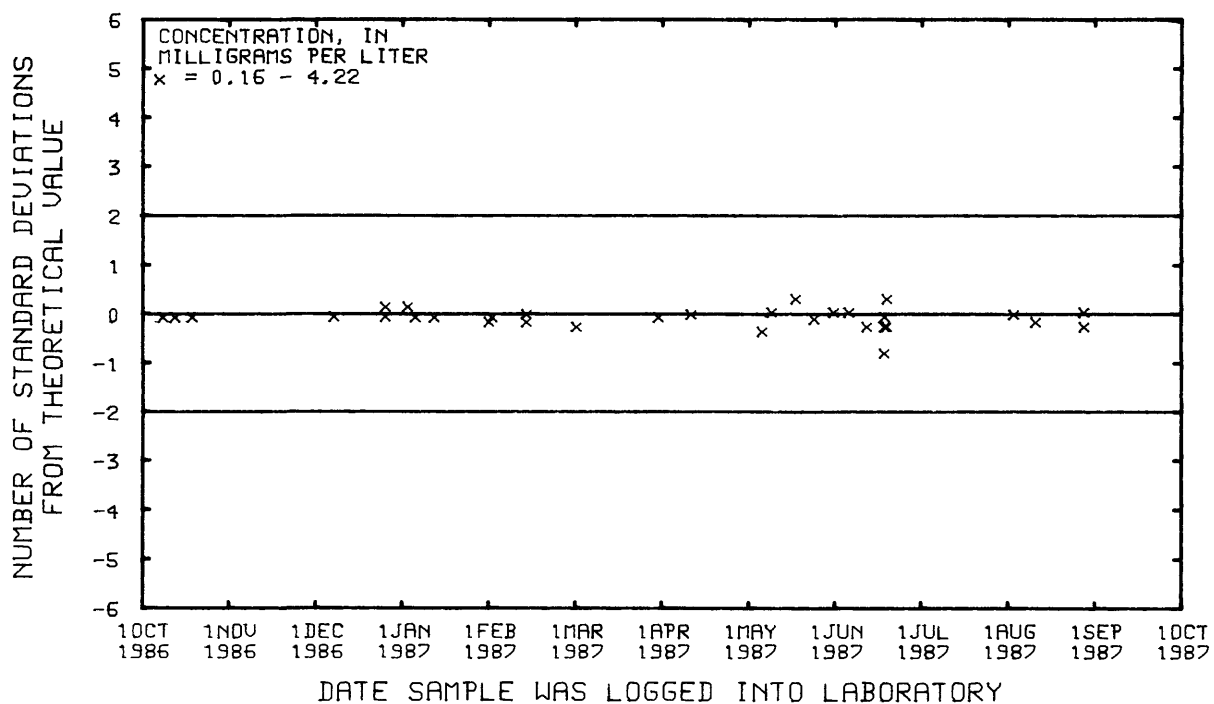


Figure 66.--Chloride, dissolved, (precipitation)
data from the National Water Quality Laboratory.

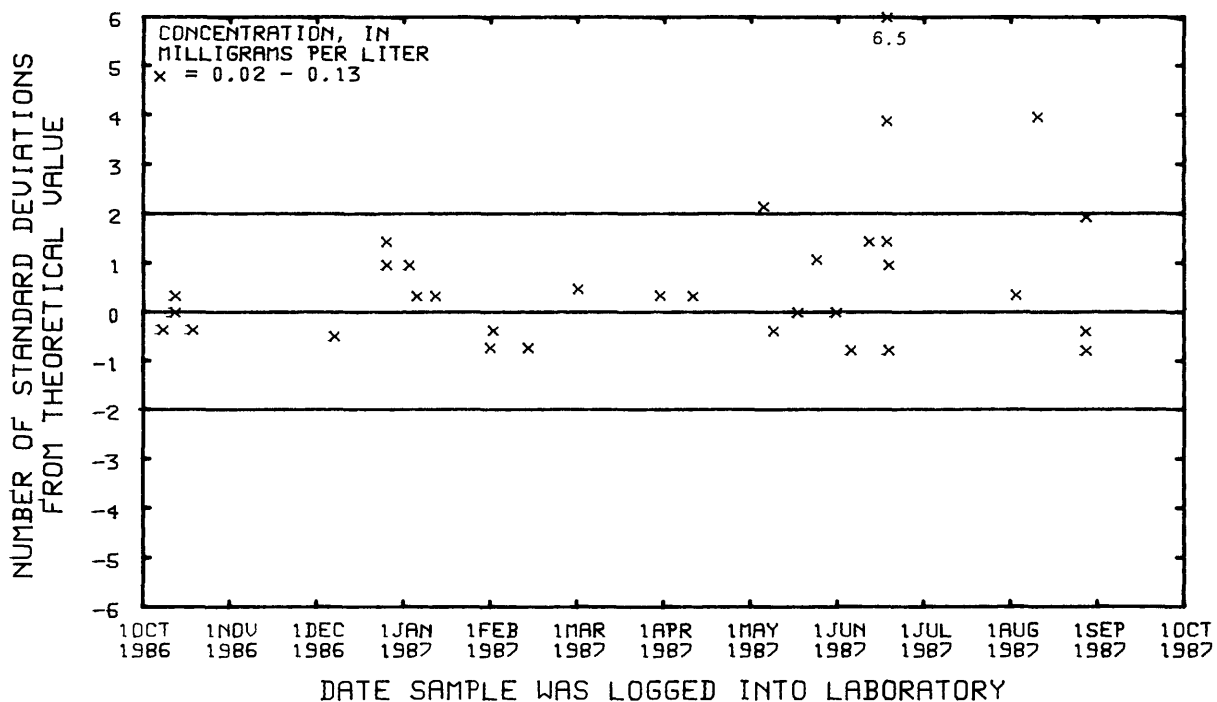


Figure 67.--Fluoride, dissolved, (precipitation)
data from the National Water Quality Laboratory.

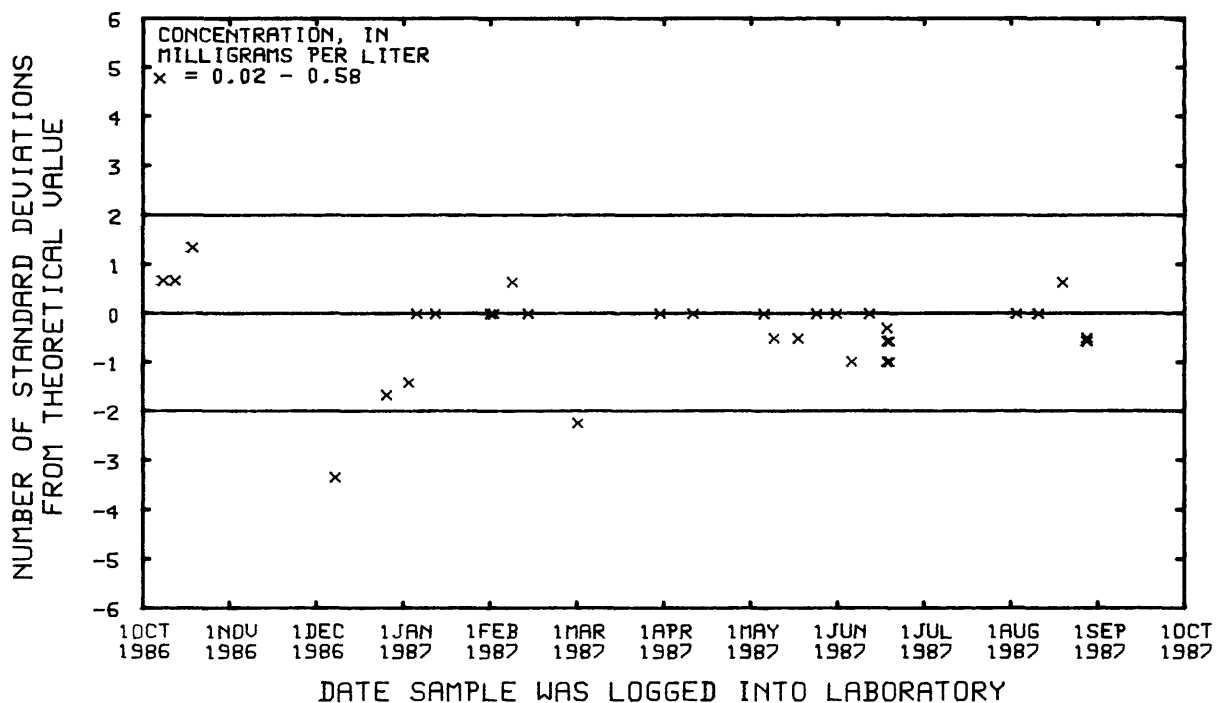


Figure 68.--Magnesium, dissolved, (precipitation)
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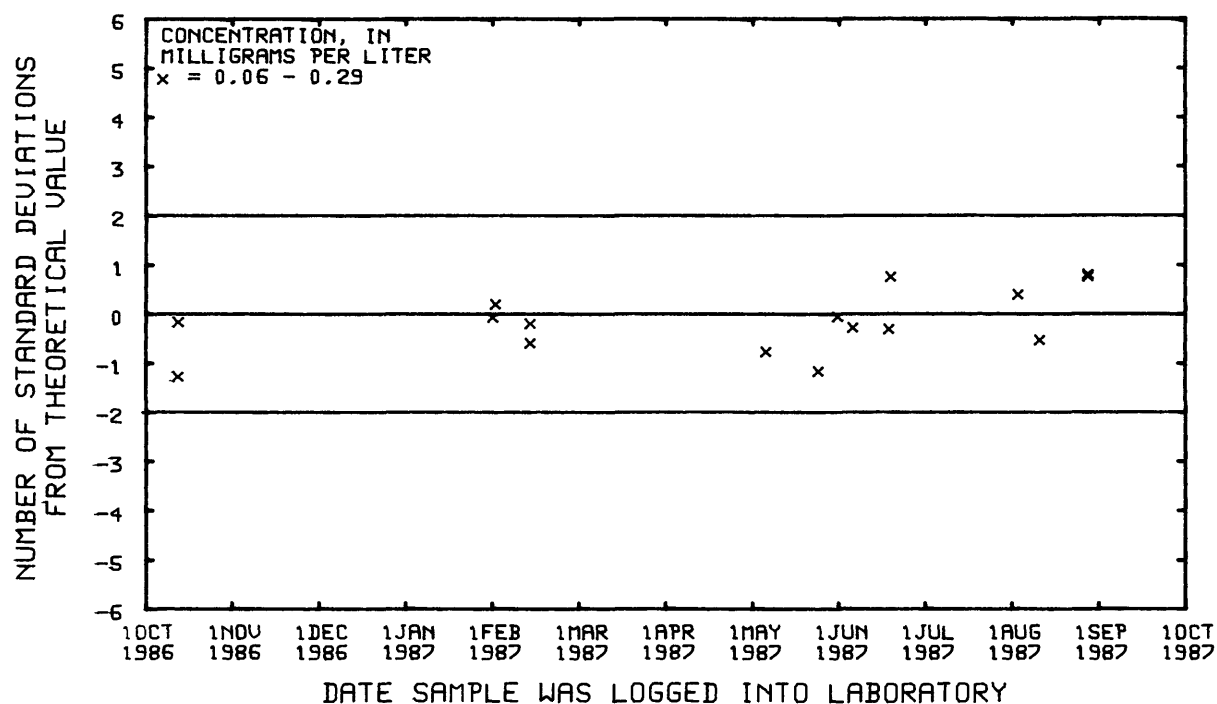


Figure 69.--Ammonia nitrogen as N, dissolved,
(precipitation) data
from the National Water Quality Laboratory.

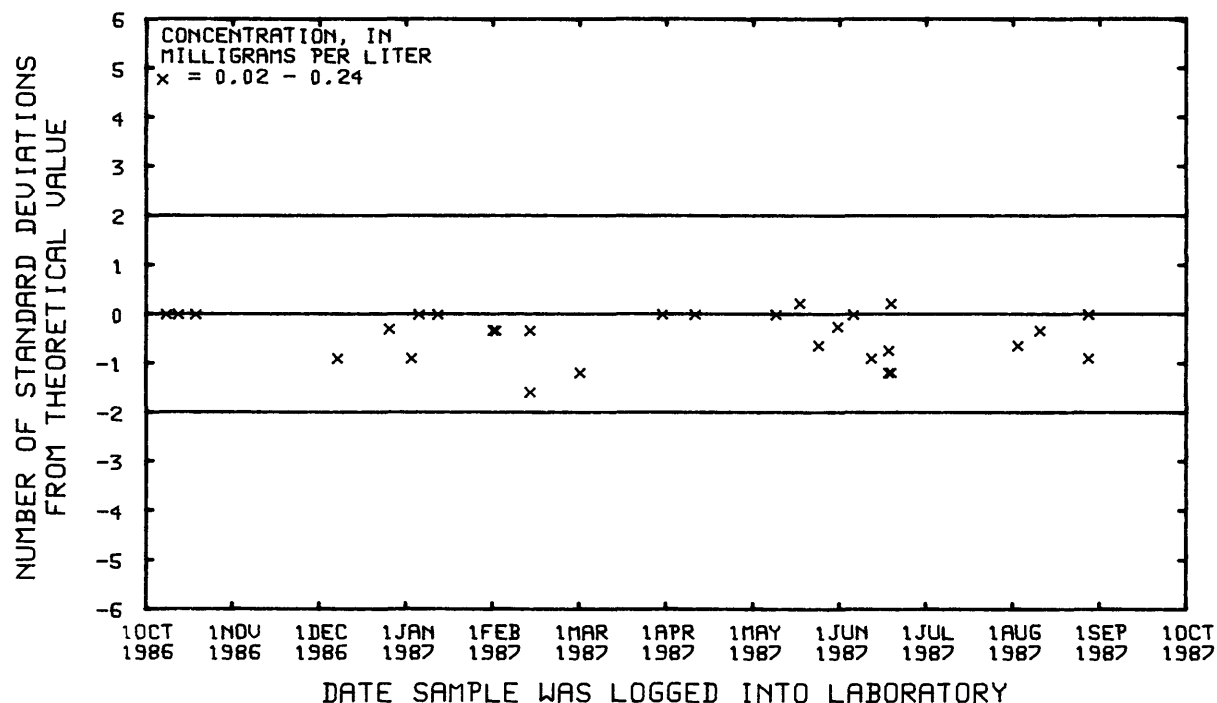


Figure 70.--Nitrate nitrogen as N, dissolved,
(precipitation) data
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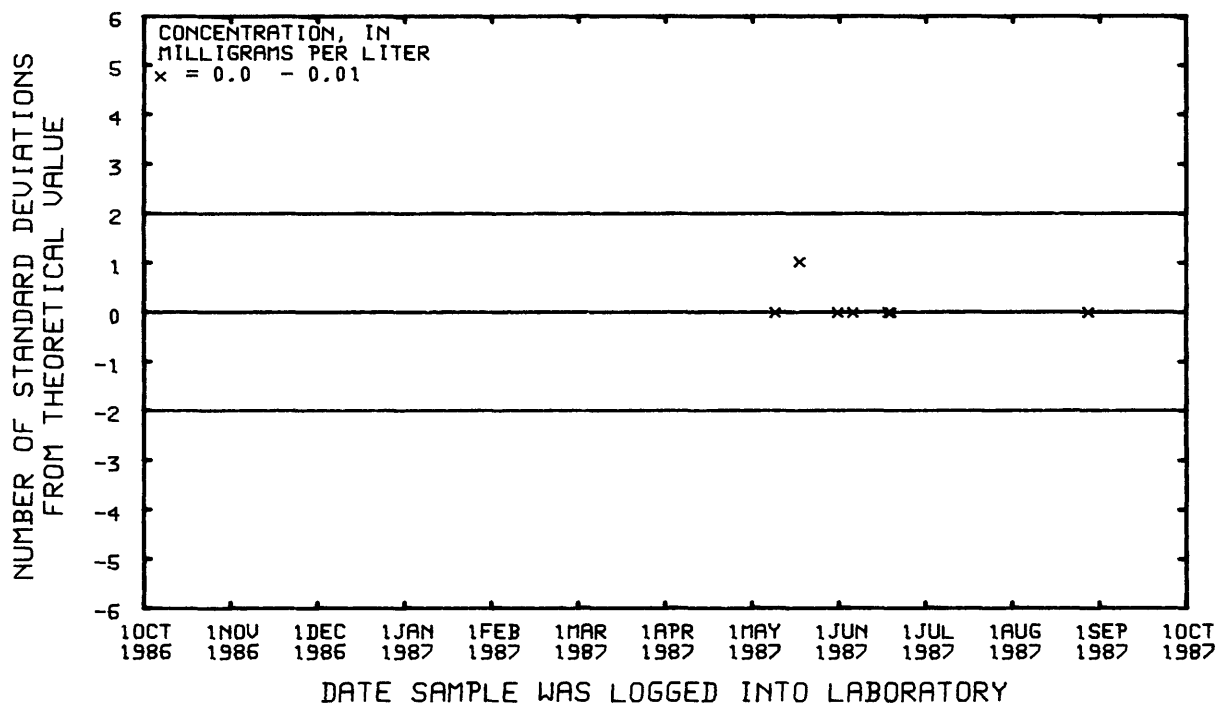


Figure 71.--Orthophosphate phosphorus as P, dissolved,
(precipitation) data
from the National Water Quality Laboratory.

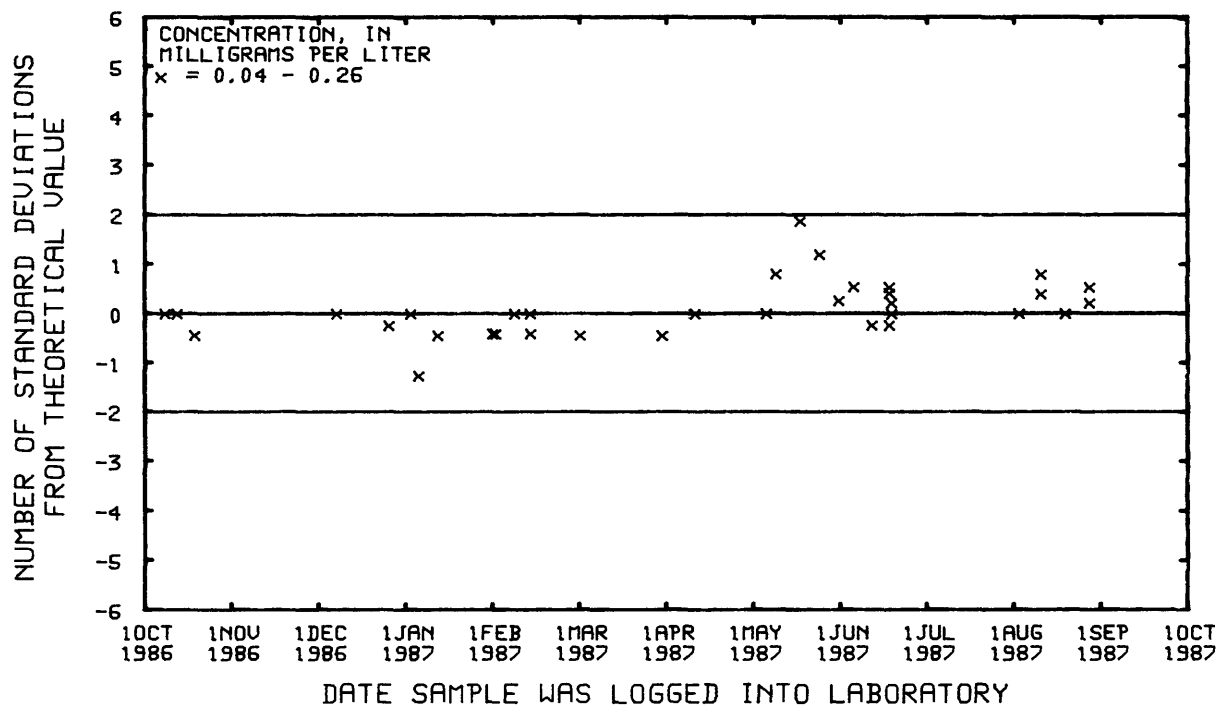


Figure 72.--Potassium, dissolved, (precipitation)
data from the National Water Quality Laboratory.

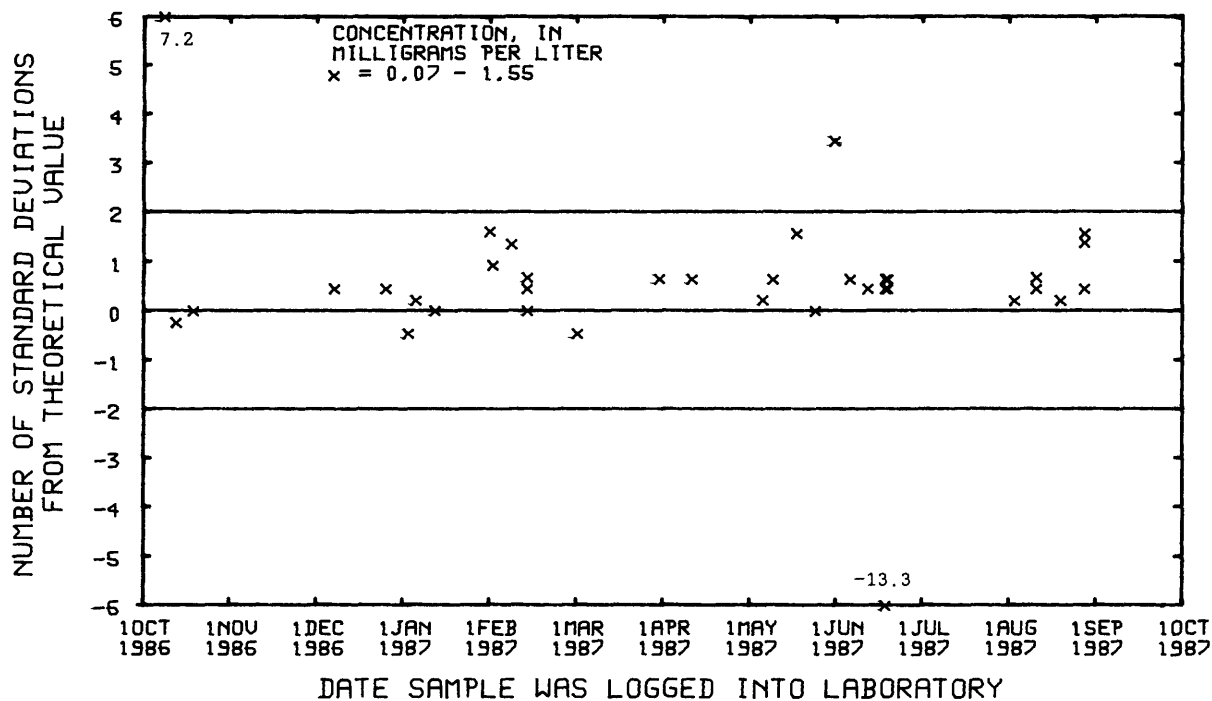


Figure 73.--Sodium, dissolved, (precipitation)
data from the National Water Quality Laboratory.

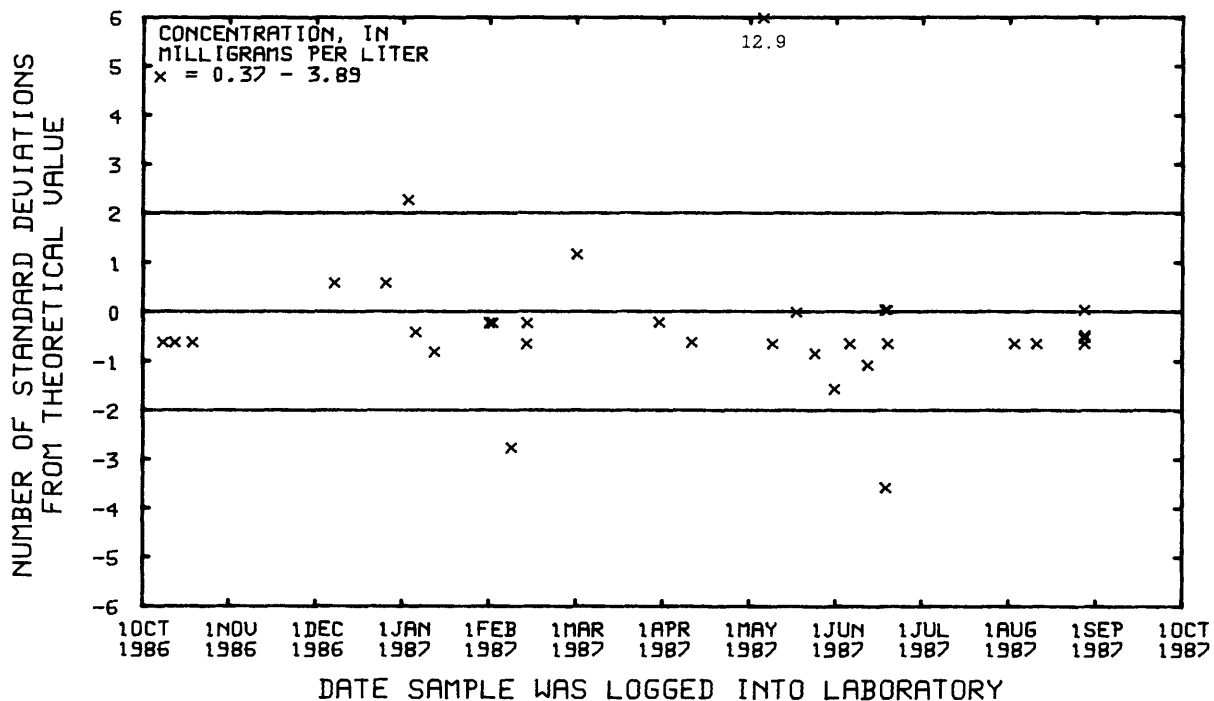


Figure 74.--Sulfate, dissolved, (precipitation)
data from the National Water Quality Laboratory.

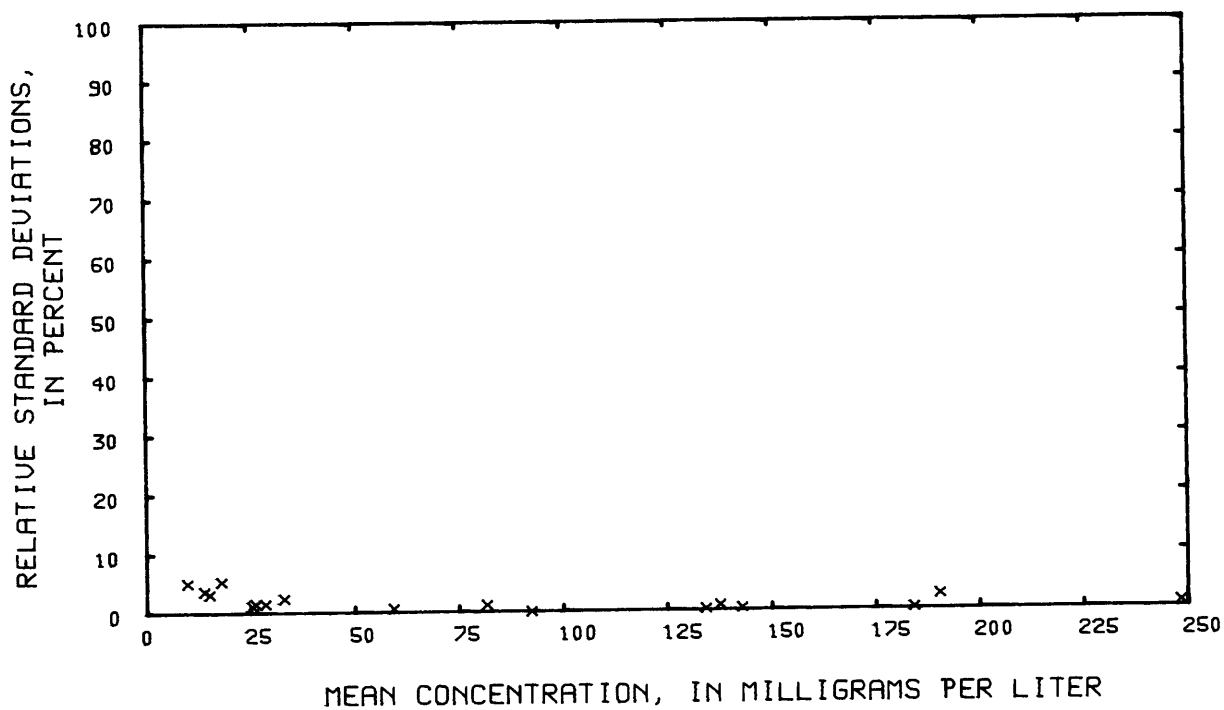


Figure 75.--Precision data for alkalinity, dissolved,
at the National Water Quality Laboratory.

