QUALITY-ASSURANCE DATA FOR ROUTINE WATER ANALYSIS IN THE NATIONAL WATER-QUALITY LABORATORY OF THE U.S. GEOLOGICAL SURVEY FOR WATER YEAR 1988

by Keith J. Lucey

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QUALITY-ASSURANCE DATA FOR ROUTINE WATER ANALYSIS IN THE NATIONAL WATER-QUALITY LABORATORY OF THE U.S. GEOLOGICAL SURVEY FOR WATER-YEAR 1988

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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, nutrient, and precipitation (low-level concentration) 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. 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.

An overall evaluation of the inorganic major ion and trace metal constituent data for water-year 1988 indicated a lack of precision in the National Water-Quality Laboratory for the determination of 8 out of 58 constituents: calcium (inductively coupled plasma emission spectrometry), fluoride, iron (atomic absorption spectrometry), iron (total recoverable), magnesium (atomic absorption spectrometry), manganese (total recoverable), potassium, and sodium (inductively coupled plasma emission spectrometry). The results for 31 constituents had positive or negative bias during water-year 1988.

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

There was acceptable precision in the determination of all 10 constituents contained in precipitation samples. Results for ammonia nitrogen as nitrogen, sodium, and fluoride 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, and 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, 1989a, 1989b) document results from February 1981 through September 1987.

Factors that need to be considered for interpretation of 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 detects errors of this type, the quality of the data can be increased 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 familiar with one of the sites or its historical data usually could detect the problem and make necessary corrections.

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 1988. Where control charts 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 entire year. The data from that period when the analytical process was in statistical 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. Sample dilutions are made routinely in the laboratory to bring sample concentrations 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 result. These kinds of errors are difficult to confirm. Their detection, confirmation through rerun requests, and correction in the field offices will increase the reliability of the data above that indicated in this report.

5. Non-analytical errors for nutrient analyses can result when the samples are not maintained at the ideal temperature of 4^{o} C during shipping and receiving.

During water-year 1988, 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, mercury, molybdenum, nickel, potassium, selenium, silica, silver, sodium, strontium, sulfate, and zinc.

Nutrients: ammonia, as nitrogen; ammonia plus organic nitrogen as nitrogen; nitrate plus nitrite as nitrogen; nitrite 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, in turn, decreases the probability that quality-assurance samples will be recognized in the laboratory because of frequency of analyses or unique sample characteristics.

The reference samples are prepared from the SRWS's 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 results. 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 cadmium, fluoride, lead, lithium, nitrite nitrogen as N, and selenium; for chromium, copper, molybdenum, and nickel when determined by inductively coupled plasma emission spectrometry; for barium, manganese, and zinc when determined by atomic absorption spectrometry; and for barium, beryllium, chromium, manganese, nickel, and zinc when determined by 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 μg/L (micrograms per liter) is set to 7.5 μg/L; the minimum standard deviation for cadmium, reported to the nearest 1 μg/L, is 0.75 μg/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.

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; DCP, direct current plasma emission spectrometry; COL, colorimetry; N, nitrogen; P, phosphorus.]

Constituent (dissolved except as indicated)	Units	Equation to determine MPSD	Minimum MPSD
	Inorganic constituents		
Alkalinity	mg/L	(0.024 x MPV) + 0.84	*
Aluminum	μg/L	(0.16 x MPV) + 21.0	*
Antimony	μg/L	(0.069 x MPV) + 1.34	*
Arsenic	μg/L	(0.12 x MPV) + 1.05	*
Barium (ICP)	μg/L	(0.46 x MPV) + 2.36	*
Barium (AA)	μg/L	(0.12 x MPV) + 24.0	75
Barium (TOT)	μg/L	(0.12 x MPV) + 24.0	75
Beryllium	μg/L	(0.045 x MPV) + 1.37	*
Beryllium (TOT)	μg/L	(0.045 x MPV) + 1.37	7.5
Boron	μg/L	(0.053 x MPV) + 32.0	*
Cadmium (ICP)	μg/L	(0.130 x MPV) + 0.59	0.75
Cadmium (AA)	μg/L	(0.130 x MPV) + 0.59	0.75
Cadmium (TOT)	μg/L	(0.130 x MPV) + 0.59	0.75
Calcium (ICP)	mg/L	(0.044 x MPV) + 0.10	*
Calcium (AA)	mg/L	(0.044 x MPV) + 0.10	*
Chloride	mg/L	(0.025 x MPV) + 0.66	*
Chromium (ICP)	μg/L	(0.16 x MPV) + 1.44	2.5
Chromium (DCP)	μg/L	(0.16 x MPV) + 1.44	*
Chromium (TOT)	μg/L	(0.16 x MPV) + 1.44	7.5
Cobalt (ICP)	μg/L	(0.120 x MPV) + 1.33	*
Cobalt (AA)	μg/L	(0.120 x MPV) + 1.33	*
Cobalt (TOT)	μg/L	(0.120 x MPV) + 1.33	*
Copper (ICP)	μg/L	(0.051 x MPV) + 2.75	7.5
Copper (AA)	μg/L	(0.051 x MPV) + 2.75	*
Copper (TOT)	μg/L	(0.051 x MPV) + 2.75	*
Dissolved solids	mg/L	(0.013 x MPV) + 10.8	*
Fluoride	mg/L	(0.033 x MPV) + 0.04	0.05
Iron (ICP)	μg/L	(0.041 x MPV) + 9.43	*
Iron (AA)	μg/L	(0.041 x MPV) + 9.43	*
Iron (TOT)	μg/L	(0.041 x MPV) + 9.43	*
Lead (ICP)	μg/L	(0.250 x MPV) + 1.62	7.5
Lead (AA)	μg/L	(0.250 x MPV) + 1.62	3.75
Lead (TOT)	μg/L	(0.250 x MPV) + 1.62	3.75
Lithium	μg/L	(0.10 x MPV) + 2.70	7.5
Lithium (TOT)	μg/L	(0.10 x MPV) + 2.70	7.5
Magnesium (ICP)	mg/L	(0.045 x MPV) + 0.09	*
Magnesium (AA)	mg/L	(0.045 x MPV) + 0.09	*

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

Constituent (dissolved except as indicated)	Units	Equation to determine MPSD	Minimum MPSD
Manganese (ICP)	µg/L	(0.042 x MPV) + 3.08	*
Manganese (AA)	µg/L	(0.042 x MPV) + 3.08	7.5
Manganese (TOT)	µg/L	(0.042 x MPV) + 3.08	7.5
Mercury	µg/L	(0.150 x MPV) + 0.07	*
Molybdenum (ICP)	µg/L	(0.047 x MPV) + 4.30	7.5
Molybdenum (AA)	µg/L	(0.047 x MPV) + 4.30	*
Nickel (ICP)	µg/L	(0.260 x MPV) + 2.83	7.5
Nickel (AA)	µg/L	(0.260 x MPV) + 2.83	*
Nickel (TOT)	µg/L	(0.260 x MPV) + 2.83	7.5
Potassium	mg/L	(0.100 x MPV) + 0.02	*
Selenium	µg/L	(0.210 x MPV) + 0.45	0.75
Silica (ICP)	mg/L	(0.041 x MPV) + 0.45	*
Silica (COL)	mg/L	(0.041 x MPV) + 0.45	*
Silver (ICP)	µg/L	(0.114 x MPV) + 1.28	*
Silver (AA)	µg/L	(0.114 x MPV) + 1.28	*
Silver (TOT)	µg/L	(0.114 x MPV) + 1.28	*
Sodium (ICP)	mg/L	(0.039 x MPV) + 0.02	*
Sodium (AA)	mg/L	(0.039 x MPV) + 0.02	*
Strontium	µg/L	(0.043 x MPV) + 5.80	*
Sulfate	mg/L	(0.046 x MPV) + 0.87	*
Zinc (ICP)	µg/L	(0.033 x MPV) + 4.63	*
Zinc (AA)	µg/L	(0.033 x MPV) + 4.63	7.5
Zinc (TOT)	µg/L	(0.033 x MPV) + 4.63	7.5
		Nutrient constituents	
Ammonia nitrogen, as N	mg/L	(0.10 x MPV) + 0.035	*
Ammonia plus organic nitrogen, as N	mg/L	(0.601 x MPV) - 0.06	*
Nitrate plus nitrite nitrogen, as N	mg/L	(0.038 x MPV) + 0.034	*
Nitrite nitrogen, as N	mg/L	(0.07 x MPV) + 0.003	.0075
Orthophosphate as P	mg/L	(0.057 x MPV) + 0.009	*
Phosphorus, as P	mg/L	(0.076 x MPV) + 0.007	*
		Constituents in precipitation samples	
Calcium	mg/L	(0.065 x MPV) + 0.05	*
Chloride	mg/L	(0.073 x MPV) + 0.20	*
Fluoride	mg/L	(-.08 x MPV) + 0.031	*
Magnesium	mg/L	(0.038 x MPV) + 0.014	*
Ammonia nitrogen, as N	mg/L	(0.32 x MPV) + 0.008	*
Nitrate nitrogen, as N	mg/L	(0.23 x MPV) + 0.018	*
Orthophosphate as P	mg/L	(0.064 x MPV) + 0.008	*
Potassium	mg/L	(0.10 x MPV) + 0.02	*
Sodium	mg/L	(0.044 x MPV) + 0.04	*
Sulfate	mg/L	(0.037 x MPV) + 0.035	*

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 constituent are shown on control charts in figures 1 through 76 in the "Supplemental Data" section of this report. Three symbols are used in figures 1 through 60 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 boron to be 436.0 mg/L (fig. 10) and still allow a correctly reported value of 440 mg/L, based on the policy to report boron 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 61 through 66 and results for precipitation samples are shown in figures 67 through 76. 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).

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 constituent with sufficient data. Because standard deviations may vary proportionally with constituent concentration in chemical analyses, these calculations were done separately for individual sample mixtures; therefore, they do not represent 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. 77 through 152 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 ±1 percent for the analyzed range of concentrations from figure 77. 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 figures 82, 85, and 111. A relative standard deviation of zero occurs when all values reported by the laboratory for a constituent in a unique mix are the same. Although this suggests that the results are from a reproducible analytical method, repetitive results can be an artifact of small sample size or reporting level. For example, the minimum reporting level for barium (AA) is 100 micrograms per liter and, since the mixes used during the 1988 water year have MPV's less than this value (fig. 6), the precision chart (fig. 82) shows a relative standard deviation of zero at a mean concentration of 100 micrograms per liter.

Table 2. **Total number of analyses from quality-assurance samples during water-year 1988 with number greater than two and six standard deviations from the most probable value**

[>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; DCP, direct current plasma emission spectrometry; COL, colorimetry; N, nitrogen; P, phosphorous.]

Constituent (dissolved except as indicated)	No. of analyses			Constituent (dissolved except as indicated)	No. of analyses		
	Total	>2SD	>6SD		Total	>2SD	>6SD
			Inorganic constituents				
Alkalinity	357	4	2	Cobalt (AA)	30	0	0
Aluminum	136	2	0	Cobalt (TOT)	58	3	0
Antimony	31	1	0	Copper (ICP)	136	0	0
Arsenic	239	7	0	Copper (AA)	184	2	0
Barium (ICP)	256	3	1	Copper (TOT)	58	2	0
Barium (AA)	30	0	0	Dissolved solids	338	3	0
Barium (TOT)	58	1	0	Fluoride	299	31	4
Beryllium	128	42	0	Iron (ICP)	256	2	0
Beryllium (TOT)	22	0	0	Iron (AA)	63	10	0
Boron	120	0	0	Iron (TOT)	58	18	1
Cadmium (ICP)	256	2	0	Lead (ICP)	136	0	0
Cadmium (AA)	63	4	3	Lead (AA)	184	10	0
Cadmium (TOT)	56	0	0	Lead (TOT)	58	1	0
Calcium (ICP)	301	31	2	Lithium	257	4	1
Calcium (AA)	42	5	1	Lithium (TOT)	29	0	0
Chloride	355	28	9	Magnesium (ICP)	301	20	0
Chromium (ICP)	255	5	0	Magnesium (AA)	42	7	1
Chromium (DCP)	65	4	0	Manganese (ICP)	256	3	0
Chromium (TOT)	59	3	0	Manganese (AA)	64	2	0
Cobalt (ICP)	256	1	1	Manganese (TOT)	58	9	1

Table 2. Total number of analyses from quality-assurance samples during water-year 1988 with number greater than two and six standard deviations from the most probable value --continued

Constituent (dissolved except as indicated)	No. of analyses Total	>2SD	>6SD	Constituent (dissolved except as indicated)	No. of analyses Total	>2SD	>6SD
Mercury	151	14	1	Silver (ICP)	256	12	0
Molybdenum (ICP)	256	1	0	Silver (AA)	30	0	0
Molybdenum (AA)	34	0	0	Silver (TOT)	58	0	0
Nickel (ICP)	256	1	1	Sodium (ICP)	301	36	0
Nickel (AA)	63	0	0	Sodium (AA)	41	5	2
Nickel (TOT)	58	1	0	Strontium	257	19	1
Potassium	342	32	12	Sulfate	357	17	0
Selenium	206	2	0	Zinc (ICP)	256	16	3
Silica (ICP)	302	4	3	Zinc (AA)	63	2	0
Silica (COL)	55	1	1	Zinc (TOT)	58	7	2
Nutrient constituents							
Ammonia nitrogen, as N	372	7	0	Nitrite nitrogen, as N	151	20	3
Ammonia + organic nitrogen, as N	370	4	1	Orthophosphate phosphorus, as P	198	32	3
Nitrate + nitrite nitrogen, as N	372	62	1	Phosphorus, as P	304	23	7
Constituents in precipitation samples							
Ammonia nitrogen, as N	32	0	0	Nitrate nitrogen, as N	46	1	1
Calcium	61	3	0	Orthophosphate phosphorus, as P	27	0	0
Chloride	60	3	0	Potassium	61	1	1
Fluoride	50	0	0	Sodium	61	3	1
Magnesium	61	0	0	Sulfate	59	6	6

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 "+").

Data for water-year 1988 for calcium (ICP), fluoride, iron (AA), iron (TOT), magnesium (AA), manganese (TOT), potassium, and sodium (ICP) indicate lack of precision in the NWQL. Only iron (TOT) failed the precision criteria during water-year 1987 (Lucey and Peart, 1989b) and again in 1988.

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; DCP, direct current plasma emission spectrometry; COL, colorimetry]

Constituent (dissolved, except as indicated)	Results from Oct. 1987-Sept. 1988	Constituent (dissolved, except as indicated)	Results from Oct. 1987-Sept. 1988
Alkalinity	+	Lead (ICP)	+
Aluminum	+	Lead (AA)	+
Antimony	+	Lead (TOT)	+
Arsenic	+	Lithium	+
Barium (ICP)	+	Lithium (TOT)	+
Barium (AA)	+	Magnesium (ICP)	+
Barium, (TOT)	+	Magnesium (AA)	LOP
Beryllium	+	Manganese (ICP)	+
Beryllium (TOT)	+	Manganese (AA)	+
Boron	+	Manganese (TOT)	LOP
Cadmium (ICP)	+	Mercury	+
Cadmium (AA)	+	Molybdenum (ICP)	+
Cadmium (TOT)	+	Molybdenum (AA)	+
Calcium (ICP)	LOP	Nickel (ICP)	+
Calcium (AA)	+	Nickel (AA)	+
Chloride	+	Nickel (TOT)	+
Chromium (ICP)	+	Potassium	LOP
Chromium (DCP)	+	Selenium	+
Chromium (TOT)	+	Silica (ICP)	+
Cobalt (ICP)	+	Silica (COL)	+
Cobalt (AA)	+	Silver (ICP)	+
Cobalt (TOT)	+	Silver (AA)	+
Copper (ICP)	+	Silver (TOT)	+
Copper (AA)	+	Sodium (ICP)	LOP
Copper (TOT)	+	Sodium (AA)	+
Dissolved solids	+	Strontium	+
Fluoride	LOP	Sulfate	+
Iron (ICP)	+	Zinc (ICP)	+
Iron (AA)	LOP	Zinc (AA)	+
Iron (TOT)	LOP	Zinc (TOT)	+

In the NWQL during water-year 1988, chloride, chromium, zinc (ICP), zinc (AA), and zinc (TOT) had acceptable results after failing the precision tests during water-year 1987 (Lucey and Peart, 1989b).

Since only one of the SRWS's used during the water year had an MPV for beryllium, the control charts for beryllium (figs. 8 and 9) have an uneven distribution of data points with several clusters corresponding to months when this reference sample was used.

Beginning October, 1987, blind-sample mixes destined for mercury analysis were preserved with a nitric acid/potassium dichromate solution at the Ocala facility. The control chart for mercury (fig. 41) shows several determinations in May that are greater than two standard deviations from the MPV which could be from a contamination problem. A possible source of mercury contamination in the blind sample program is a residue in bottles that were previously used to preserve nutrient samples with mercuric chloride tablets.

The patterns of clustered points on the control charts for copper (ICP) (fig. 23), lead (ICP) (fig. 31), and molybdenum (ICP) (fig. 42) 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.

Bias

Results of the statistical tests for bias are shown in Table 4. There were fewer constituents indicating bias for water-year 1988 than for water-year 1987 at the NWQL (Lucey and Peart, 1989b). Constituents that showed negative bias for water-years 1988 and 1987 were nickel (AA) and silver (ICP). In addition, cadmium (ICP), chromium (ICP), cobalt (ICP), lithium (TOT), mercury, molybdenum (AA), nickel (ICP), silver (AA), and silver (TOT) had negative bias during water-year 1988.

Positively biased constituents for water-years 1988 and 1987 were: arsenic, barium (AA), barium, (TOT), fluoride, iron (ICP); lead (ICP), magnesium (ICP); selenium; sodium (ICP); sulfate; and zinc (AA). Additional constituents that had a positive bias in water-year 1988 but did not during water-year 1987 were: beryllium (TOT), boron, cadmium (TOT), calcium (ICP), copper (ICP), copper (TOT), manganese (ICP), nickel (TOT), and zinc (TOT).

Results for arsenic, barium (AA), barium (TOT), fluoride, magnesium (ICP), selenium, sodium (ICP), and sulfate have indicated a positive bias for each of the last three years (1986, 1987, 1988) (Lucey and Peart, 1989a, 1989b) For barium (AA), barium (TOT), beryllium (TOT), lead (ICP), and nickel (TOT) an apparent biased condition occurred because the minimum reporting levels (barium, 100 μg/L; beryllium (TOT), 10 μg/L; lead (ICP), 10 μg/L; and nickel (TOT), 10 μg/L) were greater than the MPV's.

The control chart for alkalinity (fig. 1) shows a change to a positive bias in March, 1988, for samples with dissolved alkalinity concentrations less than 100 mg/L which continues for the remainder of the water year. The determination could have been affected by instrument adjustments or the calibration of standards.

Control charts for calcium (ICP) (fig. 14) and magnesium (ICP) (fig. 36) indicate a trend to a positive bias toward the end of the water year.

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; DCP, direct current plasma emission spectrometry; COL, colorimetry]

Constituent (dissolved, except as indicated)	Results from Oct. 1987- Sept. 1988	Constituent (dissolved, except as indicated)	Results from Oct. 1987- Sept. 1988
Alkalinity	+	Lead (ICP)	P[1]
Aluminum	+	Lead (AA)	+
Antimony	+	Lead (TOT)	+
Arsenic	P	Lithium	+
Barium (ICP)	+	Lithium (TOT)	N
Barium (AA)	P[1]	Magnesium (ICP)	P
Barium (TOT)	P[1]	Magnesium (AA)	+
Beryllium	+	Manganese (ICP)	P
Beryllium (TOT)	P[1]	Manganese (AA)	+
Boron	P	Manganese (TOT)	+
Cadmium (ICP)	N	Mercury	N
Cadmium (AA)	+	Molybdenum (ICP)	+
Cadmium (TOT)	P	Molybdenum (AA)	N
Calcium (ICP)	P	Nickel (ICP)	N
Calcium (AA)	+	Nickel (AA)	N
Chloride	+	Nickel (TOT)	P[1]
Chromium (ICP)	N	Potassium	+
Chromium (DCP)	+	Selenium	P
Chromium (TOT)	+	Silica (ICP)	+
Cobalt (ICP)	N	Silica (COL)	+
Cobalt (AA)	+	Silver (ICP)	N
Cobalt (TOT)	+	Silver (AA)	N
Copper (ICP)	P	Silver (TOT)	N
Copper (AA)	+	Sodium (ICP)	P
Copper (TOT)	P	Sodium (AA)	+
Dissolved solids	+	Strontium	+
Fluoride	P	Sulfate	P
Iron (ICP)	P	Zinc (ICP)	+
Iron (AA)	+	Zinc (AA)	P
Iron (TOT)	+	Zinc (TOT)	P

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

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 or lower than the MPV's or undetected contamination of the SRWS. When bias is indicated statistically but precision is good during the water year, 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 plus nitrite nitrogen as N, nitrite nitrogen as N, and orthophosphate phosphorus as P failed the precision test at the NWQL in water-year 1988. Nitrate plus nitrite nitrogen as N and orthophosphate phosphorus as P had also failed the precision test during water-year 1987 (Lucey and Peart, 1989b).

Bias

Results of the statistical tests for bias are presented in table 6. Results for ammonia nitrogen as N indicated a positive bias, while the results for ammonia plus organic nitrogen as N and nitrite nitrogen as N indicated a negative bias. During water-year 1987, ammonia plus organic nitrogen as N indicated a positive bias (Lucey and Peart, 1989b).

QUALITY-ASSURANCE DATA FOR PRECIPITATION SAMPLES

The results for statistical testing for lack of precision and bias for each constituent in the 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 1988, as they did in water-year 1987. Results for ammonia nitrogen as N and sodium indicate a positive bias and results for fluoride a negative bias. Sodium data also indicated a positive bias in water-year 1987 (Lucey and Peart, 1989b).

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. 1987-Sept. 1988	Constituent (dissolved)	Results from Oct. 1987-Sept. 1988
Ammonia nitrogen, as N	+	Nitrite nitrogen, as N	LOP
Ammonia+organic nitrogen, as N	+	Orthophosphate phosphorus, as P	LOP
Nitrate+nitrite nitrogen, as N	LOP	Phosphorus, as P	+

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

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

Constituent (dissolved)	Results from Oct. 1987-Sept. 1988	Constituent (dissolved)	Results from Oct. 1987-Sept. 1988
Ammonia nitrogen, as N	p	Nitrite nitrogen, as N	+
Ammonia+organic nitrogen, as N	n	Orthophosphate phosphorus, as P	+
Nitrate+nitrite nitrogen, as N	n	Phosphorus, as P	+

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. 1987-Sept. 1988	Constituent (dissolved)	Results from Oct. 1987-Sept. 1988
Ammonia nitrogen, as N	+	Nitrate nitrogen, as N	+
Calcium	+	Orthophosphate phosphorus, as P	+
Chloride	+	Potassium	+
Fluoride	+	Sodium	+
Magnesium	+	Sulfate	+

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

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

Constituent (dissolved)	Results from Oct. 1987-Sept. 1988	Constituent (dissolved)	Results from Oct. 1987-Sept. 1988
Ammonia nitrogen, as N	p	Nitrate nitrogen, as N	+
Calcium	+	Orthophosphate phosphorus, as P	+
Chloride	+	Potassium	+
Fluoride	n	Sodium	p
Magnesium	+	Sulfate	+

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 U.S. Geological Survey to the National Water-Quality Laboratory in Denver, Colo. The resulting data are 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. When bias is indicated statistically but precision is good during the water year, the bias may have minimal effect on data interpretation and minimal practical significance.

An overall evaluation of the data for water-year 1988 indicates a lack of precision in results from the NWQL for calcium (ICP), fluoride, iron (AA), iron (TOT), magnesium (AA), manganese (TOT), potassium, and sodium (ICP). Iron (TOT) failed the precision criteria for both water-years 1987 and 1988 (Lucey and Peart, 1989b).

An overall evaluation of the data for water-year 1988 indicates a significant bias in results from the NWQL for arsenic, barium (AA), barium (TOT), beryllium (TOT), boron, cadmium (ICP), cadmium (TOT), calcium (ICP), chromium (ICP), cobalt (ICP), copper (ICP), copper (TOT), fluoride, iron (ICP), lead (ICP), lithium (TOT), magnesium (ICP), manganese (ICP), mercury, molybdenum (AA), nickel (ICP), nickel (AA), nickel (TOT), selenium, silver (ICP), silver (AA), silver (TOT), sodium (ICP), sulfate, zinc (AA), and zinc (TOT).

Constituents with results that showed negative bias for water-years 1987 and 1988 were nickel (AA) and silver (ICP). Constituents with results that showed positive bias for water-years 1987 and 1988 were: arsenic, barium (AA), barium (TOT), fluoride, iron (ICP); lead (ICP), magnesium (ICP), selenium, sodium (ICP), sulfate, and zinc (AA). Results for arsenic, barium (AA), barium (TOT), fluoride, magnesium (ICP), selenium, sodium (ICP), and sulfate have indicated positive bias for each of the last three years (Lucey and Peart, 1989a, 1989b).

For nutrient constituents, results for nitrate plus nitrite nitrogen as N, nitrite nitrogen as N, and orthophosphate phosphorus as P failed the precision test at the NWQL during water-year 1988. Results for ammonia plus organic nitrogen as N and nitrite nitrogen as N indicate a negative bias, while results for ammonia nitrogen as N indicate a positive bias.

Results for all constituents in precipitation samples indicate acceptable precision. Results for sodium and ammonia nitrogen as N indicate a positive bias, while results for fluoride indicate a negative bias.

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SUPPLEMENTAL DATA

page 21 follows

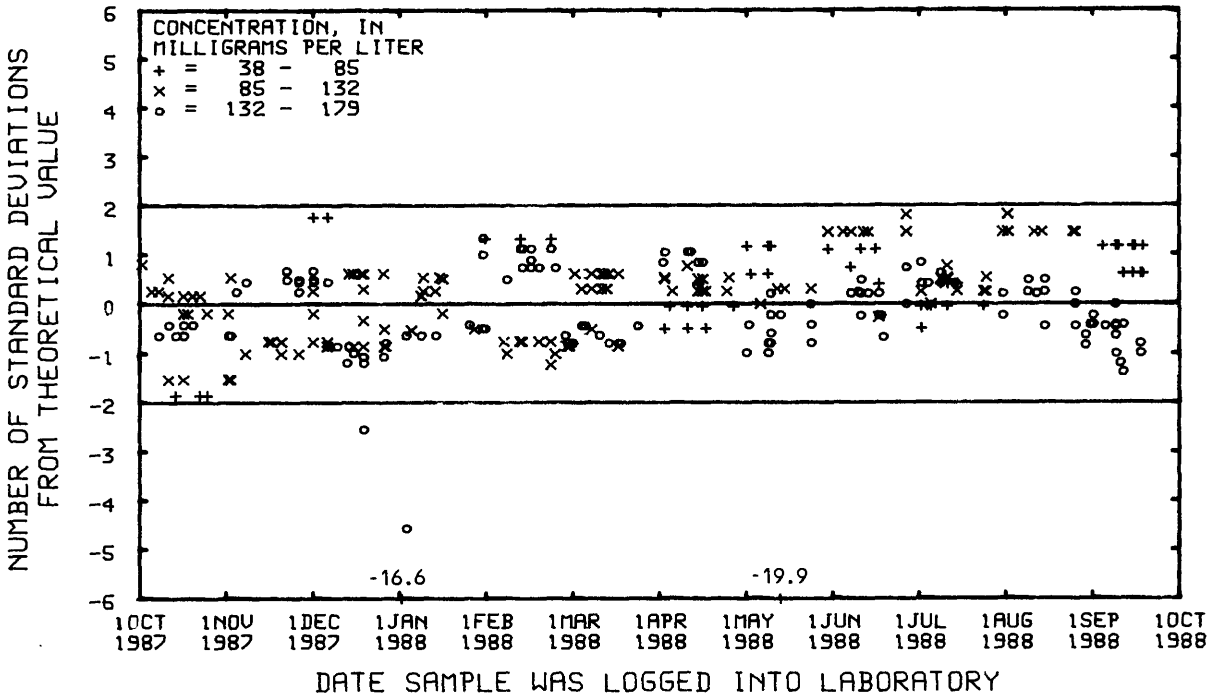

Figure 1.--Alkalinity, dissolved, data from the National Water Quality Laboratory.

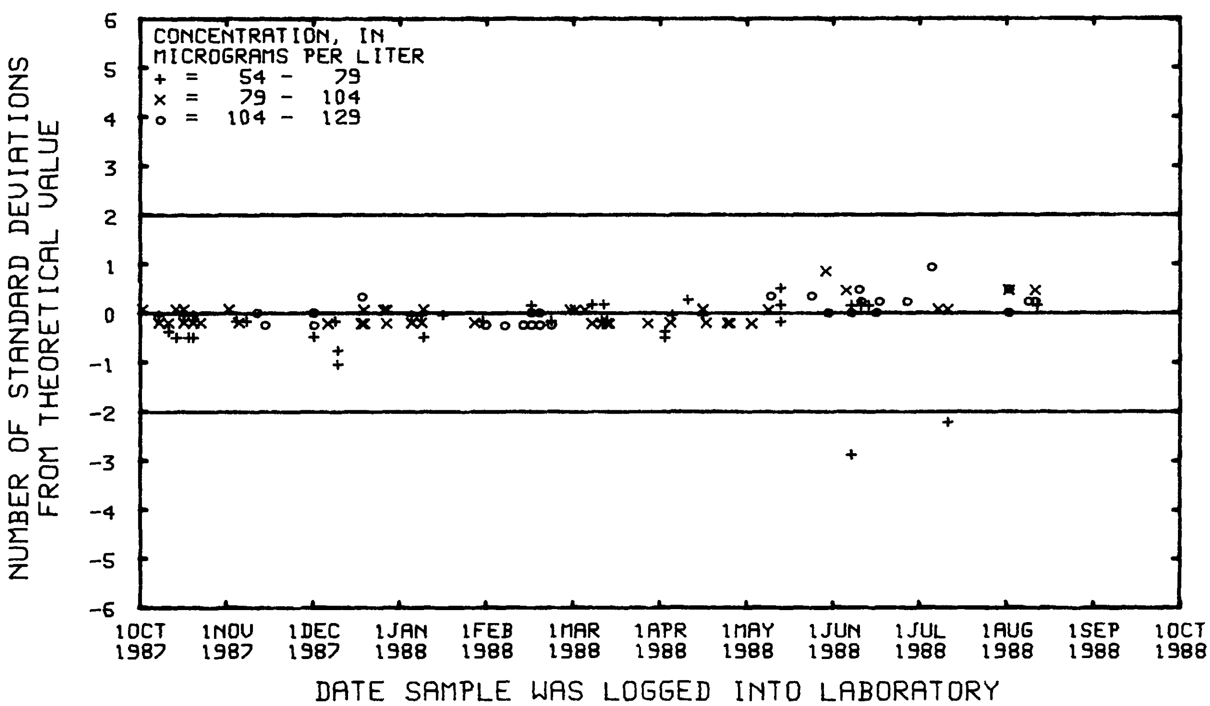

Figure 2.--Aluminum, dissolved, data from the National Water Quality Laboratory.

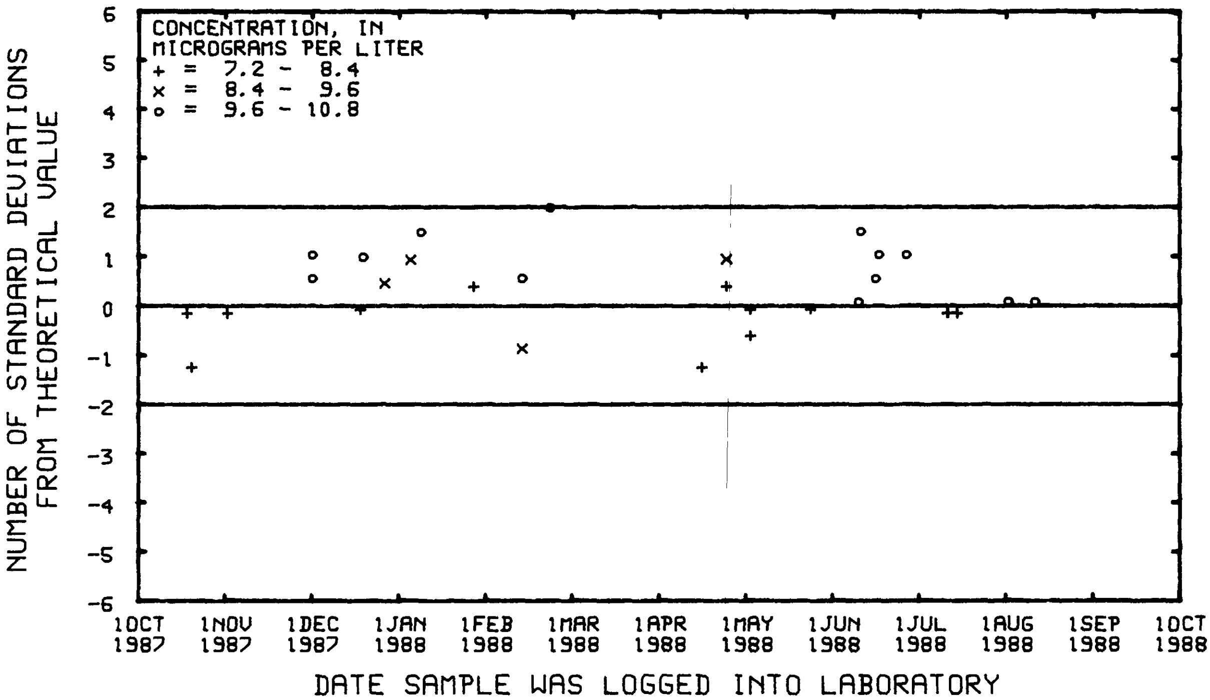

Figure 3.--Antimony, dissolved, data from the National Water Quality Laboratory.

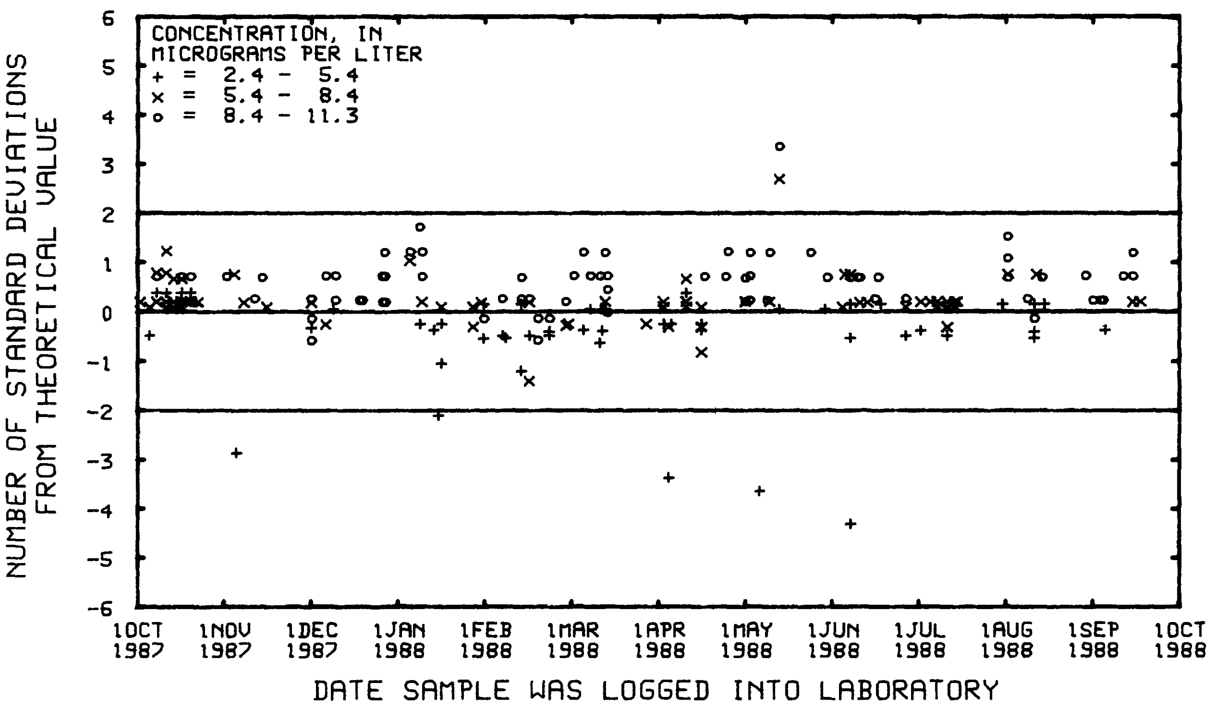

Figure 4.--Arsenic, dissolved, data from the National Water Quality Laboratory.

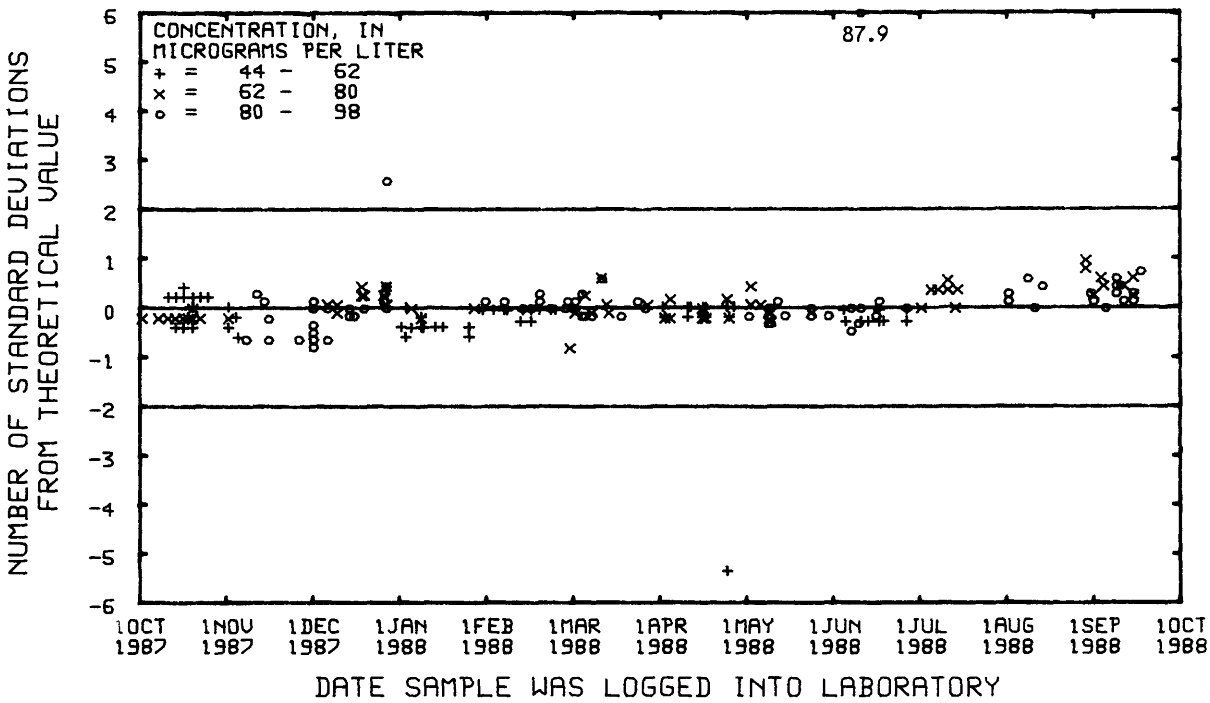

Figure 5.--Barium, dissolved, (inductively coupled plasma emission spectrometry) data from the National Water Quality Laboratory.

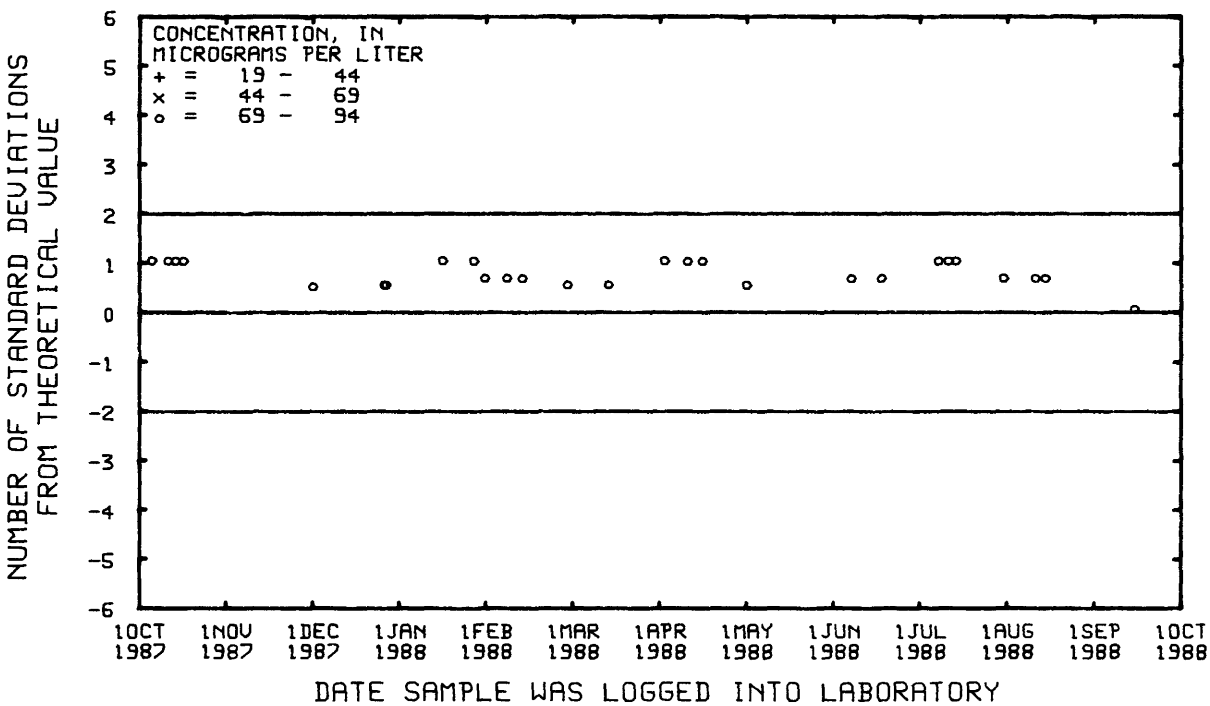

Figure 6.--Barium, dissolved, (atomic absorption spectrometry) data from the National Water Quality Laboratory.