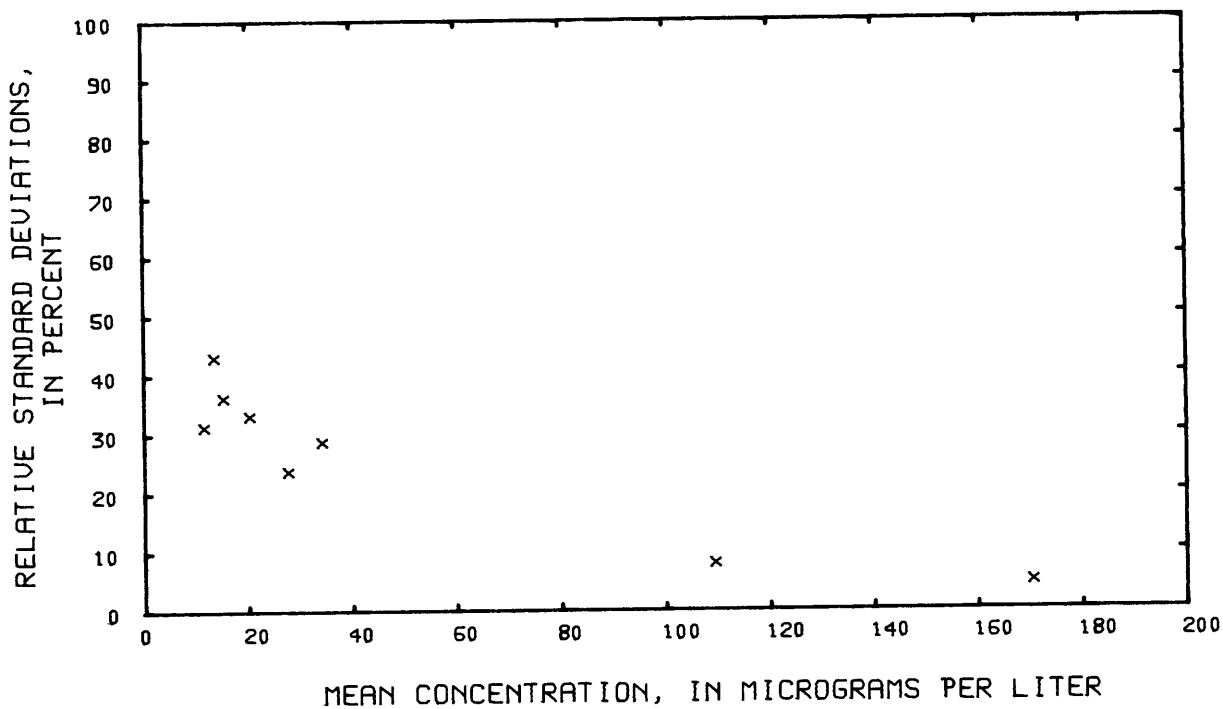


Figure 76.--Precision data for aluminum, dissolved,
at the National Water Quality Laboratory.

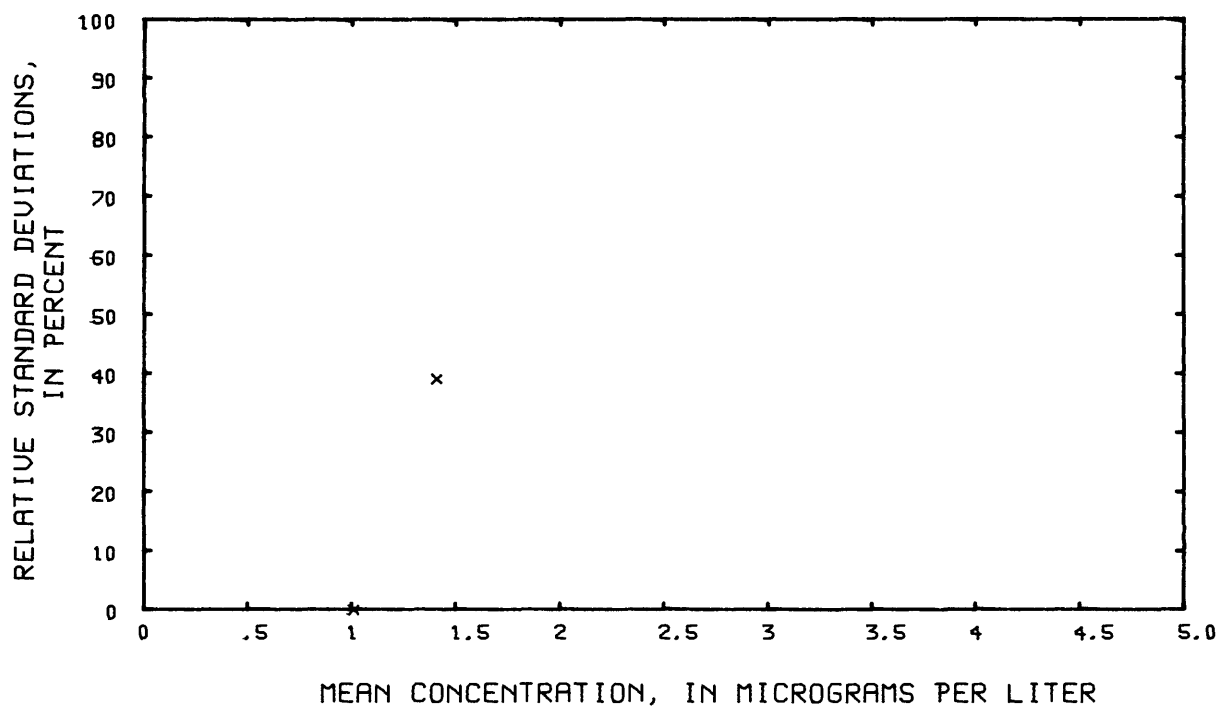


Figure 77.--Precision data for antimony, dissolved,
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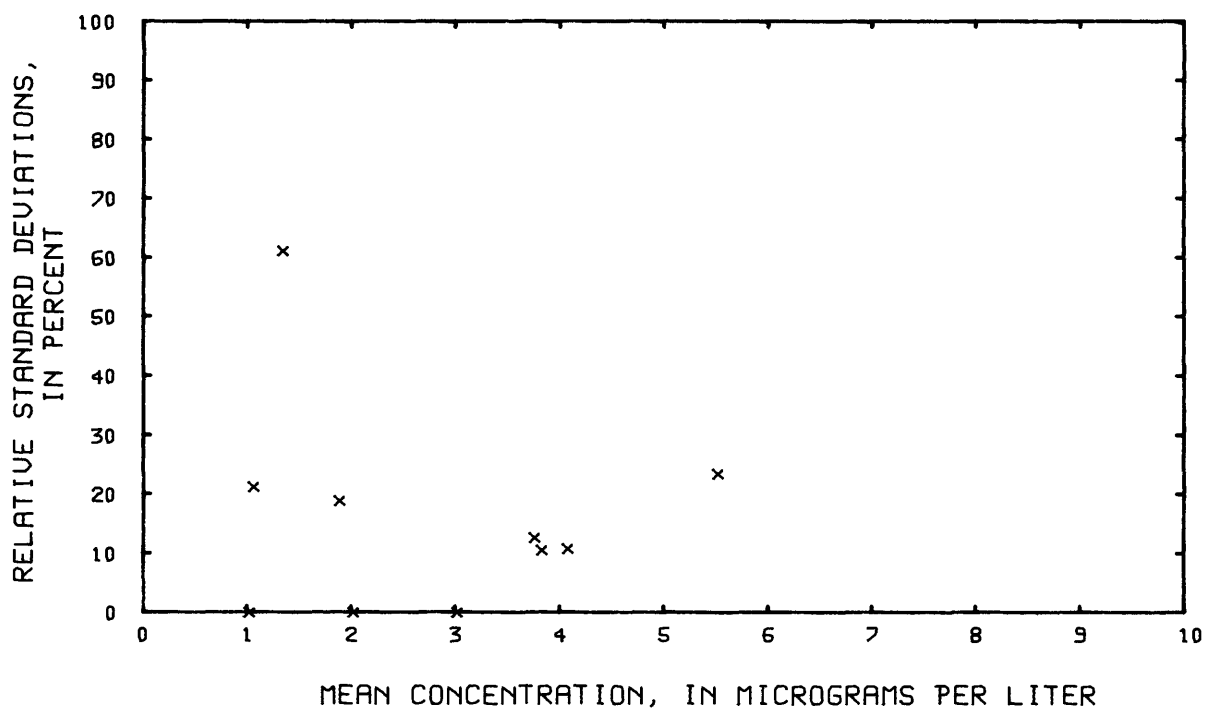


Figure 78.--Precision data for arsenic, dissolved,
at the National Water Quality Laboratory.

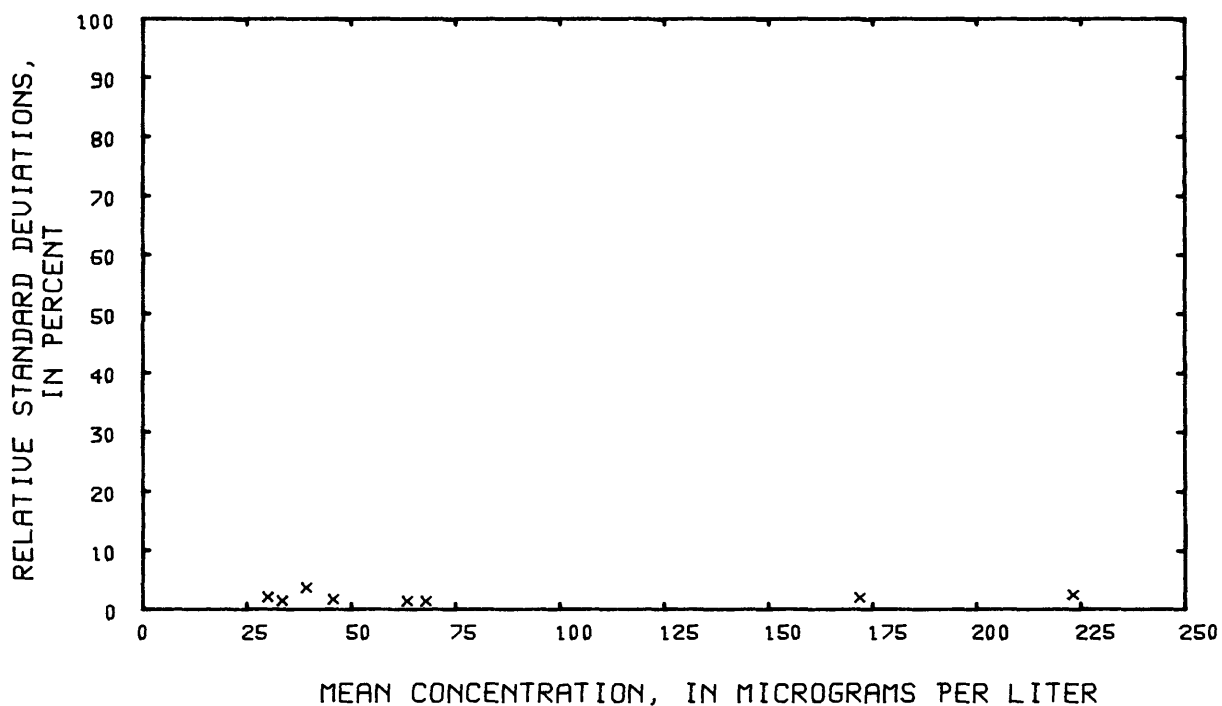


Figure 79.--Precision data for barium, dissolved,
(inductively coupled plasma emission spectrometry)
at the National Water Quality Laboratory.

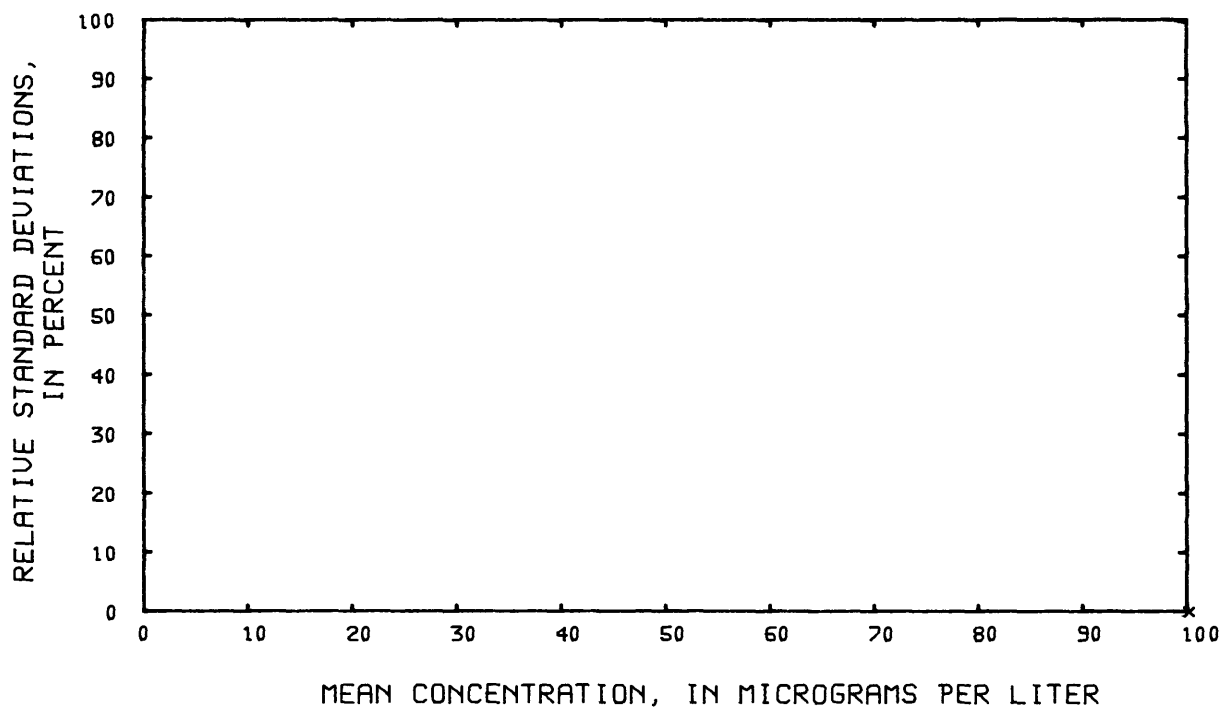


Figure 80.--Precision data for barium, dissolved,
(atomic absorption spectrometry)
at the National Water Quality Laboratory.

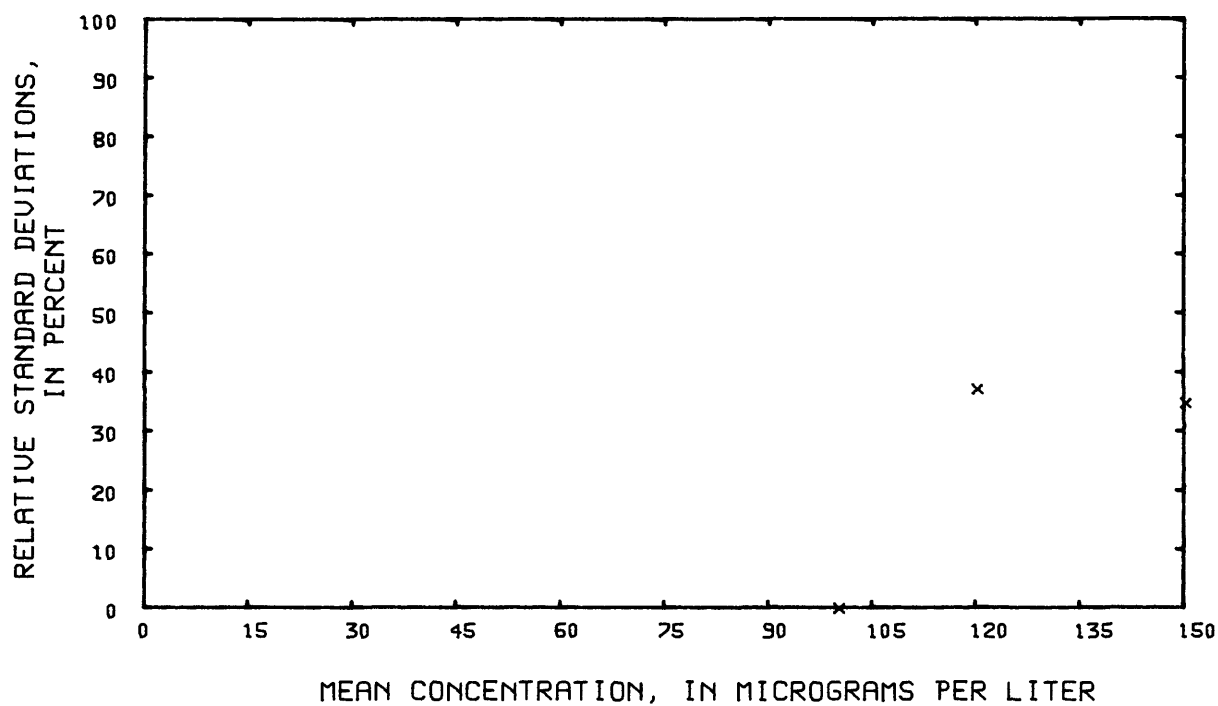


Figure 81.--Precision data for barium, total recoverable, at the National Water Quality Laboratory.

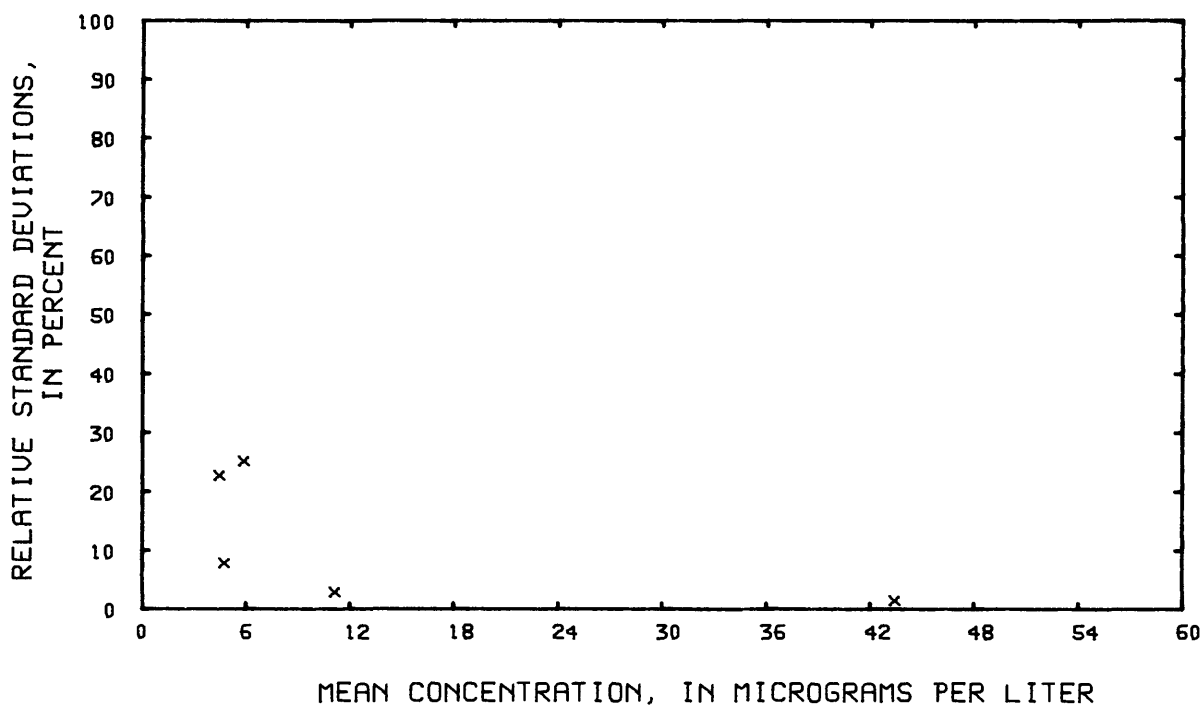


Figure 82.--Precision data for beryllium, dissolved, at the National Water Quality Laboratory.

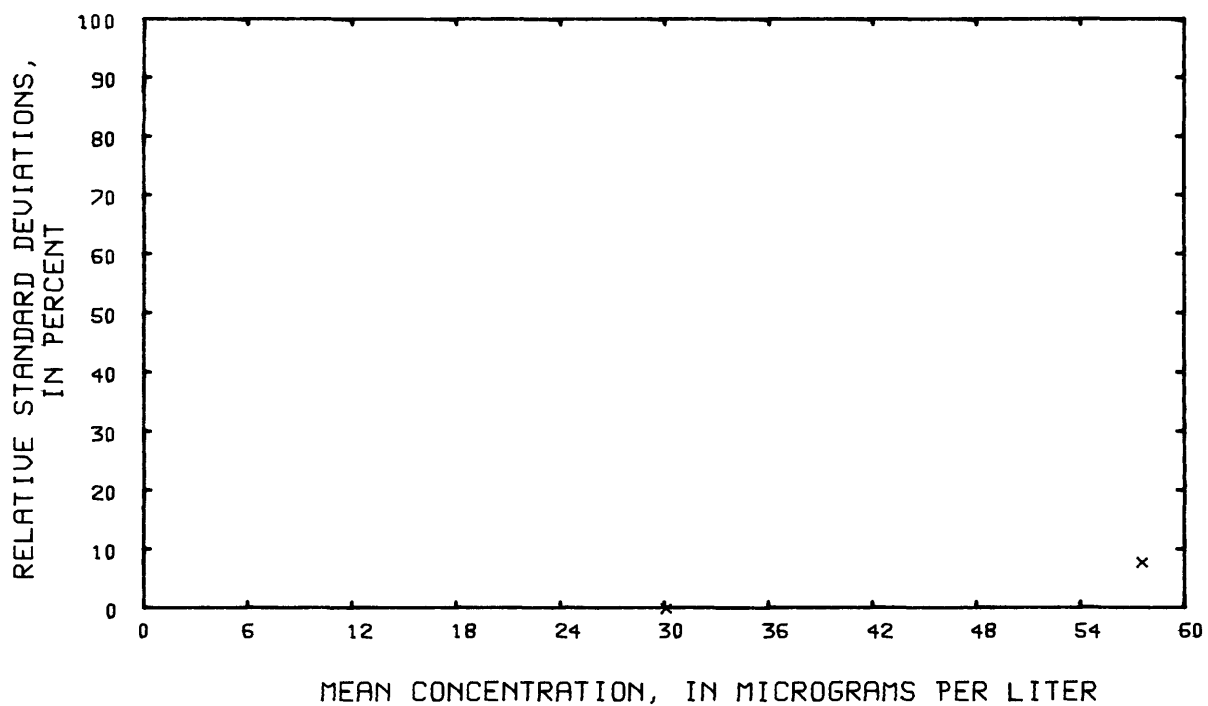


Figure 83.--Precision data for beryllium, total recoverable, at the National Water Quality Laboratory.

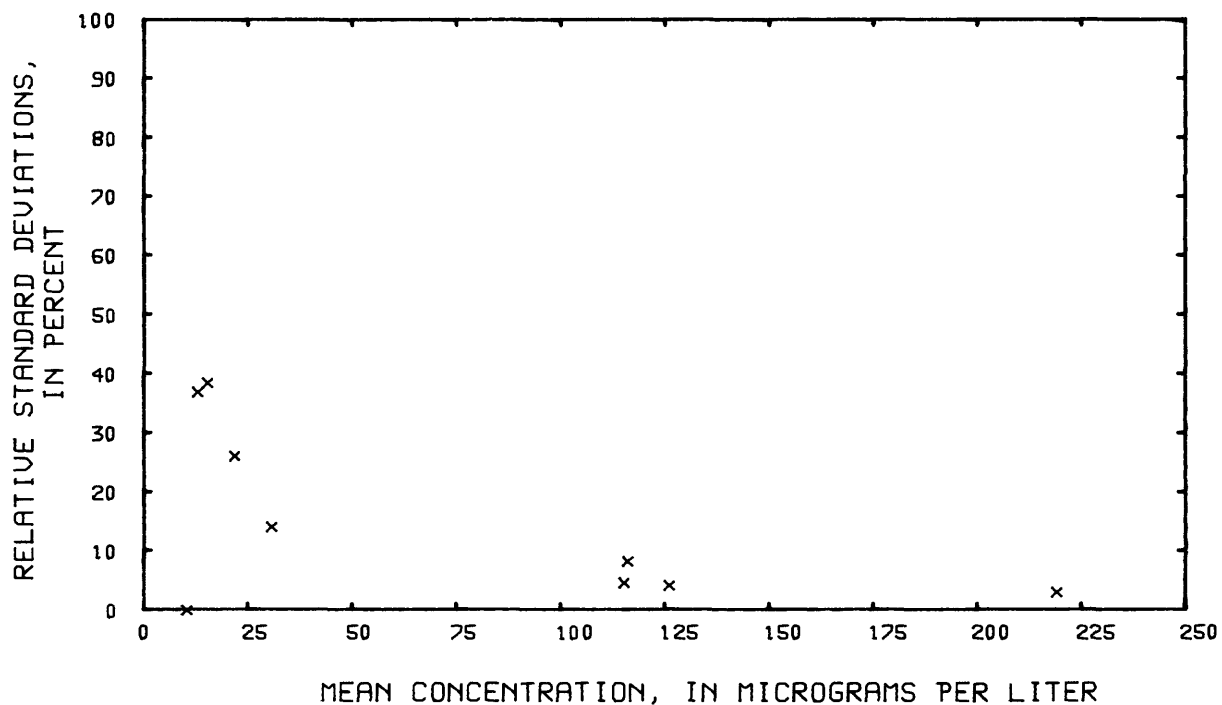


Figure 84.--Precision data for boron, dissolved, at the National Water Quality Laboratory.

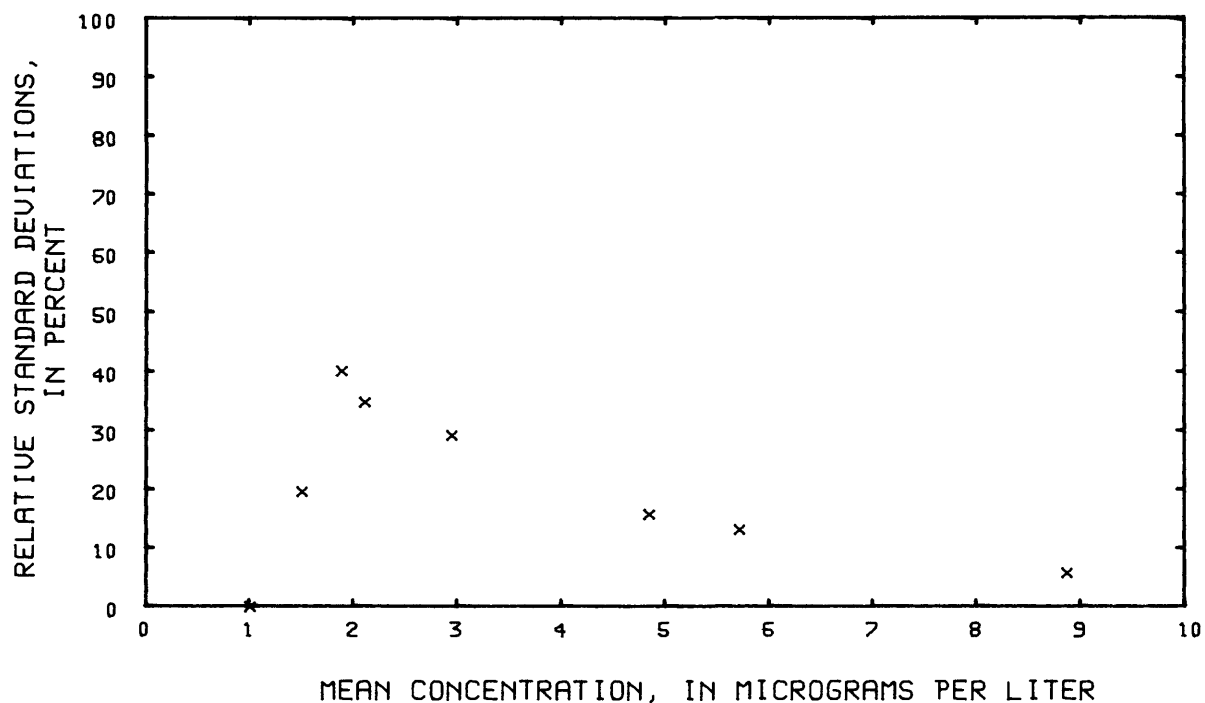


Figure 85.--Precision data for cadmium, dissolved,
(inductively coupled plasma emission spectrometry)
at the National Water Quality Laboratory.

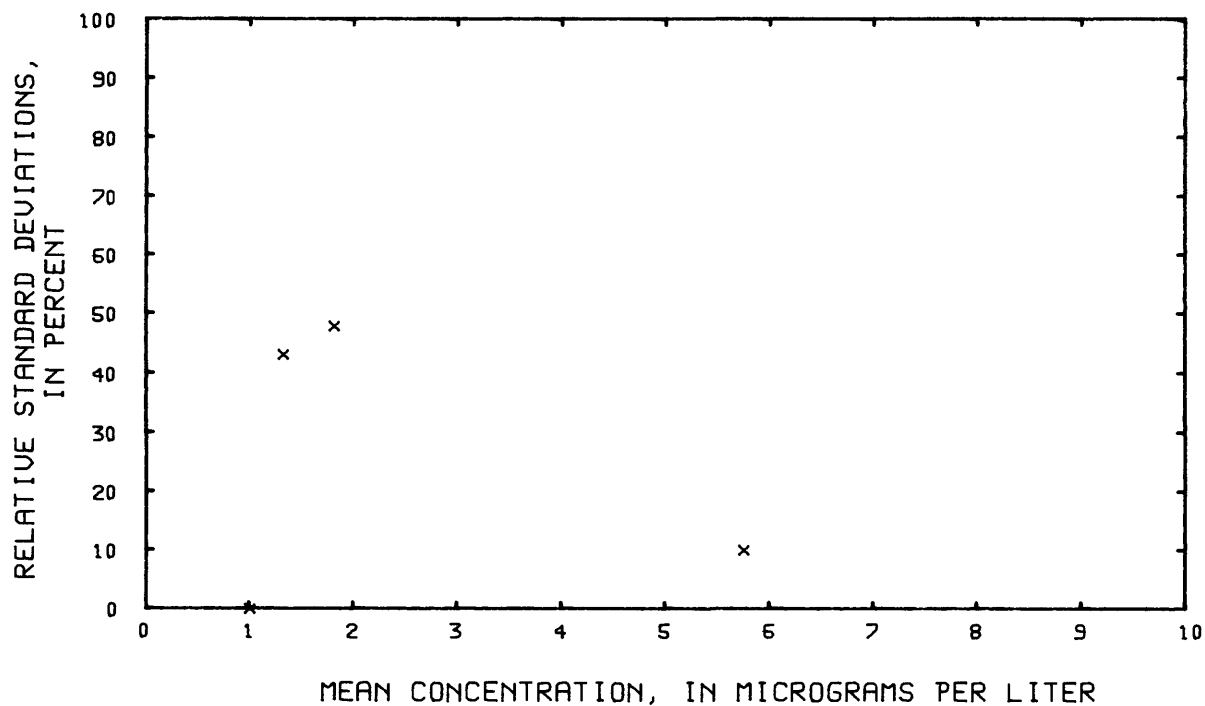


Figure 86.--Precision data for cadmium, dissolved,
(atomic absorption spectrometry)
at the National Water Quality Laboratory.