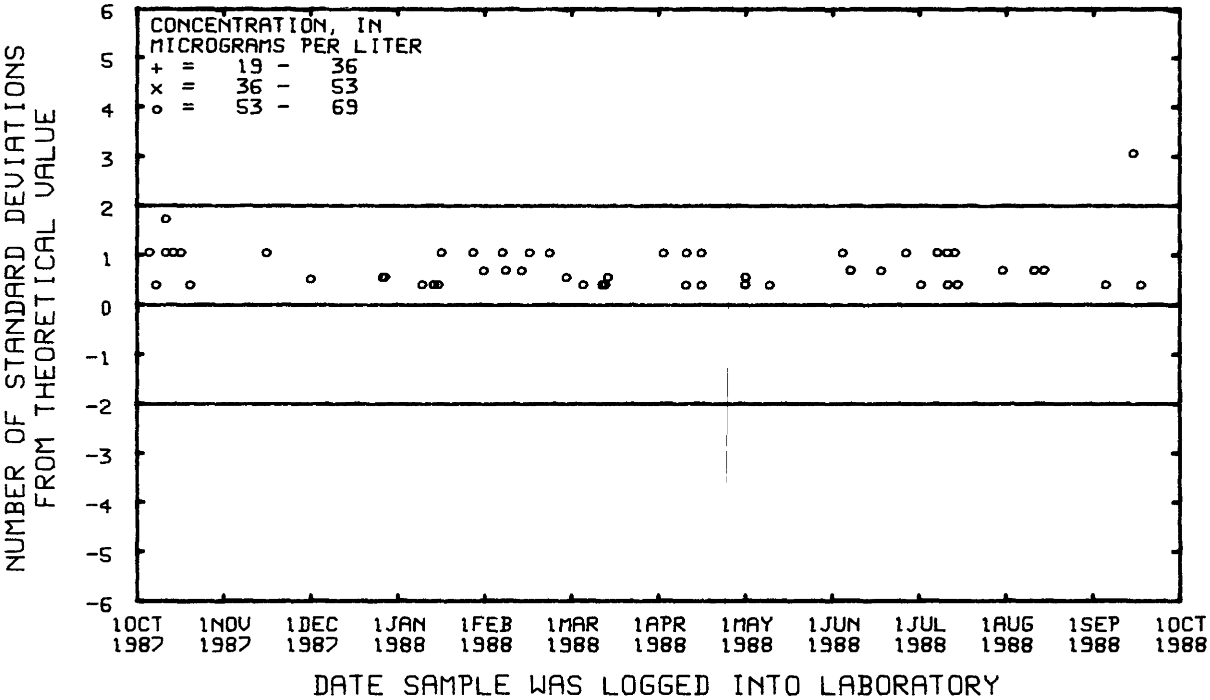

Figure 7.--Barium, total recoverable, data from the National Water Quality Laboratory.

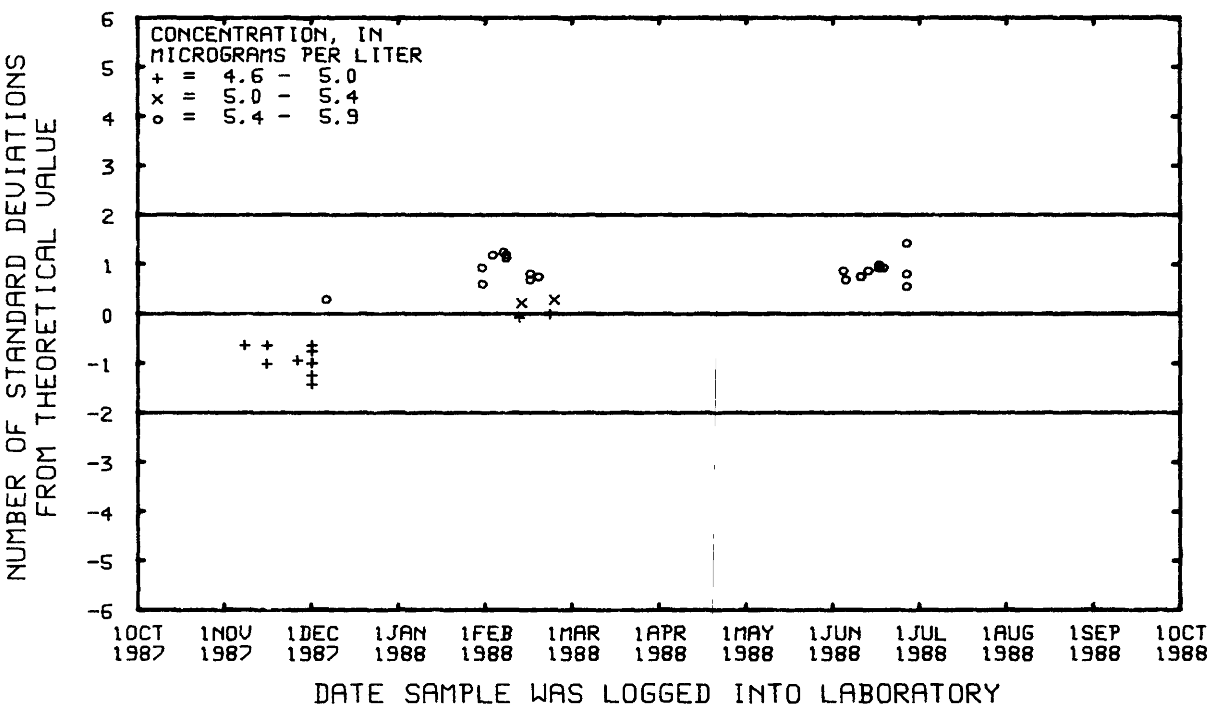

Figure 8.--Beryllium, dissolved, data from the National Water Quality Laboratory.

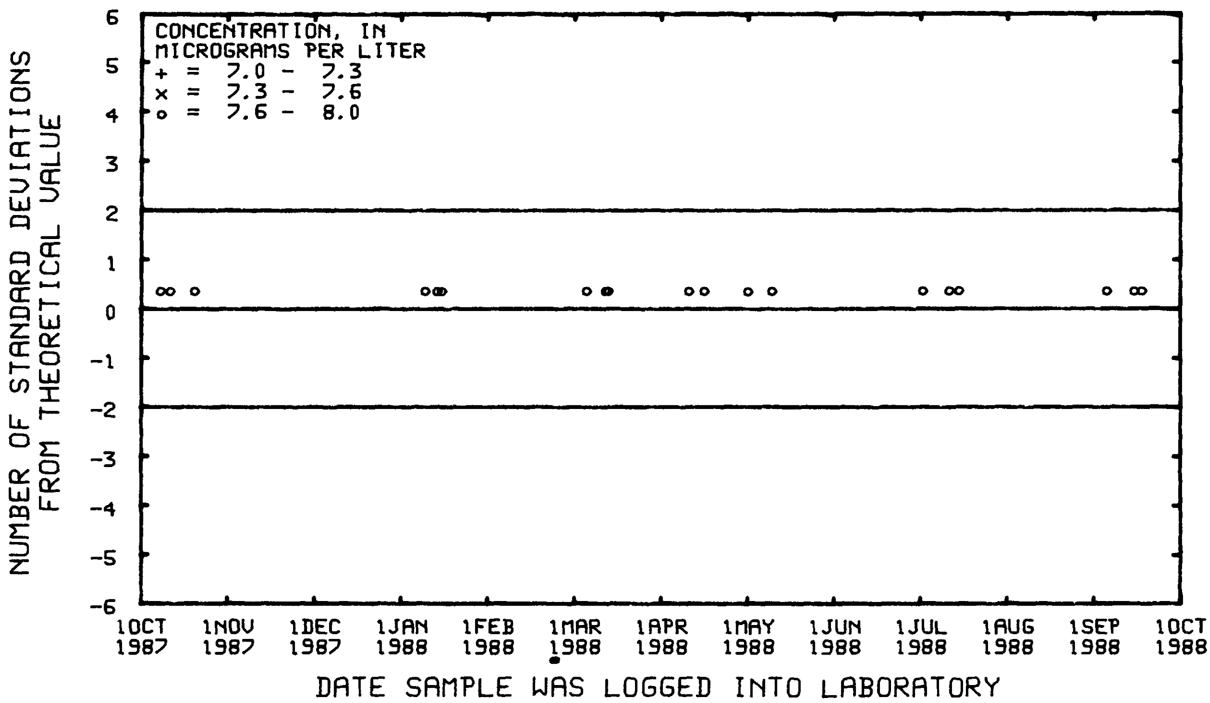

Figure 9.--Beryllium, total recoverable, data from the National Water Quality Laboratory.

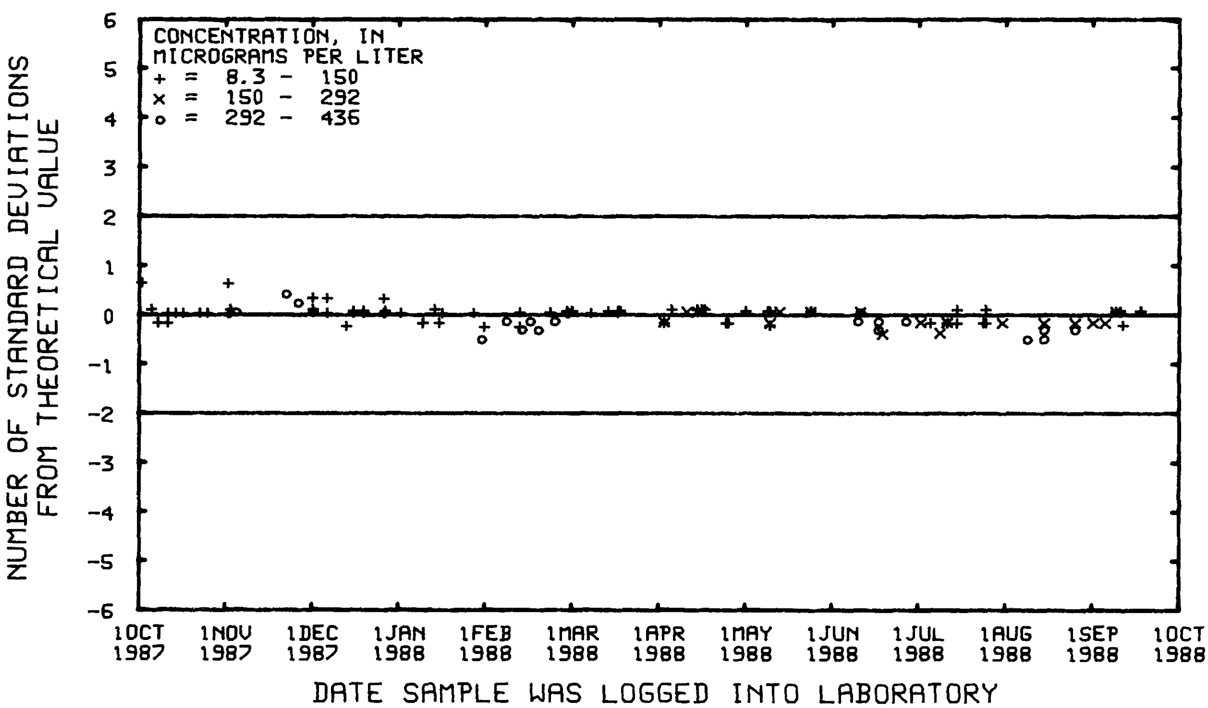

Figure 10.--Boron, dissolved, data from the National Water Quality Laboratory.

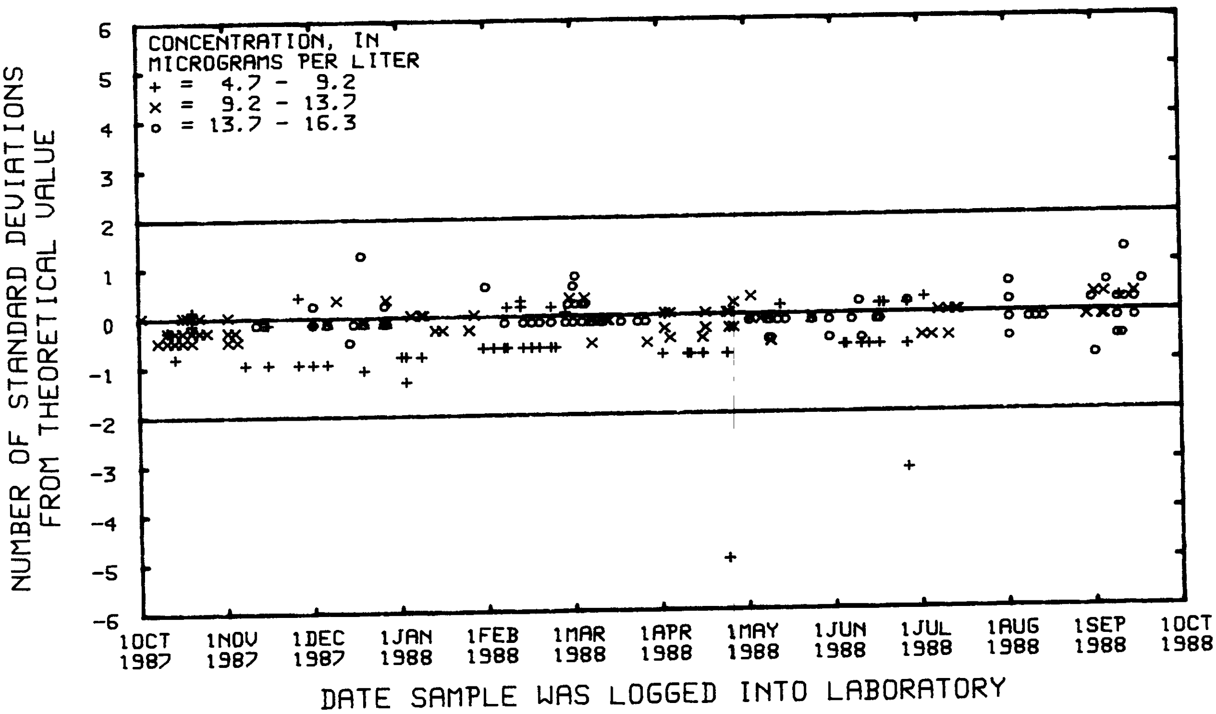

Figure 11.--Cadmium, dissolved,
(inductively coupled plasma emission spectrometry)
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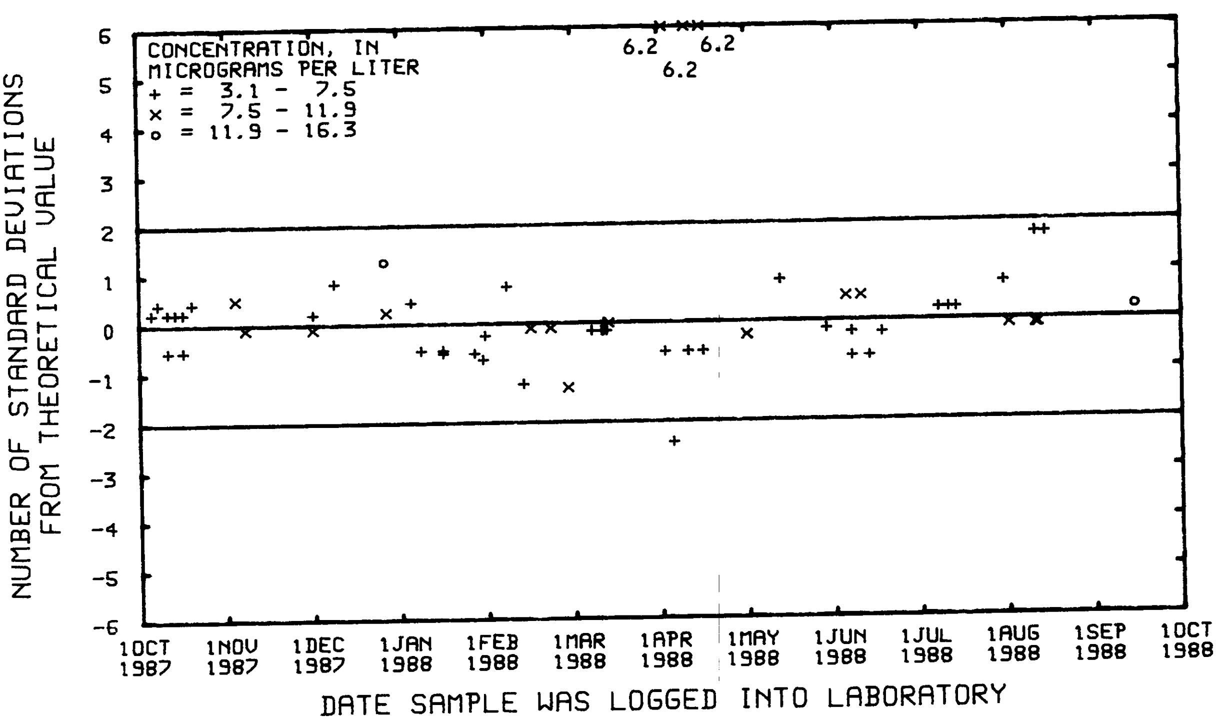

Figure 12.--Cadmium, dissolved,
(atomic absorption spectrometry)
data from the National Water Quality Laboratory.

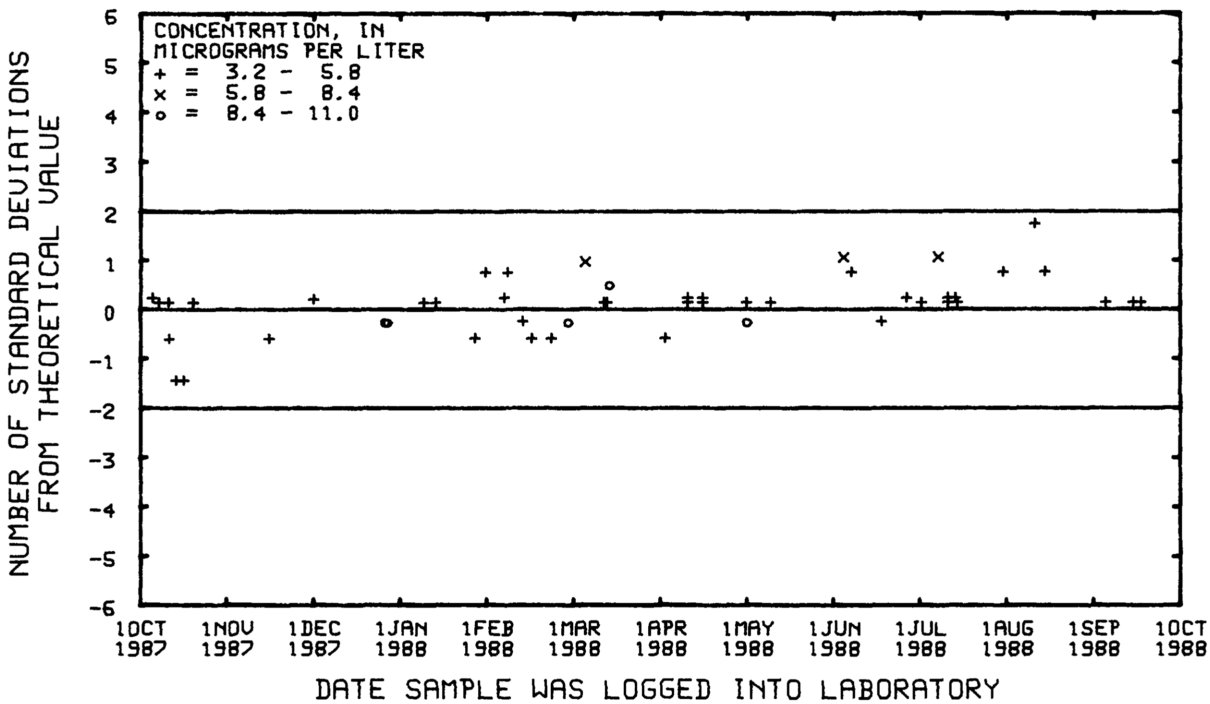

Figure 13.--Cadmium, total recoverable, data from the National Water Quality Laboratory.

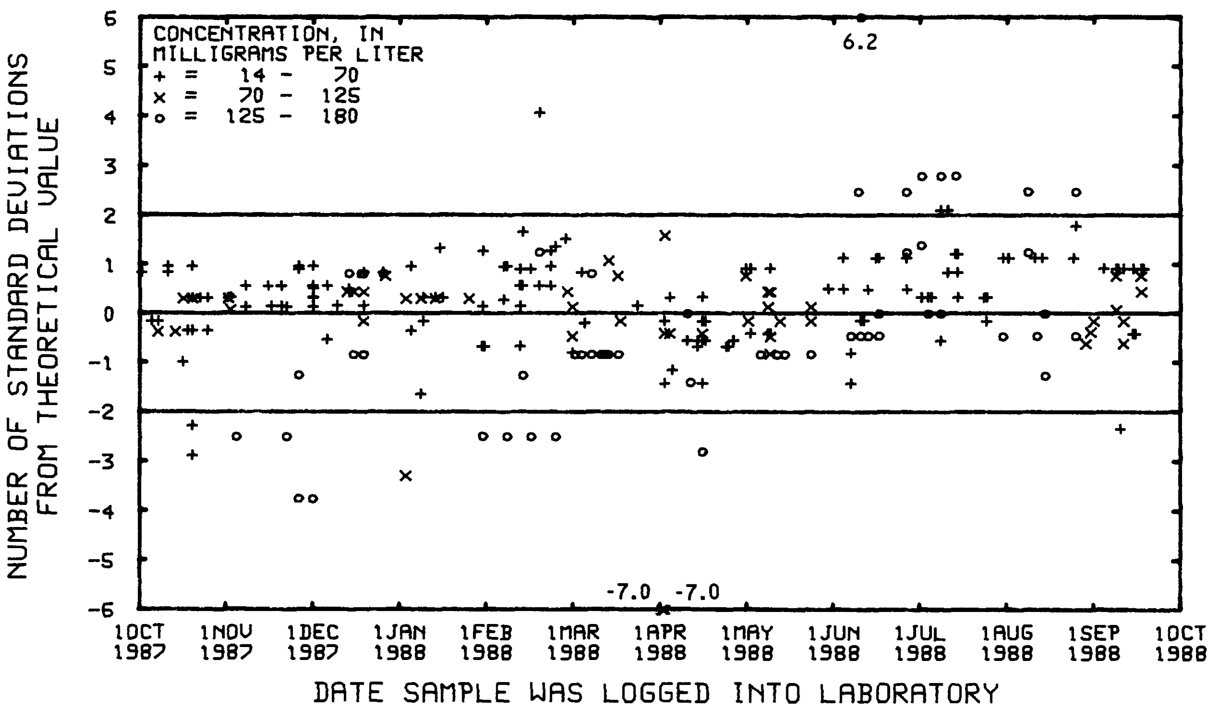

Figure 14.--Calcium, dissolved, (inductively coupled plasma emission spectrometry) data from the National Water Quality Laboratory.

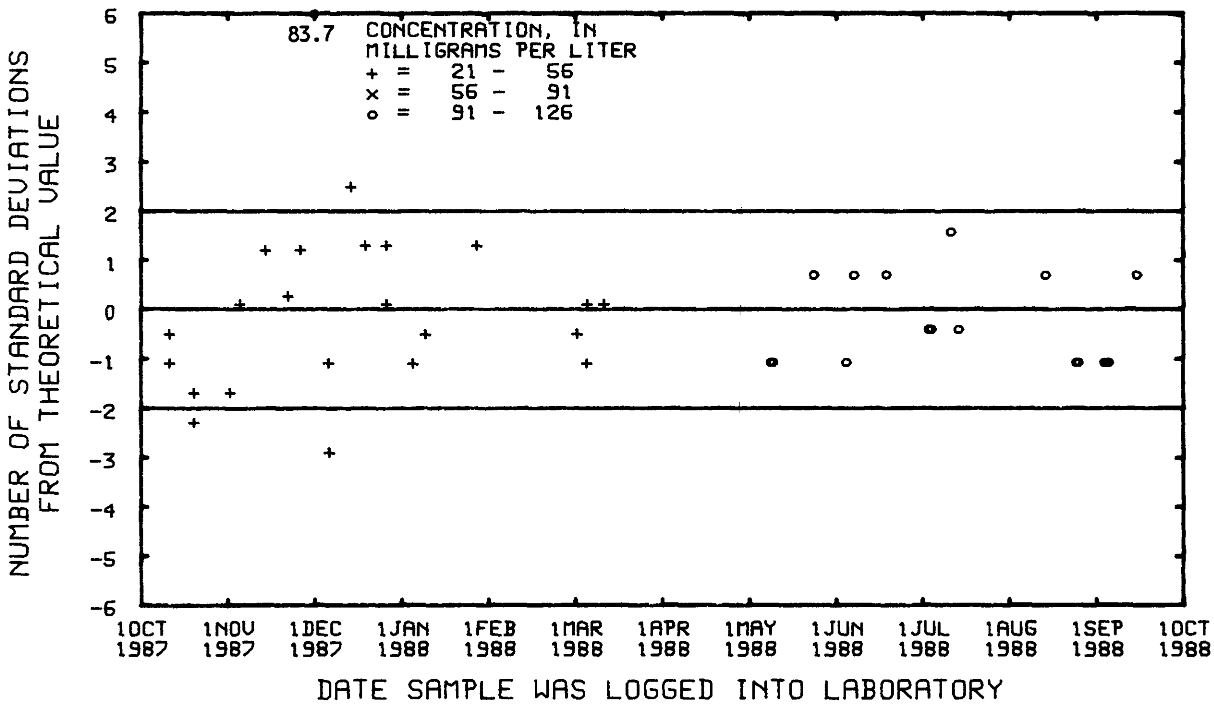

Figure 15.--Calcium, dissolved, (atomic absorption spectrometry) data from the National Water Quality Laboratory.

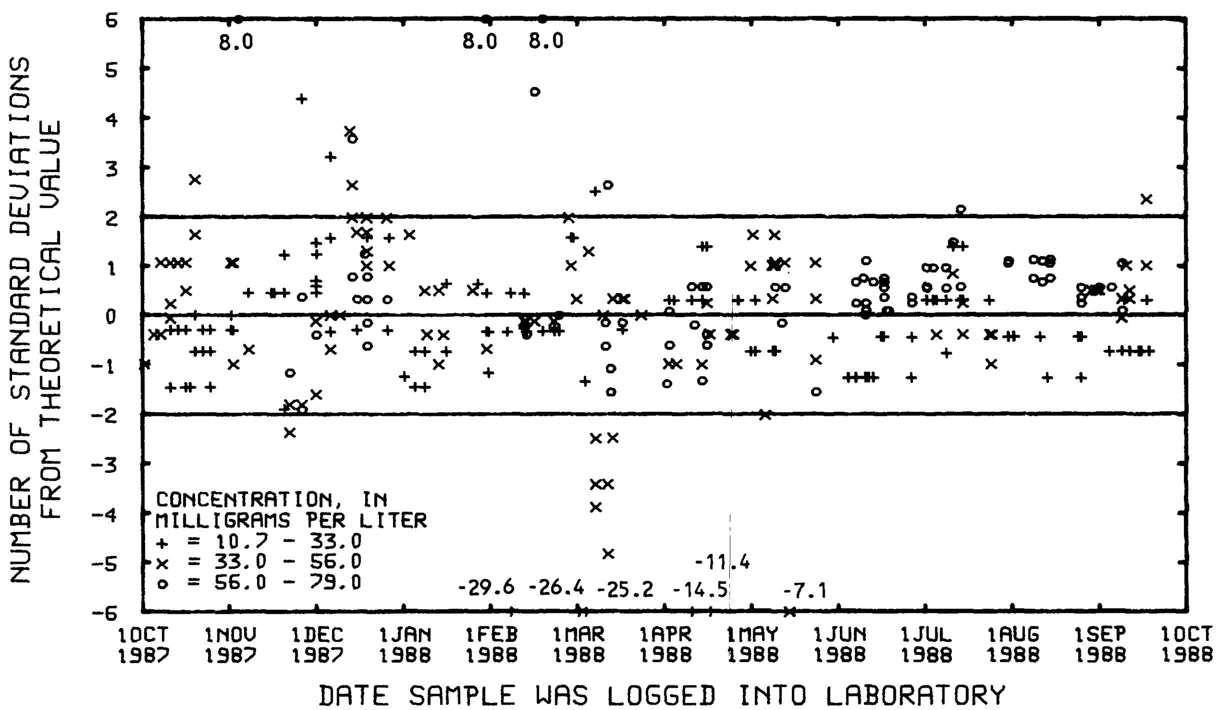

Figure 16.--Chloride, dissolved, data from the National Water Quality Laboratory.

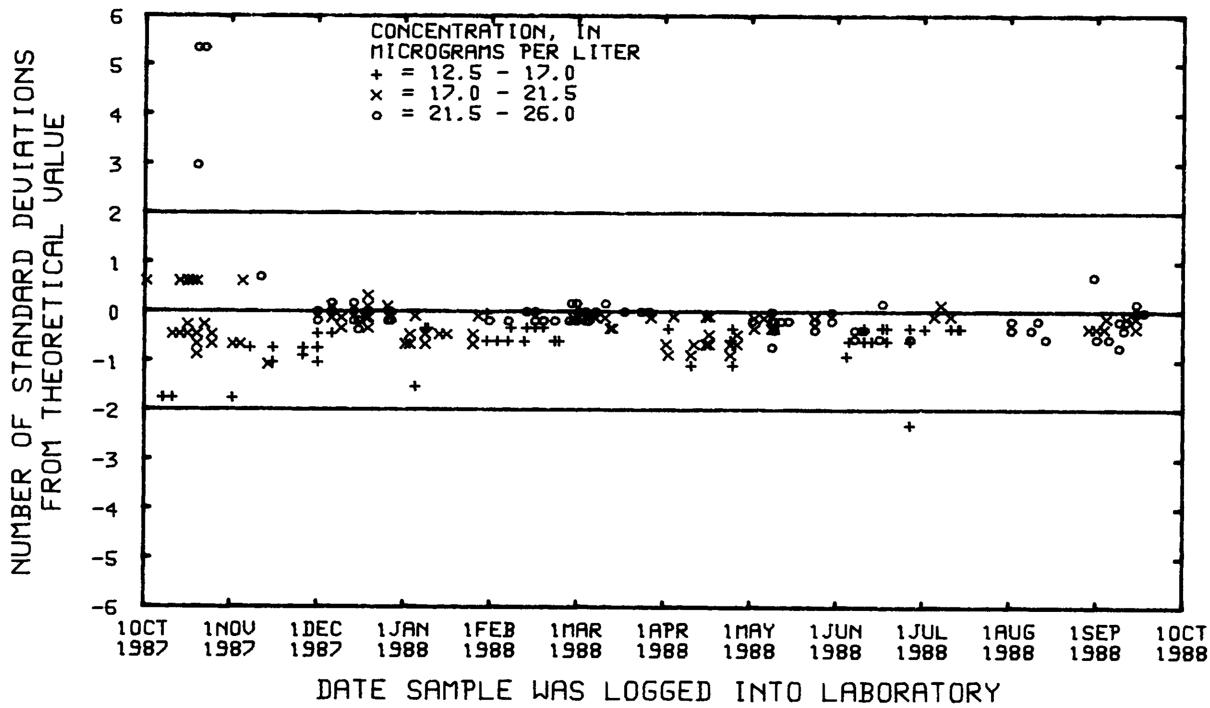

Figure 17.--Chromium, dissolved,
(inductively coupled plasma emission spectrometry)
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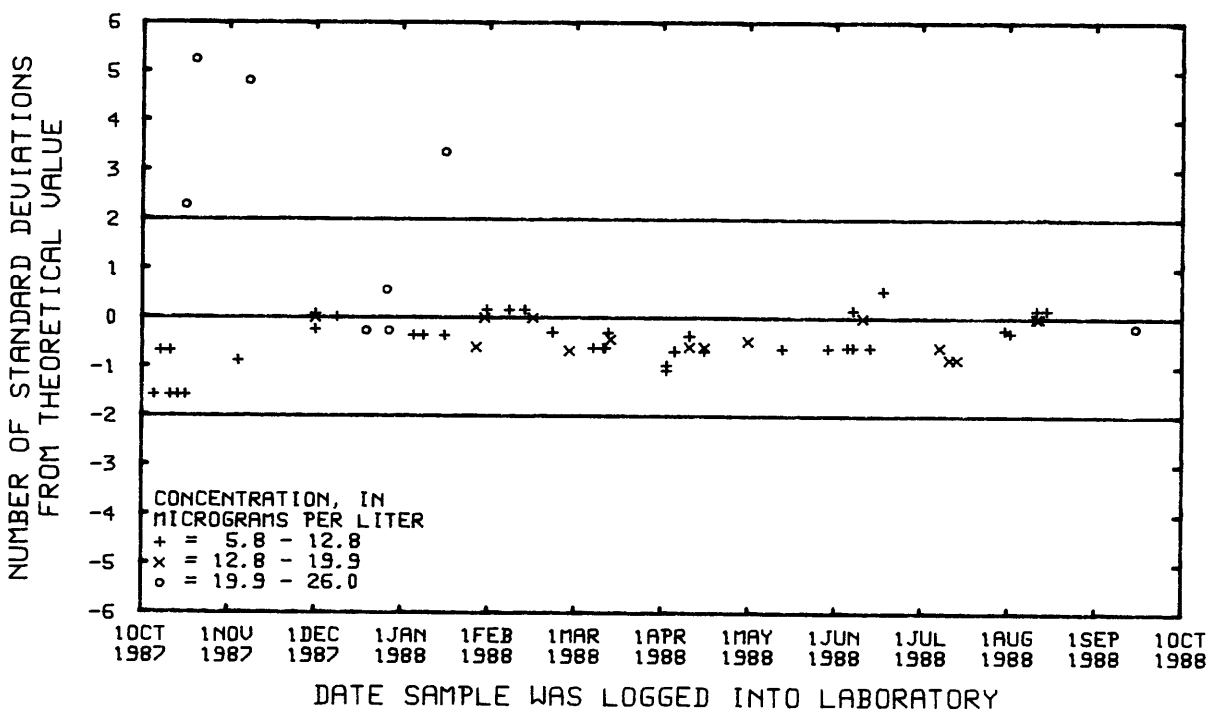

Figure 18.--Chromium, dissolved,
(direct current plasma emission spectrometry)
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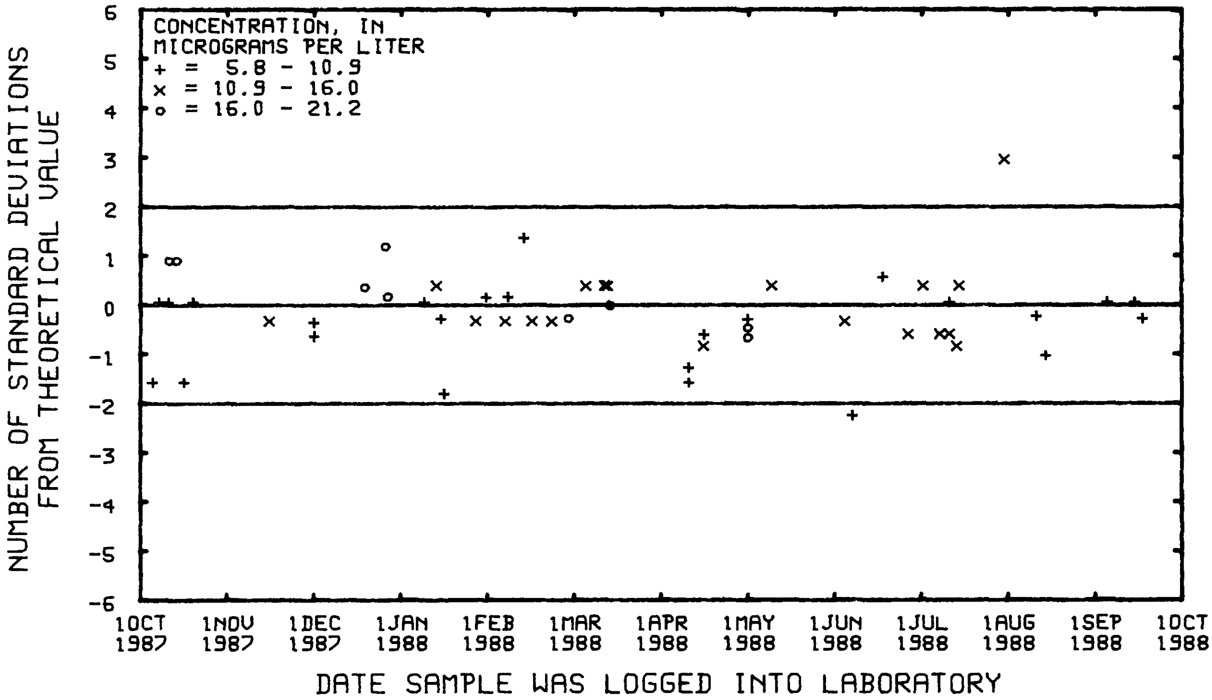

Figure 19.--Chromium, total recoverable, data from the National Water Quality Laboratory.

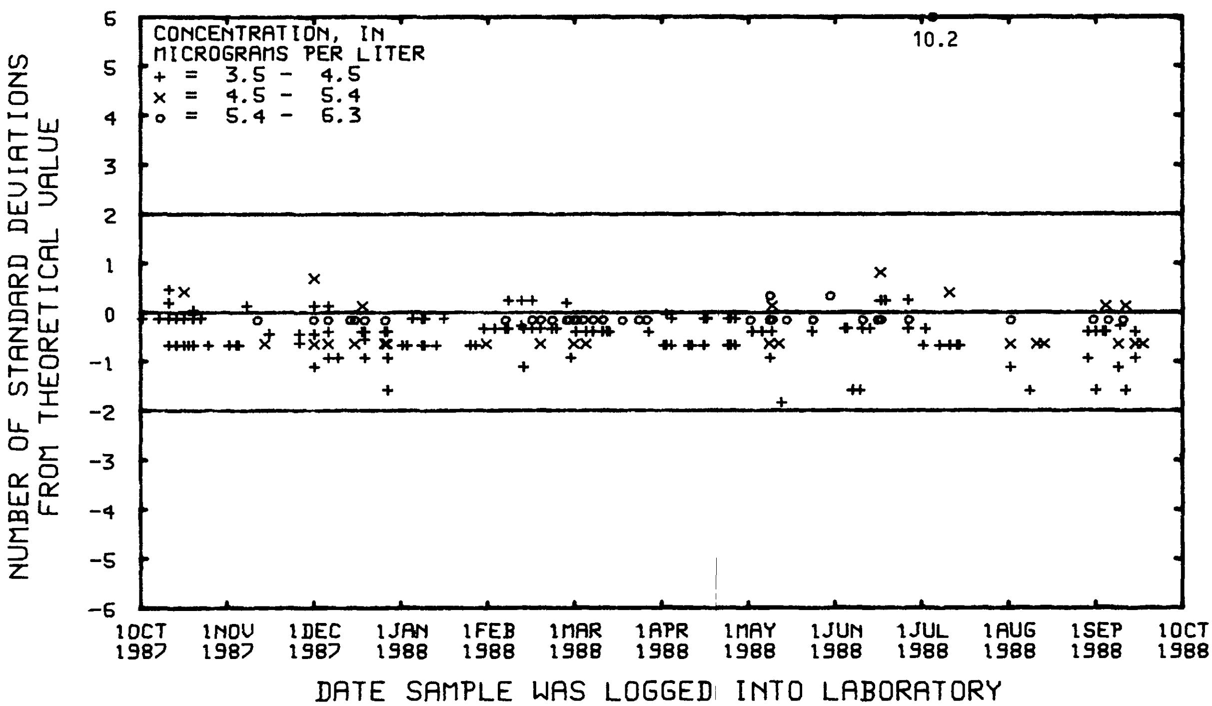

Figure 20.--Cobalt, dissolved, (inductively coupled plasma emission spectrometry) data from the National Water Quality Laboratory.

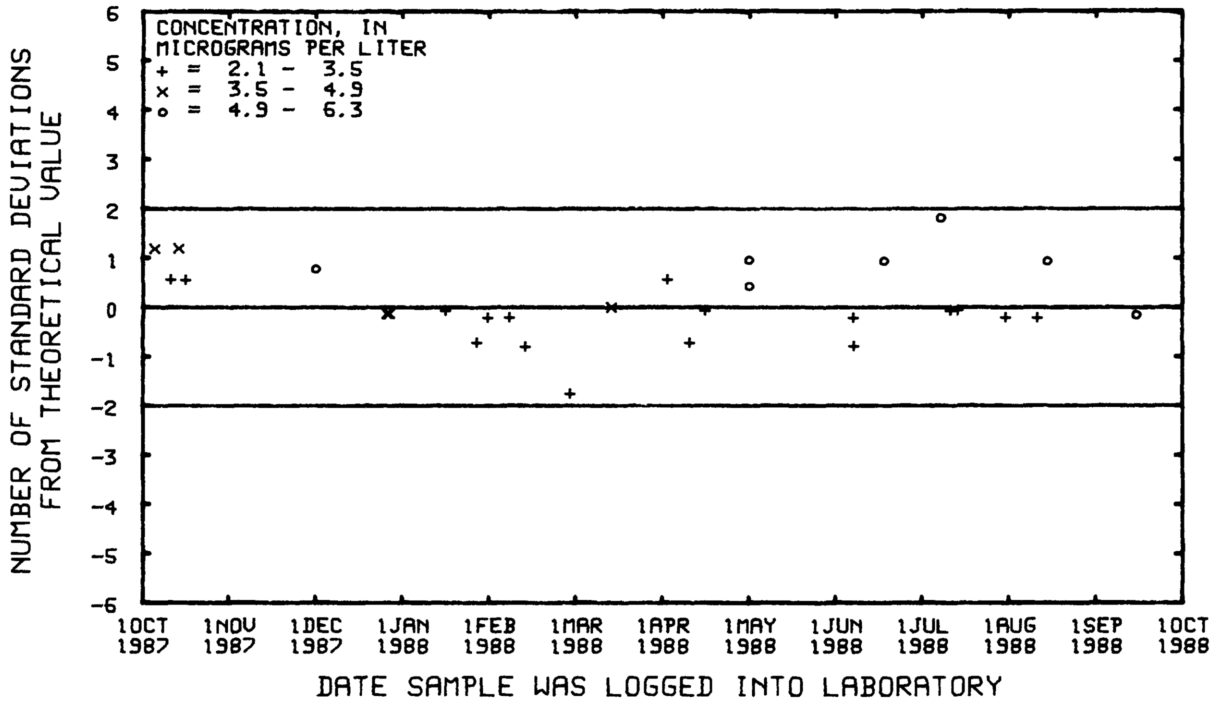

Figure 21.--Cobalt, dissolved,
(atomic absorption spectrometry)
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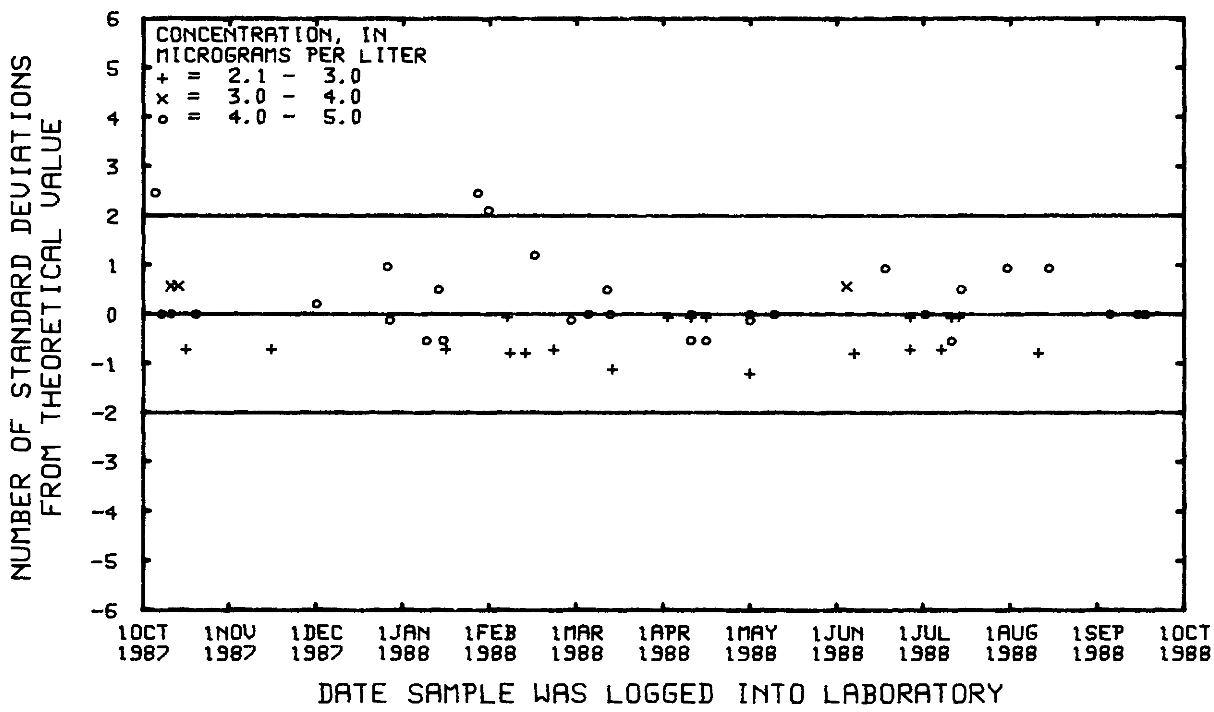