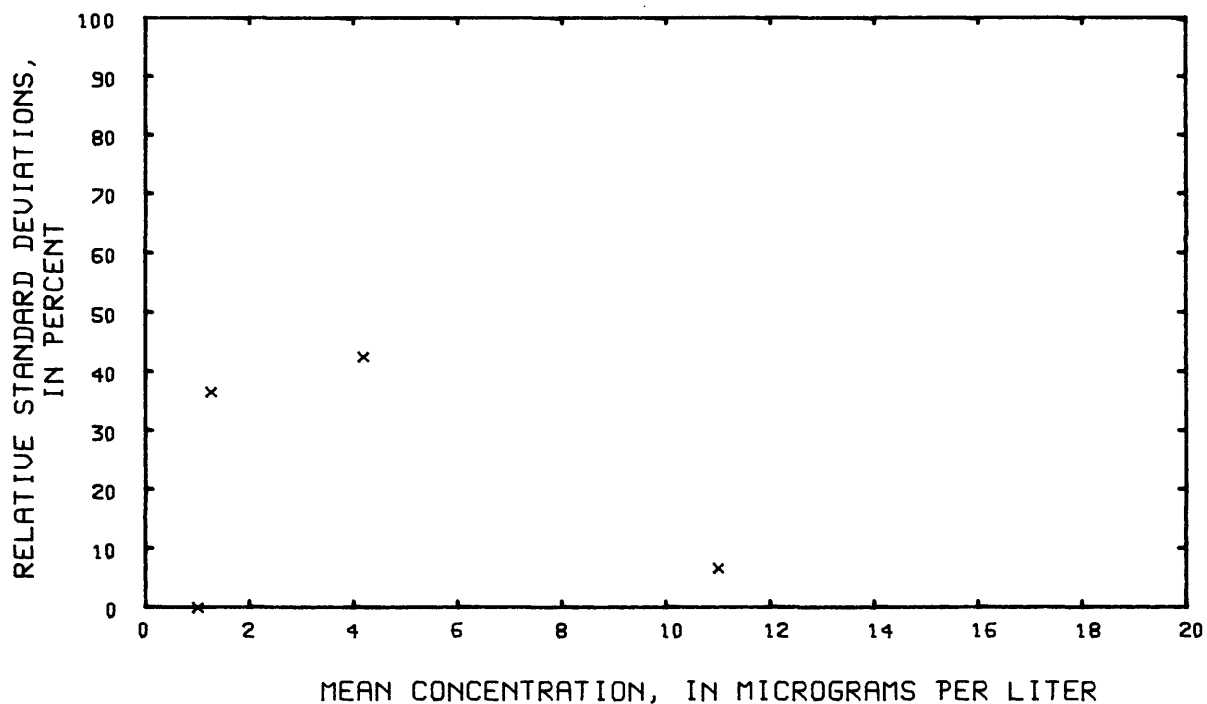


Figure 87.--Precision data for cadmium, total recoverable,
at the National Water Quality Laboratory.

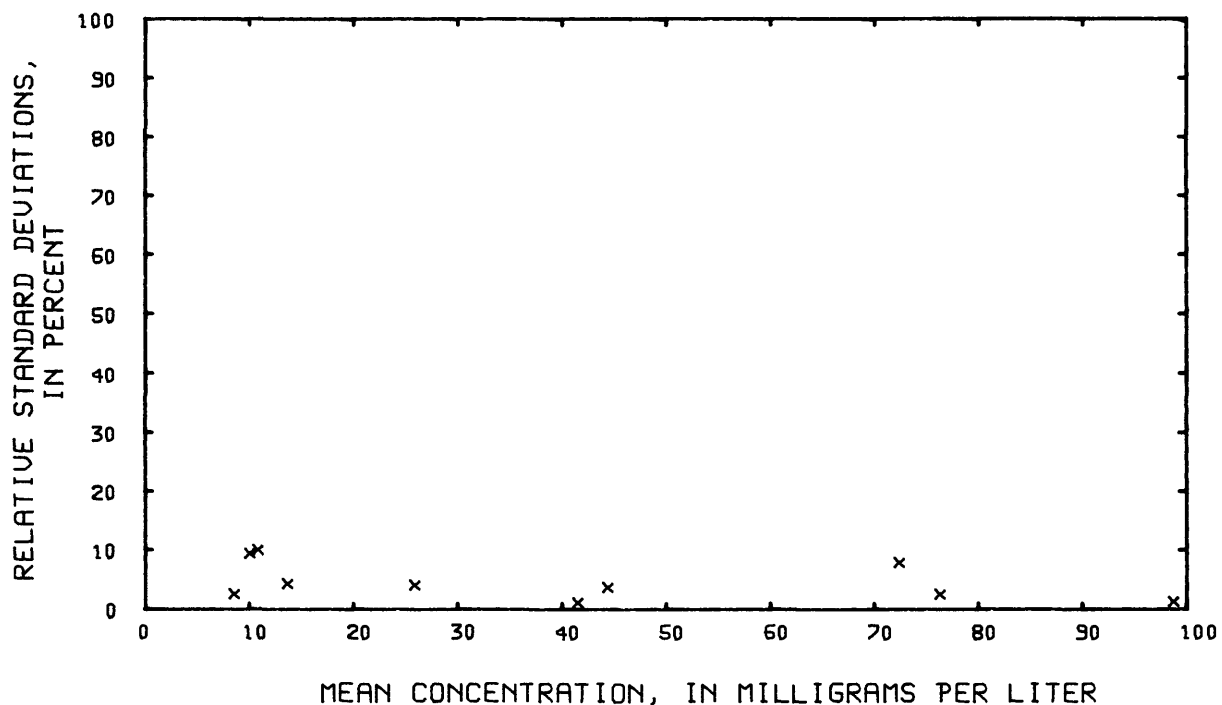


Figure 88.--Precision data for calcium, dissolved,
(inductively coupled plasma emission spectrometry)
at the National Water Quality Laboratory.

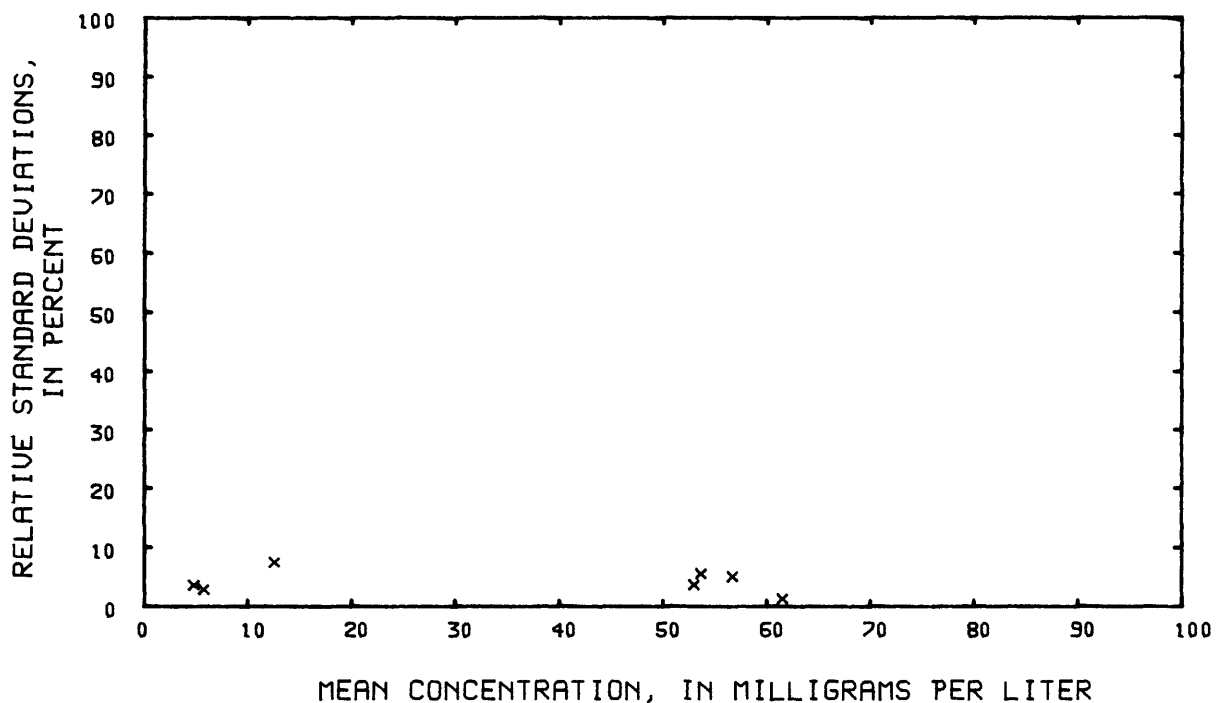


Figure 89.--Precision data for calcium, dissolved,
(atomic absorption spectrometry)
at the National Water Quality Laboratory.

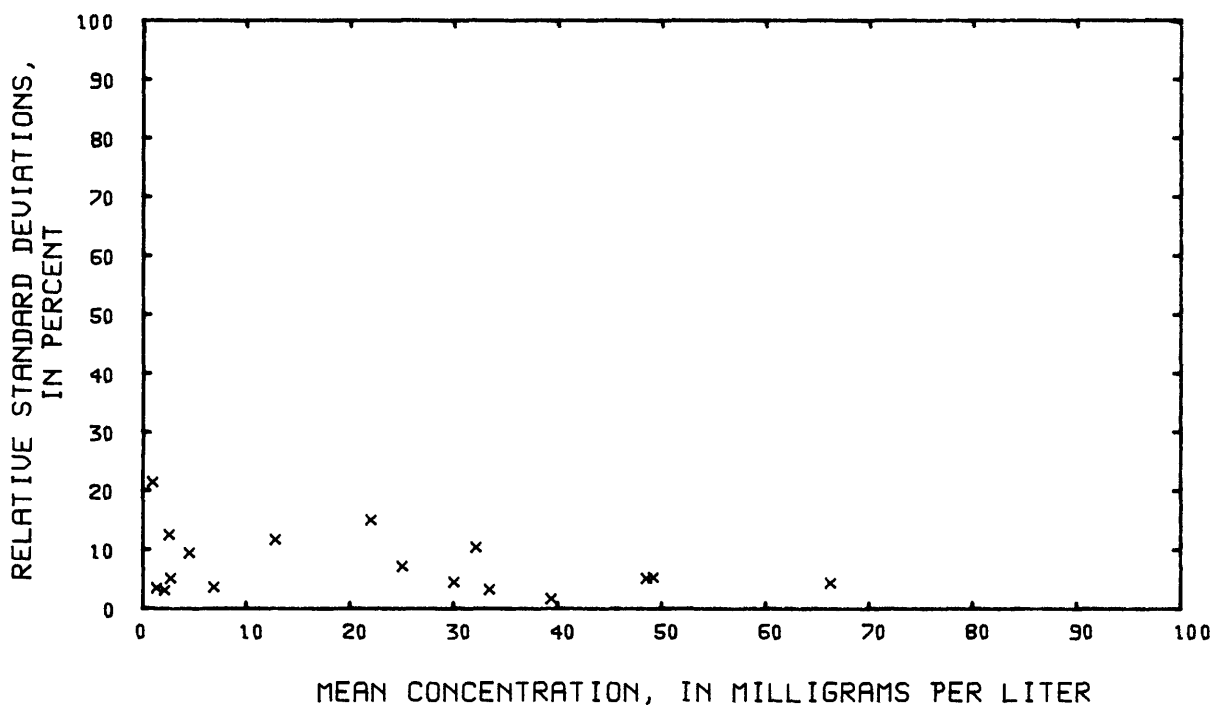


Figure 90.--Precision data for chloride, dissolved,
at the National Water Quality Laboratory.

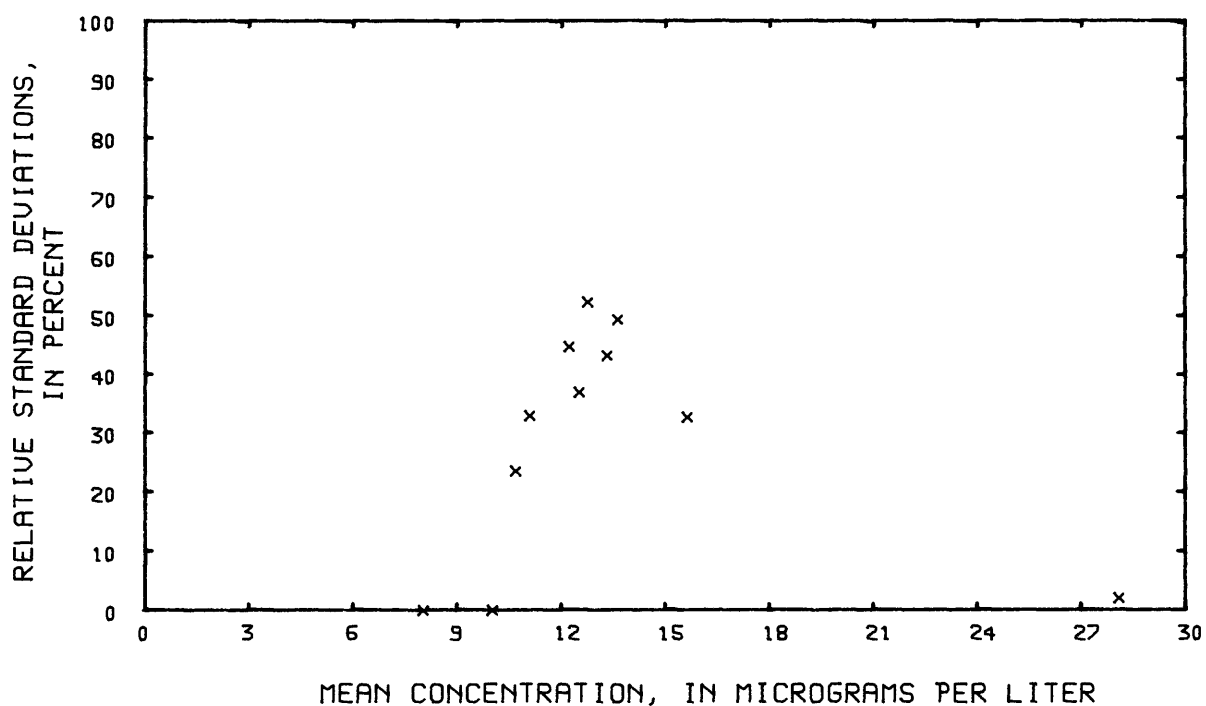


Figure 91.--Precision data for chromium, dissolved,
at the National Water Quality Laboratory.

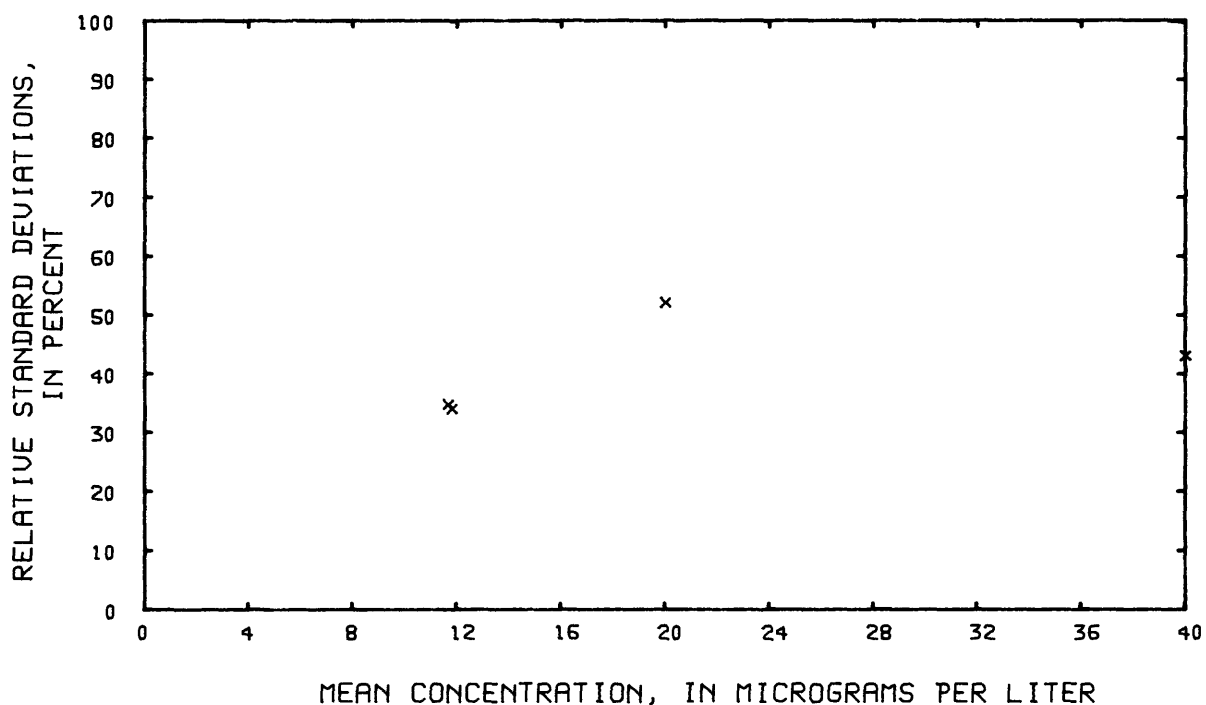


Figure 92.--Precision data for chromium, total recoverable,
at the National Water Quality Laboratory.

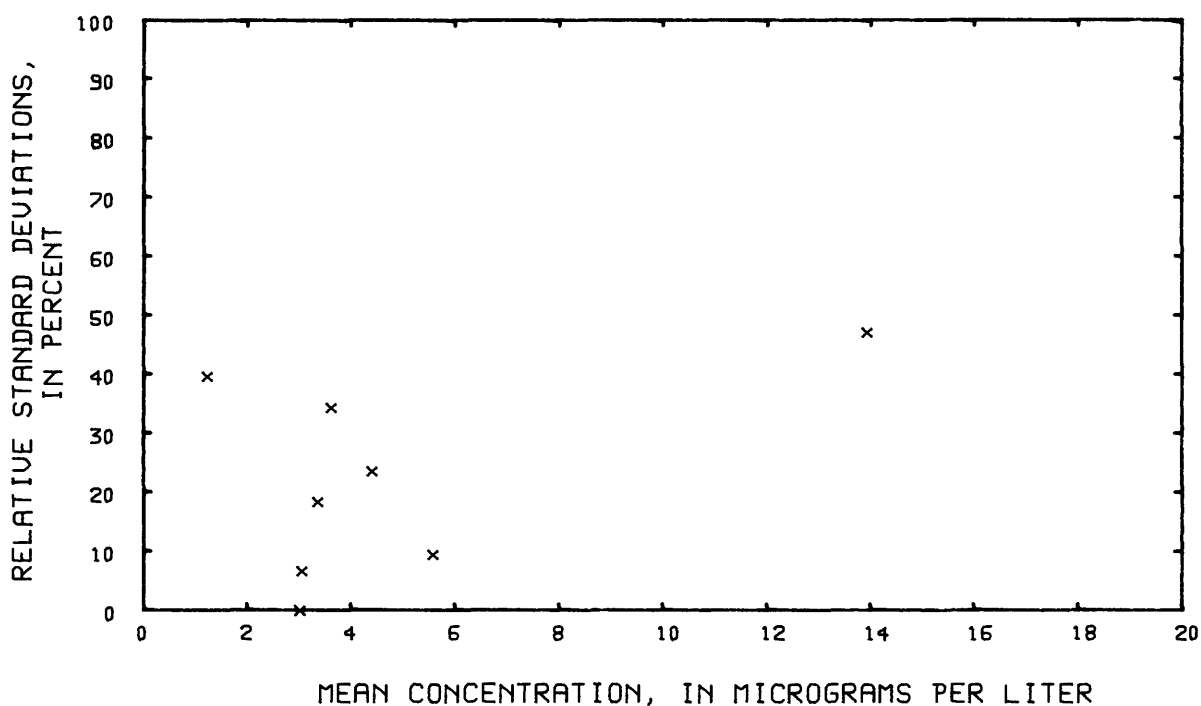


Figure 93.--Precision data for cobalt, dissolved,
(inductively coupled plasma emission spectrometry)
at the National Water Quality Laboratory.

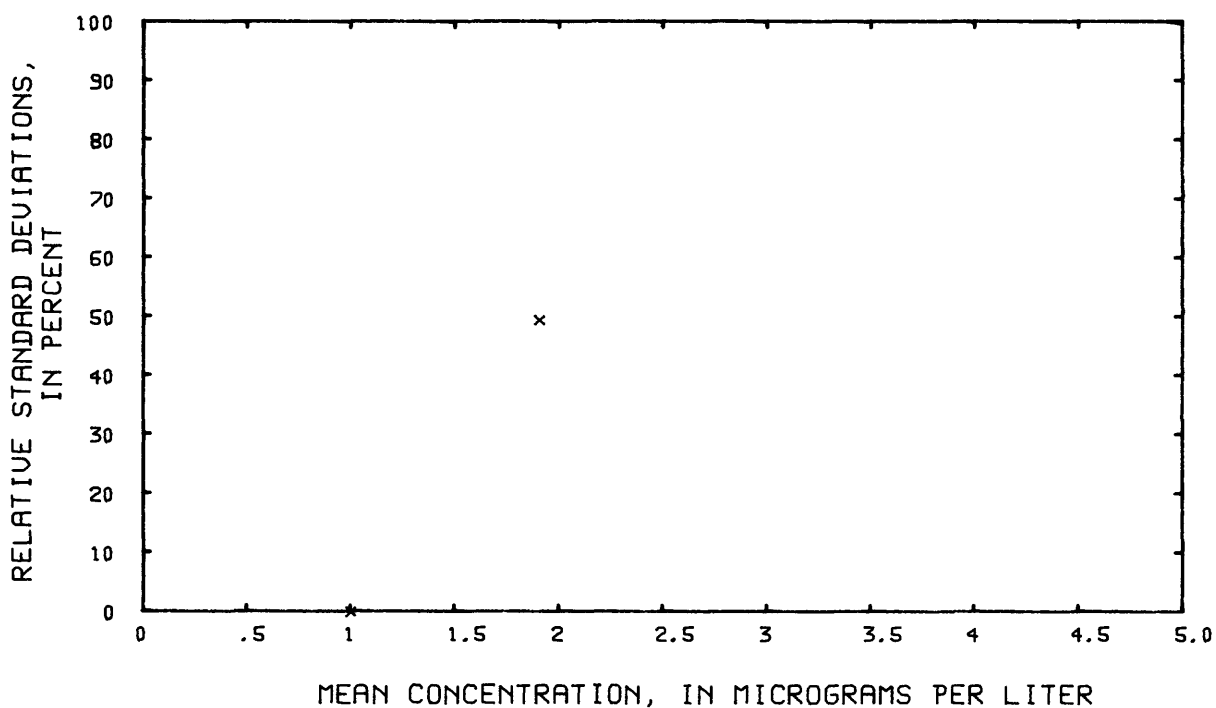


Figure 94.--Precision data for cobalt, dissolved,
(atomic absorption spectrometry)
at the National Water Quality Laboratory.

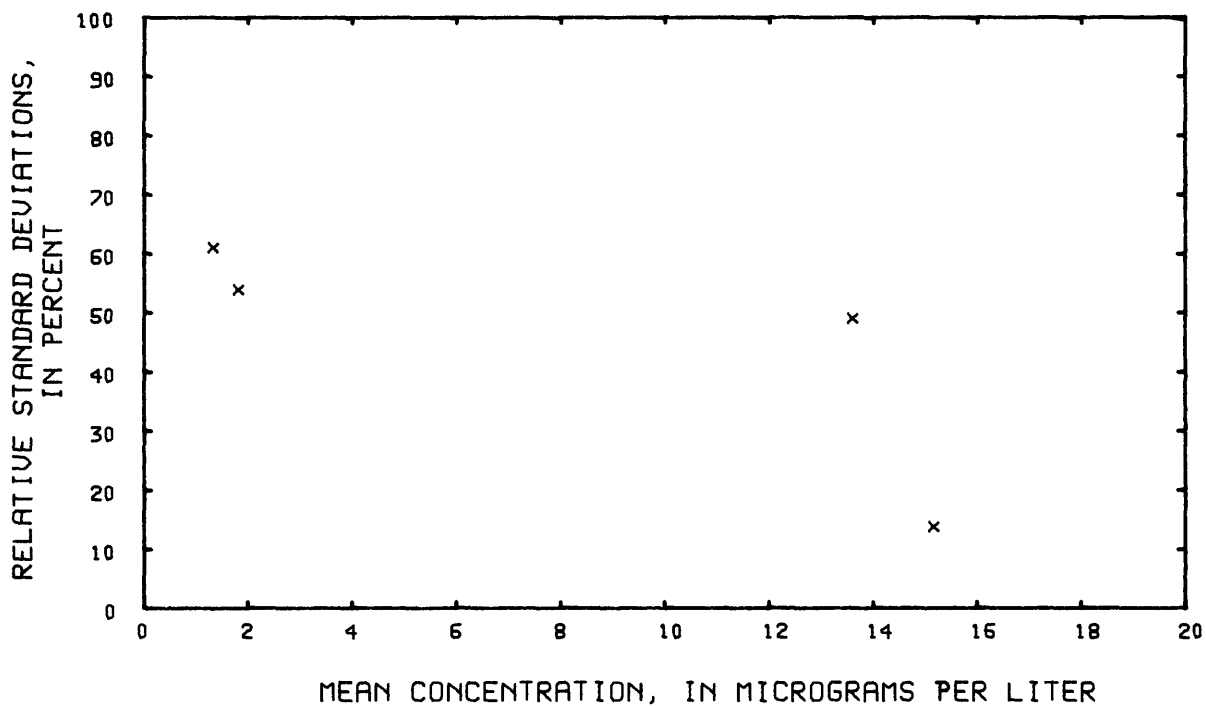


Figure 95.--Precision data for cobalt, total recoverable,
at the National Water Quality Laboratory.

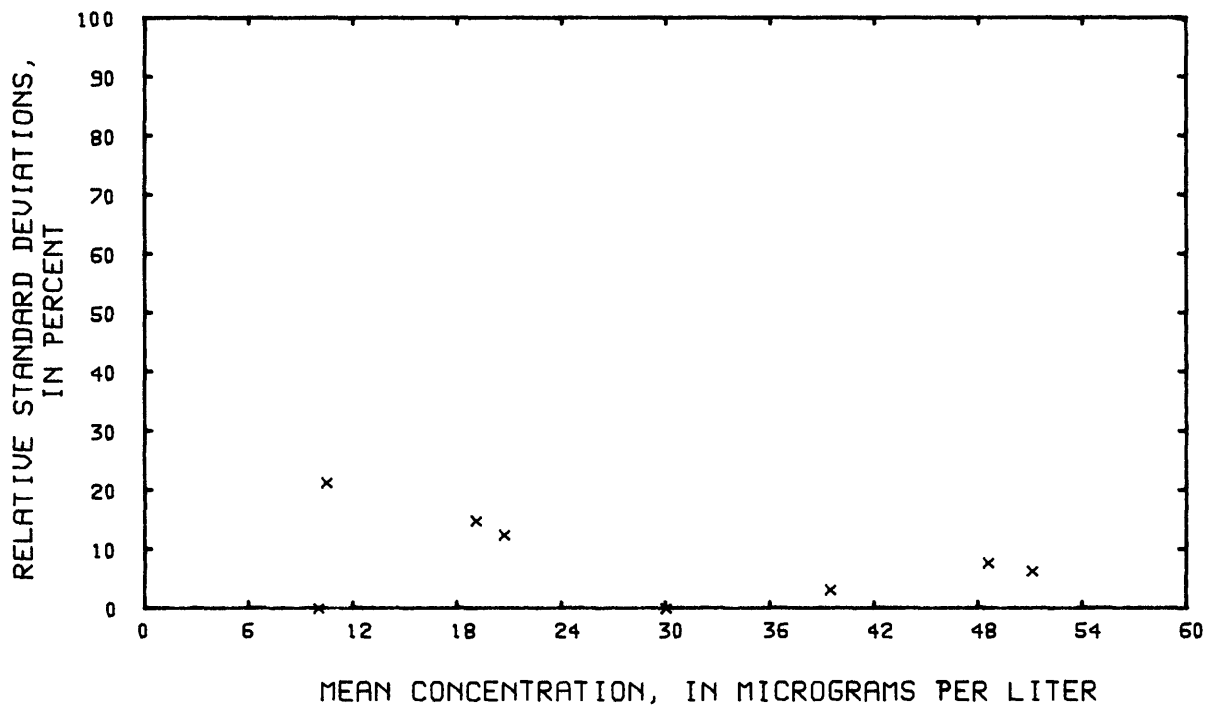


Figure 96.--Precision data for copper, dissolved,
(inductively coupled plasma emission spectrometry)
at the National Water Quality Laboratory.