Figure 22.--Cobalt, total recoverable,
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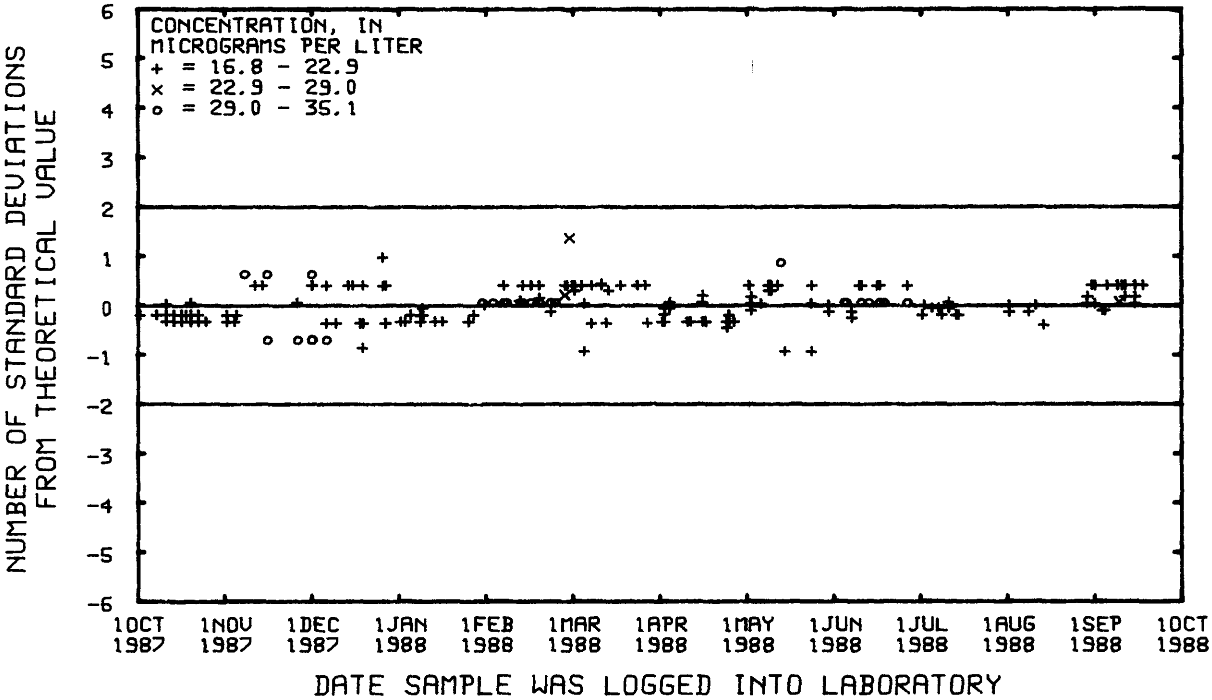

Figure 23.--Copper, dissolved,
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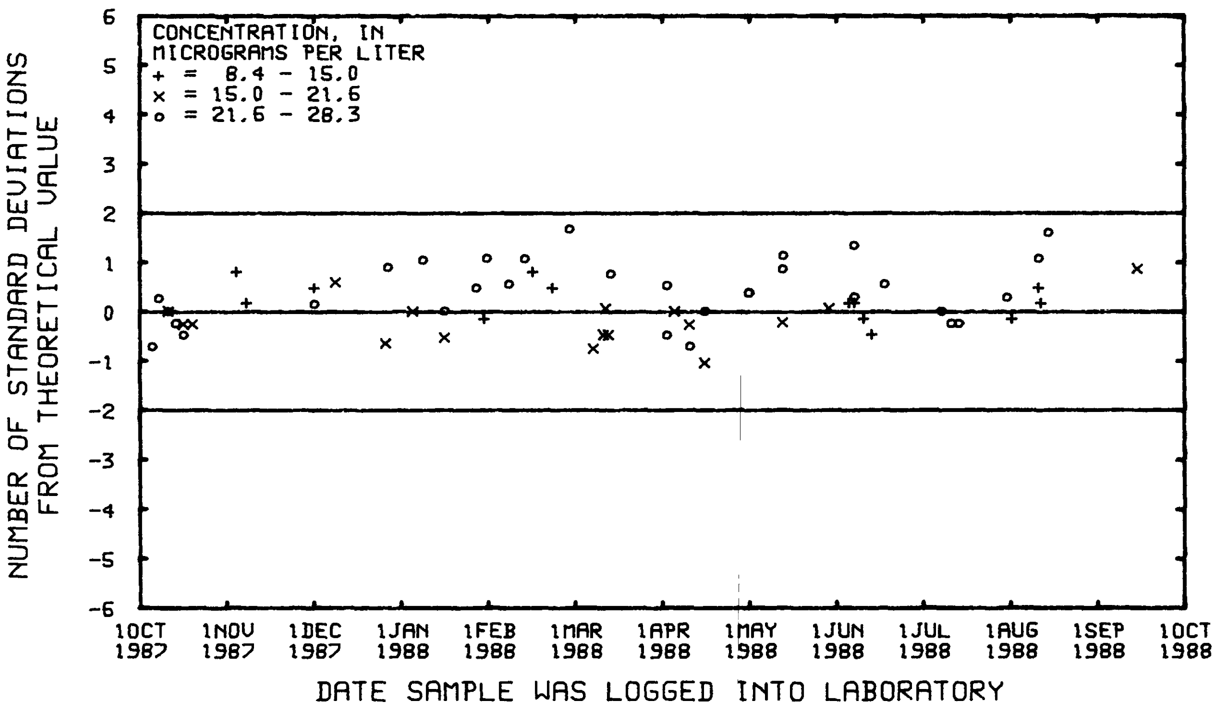

Figure 24.--Copper, dissolved,
(atomic absorption spectrometry)
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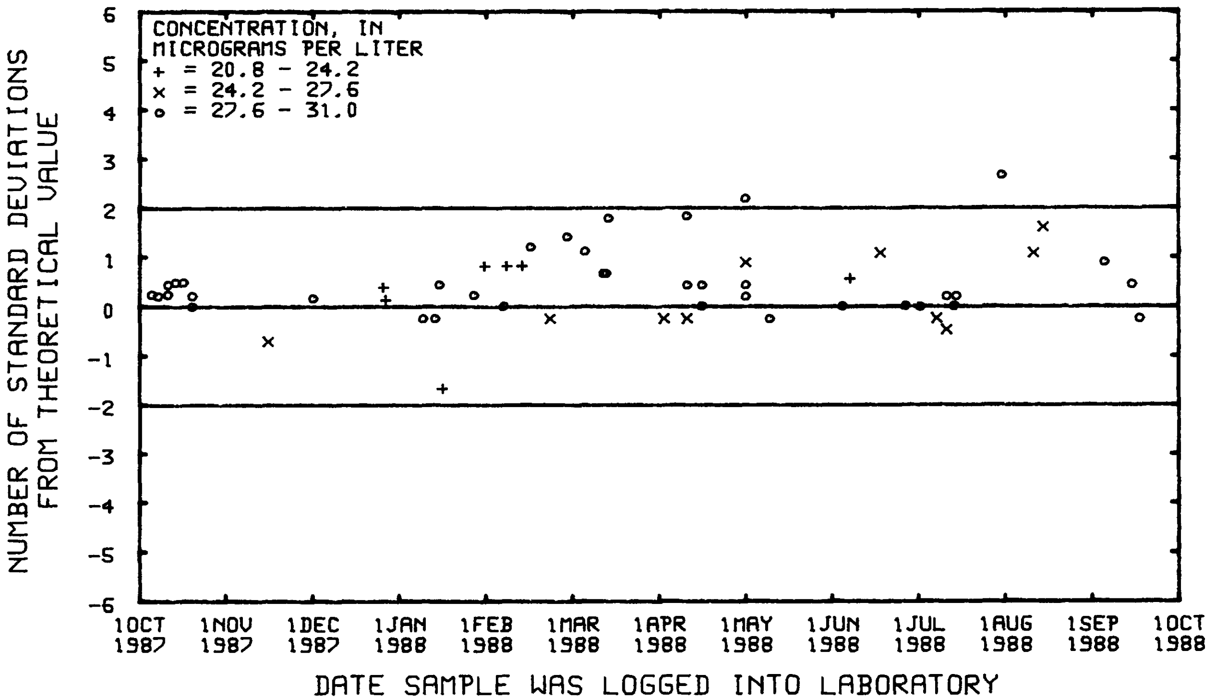

Figure 25.--Copper, total recoverable, data from the National Water Quality Laboratory.

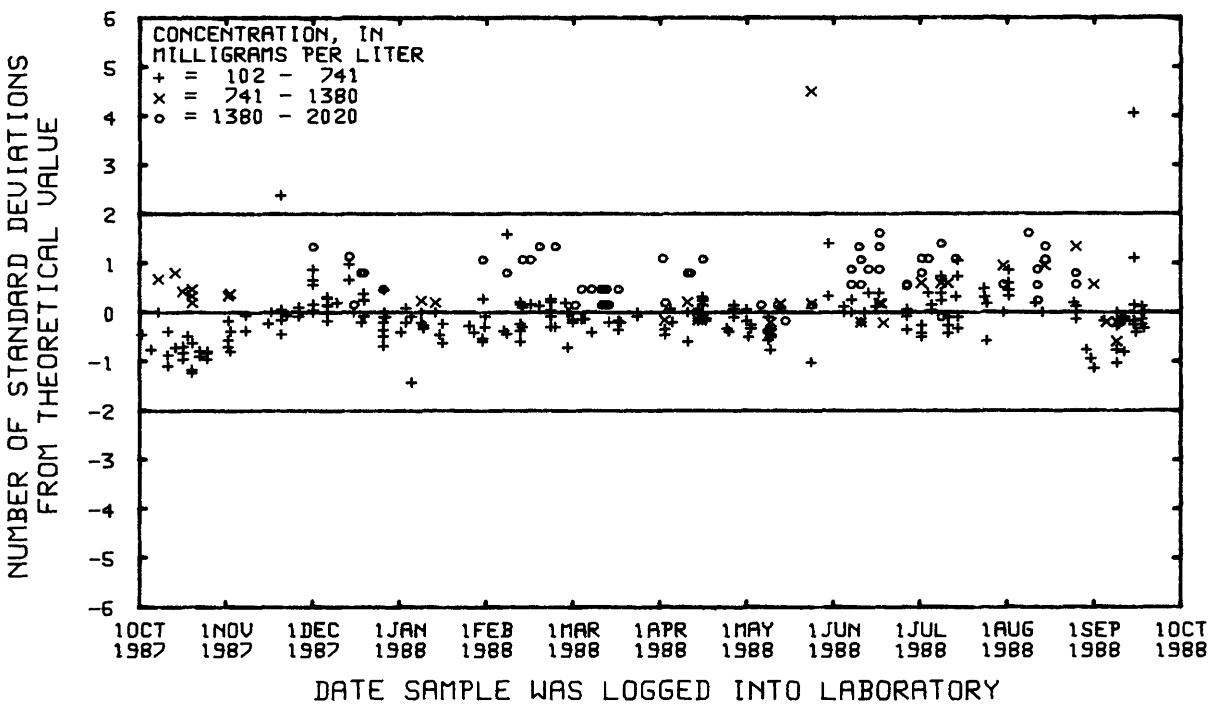

Figure 26.--Dissolved solids data from the National Water Quality Laboratory.

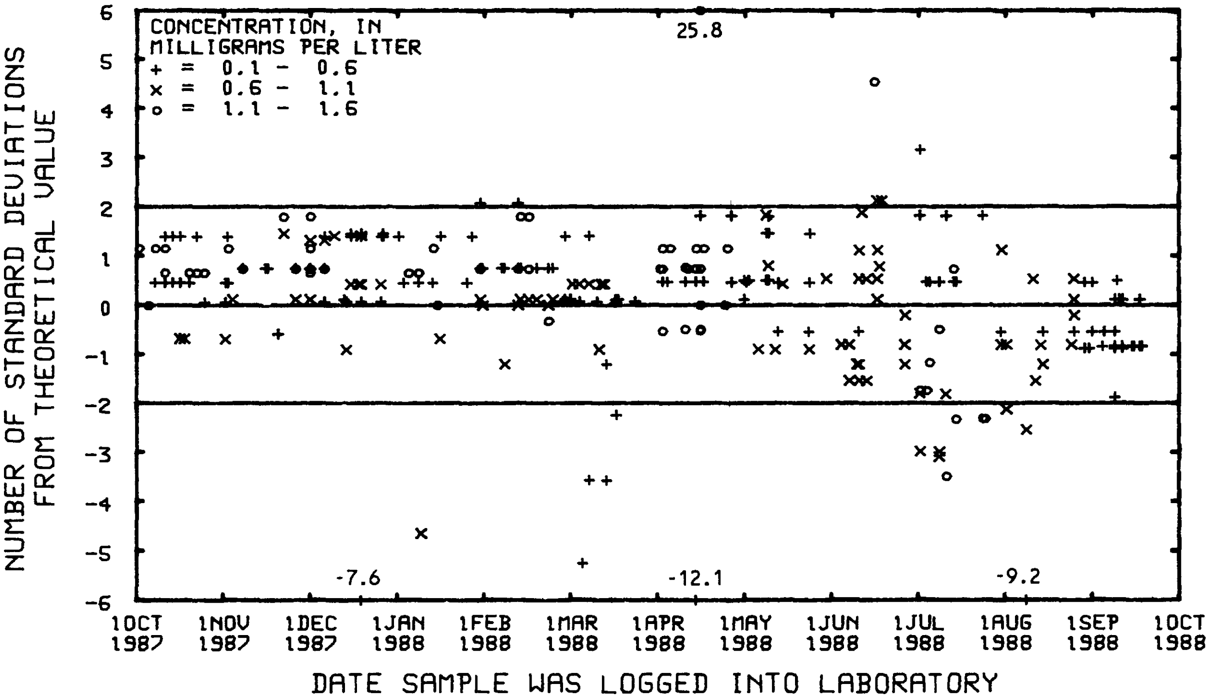

Figure 27.--Fluoride, dissolved, data from the National Water Quality Laboratory.

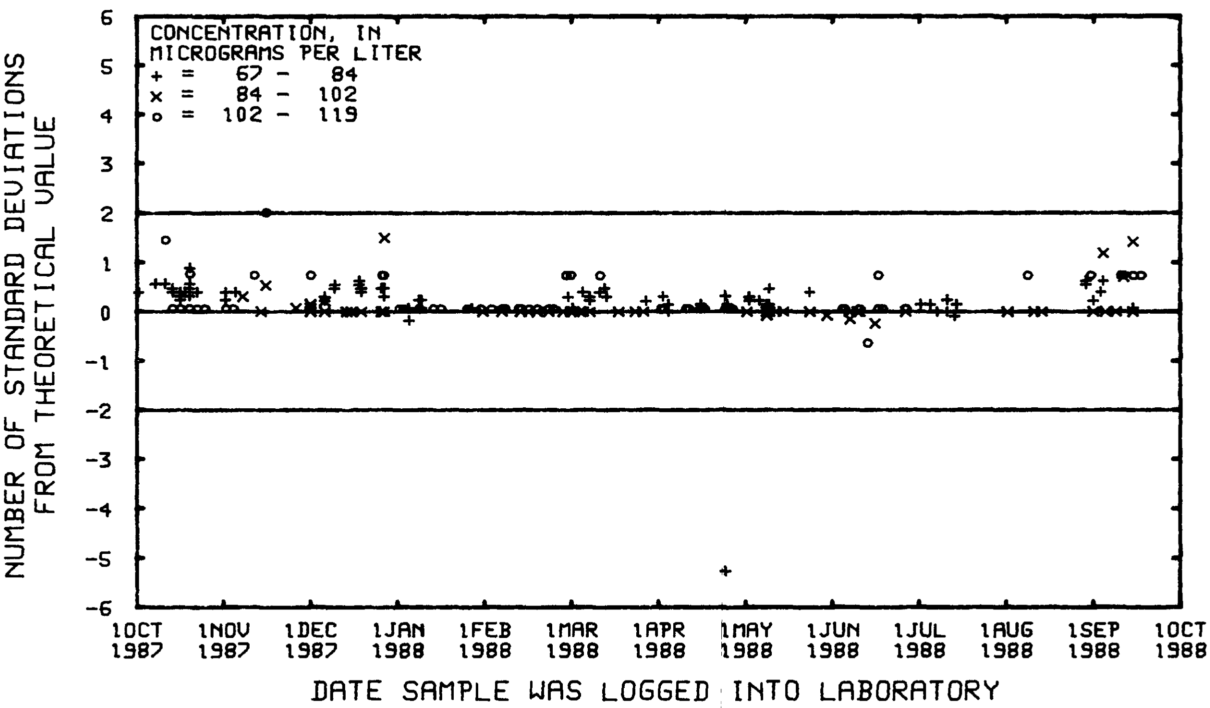

Figure 28.--Iron, dissolved, (inductively coupled plasma emission spectrometry) data from the National Water Quality Laboratory.

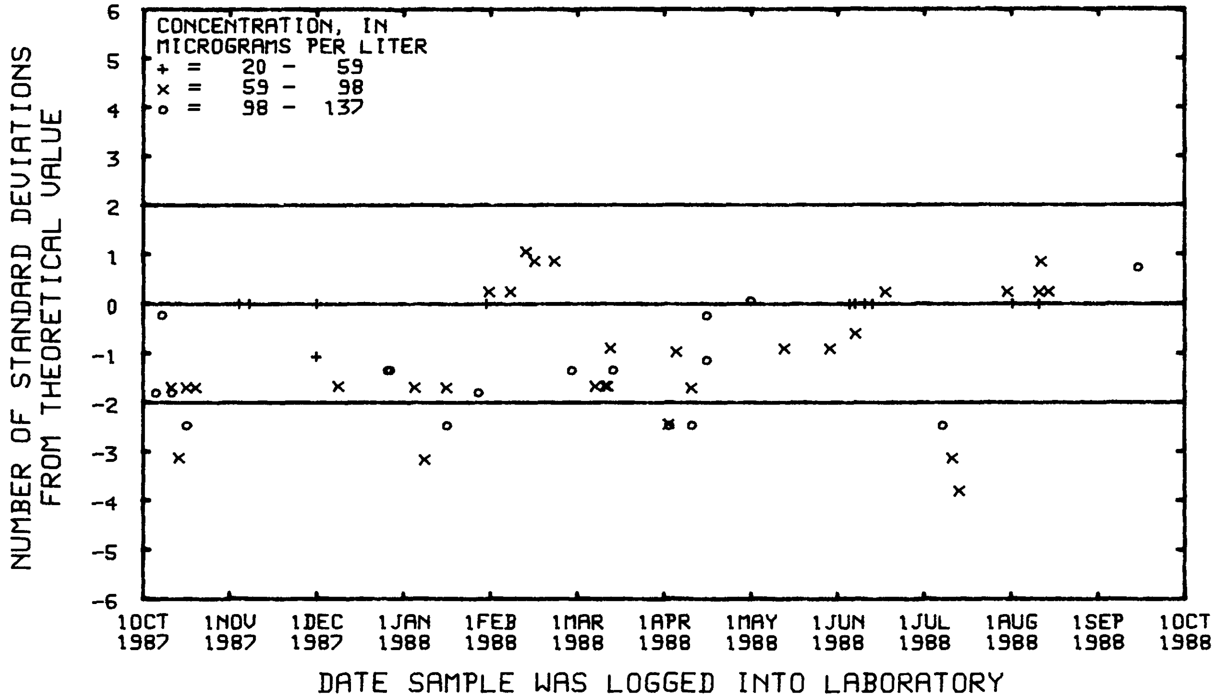

Figure 29.--Iron, dissolved, (atomic absorption spectrometry) data from the National Water Quality Laboratory.