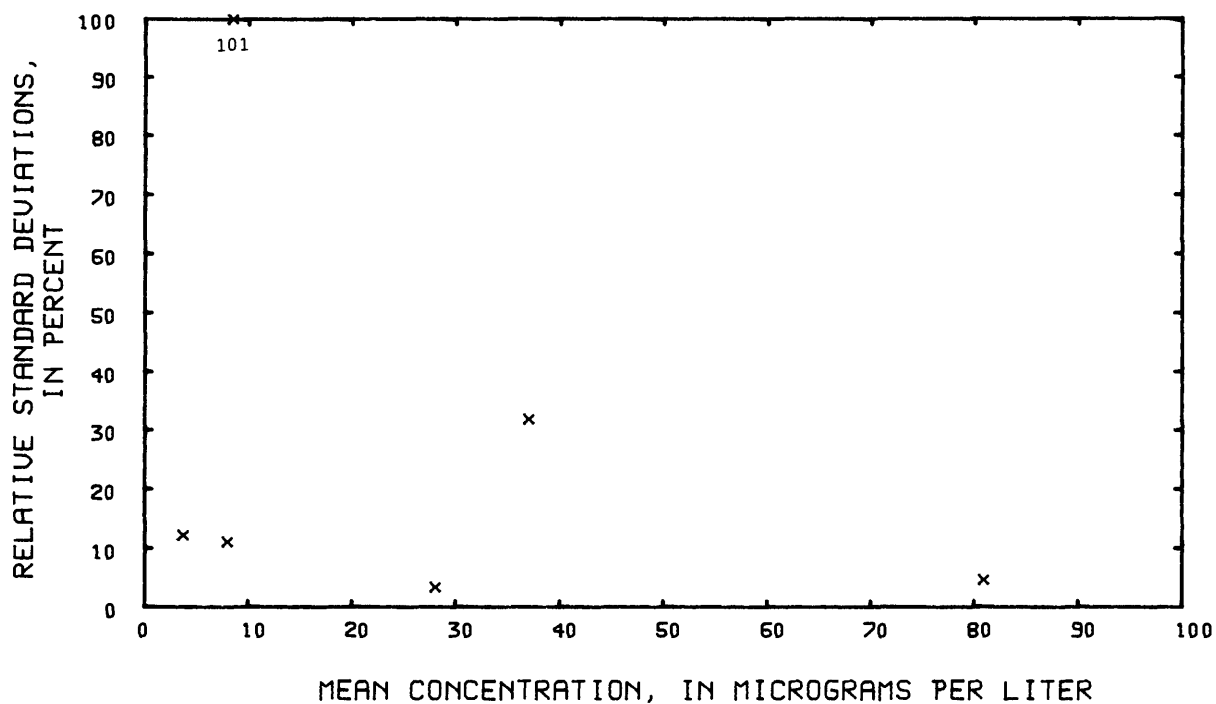


Figure 97.--Precision data for copper, dissolved,
(atomic absorption spectrometry)
at the National Water Quality Laboratory.

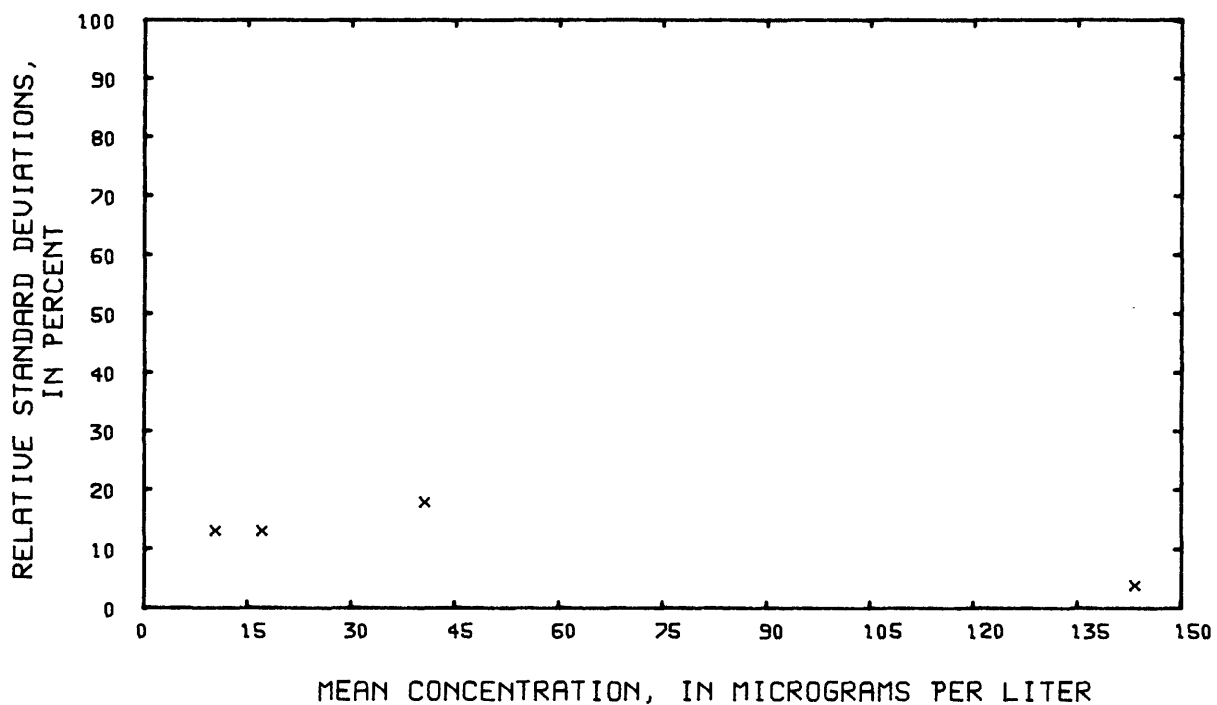


Figure 98.--Precision data for copper, total recoverable,
at the National Water Quality Laboratory.

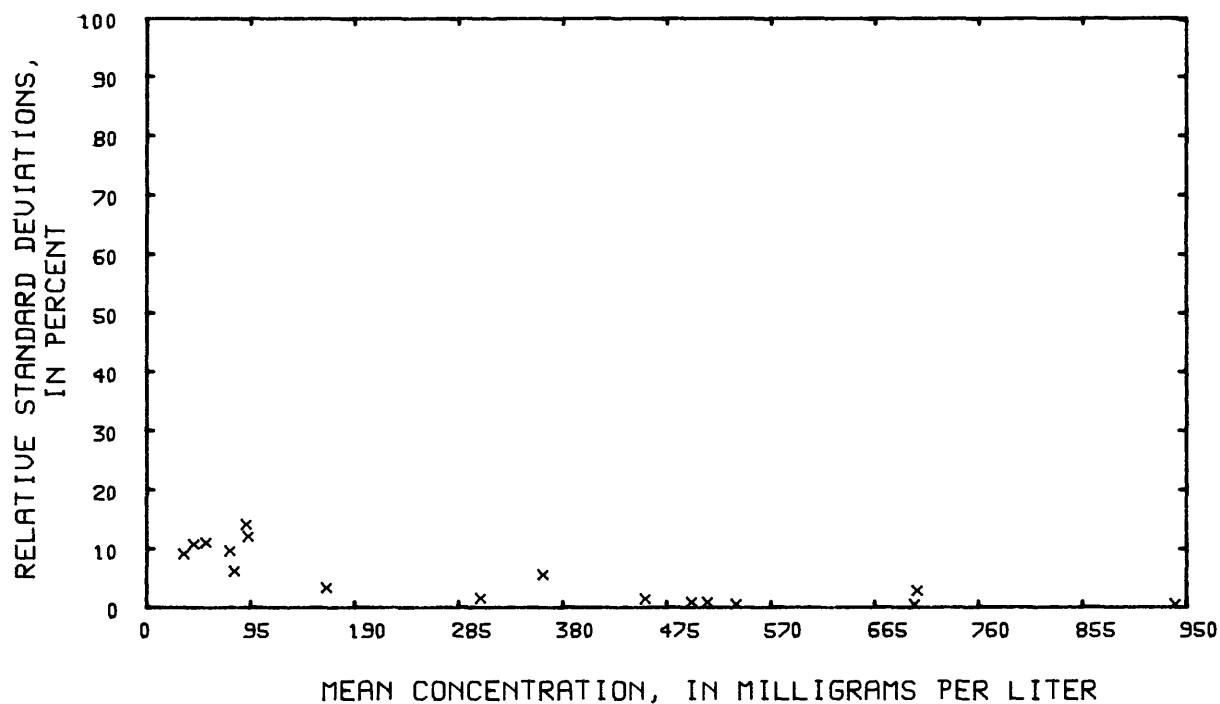


Figure 99.--Precision data for dissolved solids
at the National Water Quality Laboratory.

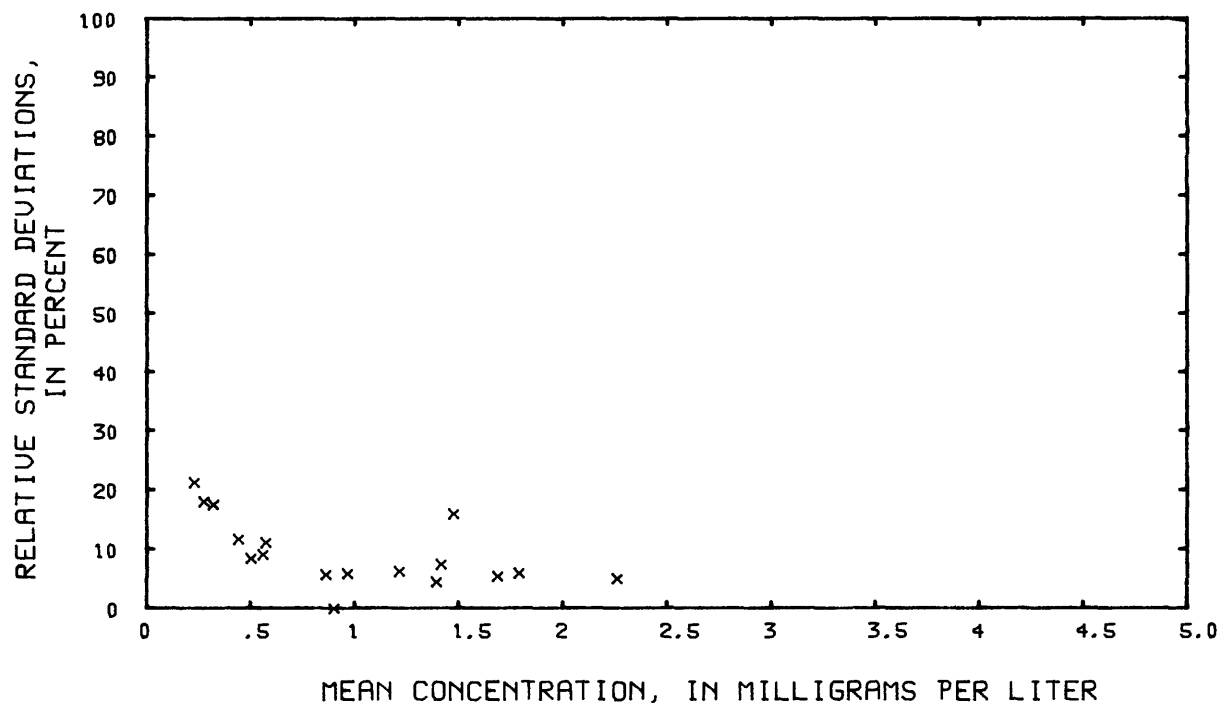


Figure 100.--Precision data for fluoride, dissolved,
at the National Water Quality Laboratory.

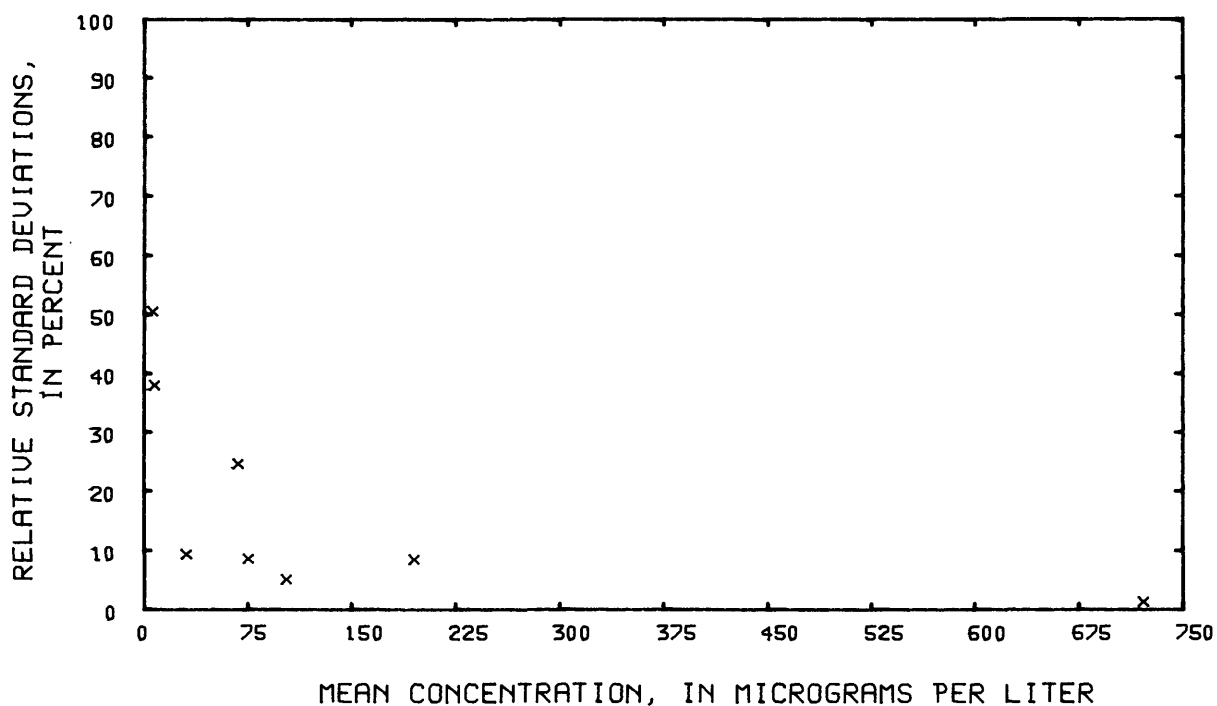


Figure 101.--Precision data for Iron, dissolved,
(inductively coupled plasma emission spectrometry)
at the National Water Quality Laboratory.

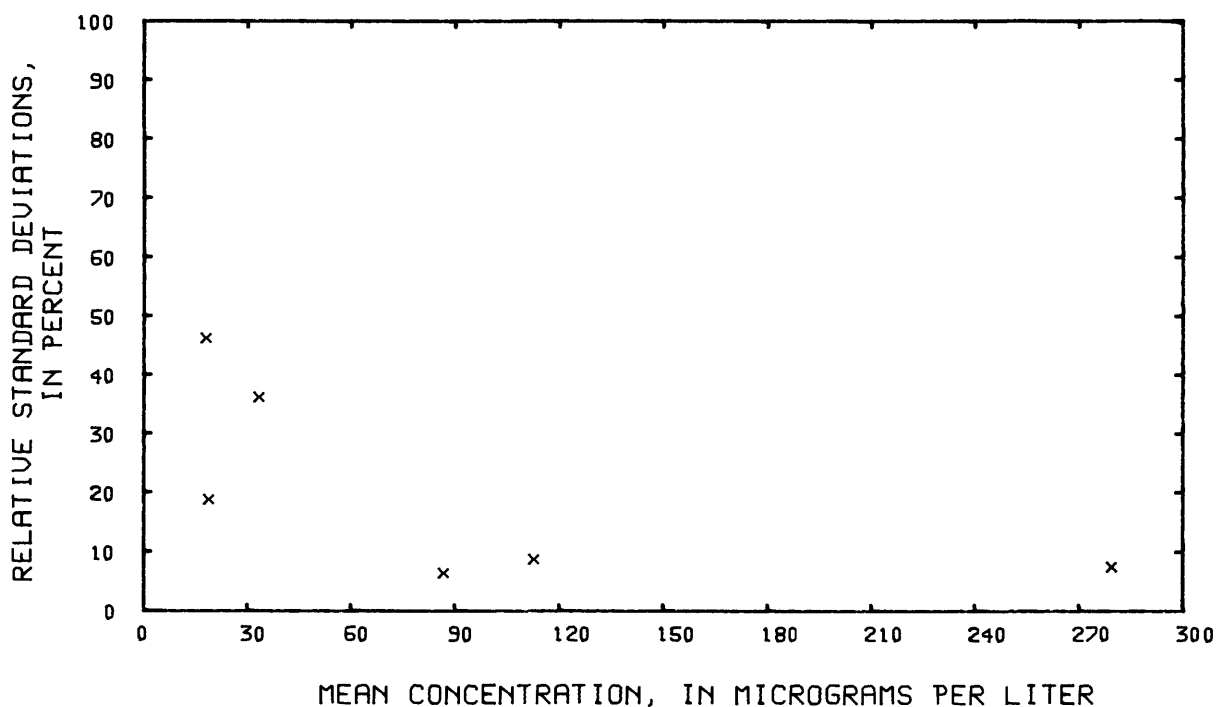


Figure 102.--Precision data for Iron, dissolved,
(atomic absorption spectrometry)
at the National Water Quality Laboratory.

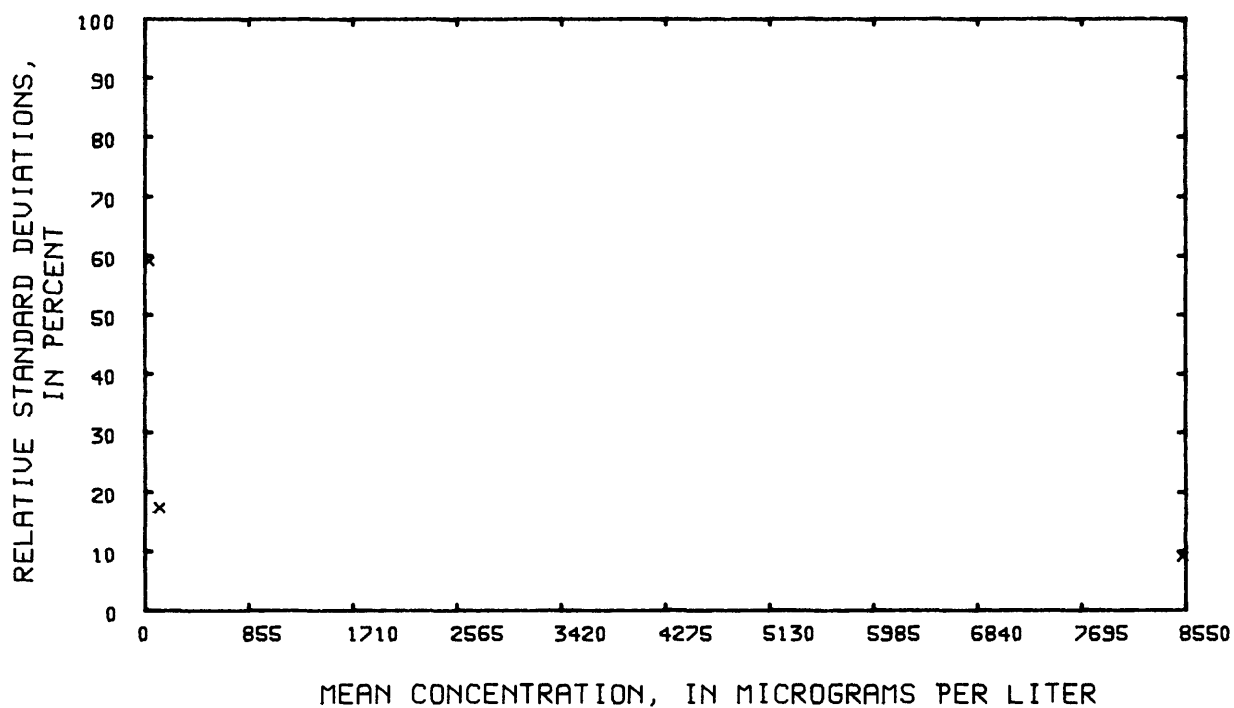


Figure 103.--Precision data for iron, total recoverable,
at the National Water Quality Laboratory.

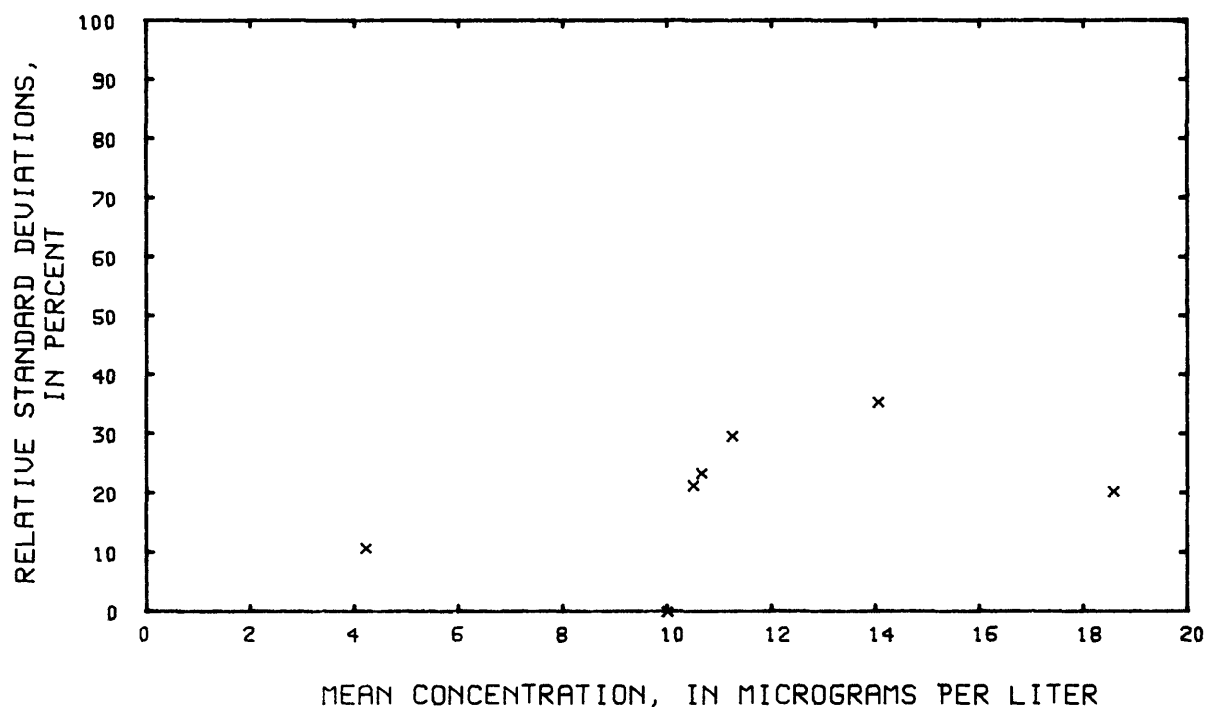


Figure 104.--Precision data for lead, dissolved,
(inductively coupled plasma emission spectrometry)
at the National Water Quality Laboratory.

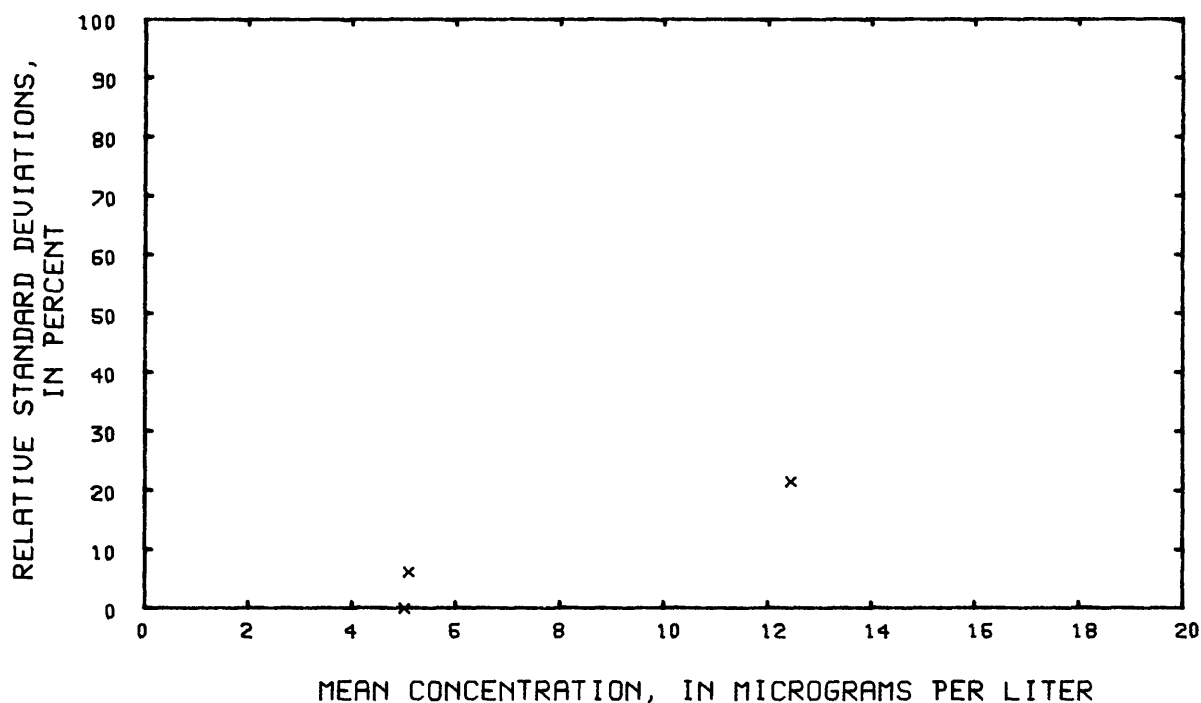


Figure 105.--Precision data for lead, dissolved,
(atomic absorption spectrometry)
at the National Water Quality Laboratory.

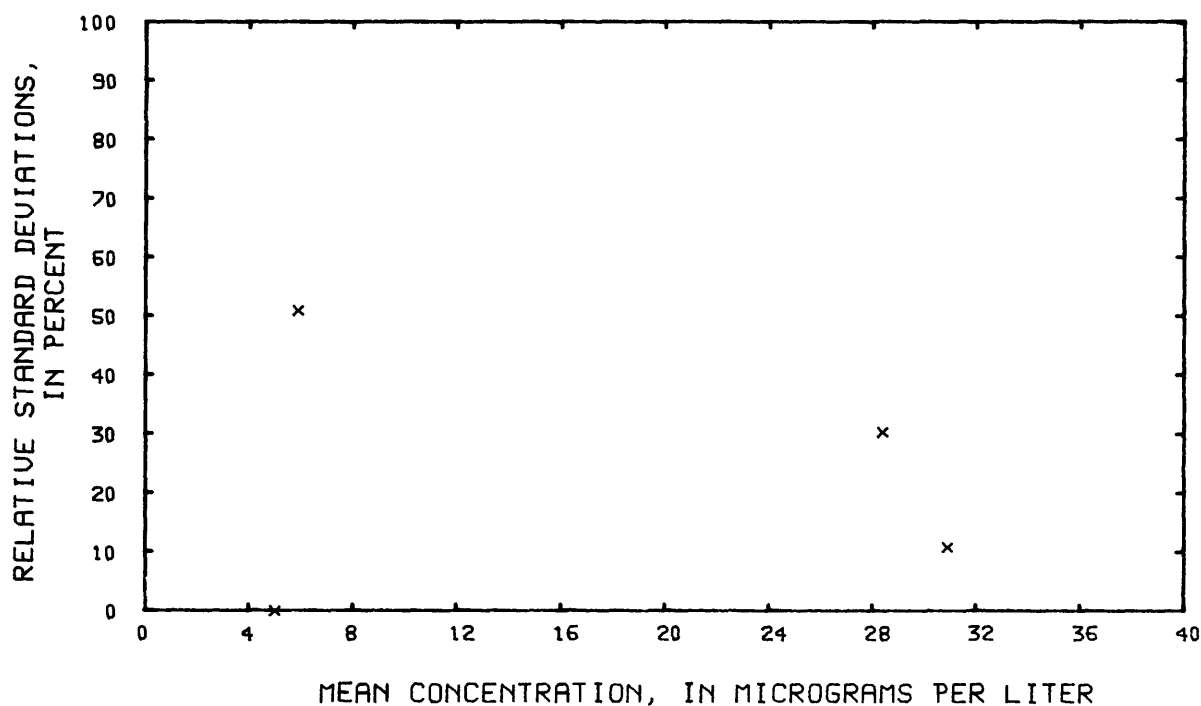


Figure 106.--Precision data for lead, total recoverable,
at the National Water Quality Laboratory.