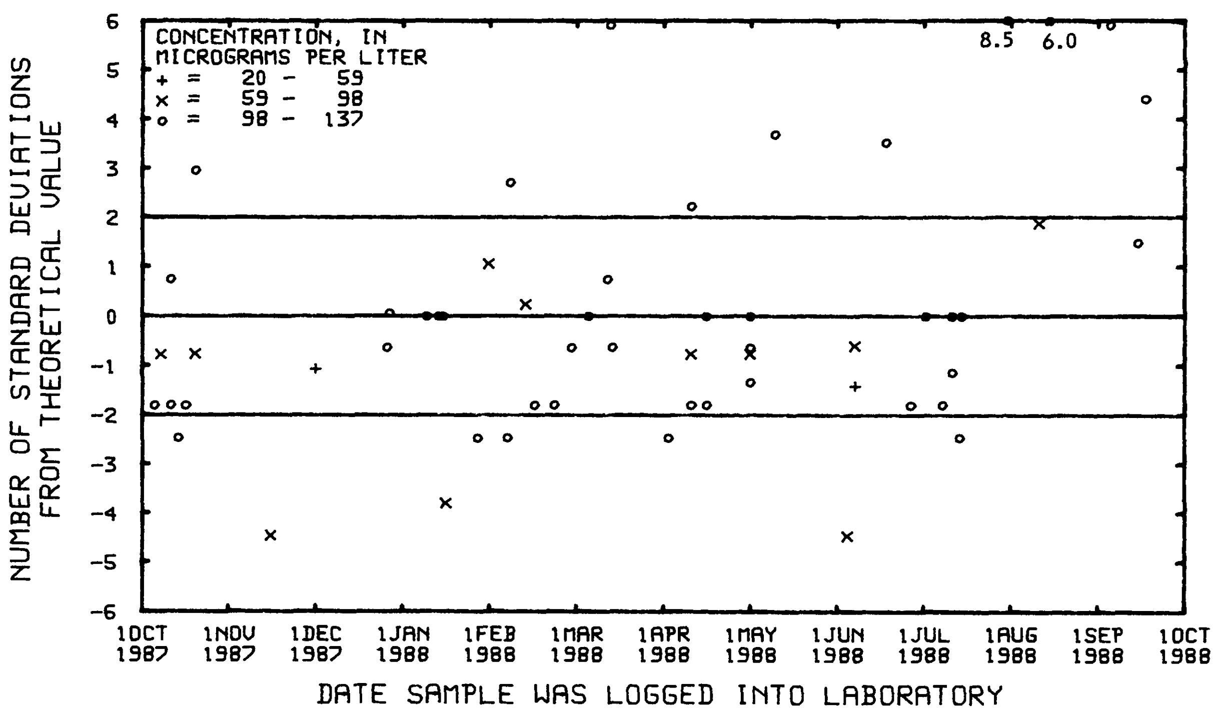

Figure 30.--Iron, total recoverable, data from the National Water Quality Laboratory.

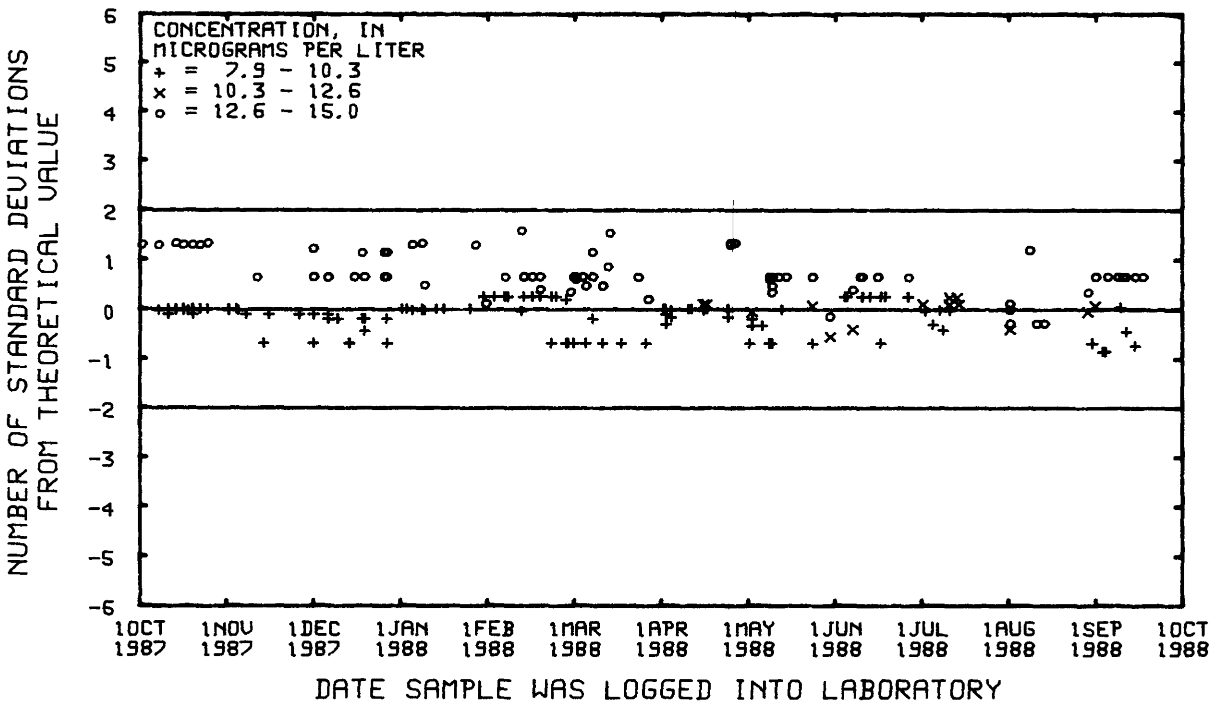

Figure 31.--Lead, dissolved, (inductively coupled plasma emission spectrometry) data from the National Water Quality Laboratory.

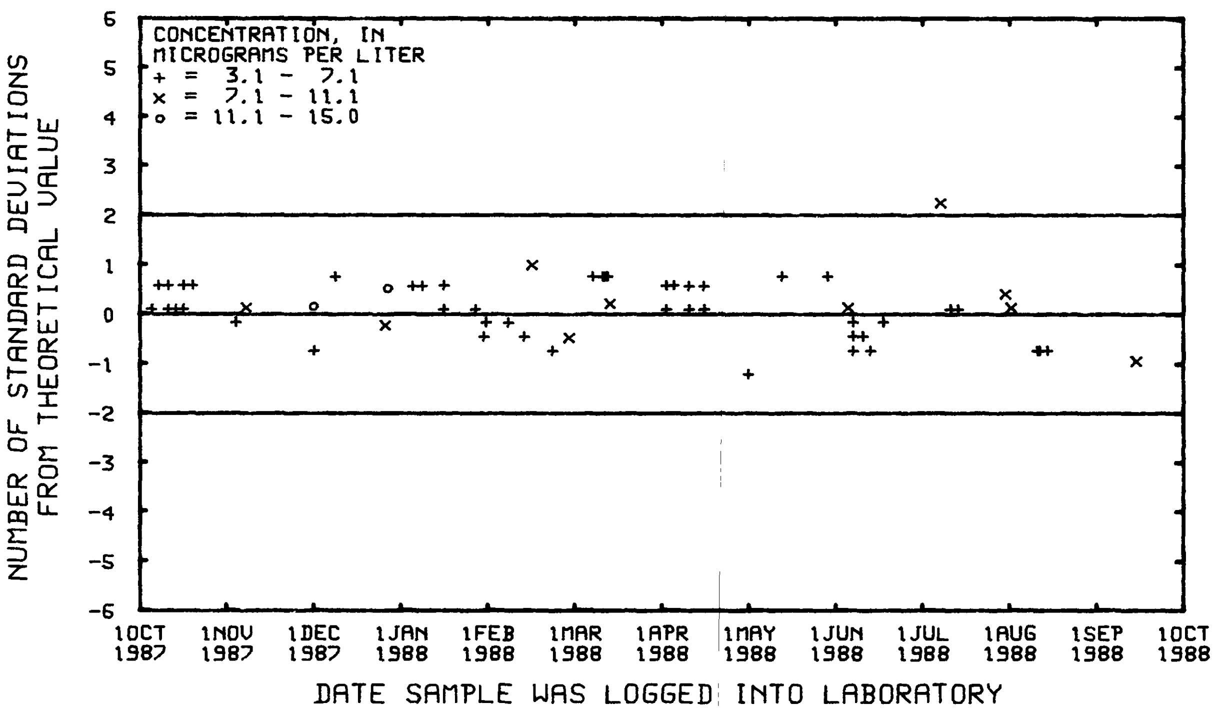

Figure 32.--Lead, dissolved, (atomic absorption spectrometry) data from the National Water Quality Laboratory.

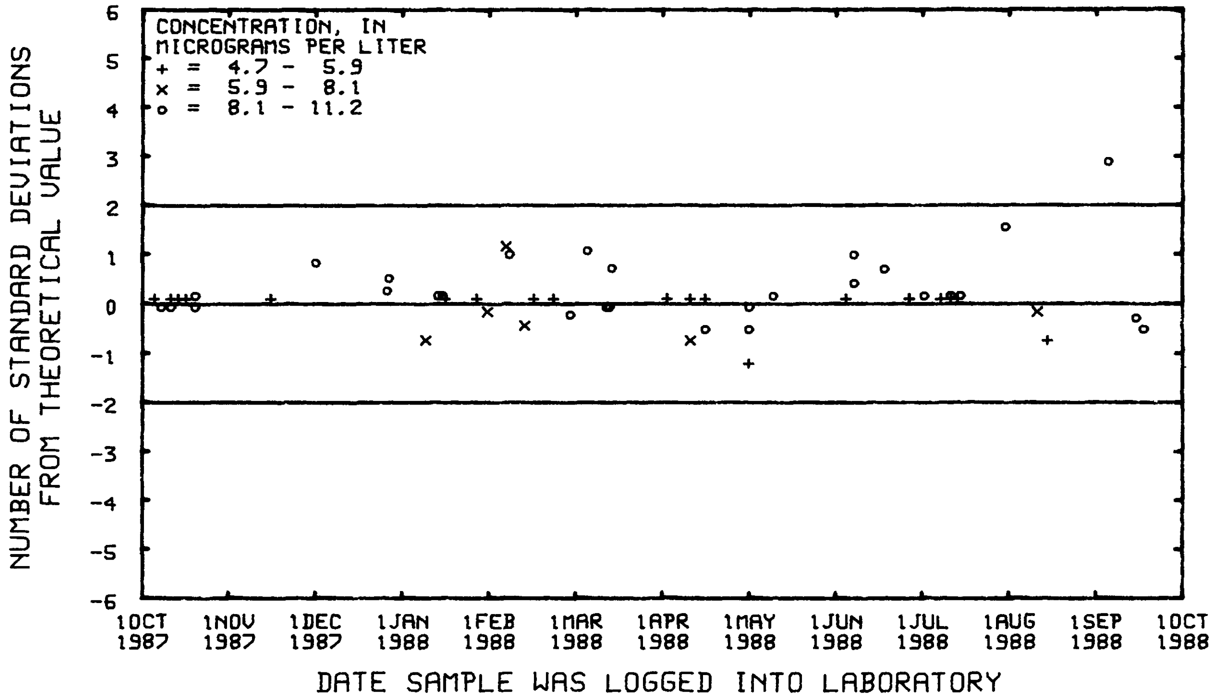

Figure 33.--Lead, total recoverable, data from the National Water Quality Laboratory.

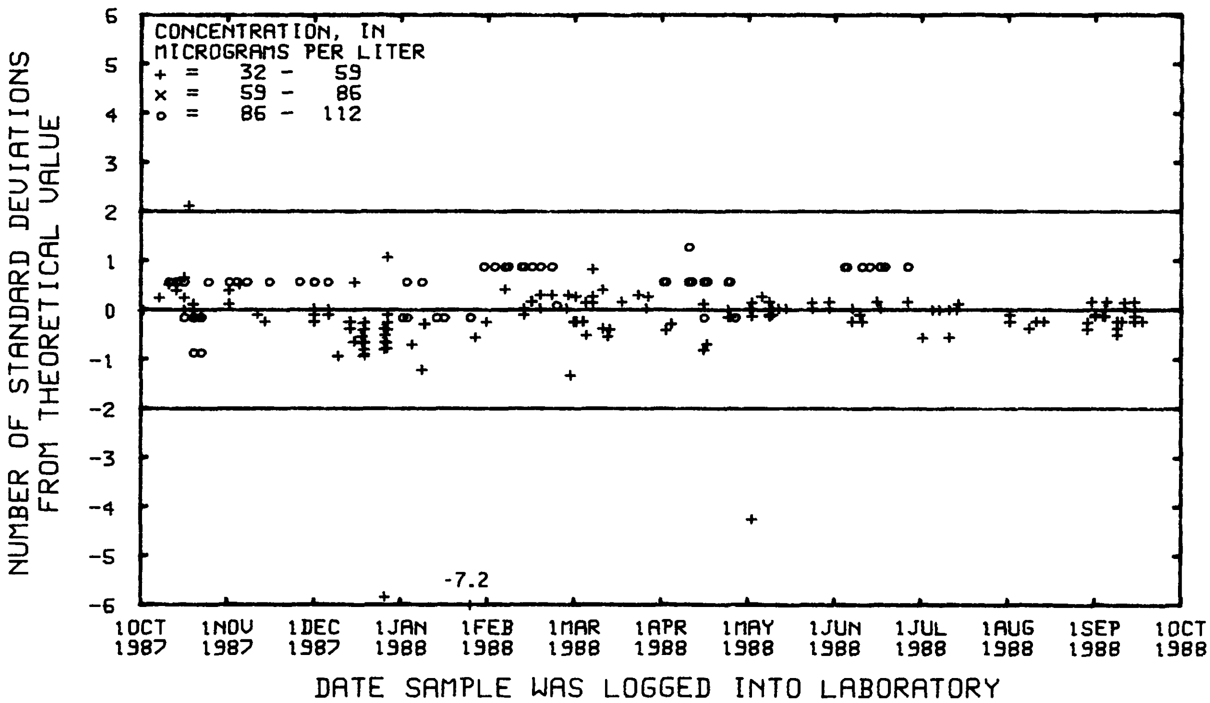

Figure 34.--Lithium, dissolved, data from the National Water Quality Laboratory.

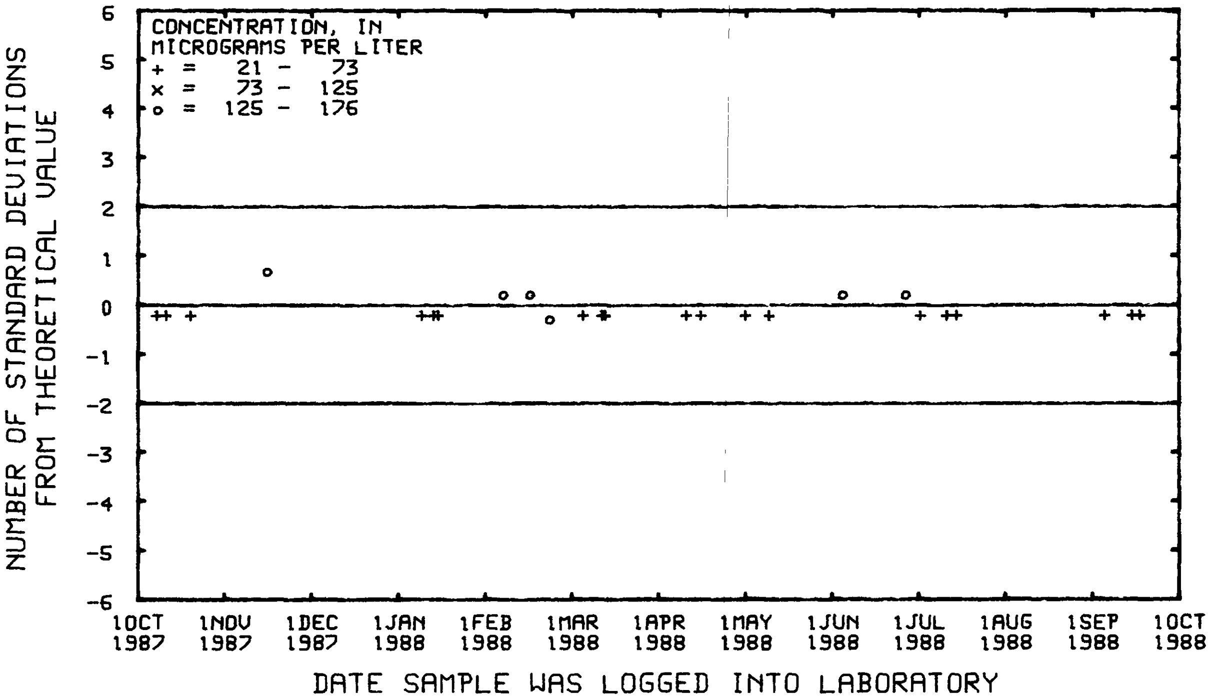

Figure 35.--Lithium, total recoverable, data from the National Water Quality Laboratory.

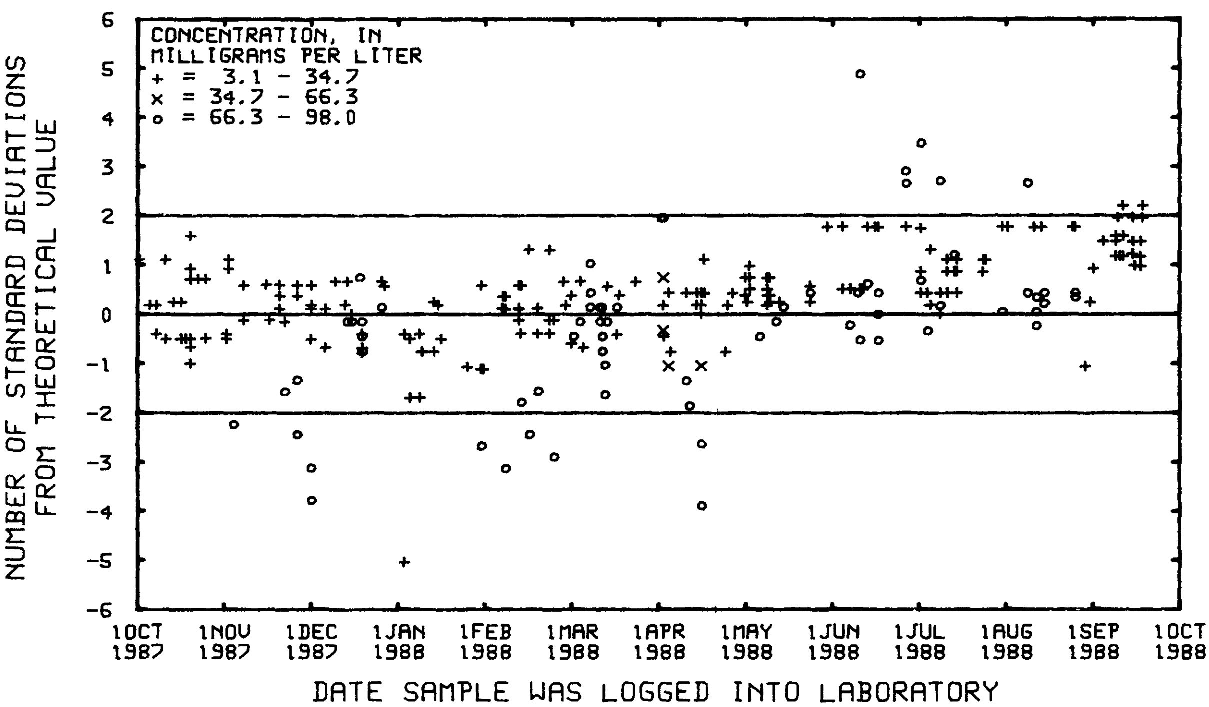

Figure 36.--Magnesium, dissolved, (inductively coupled plasma emission spectrometry) data from the National Water Quality Laboratory.

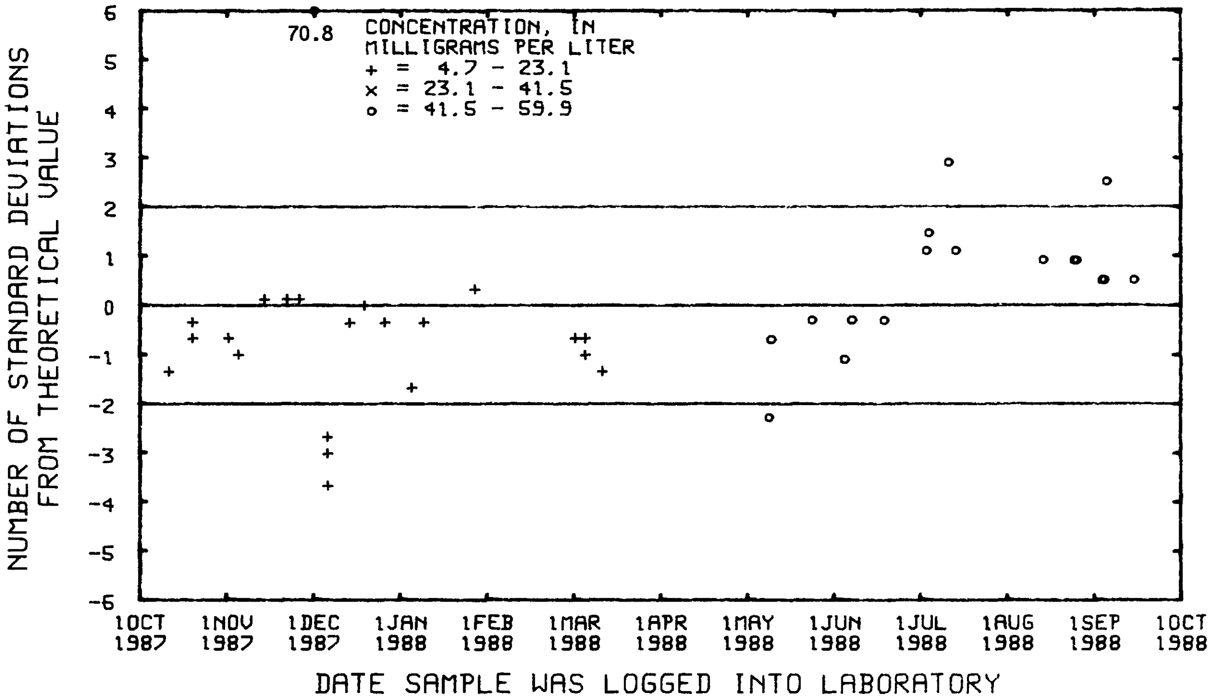

Figure 37.--Magnesium, dissolved,
(atomic absorption spectrometry)
data from the National Water Quality Laboratory.

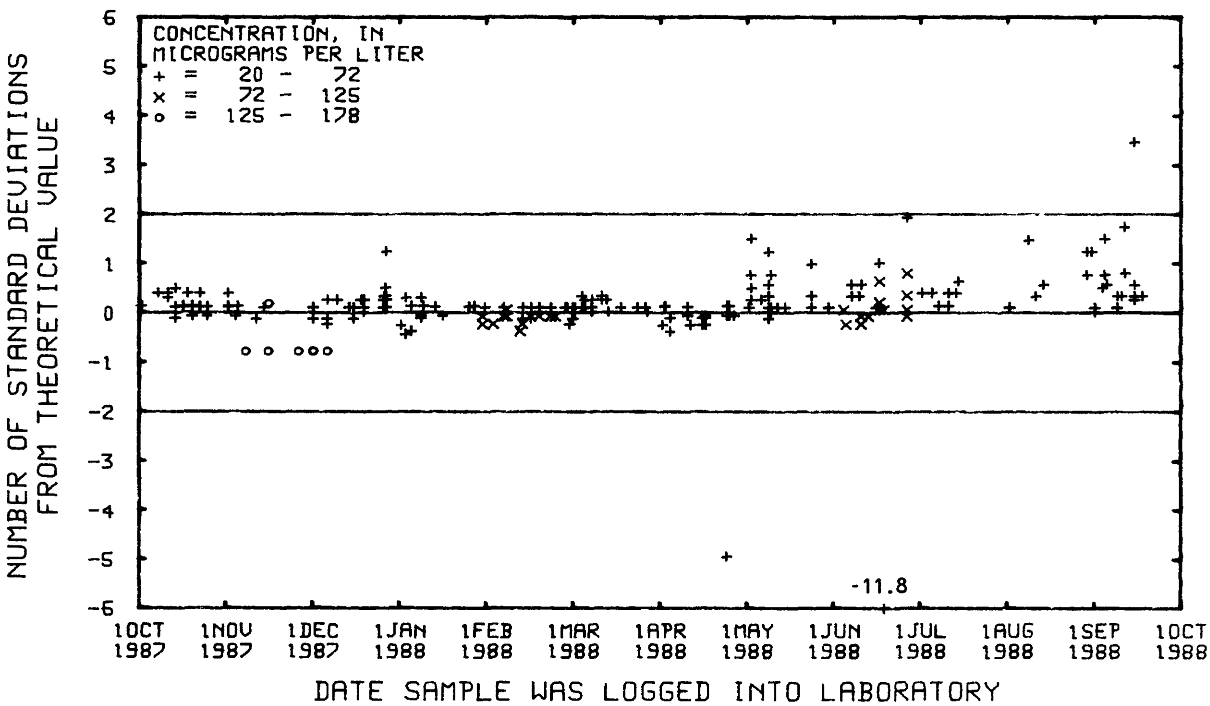

Figure 38.--Manganese, dissolved,
(inductively coupled plasma emission spectrometry)
data from the National Water Quality Laboratory.

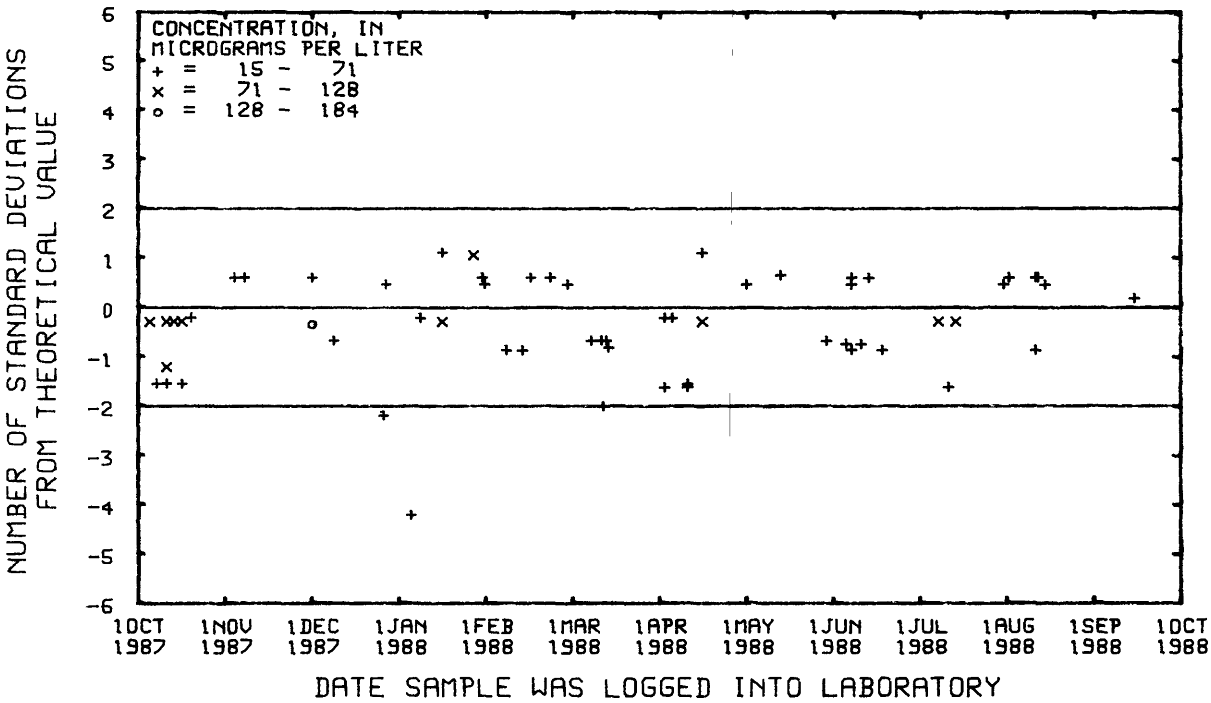

Figure 39.--Manganese, dissolved,
(atomic absorption spectrometry)
data from the National Water Quality Laboratory.

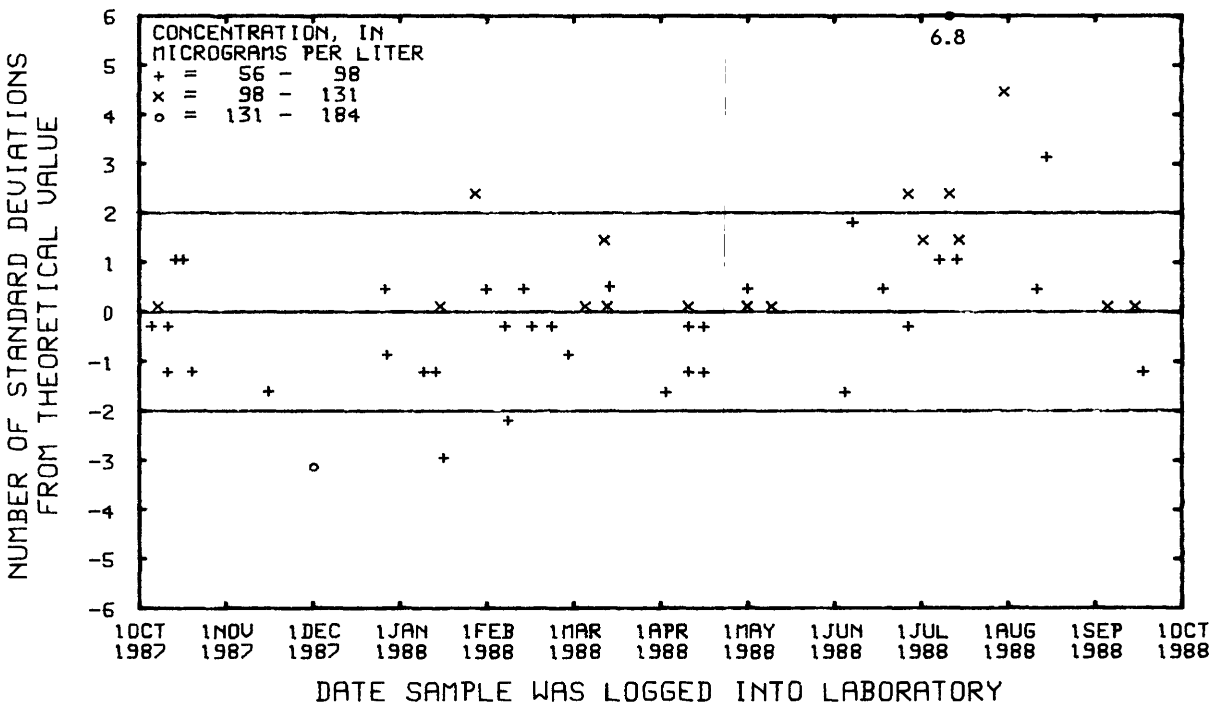

Figure 40.--Manganese, total recoverable,
data from the National Water Quality Laboratory.

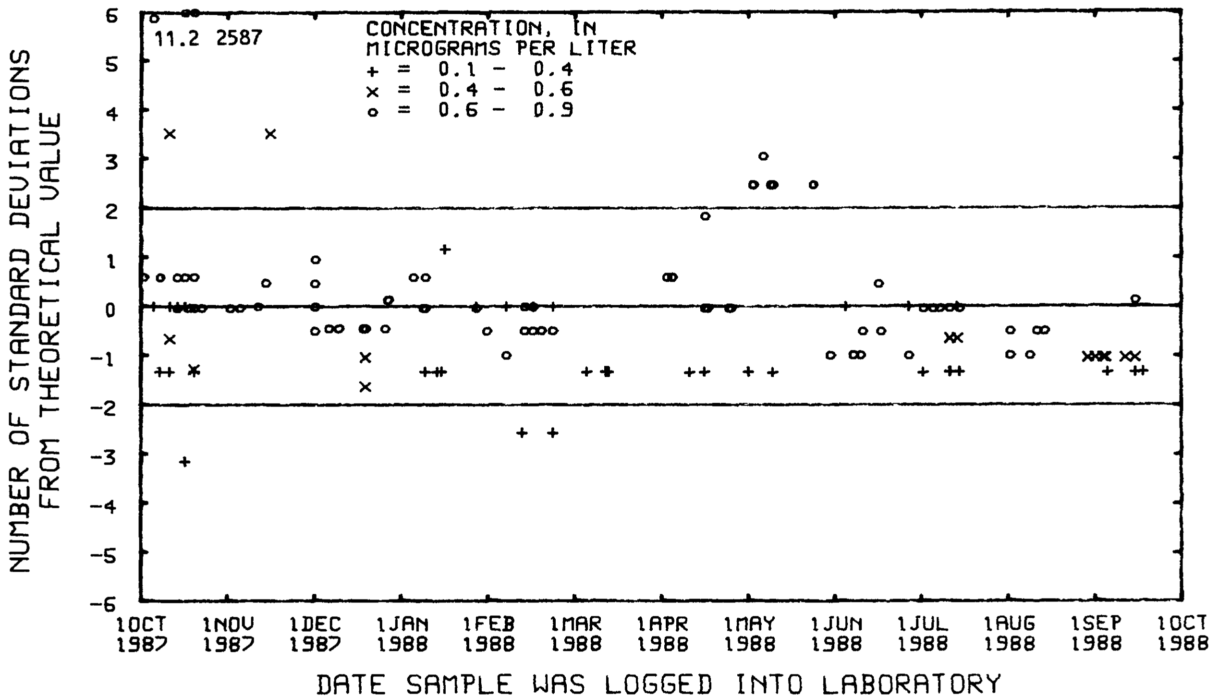

Figure 41.--Mercury, dissolved, data from the National Water Quality Laboratory.

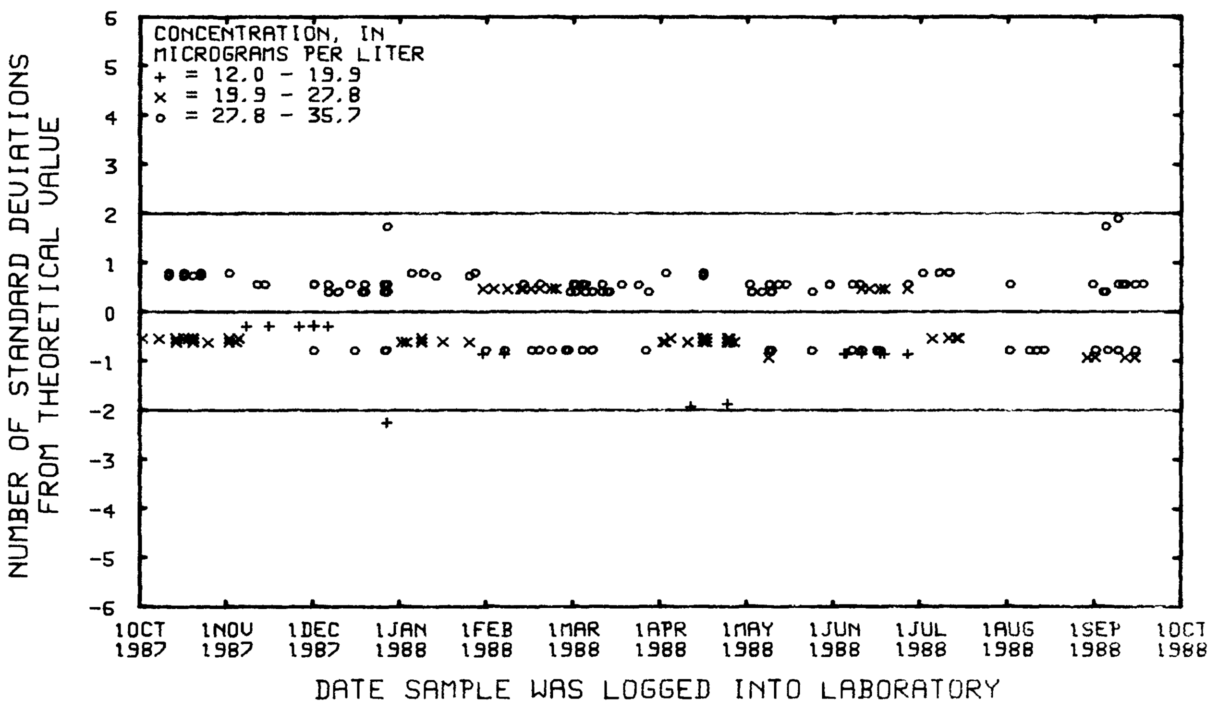

Figure 42.--Molybdenum, dissolved, (inductively coupled plasma emission spectrometry) data from the National Water Quality Laboratory.

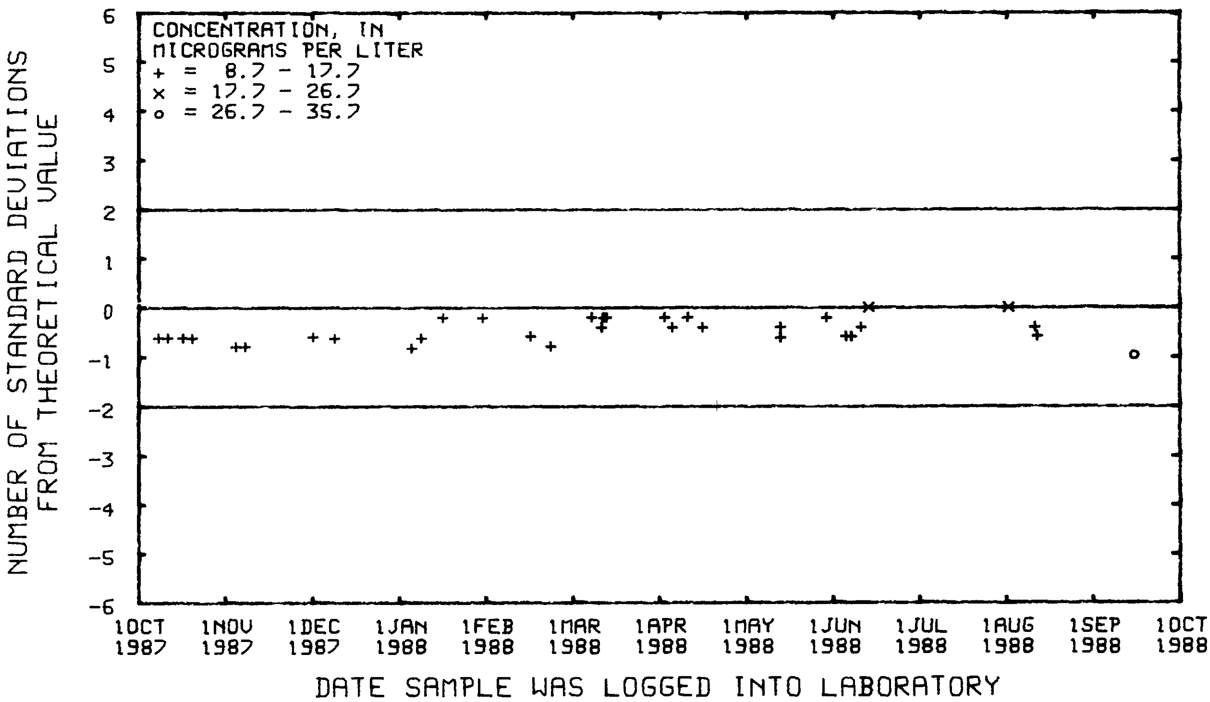

Figure 43.--Molybdenum, dissolved,
(atomic absorption spectrometry)
data from the National Water Quality Laboratory.

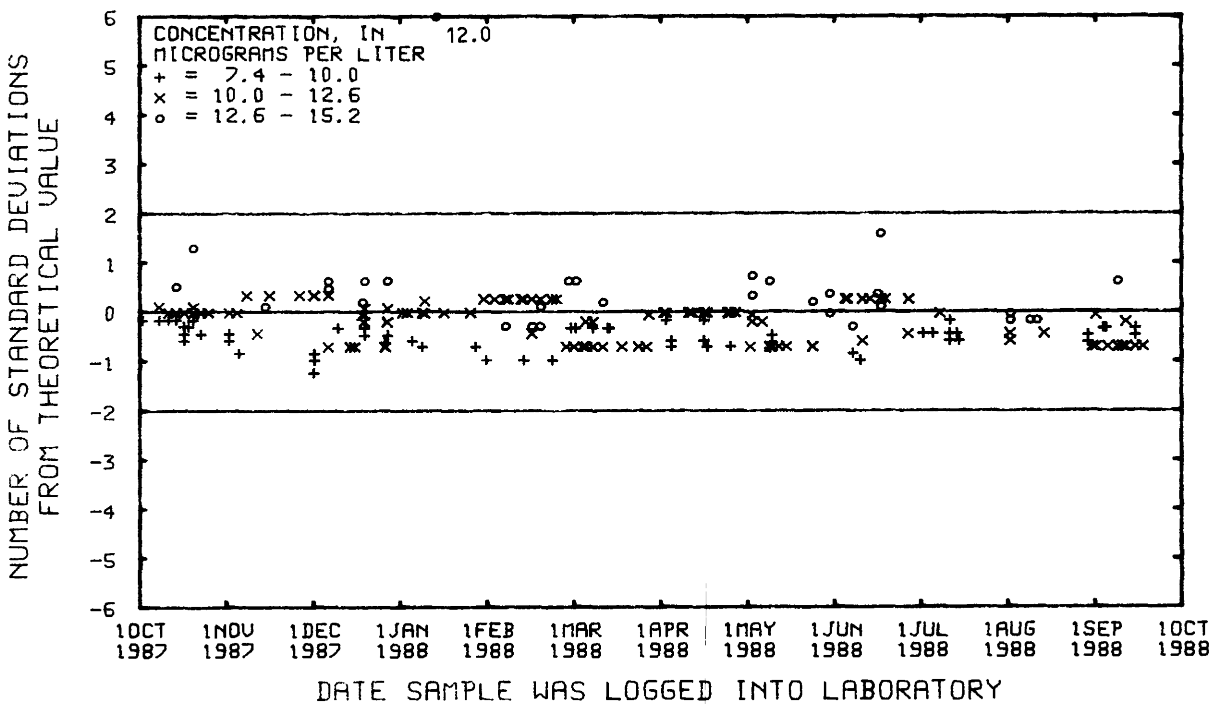

Figure 44.--Nickel, dissolved,
(inductively coupled plasma emission spectrometry)
data from the National Water Quality Laboratory.