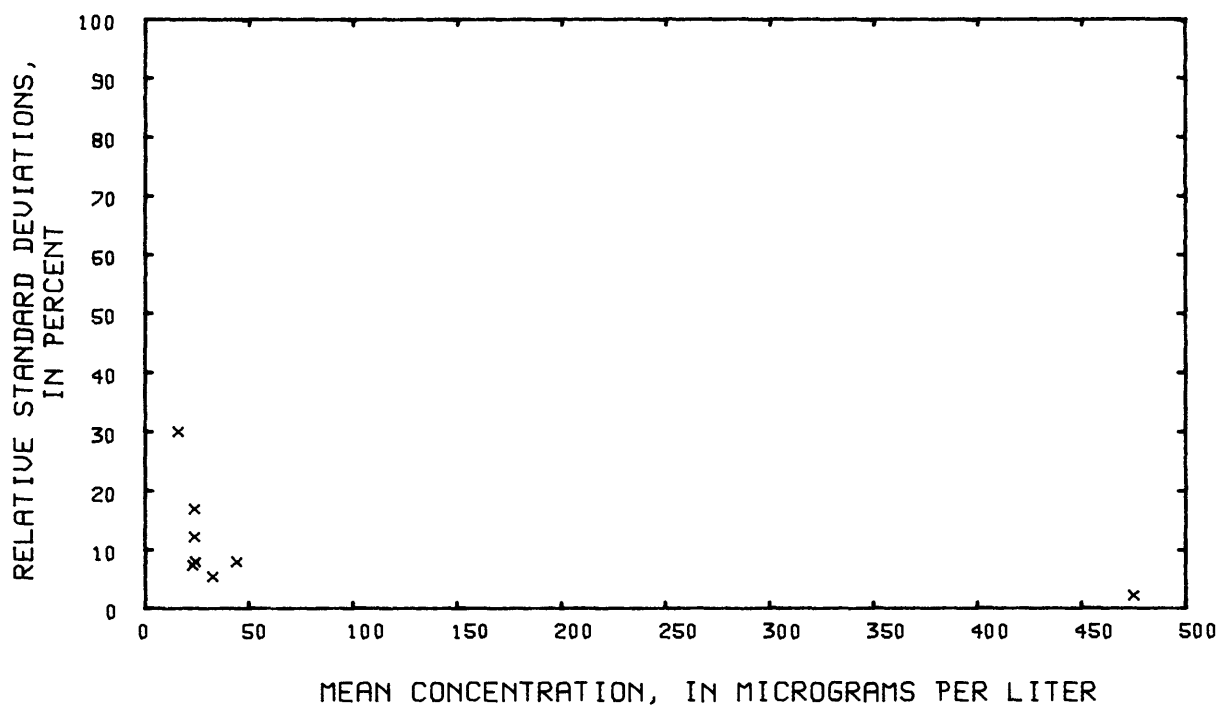


Figure 107.--Precision data for lithium, dissolved,
at the National Water Quality Laboratory.

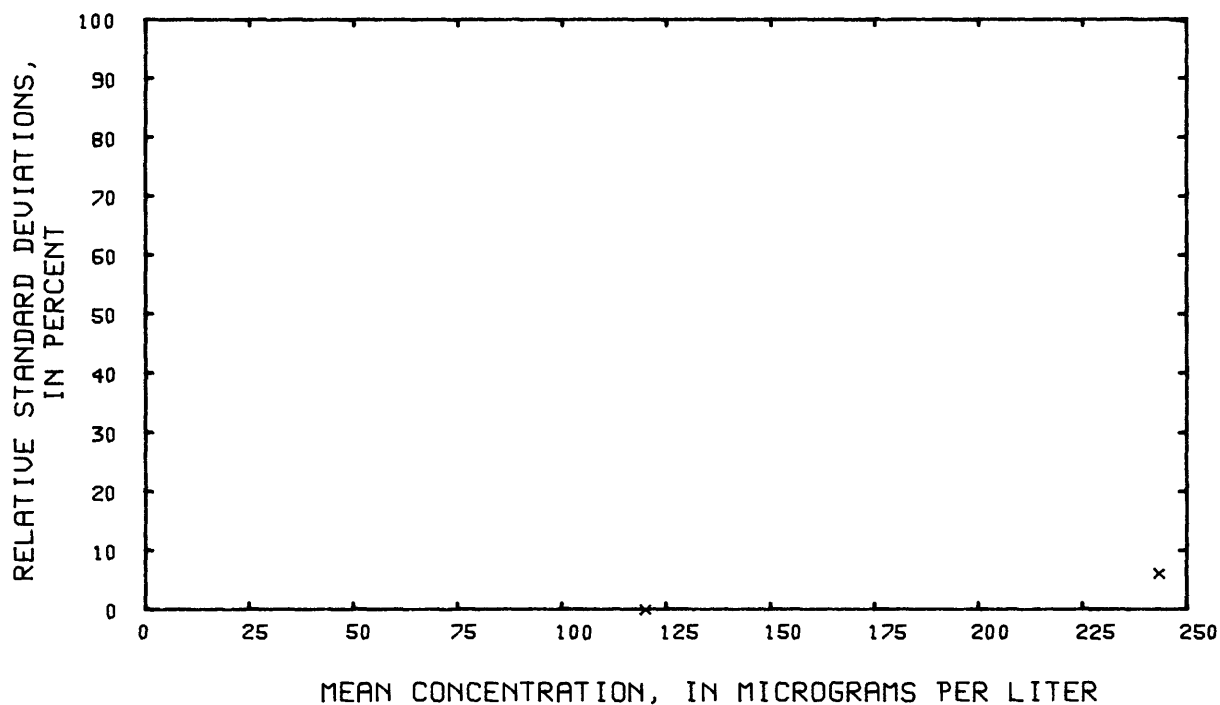


Figure 108.--Precision data for lithium, total recoverable,
at the National Water Quality Laboratory.

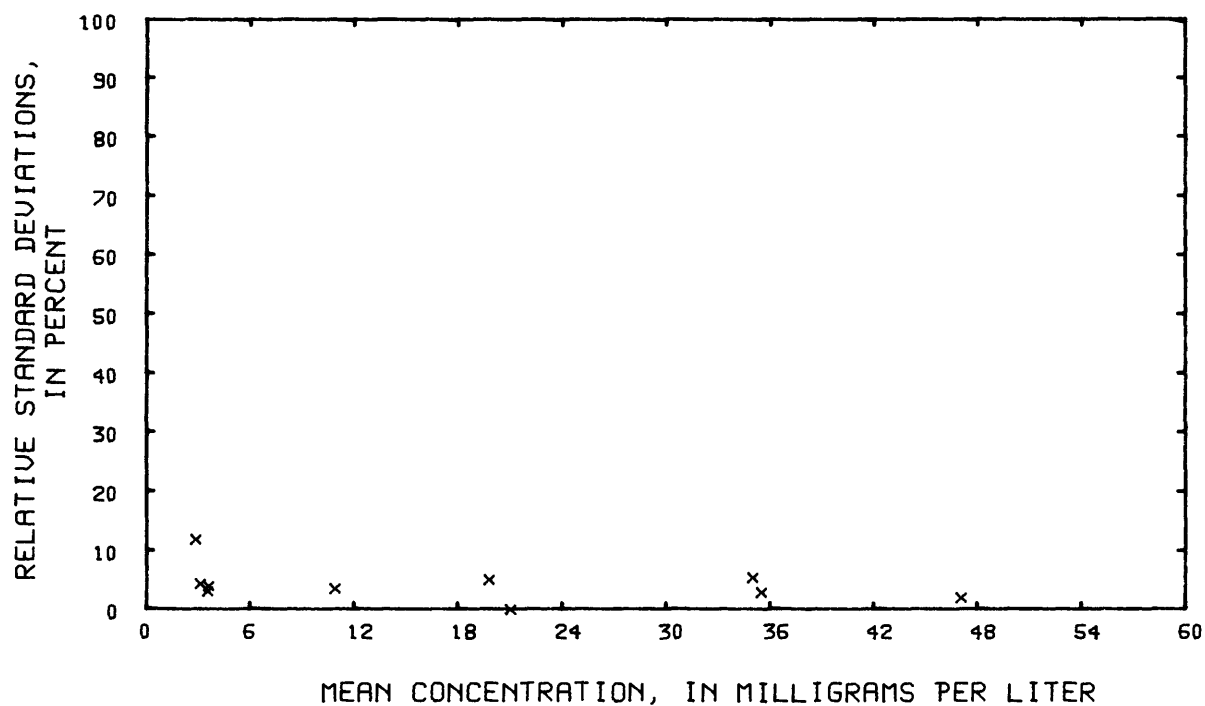


Figure 109.--Precision data for magnesium, dissolved, (inductively coupled plasma emission spectrometry) at the National Water Quality Laboratory.

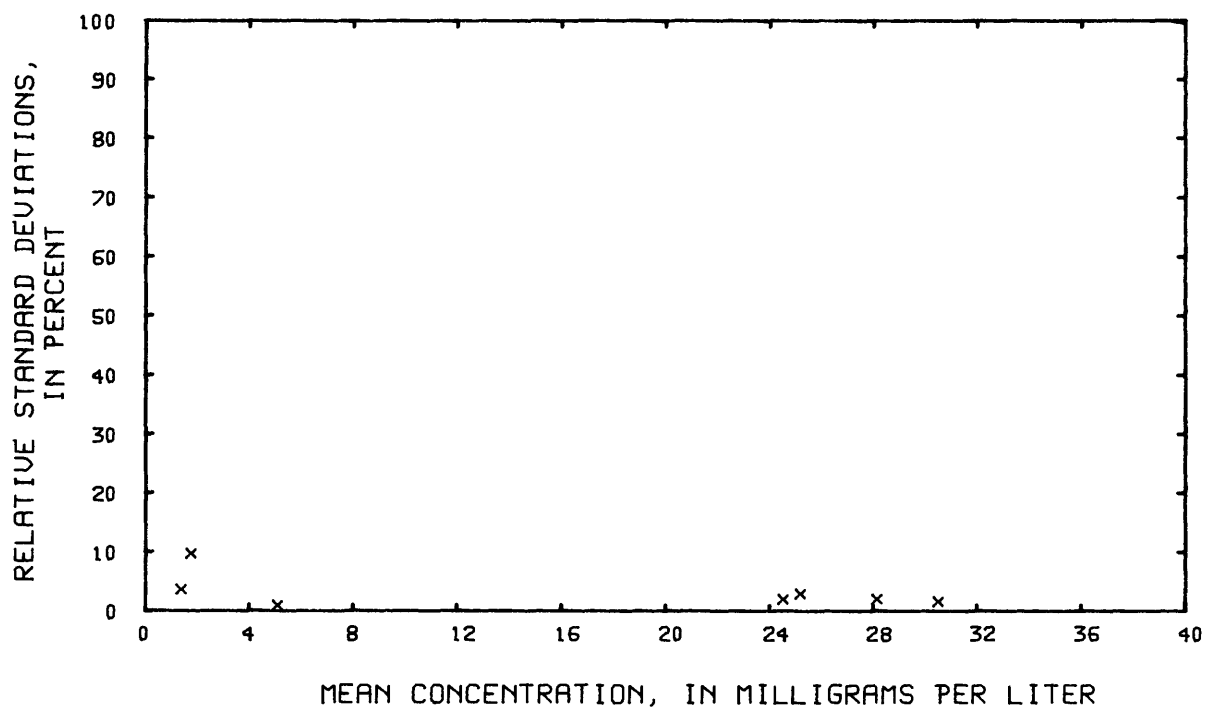


Figure 110.--Precision data for magnesium, dissolved, (atomic absorption spectrometry) at the National Water Quality Laboratory.

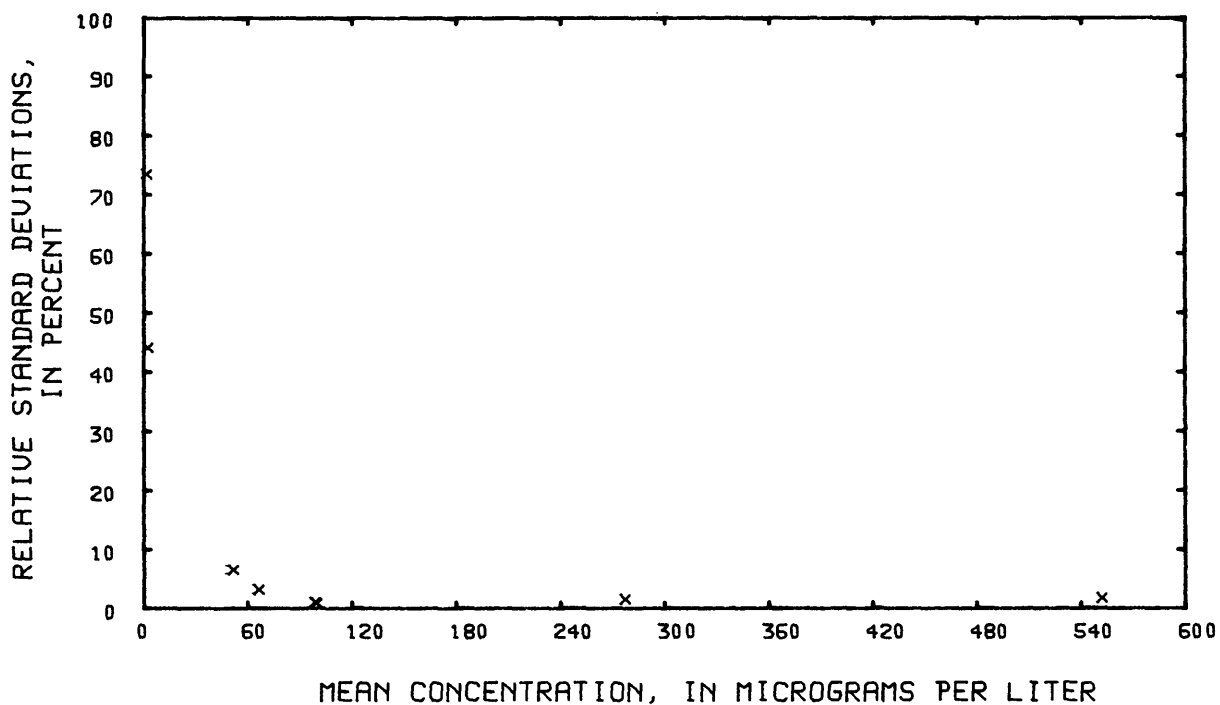


Figure 111.--Precision data for manganese, dissolved,
(inductively coupled plasma emission spectrometry)
at the National Water Quality Laboratory.

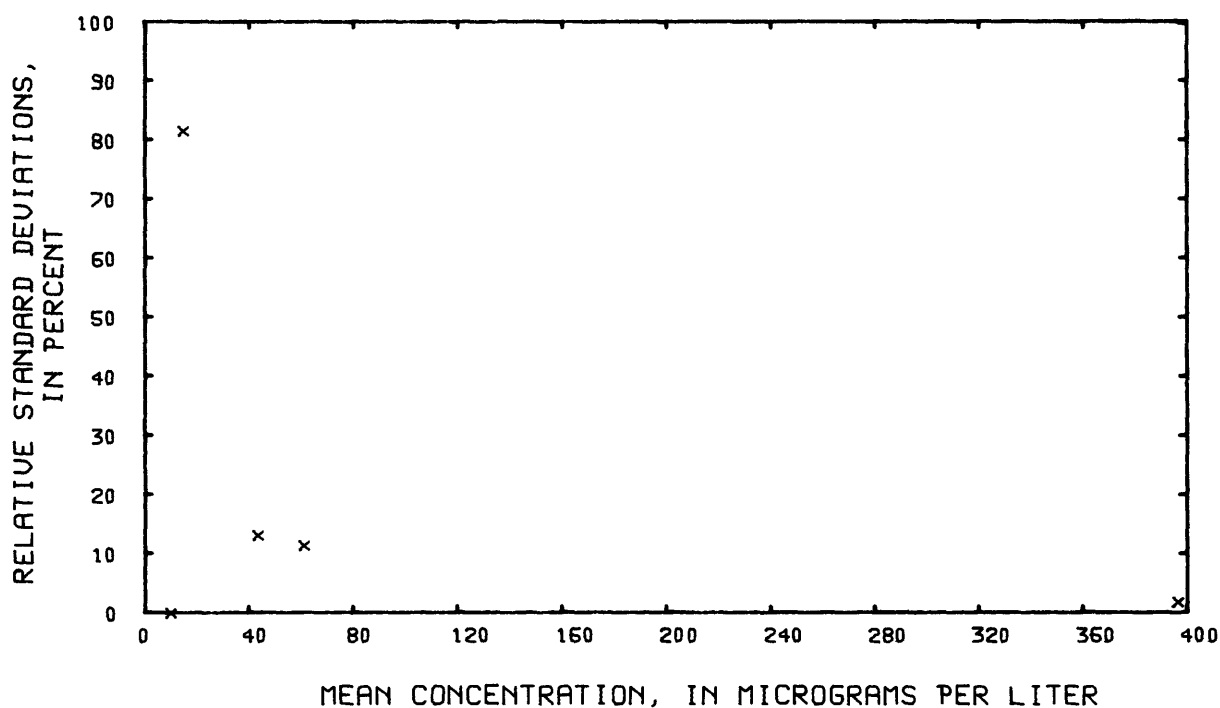


Figure 112.--Precision data for manganese, dissolved,
(atomic absorption spectrometry)
at the National Water Quality Laboratory.

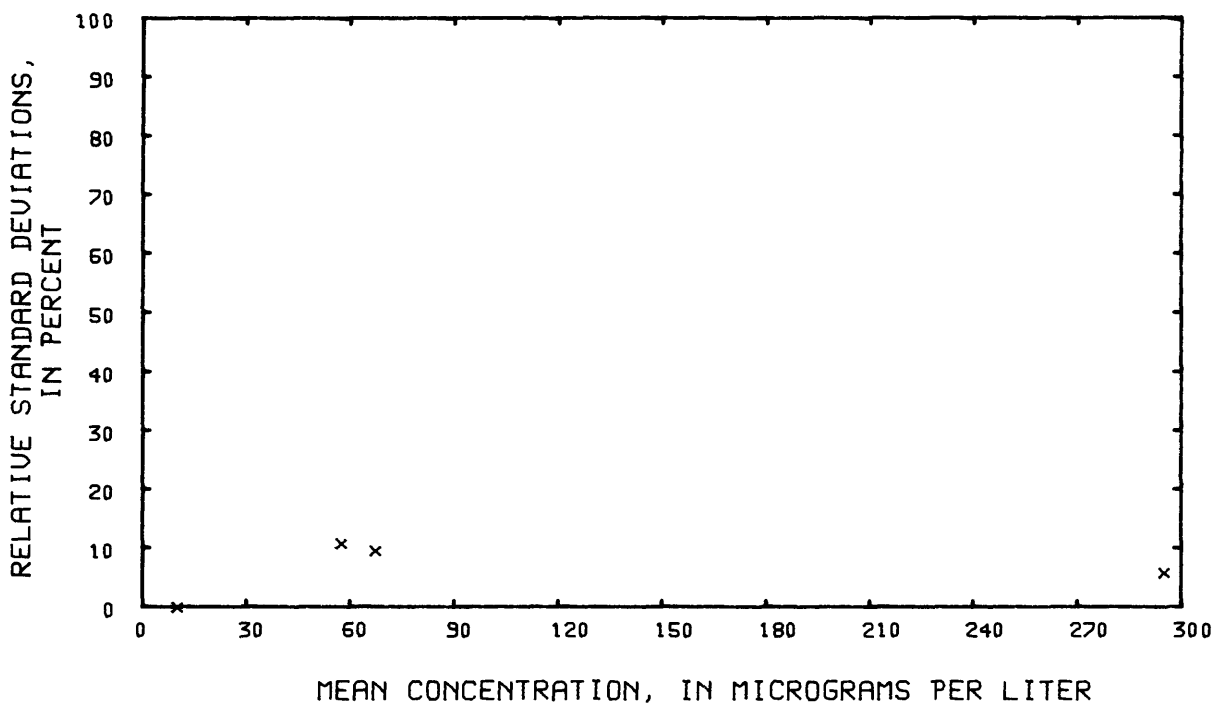


Figure 113.--Precision data for manganese, total recoverable, at the National Water Quality Laboratory.

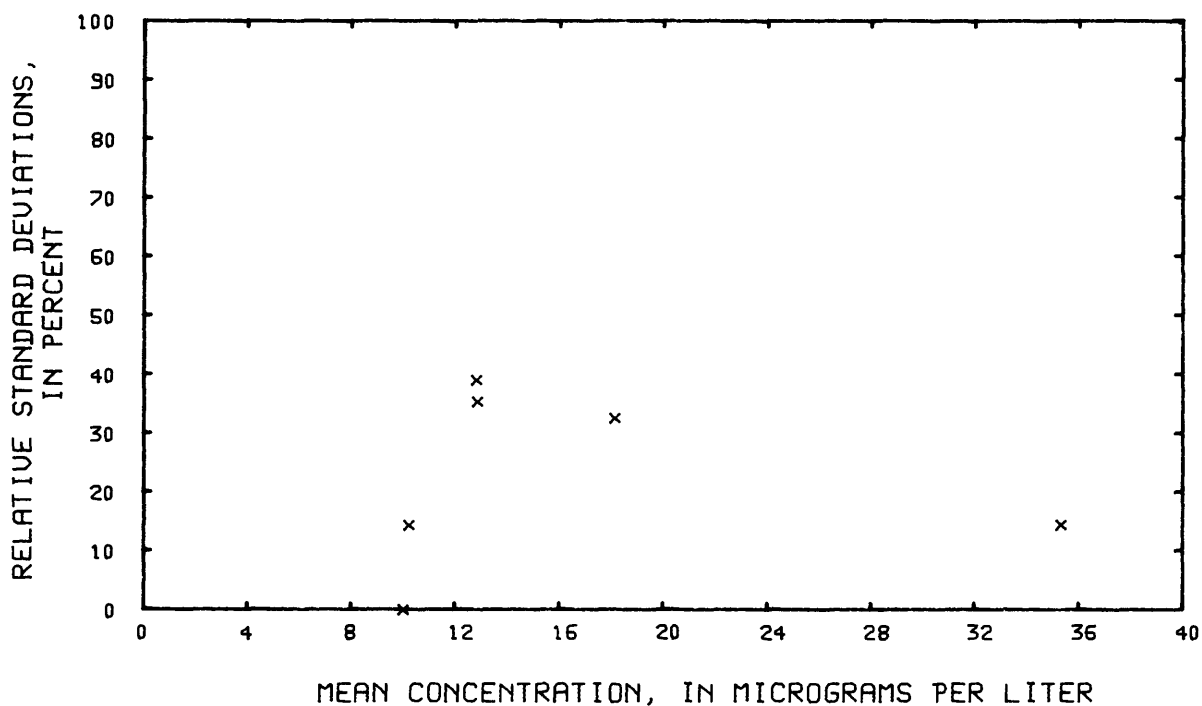


Figure 114.--Precision data for molybdenum, dissolved, (inductively coupled plasma emission spectrometry) at the National Water Quality Laboratory.

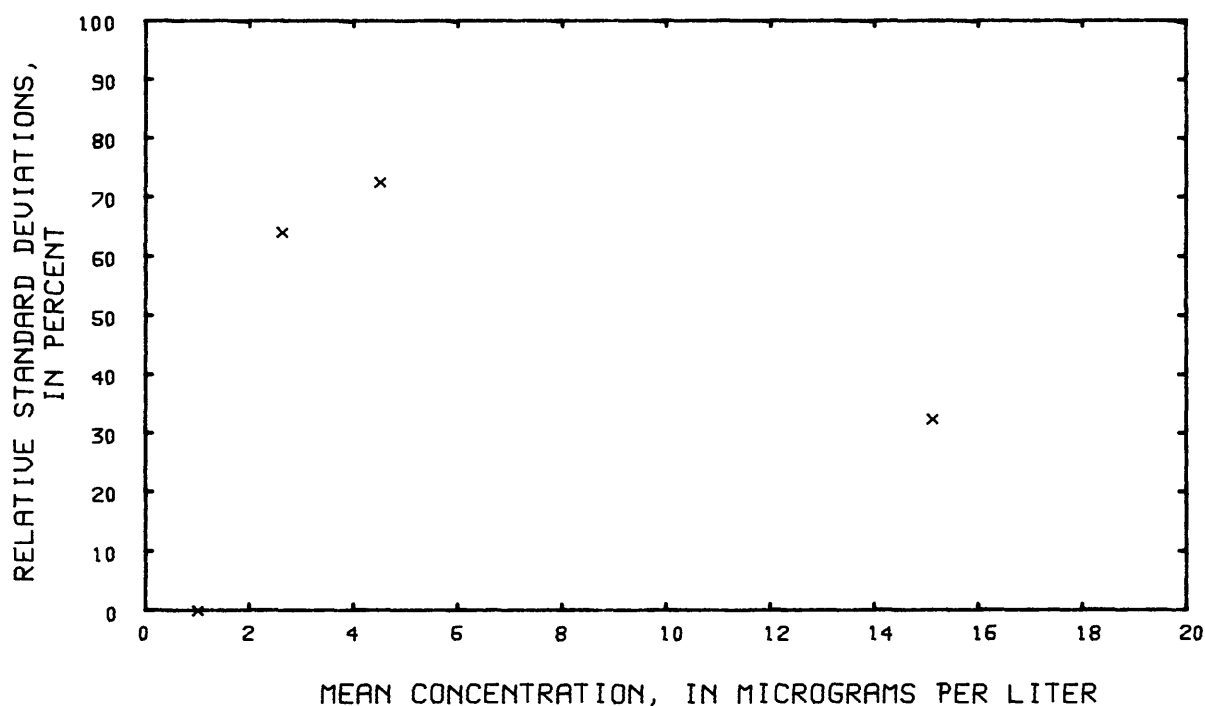


Figure 115.--Precision data for molybdenum, dissolved,
(atomic absorption spectrometry)
at the National Water Quality Laboratory.

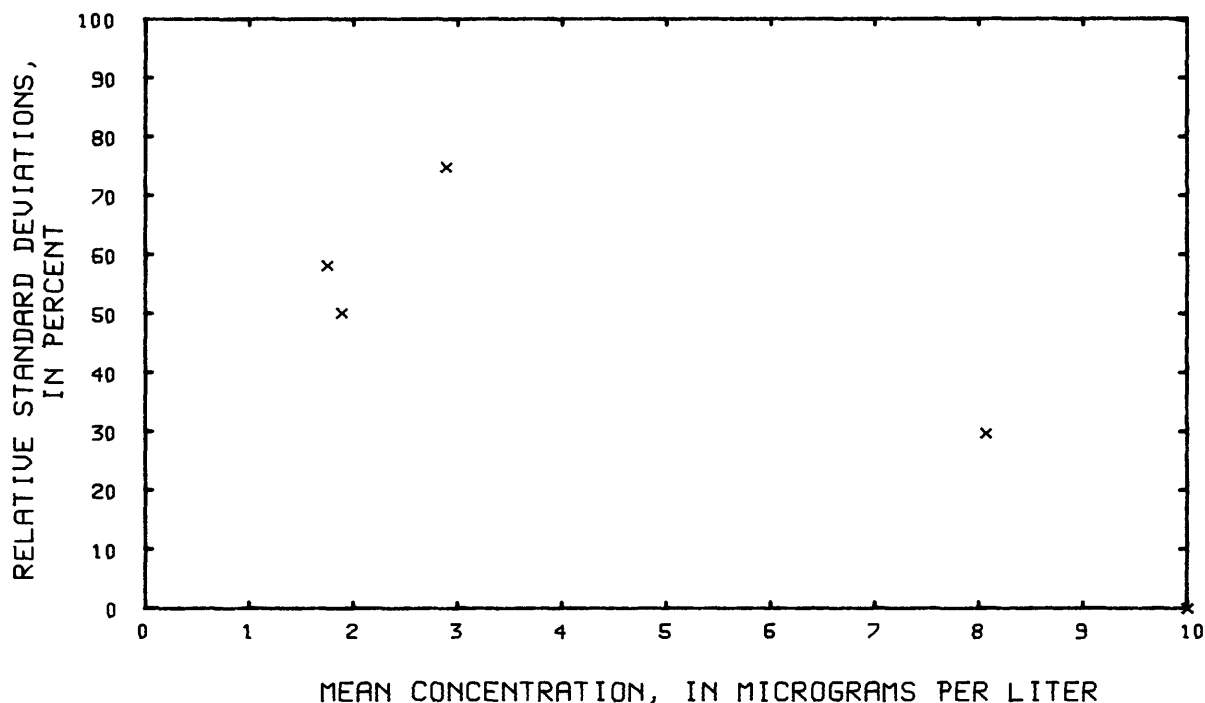


Figure 116.--Precision data for nickel, dissolved,
(inductively coupled plasma emission spectrometry)
at the National Water Quality Laboratory.

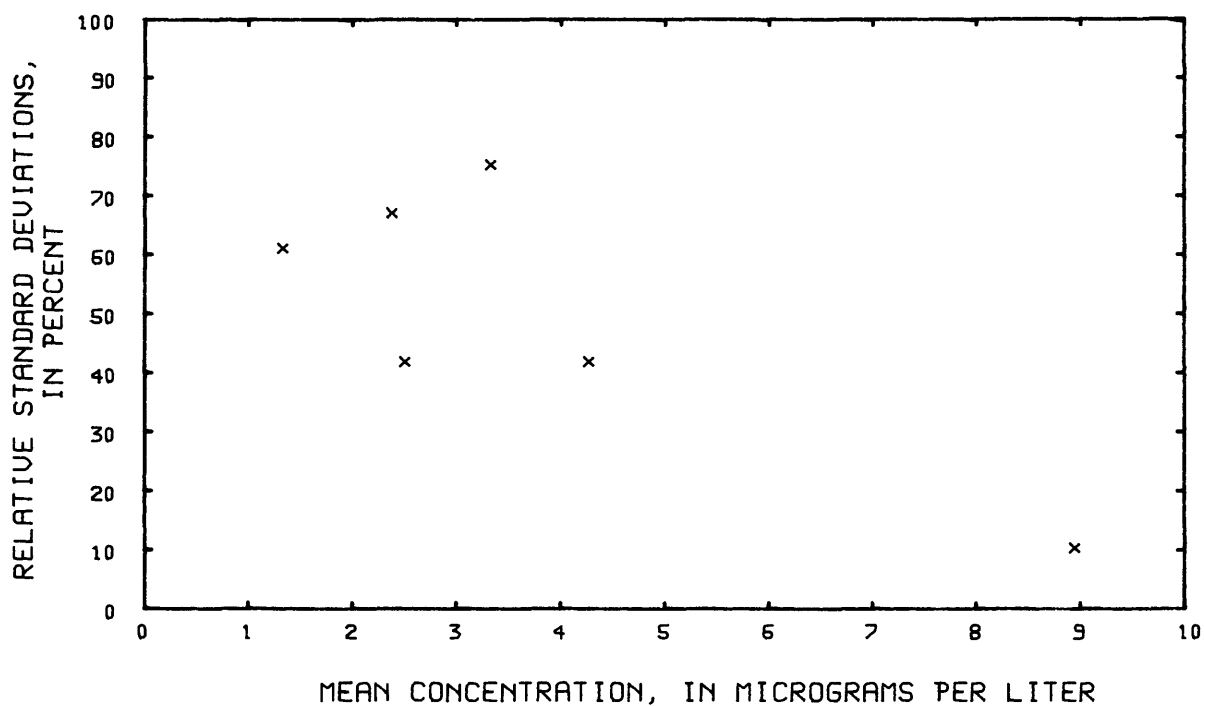


Figure 117.--Precision data for nickel, dissolved,
(atomic absorption spectrometry)
at the National Water Quality Laboratory.

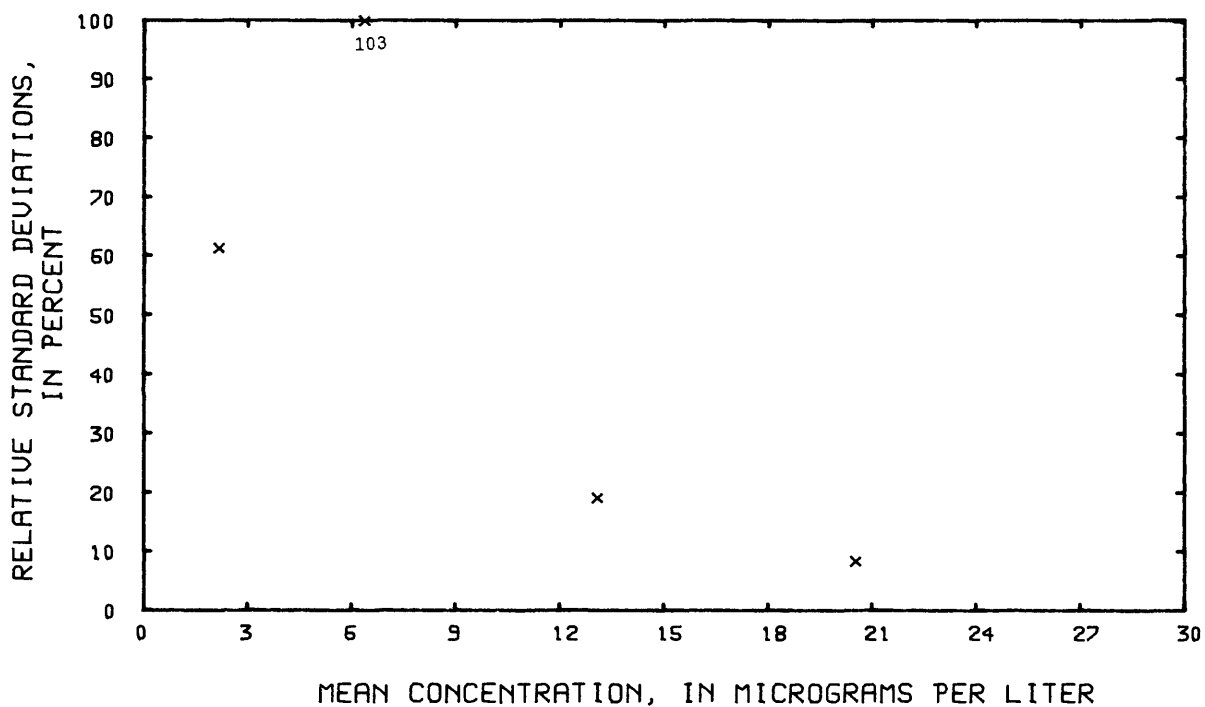


Figure 118.--Precision data for nickel, total recoverable,
at the National Water Quality Laboratory.

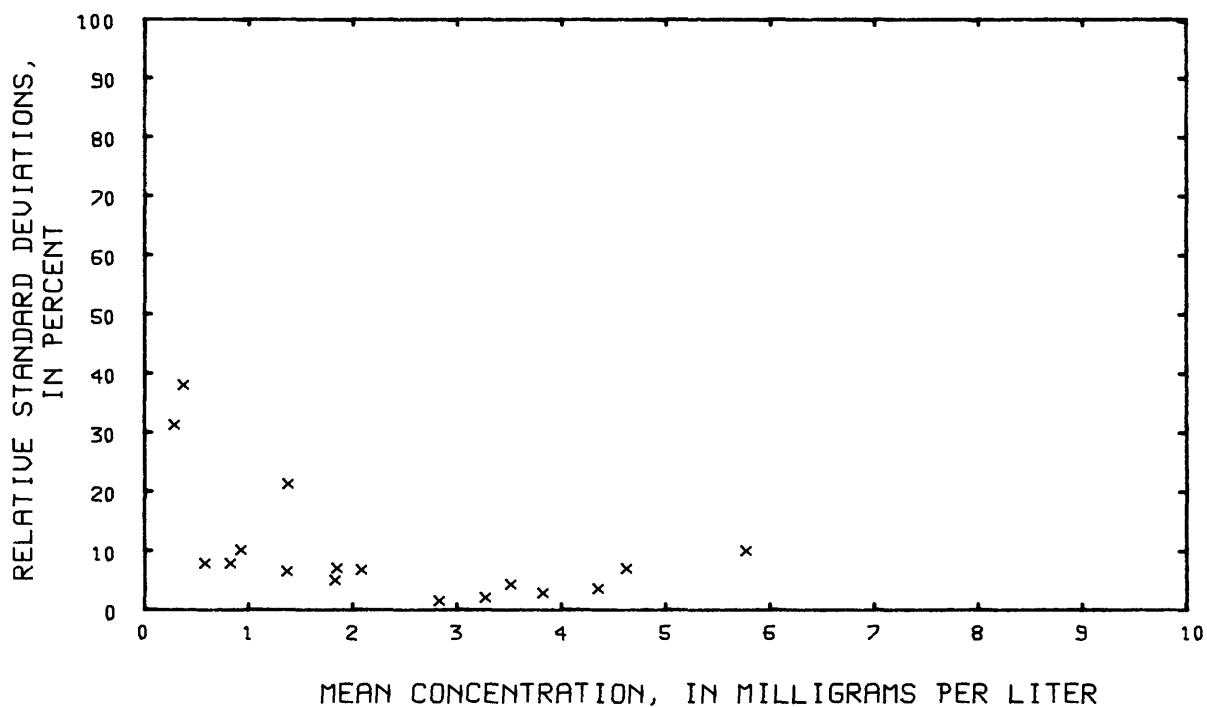


Figure 119.--Precision data for potassium, dissolved,
at the National Water Quality Laboratory.

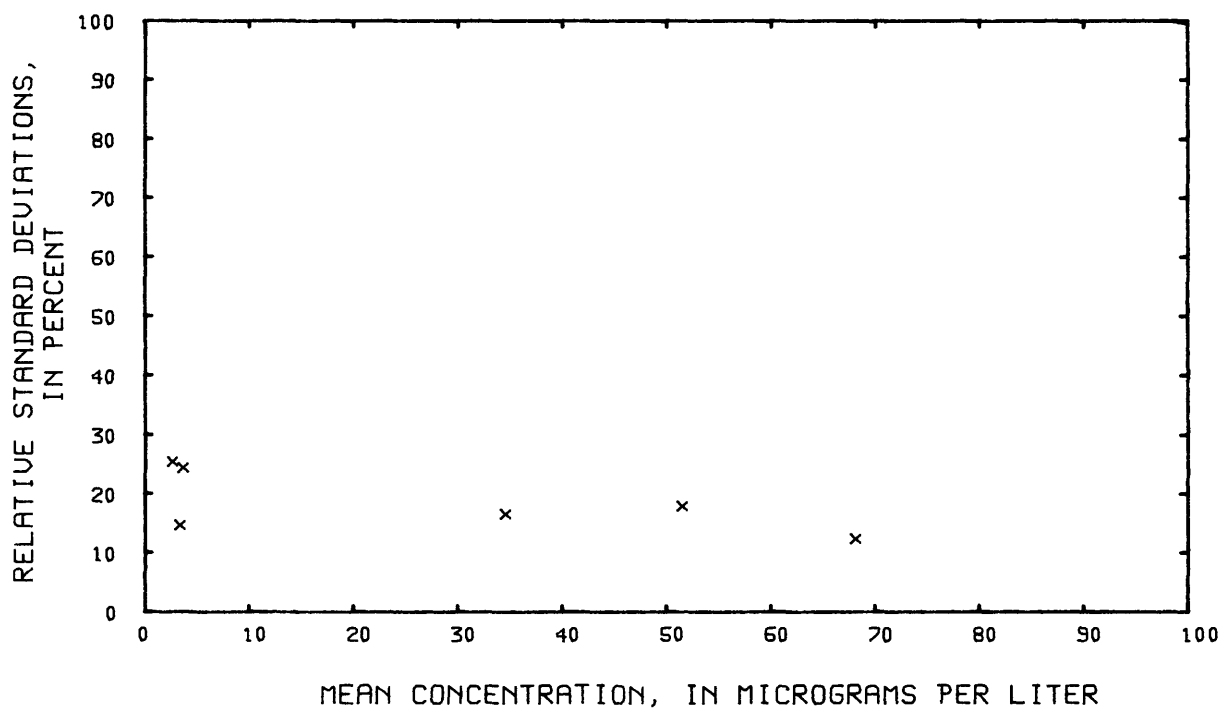


Figure 120.--Precision data for selenium, dissolved,
at the National Water Quality Laboratory.

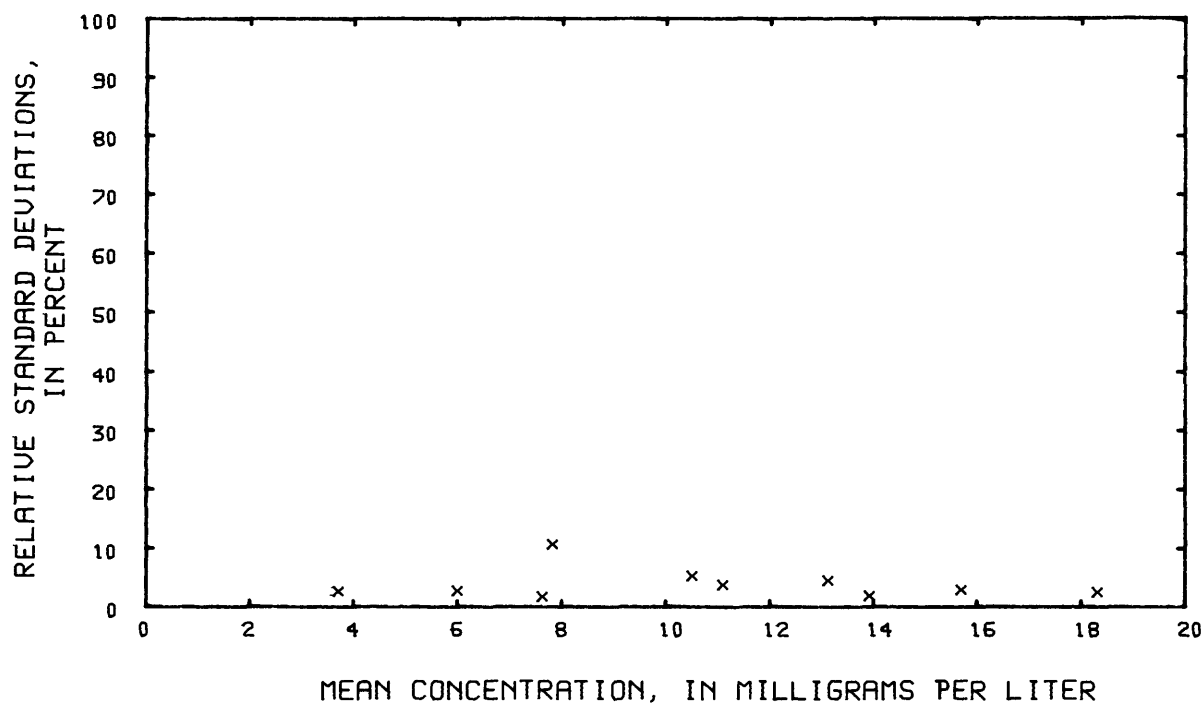


Figure 121.--Precision data for silica, dissolved,
(inductively coupled plasma emission spectrometry)
at the National Water Quality Laboratory.

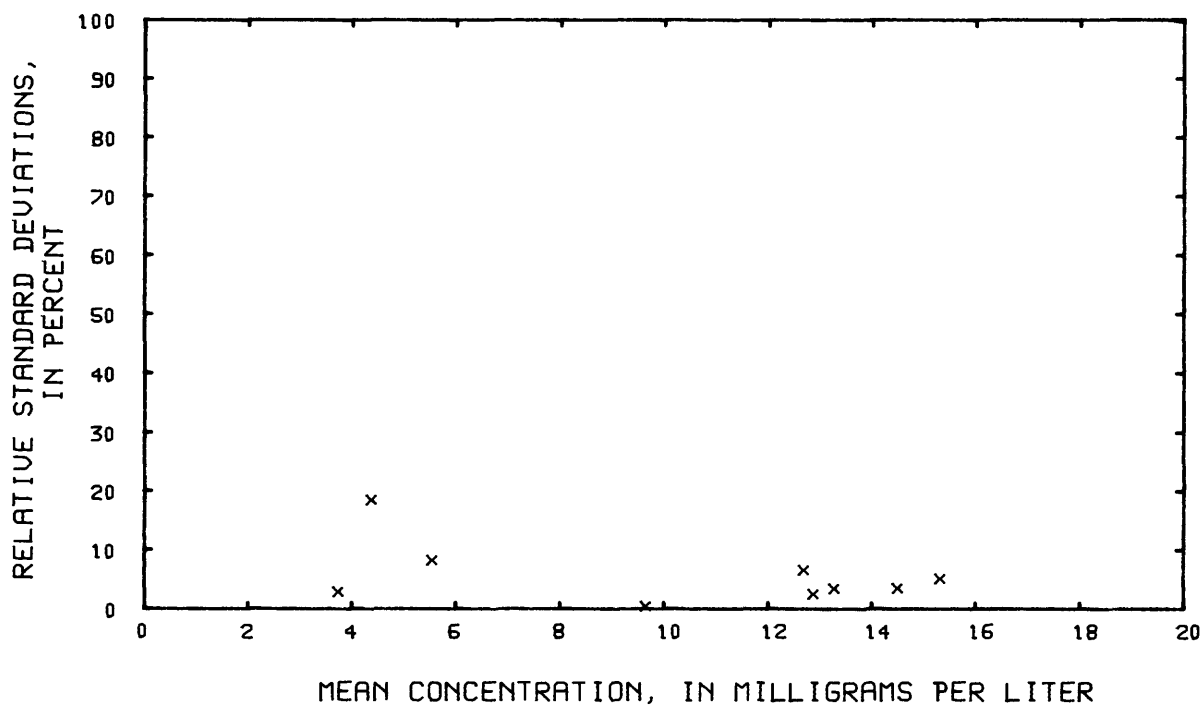


Figure 122.--Precision data for silica, dissolved,
(colorimetry)
at the National Water Quality Laboratory.

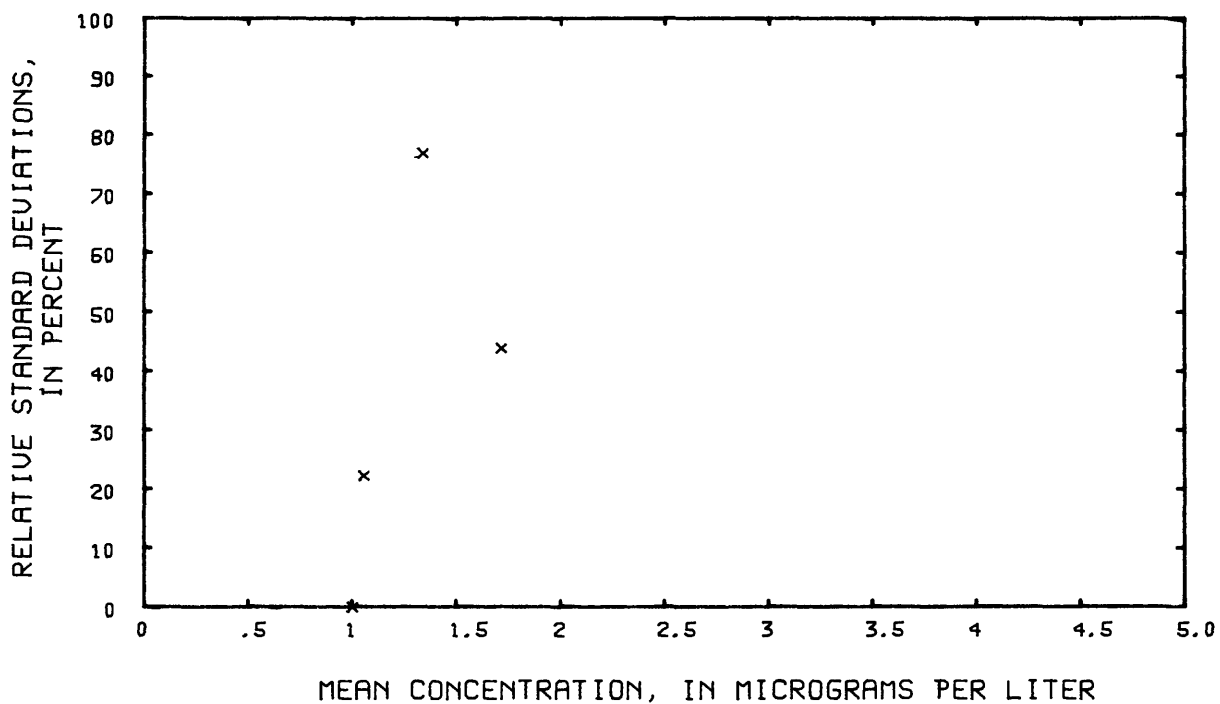


Figure 123.--Precision data for silver, dissolved,
(inductively coupled plasma emission spectrometry)
at the National Water Quality Laboratory.

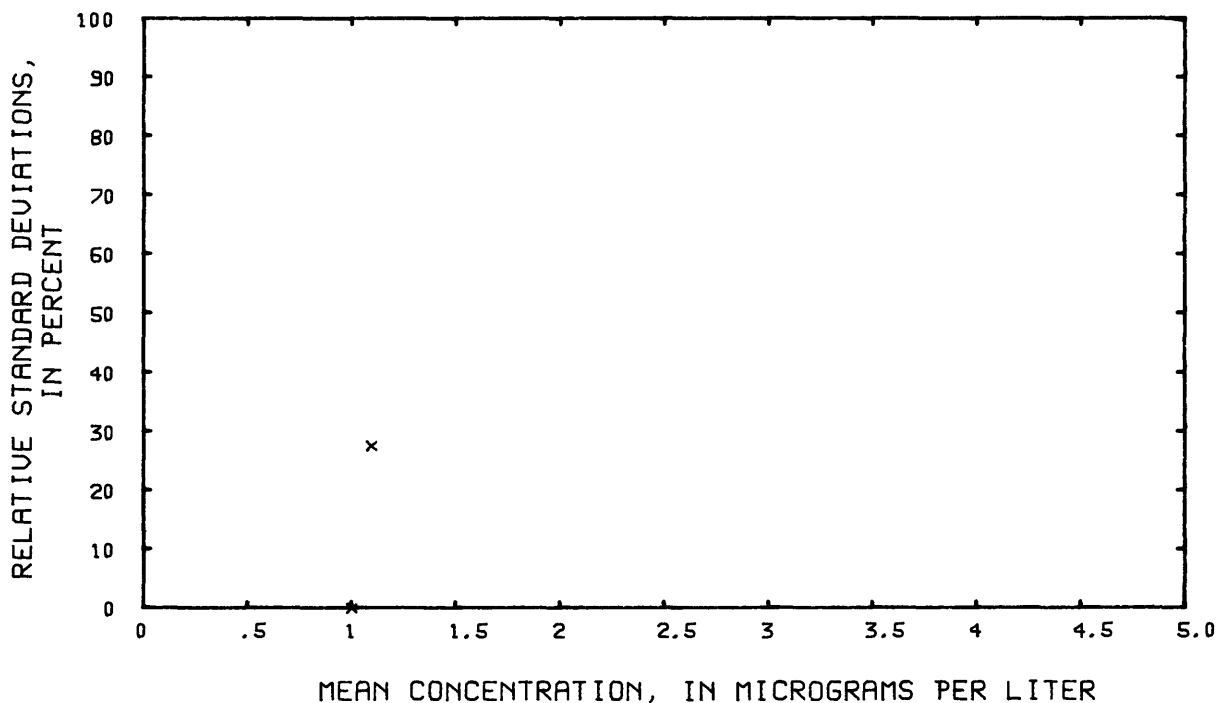


Figure 124.--Precision data for silver, dissolved,
(atomic absorption spectrometry)
at the National Water Quality Laboratory.

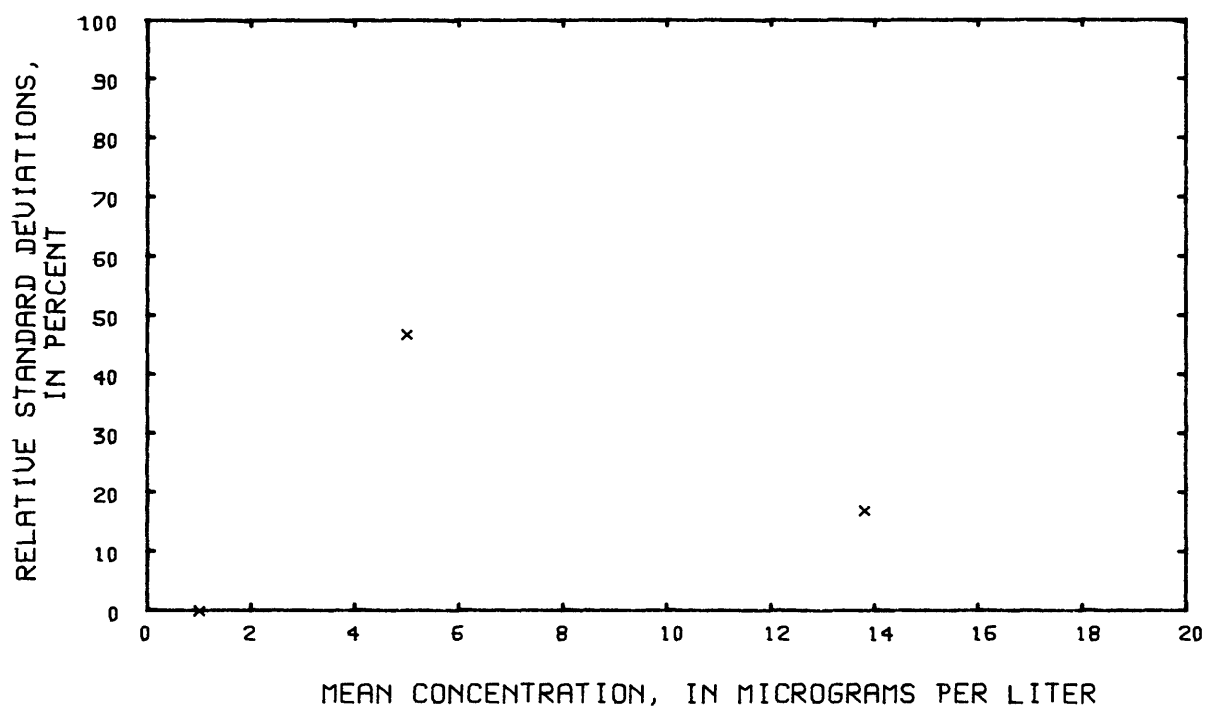


Figure 125.--Precision data for silver, total recoverable, at the National Water Quality Laboratory.

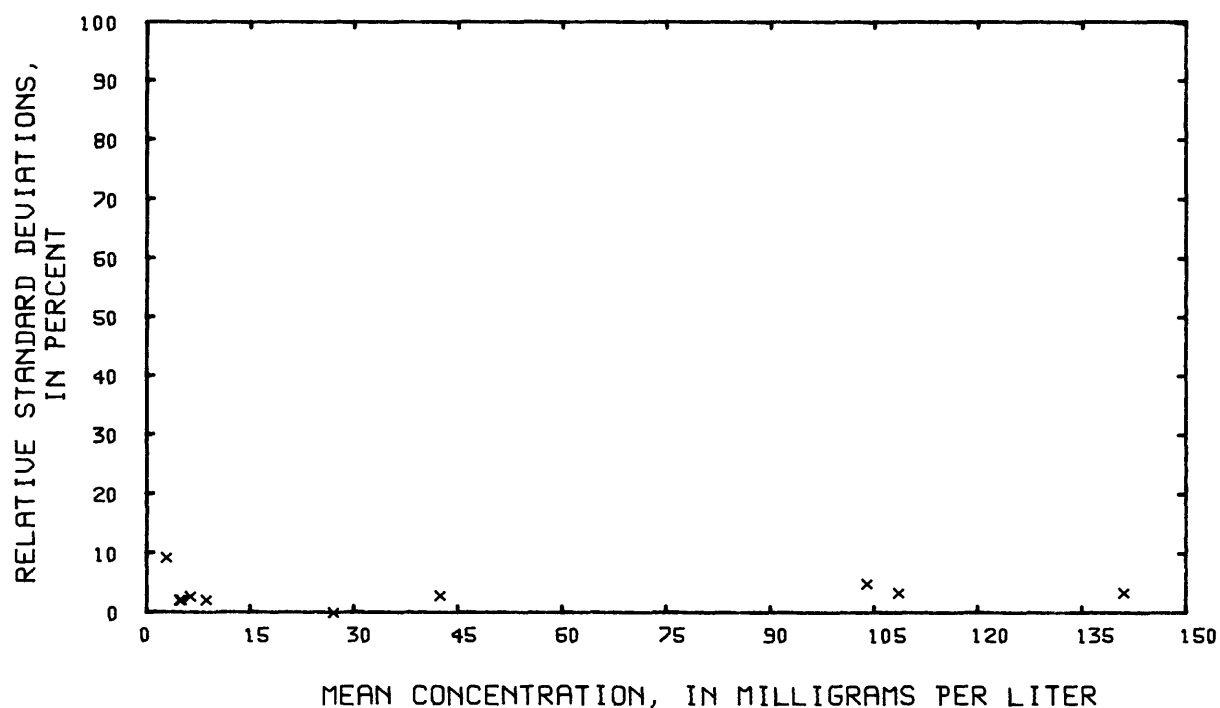


Figure 126.--Precision data for sodium, dissolved, (inductively coupled plasma emission spectrometry) at the National Water Quality Laboratory.

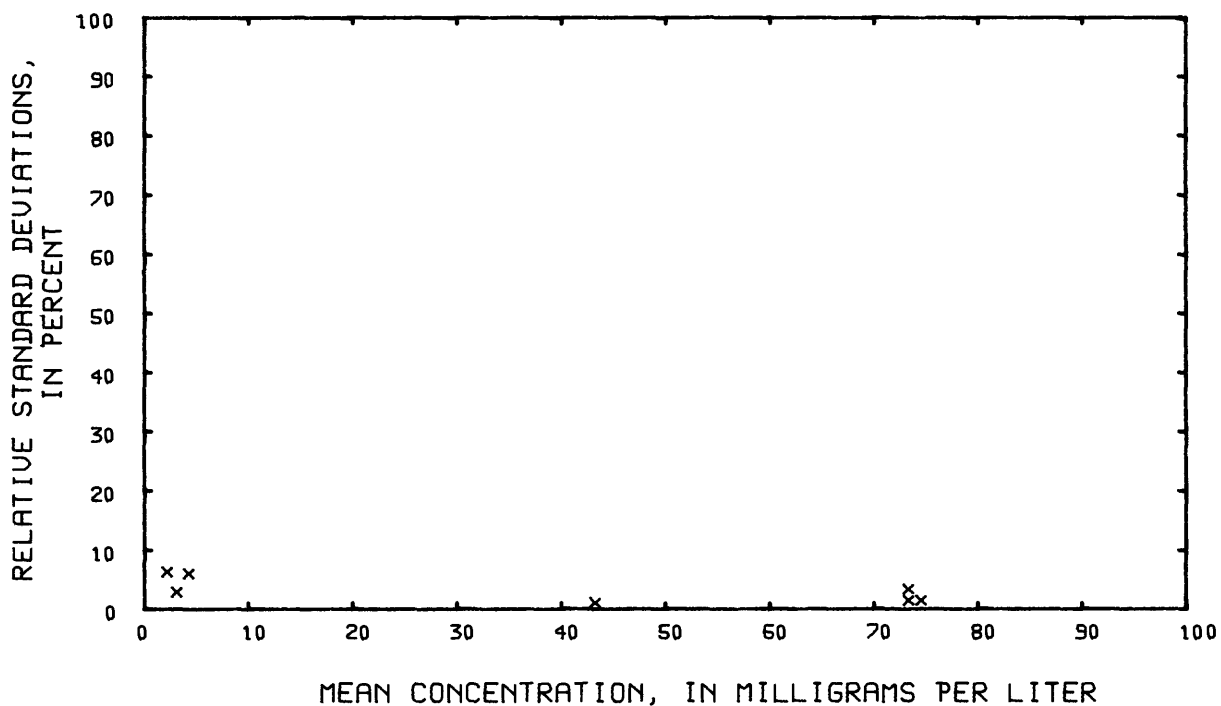


Figure 127.--Precision data for sodium, dissolved,
(atomic absorption spectrometry)
at the National Water Quality Laboratory.

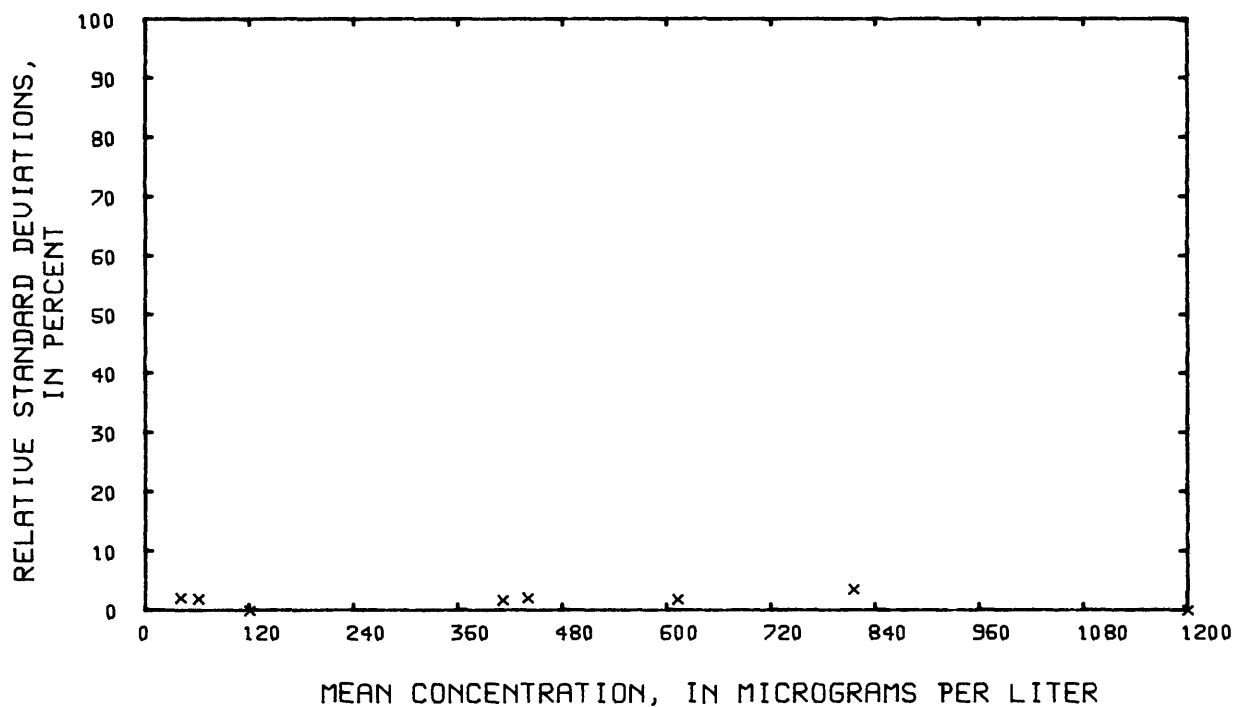


Figure 128.--Precision data for strontium, dissolved,
at the National Water Quality Laboratory.

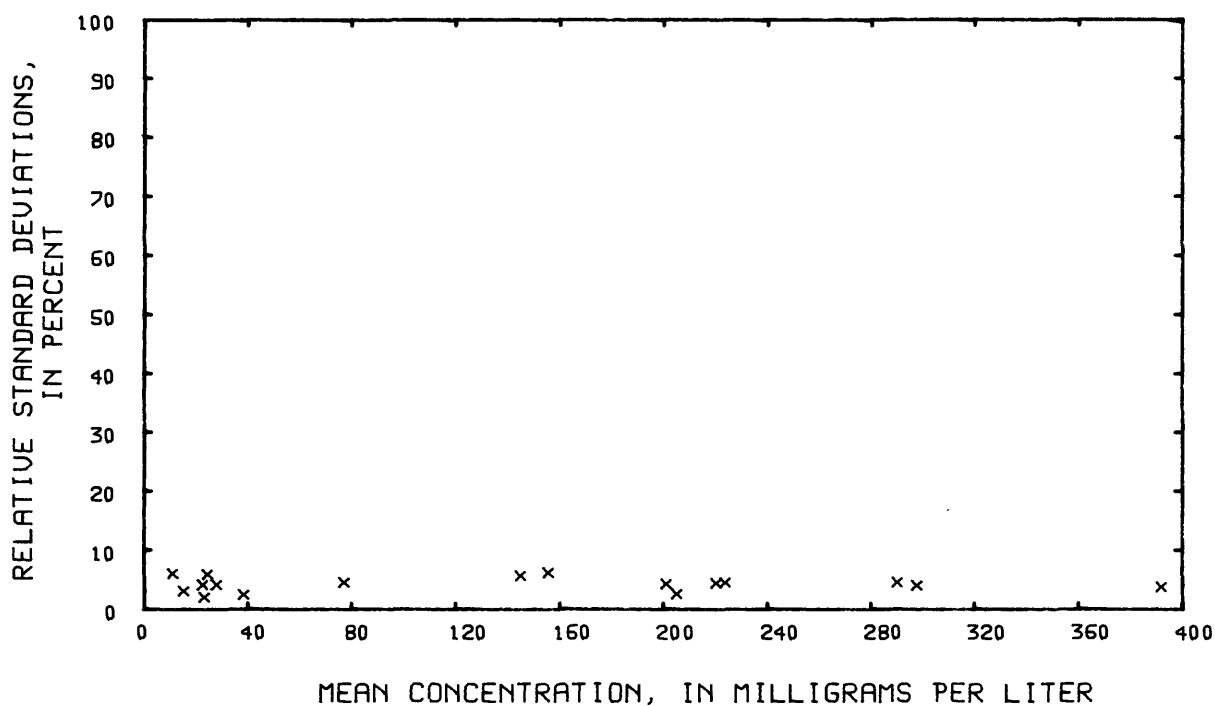


Figure 129.--Precision data for sulfate, dissolved,
at the National Water Quality Laboratory.

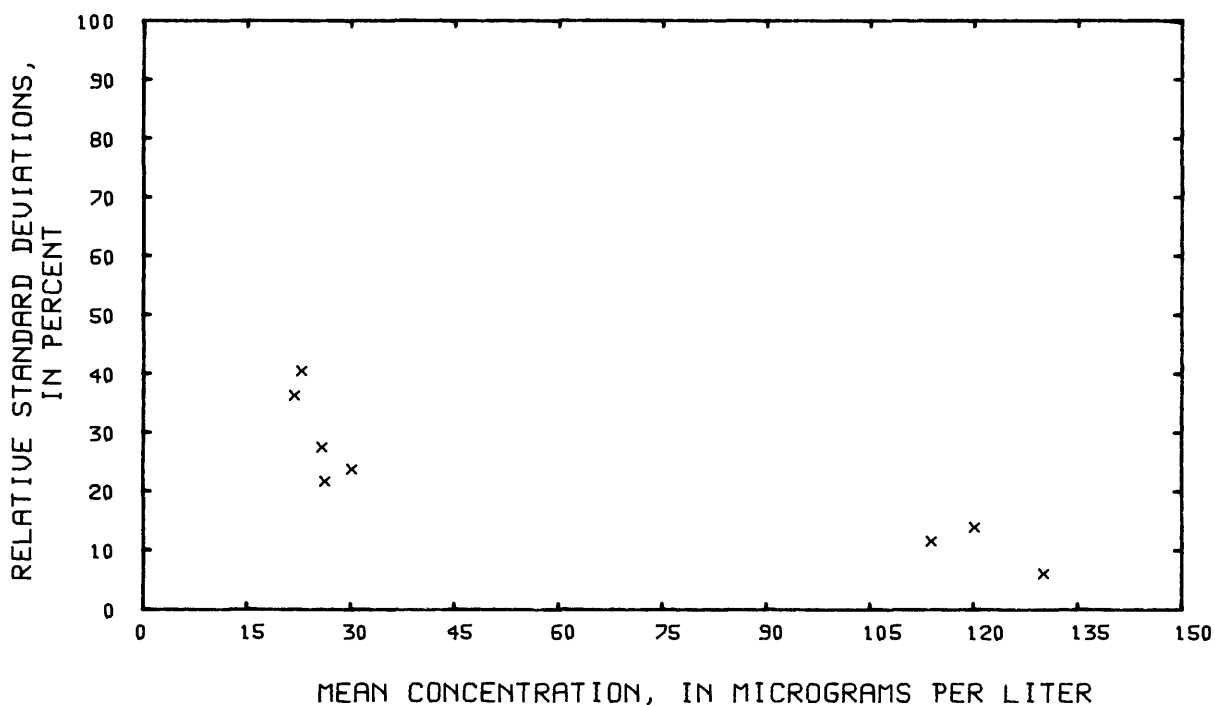


Figure 130.--Precision data for zinc, dissolved,
(inductively coupled plasma emission spectrometry)
at the National Water Quality Laboratory.

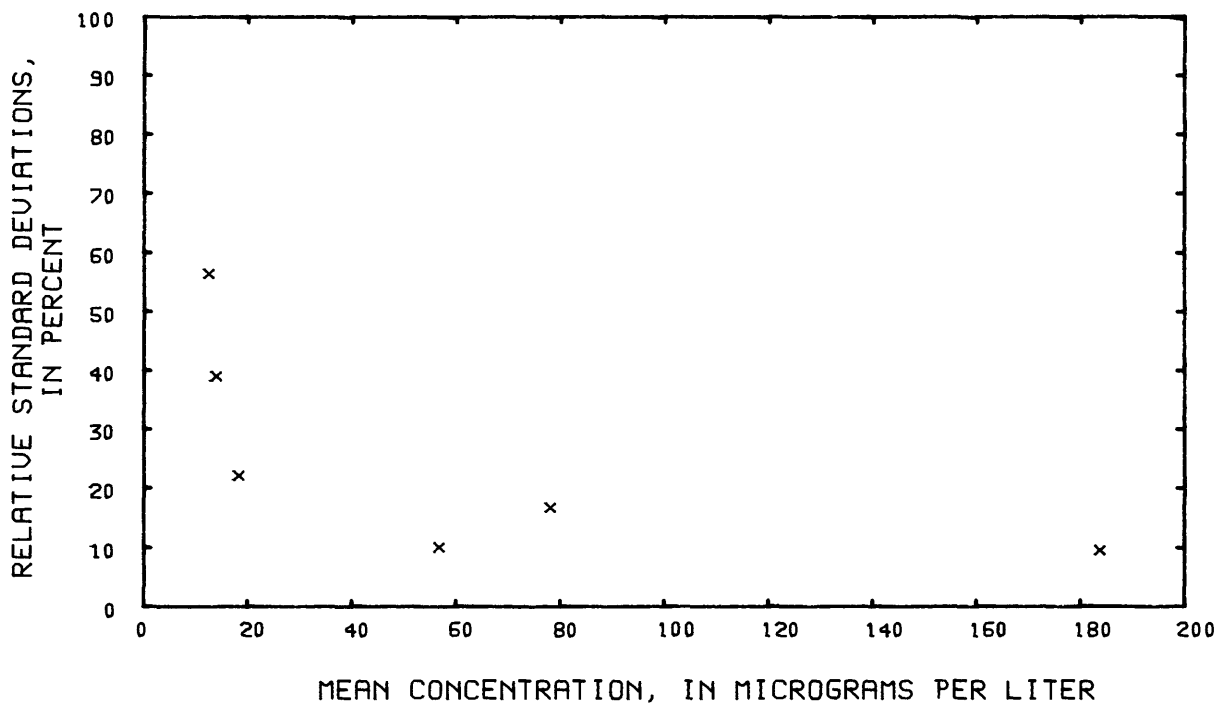


Figure 131.--Precision data for zinc, dissolved,
(atomic absorption spectrometry)
at the National Water Quality Laboratory.

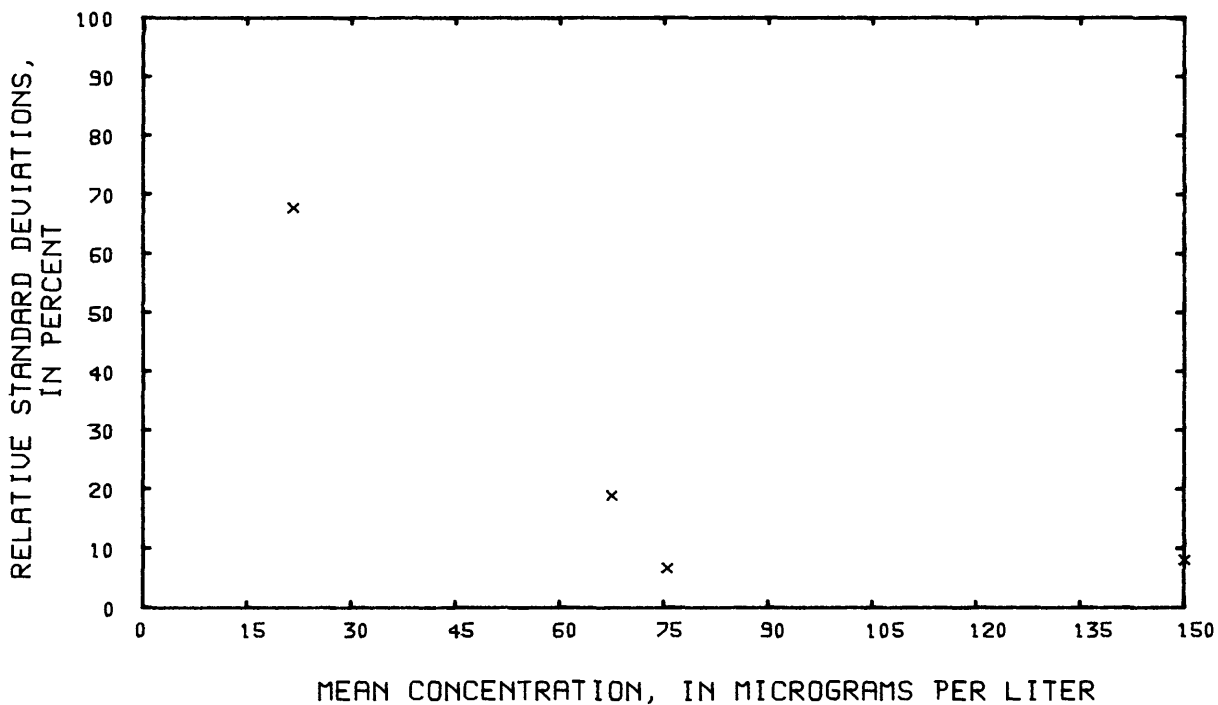


Figure 132.--Precision data for zinc, total recoverable,
at the National Water Quality Laboratory.

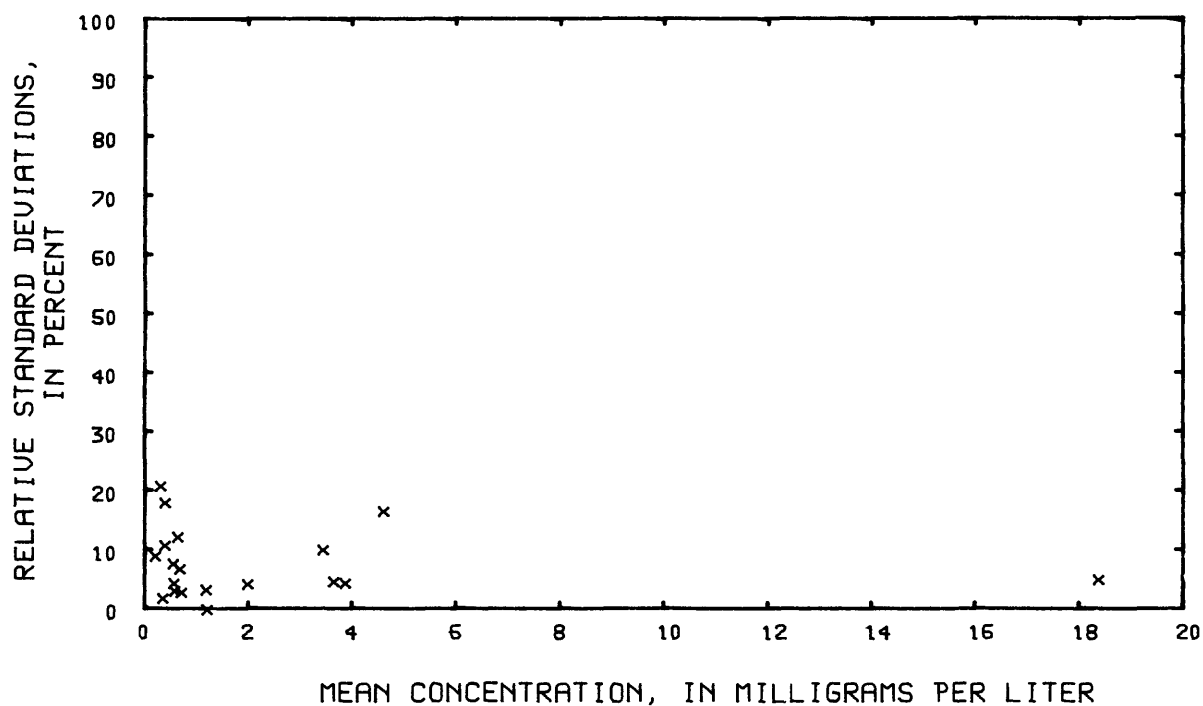


Figure 133.--Precision data for ammonia nitrogen as N, dissolved, at the National Water Quality Laboratory.

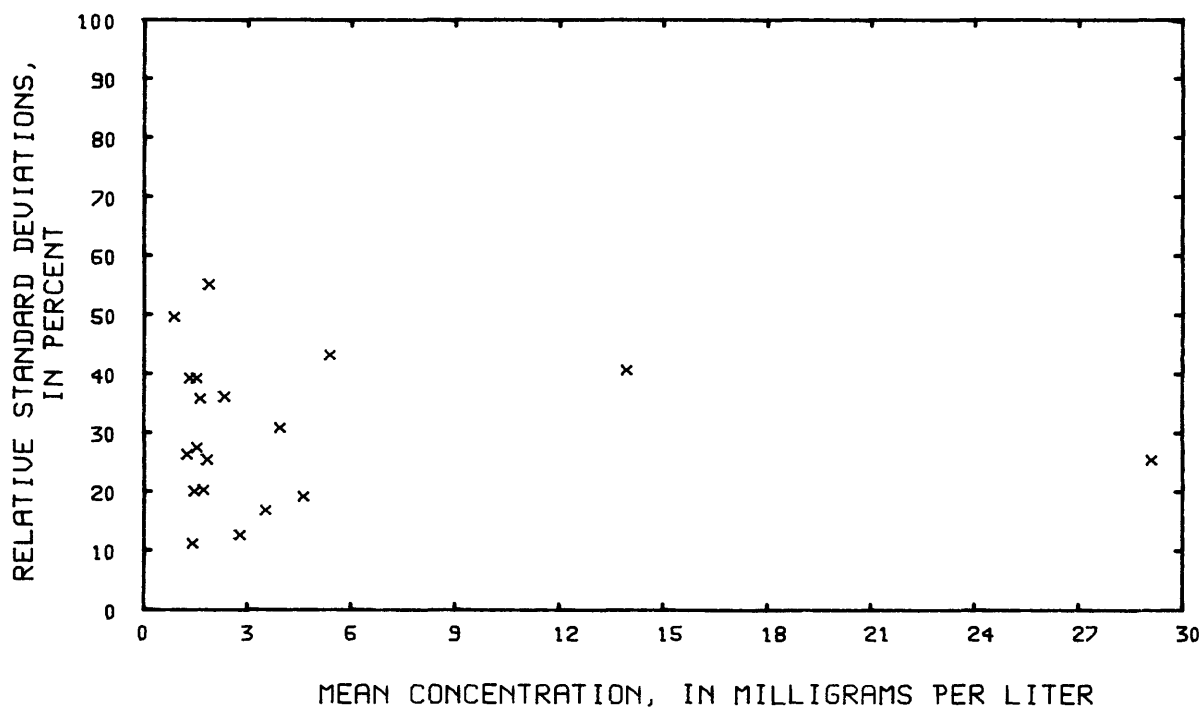


Figure 134.--Precision data for ammonia + organic nitrogen as N, dissolved, at the National Water Quality Laboratory.

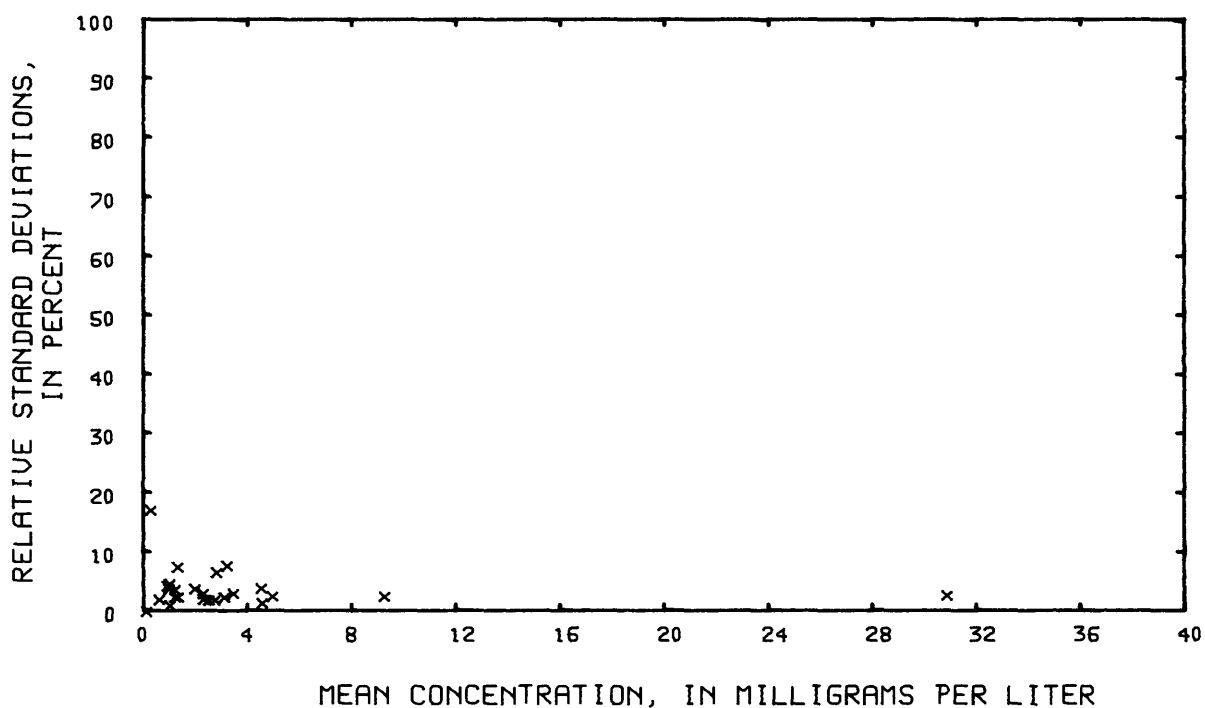


Figure 135.--Precision data for nitrite + nitrate nitrogen as N, dissolved, at the National Water Quality Laboratory.

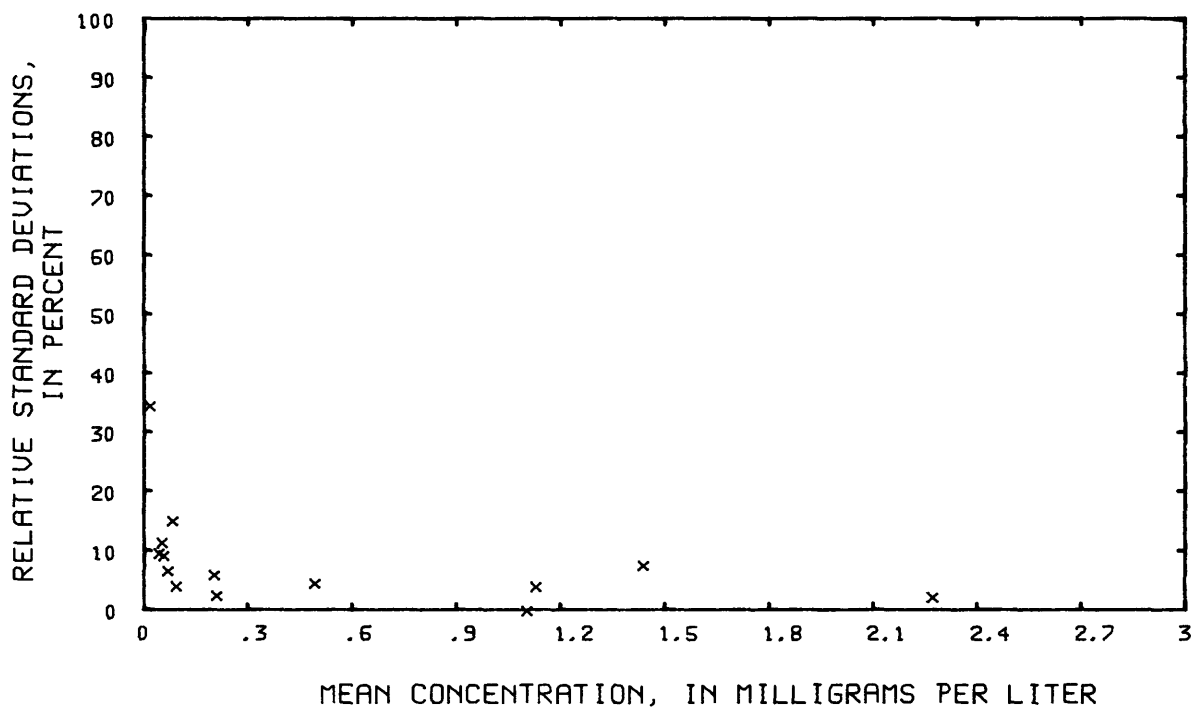


Figure 136.--Precision data for nitrite nitrogen as N, dissolved, at the National Water Quality Laboratory.

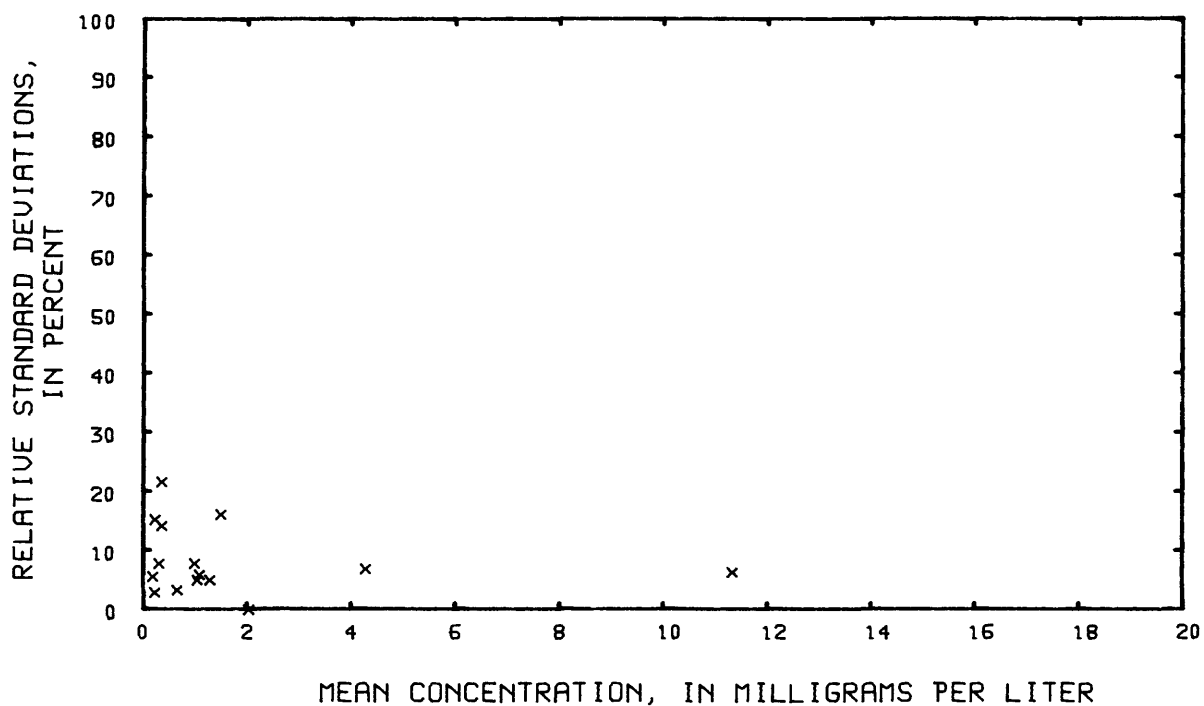


Figure 137.--Precision data for orthophosphate phosphorus as P, dissolved, at the National Water Quality Laboratory.

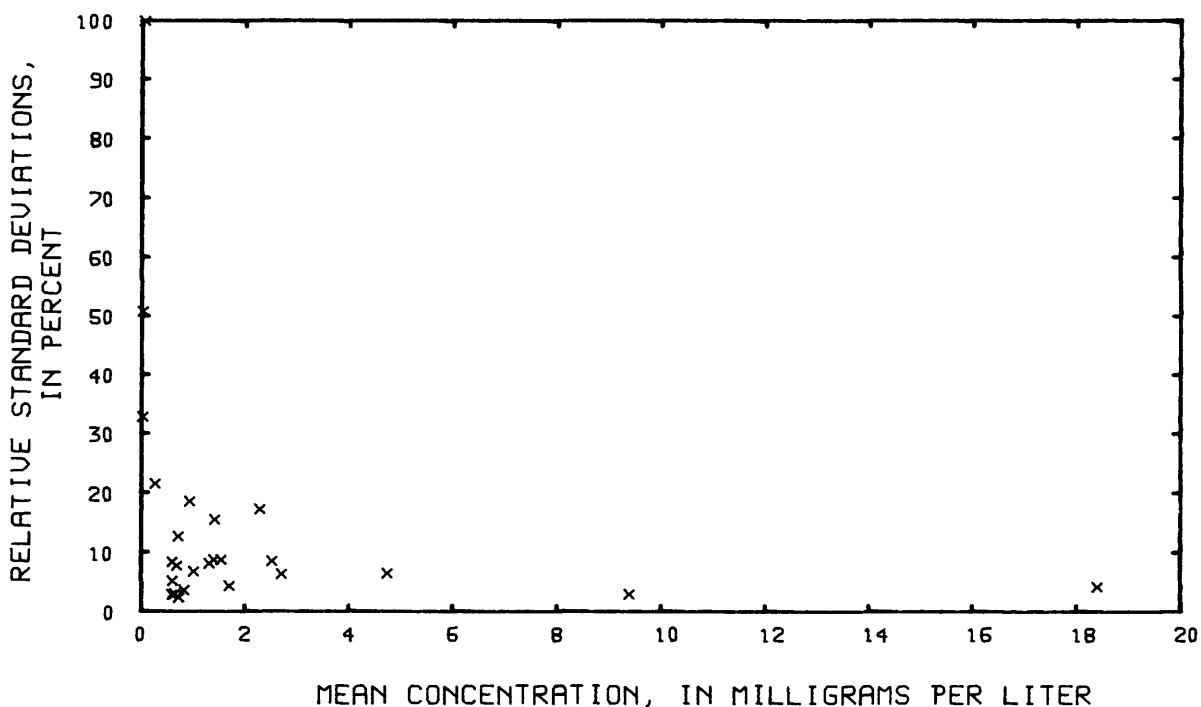


Figure 138.--Precision data for phosphorus as P, dissolved, at the National Water Quality Laboratory.

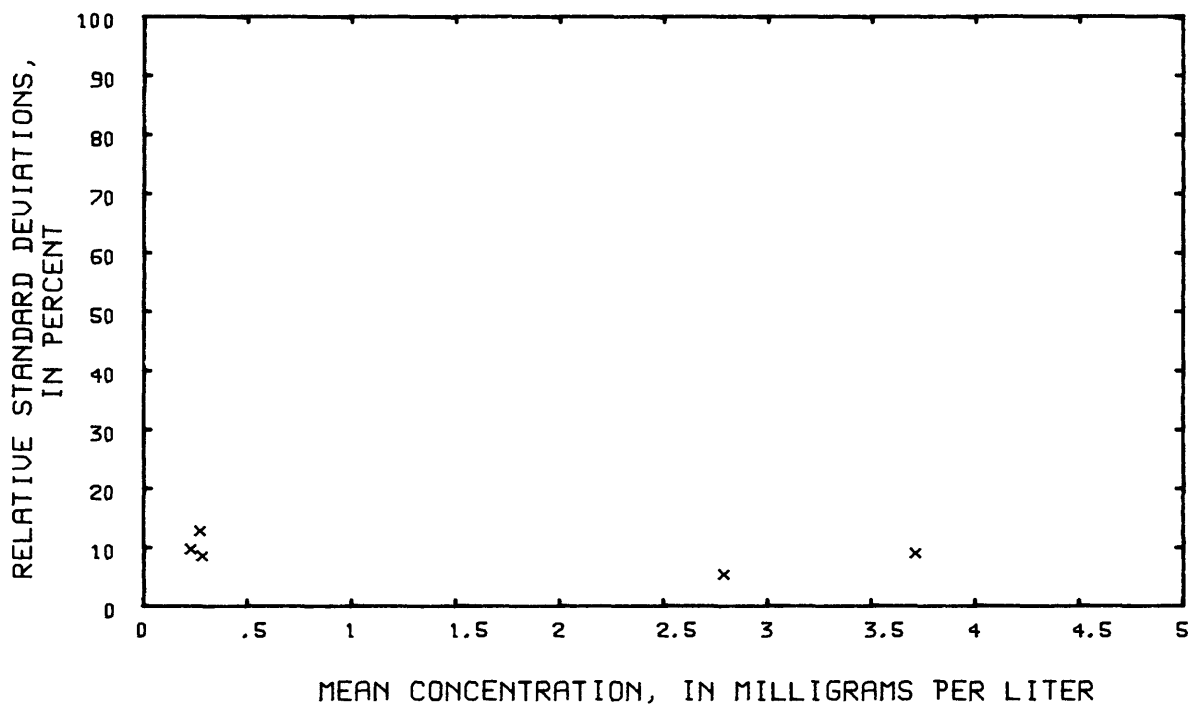


Figure 139.--Precision data for calcium,
dissolved, (precipitation)
at the National Water Quality Laboratory.

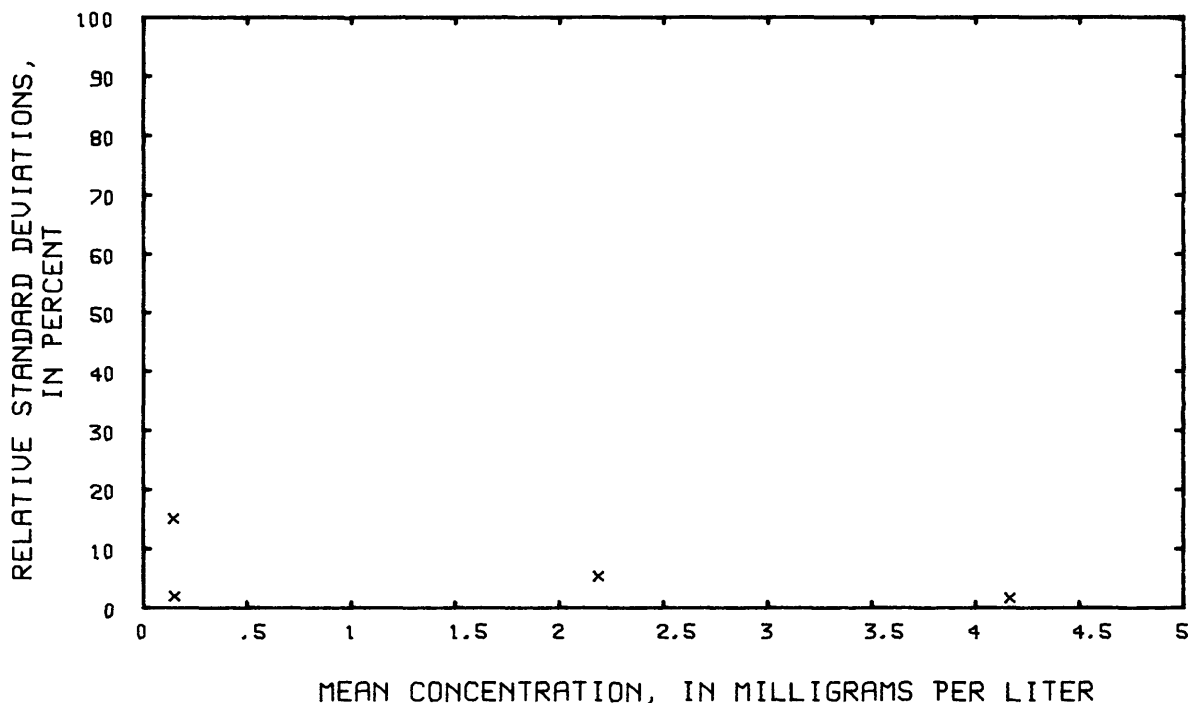


Figure 140.--Precision data for chloride,
dissolved, (precipitation)
at the National Water Quality Laboratory.

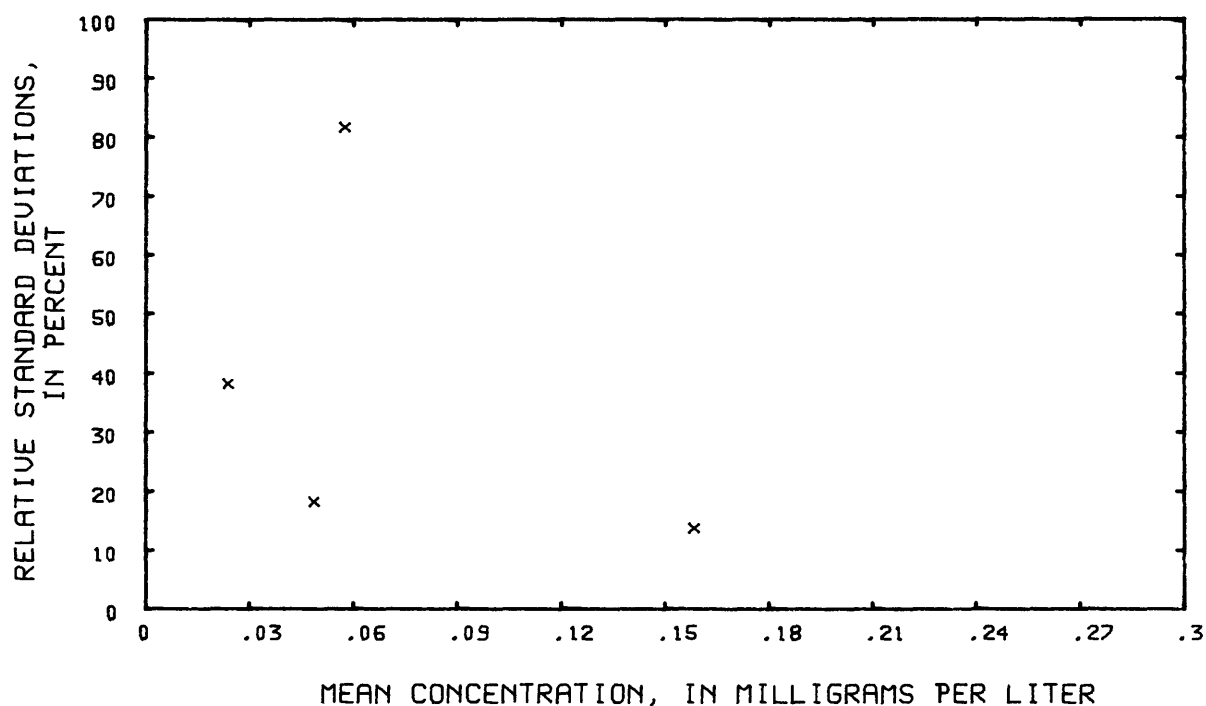


Figure 141.--Precision data for fluoride,
dissolved, (precipitation)
at the National Water Quality Laboratory.

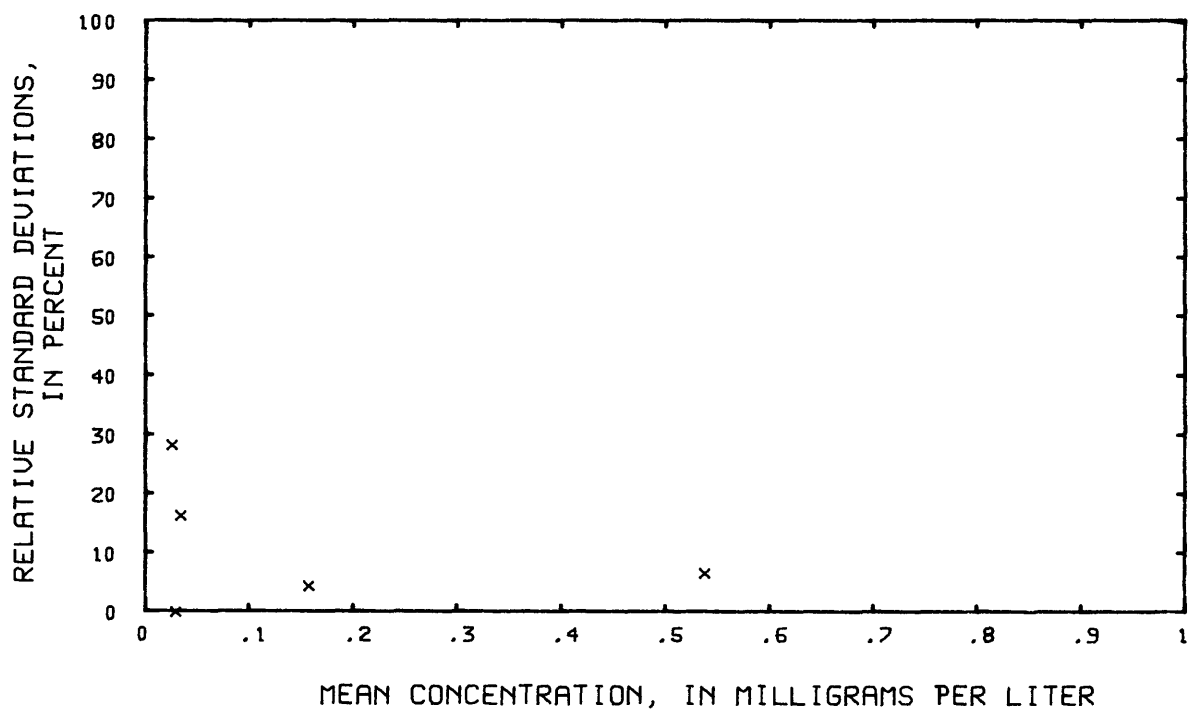


Figure 142.--Precision data for magnesium,
dissolved, (precipitation)
at the National Water Quality Laboratory.

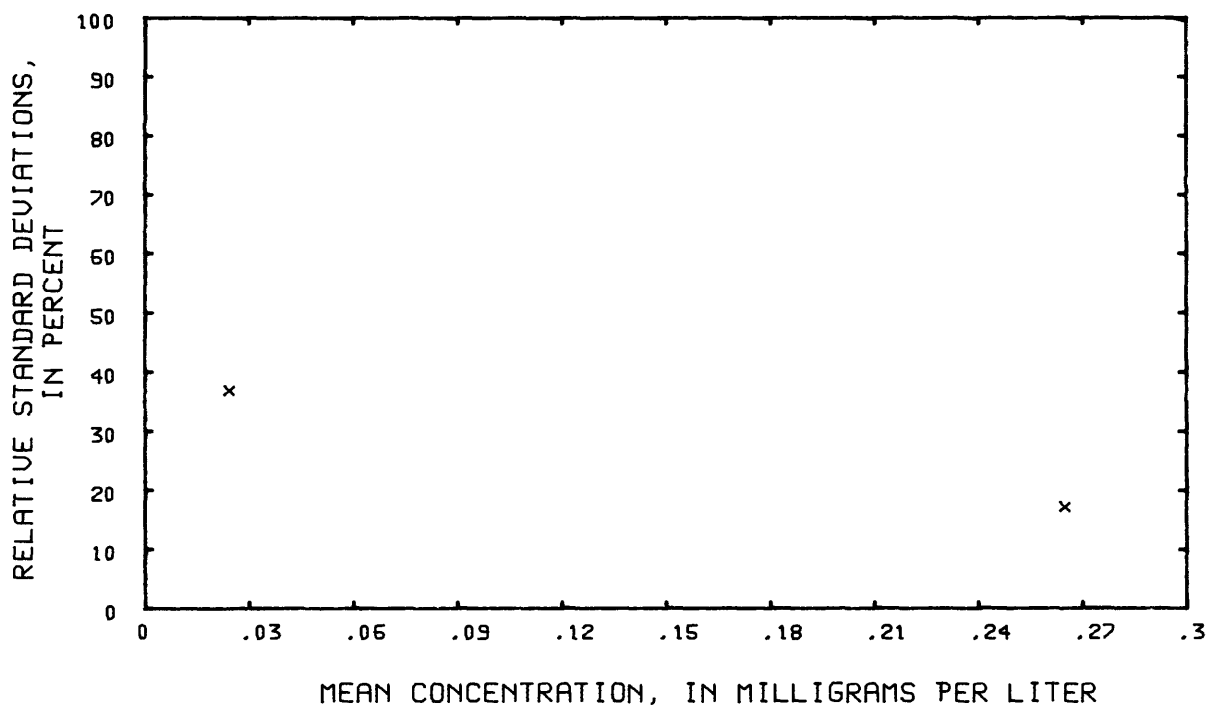


Figure 143.--Precision data for ammonia nitrogen as N, dissolved, (precipitation) at the National Water Quality Laboratory.

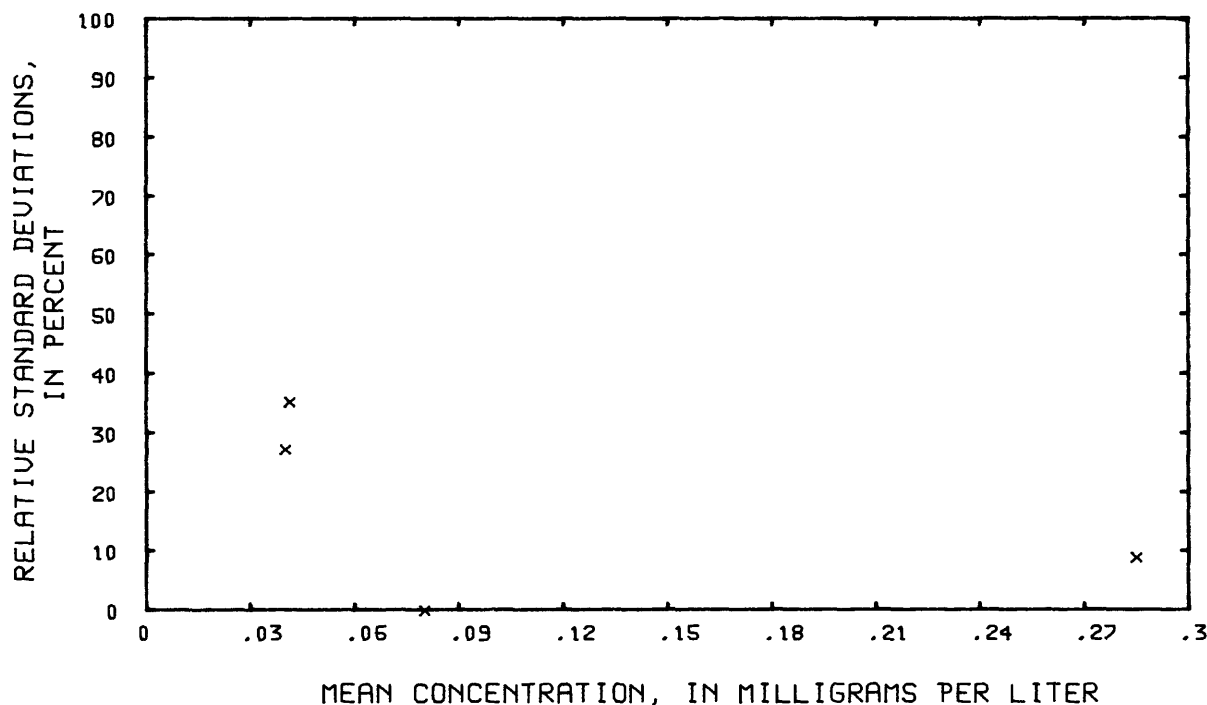


Figure 144.--Precision data for nitrate nitrogen as N, dissolved, (precipitation) at the National Water Quality Laboratory.

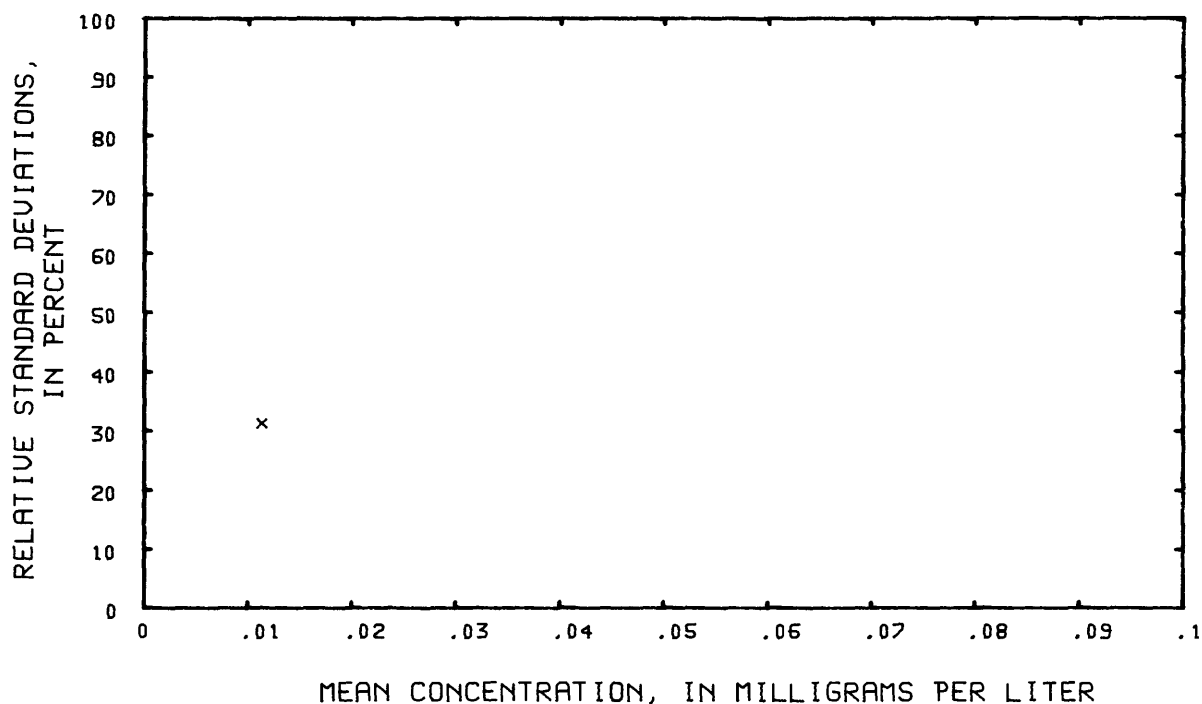


Figure 145.--Precision data for orthophosphate phosphorus as P, dissolved, (precipitation) at the National Water Quality Laboratory.

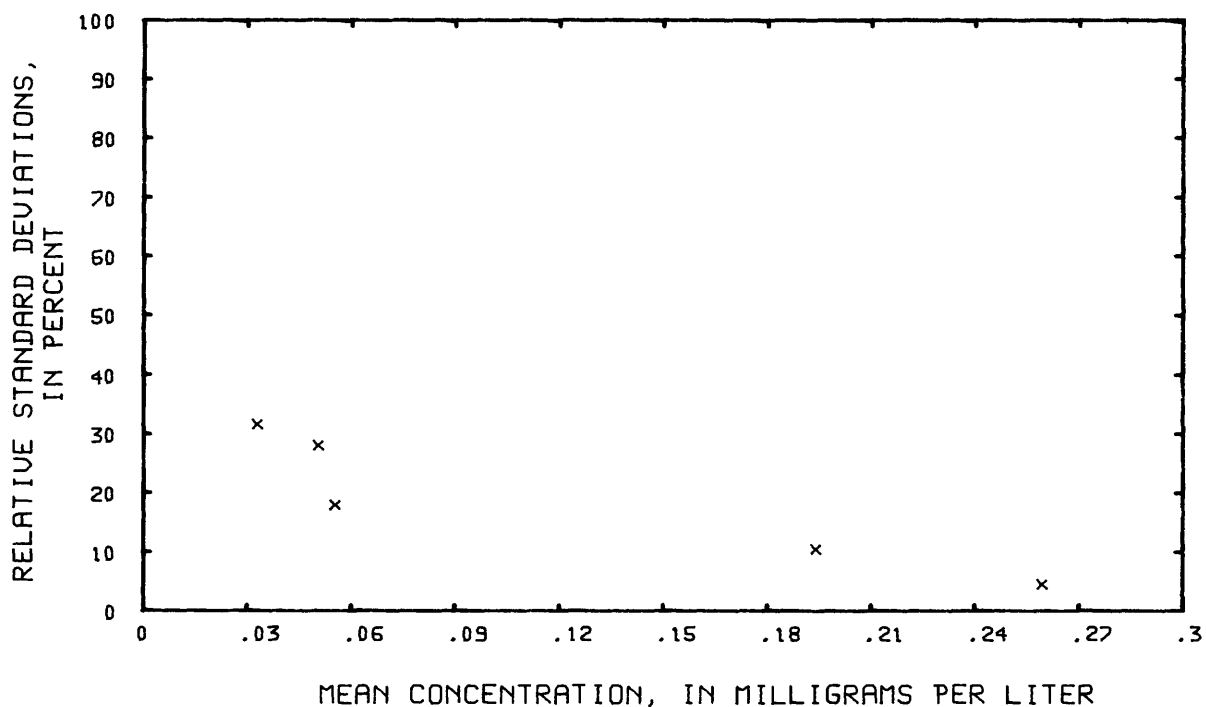


Figure 146.--Precision data for potassium, dissolved, (precipitation) at the National Water Quality Laboratory.

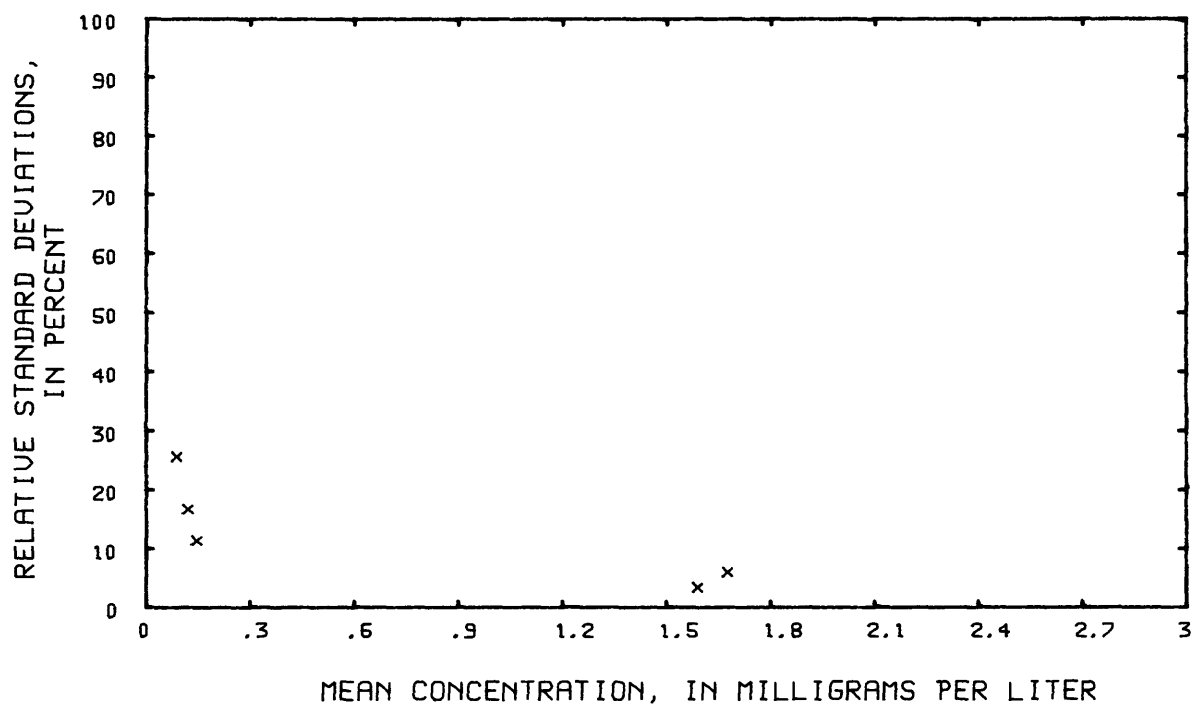


Figure 147.--Precision data for sodium,
dissolved, (precipitation)
at the National Water Quality Laboratory.

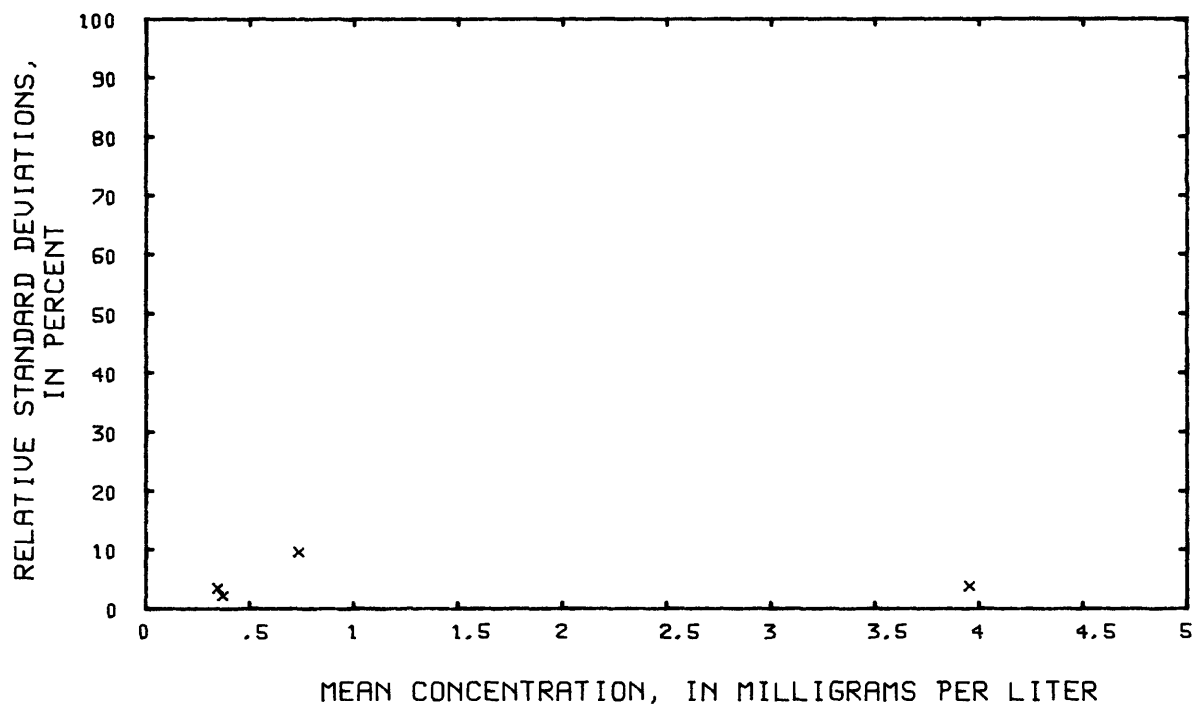


Figure 148.--Precision data for sulfate,
dissolved, (precipitation)
at the National Water Quality Laboratory.