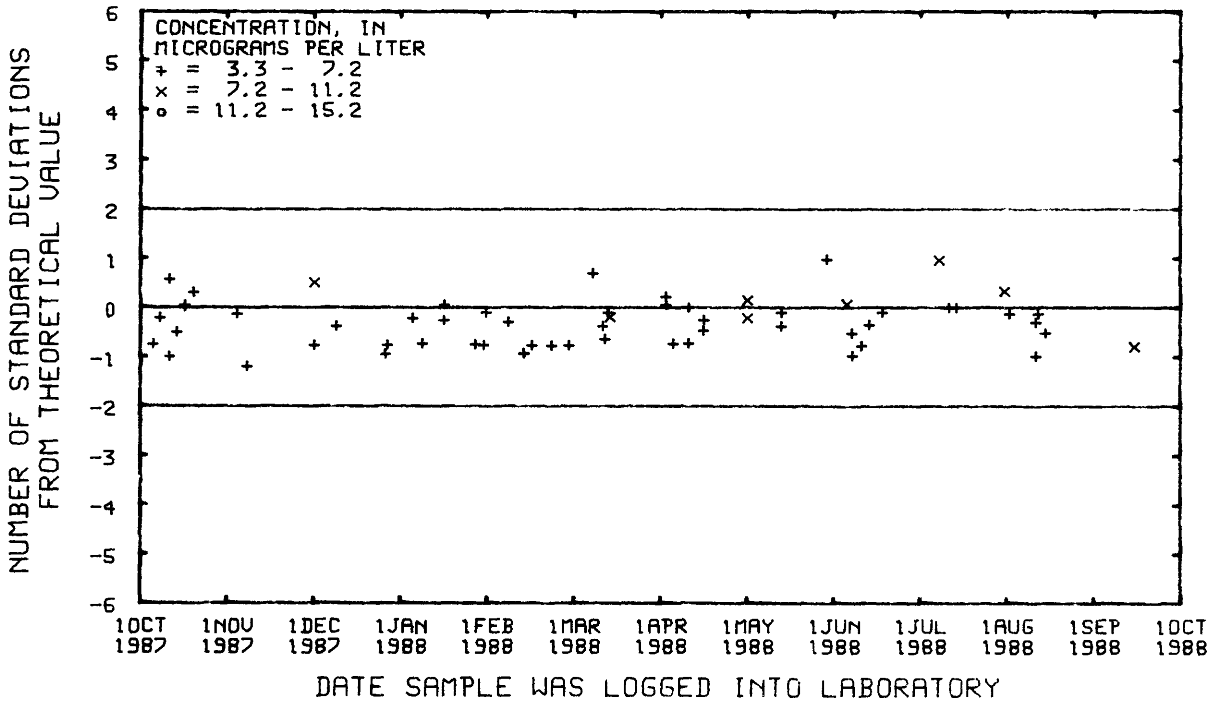

Figure 45.--Nickel, dissolved,
(atomic absorption spectrometry)
data from the National Water Quality Laboratory.

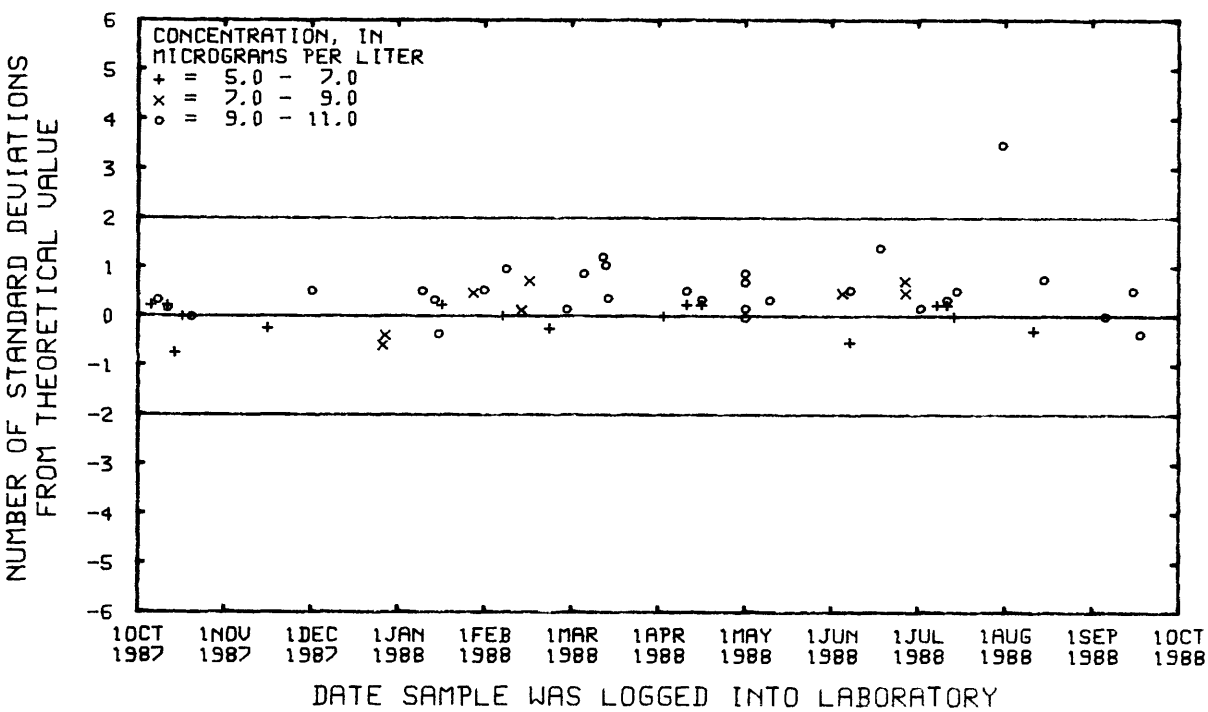

Figure 46.--Nickel, total recoverable,
data from the National Water Quality Laboratory.

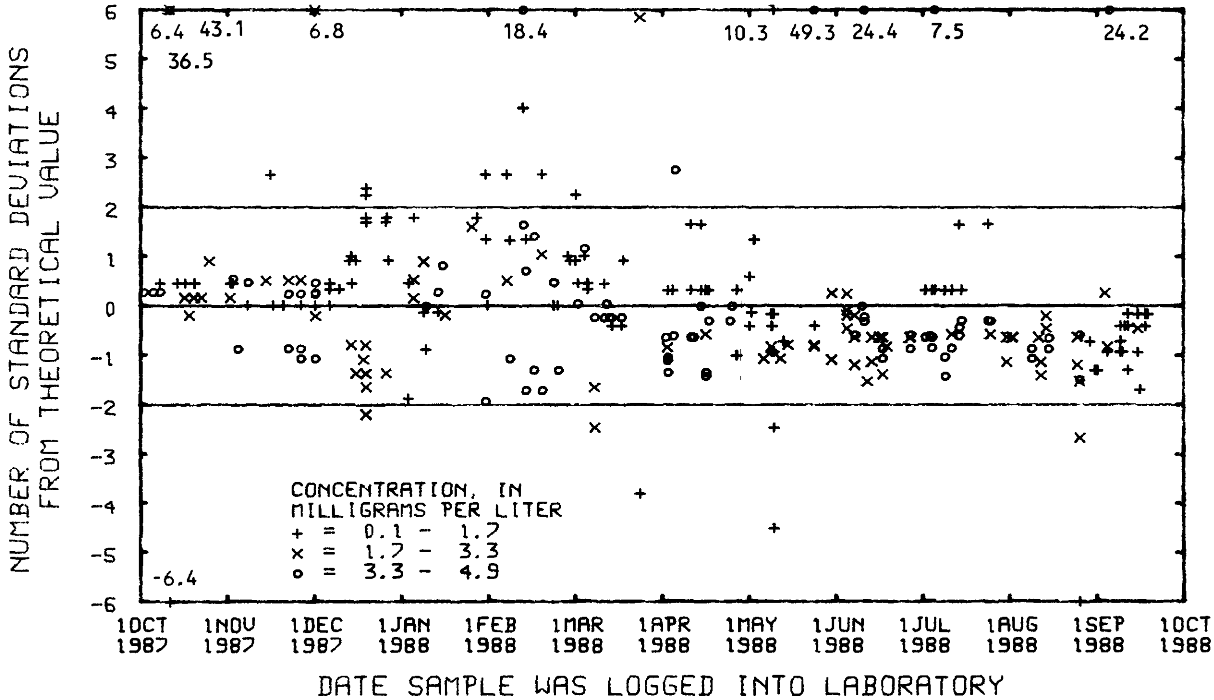

Figure 47.--Potassium, dissolved, data from the National Water Quality Laboratory.

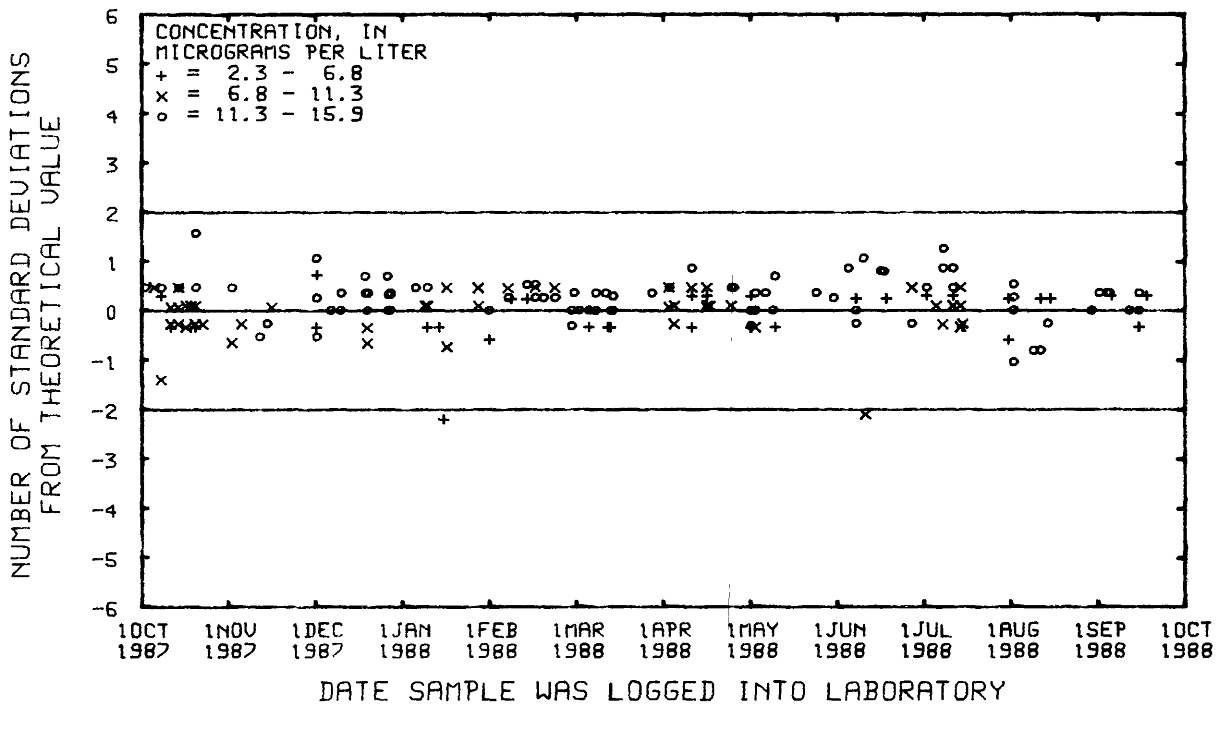

Figure 48.--Selenium, dissolved, data from the National Water Quality Laboratory.

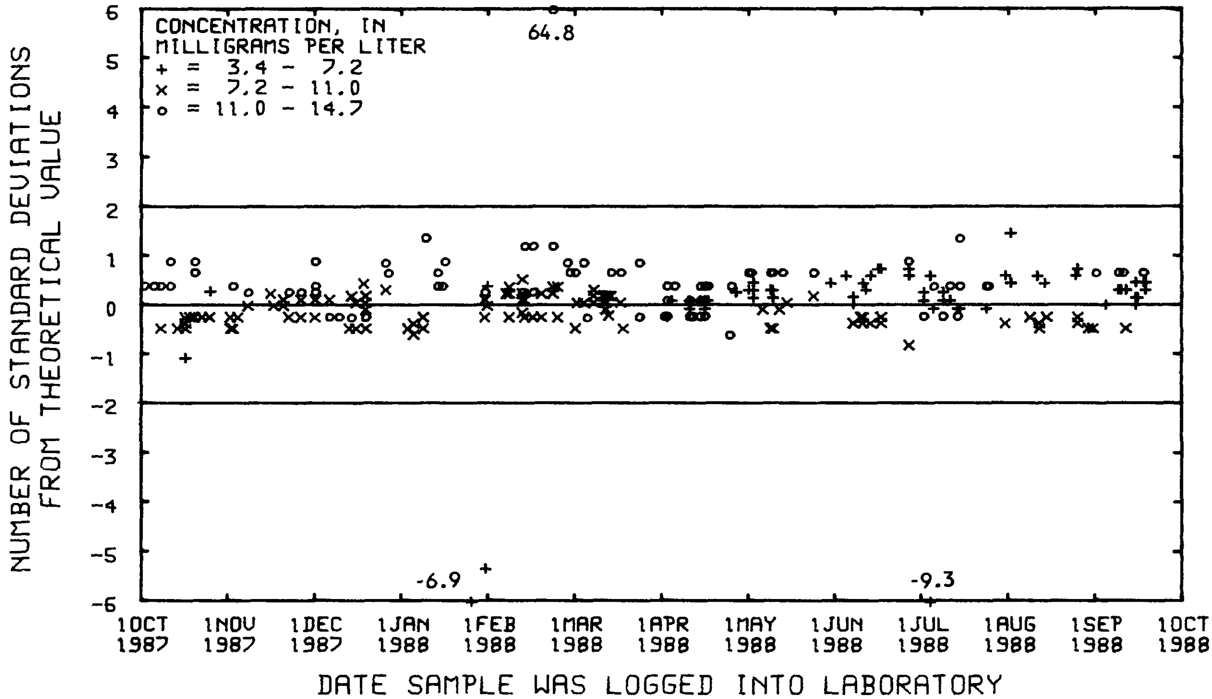

Figure 49.--Silica, dissolved, (inductively coupled plasma emission spectrometry) data from the National Water Quality Laboratory.

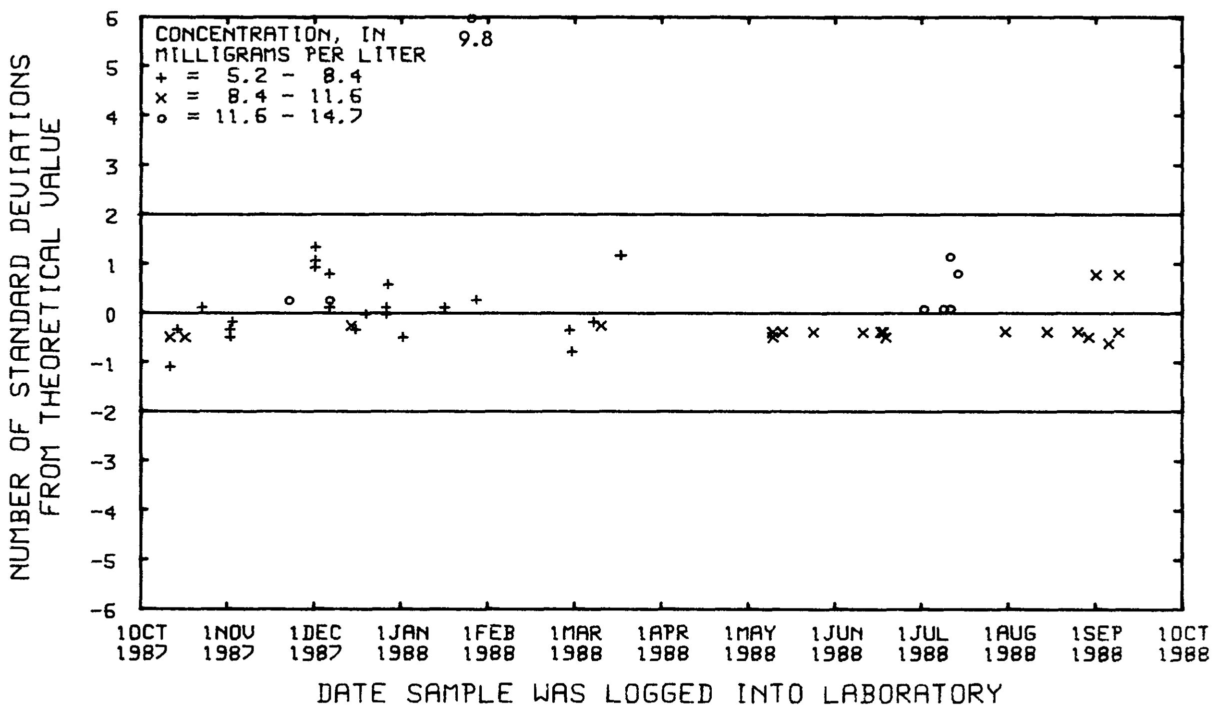

Figure 50.--Silica, dissolved, (colorimetry) data from the National Water Quality Laboratory.

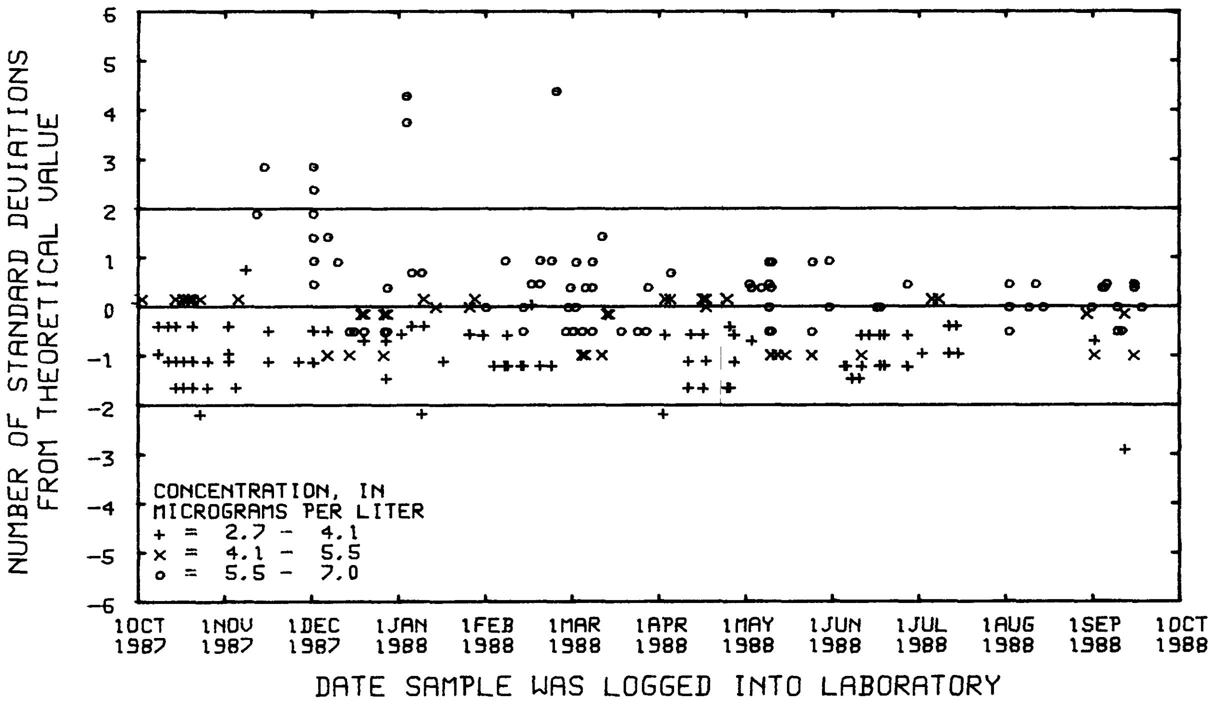

Figure 51.--Silver, dissolved, (inductively coupled plasma emission spectrometry) data from the National Water Quality Laboratory.

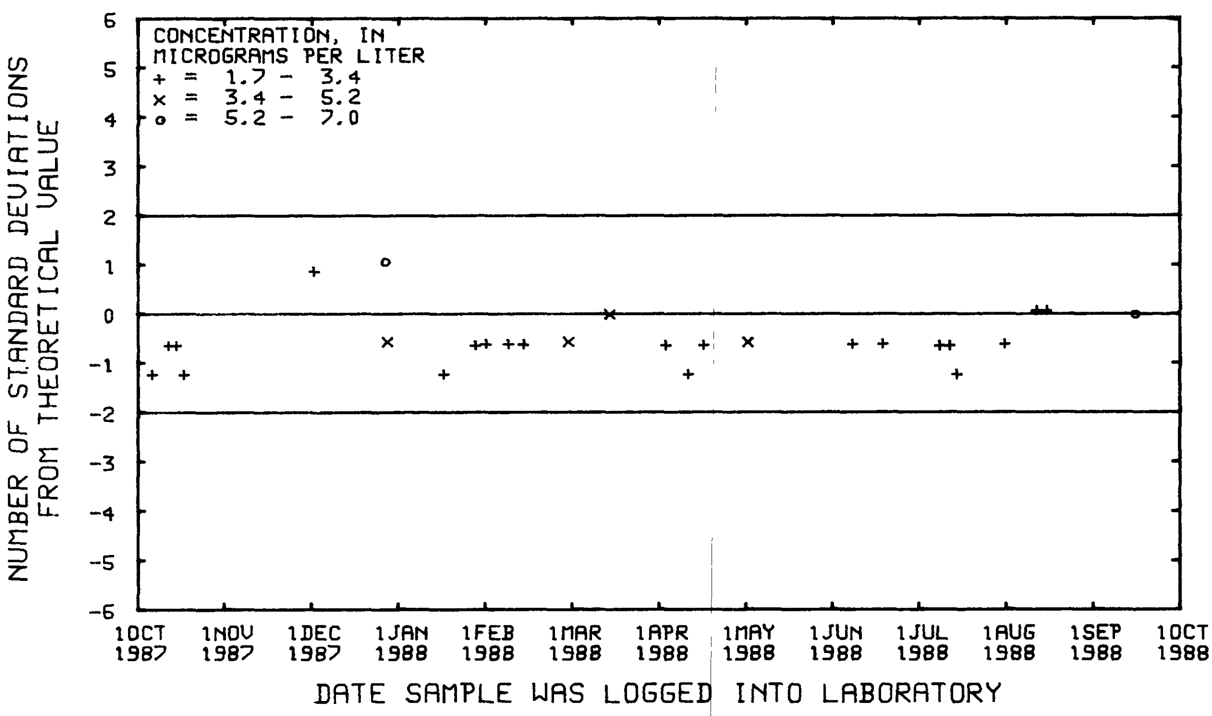

Figure 52.--Silver, dissolved, (atomic absorption spectrometry) data from the National Water Quality Laboratory.

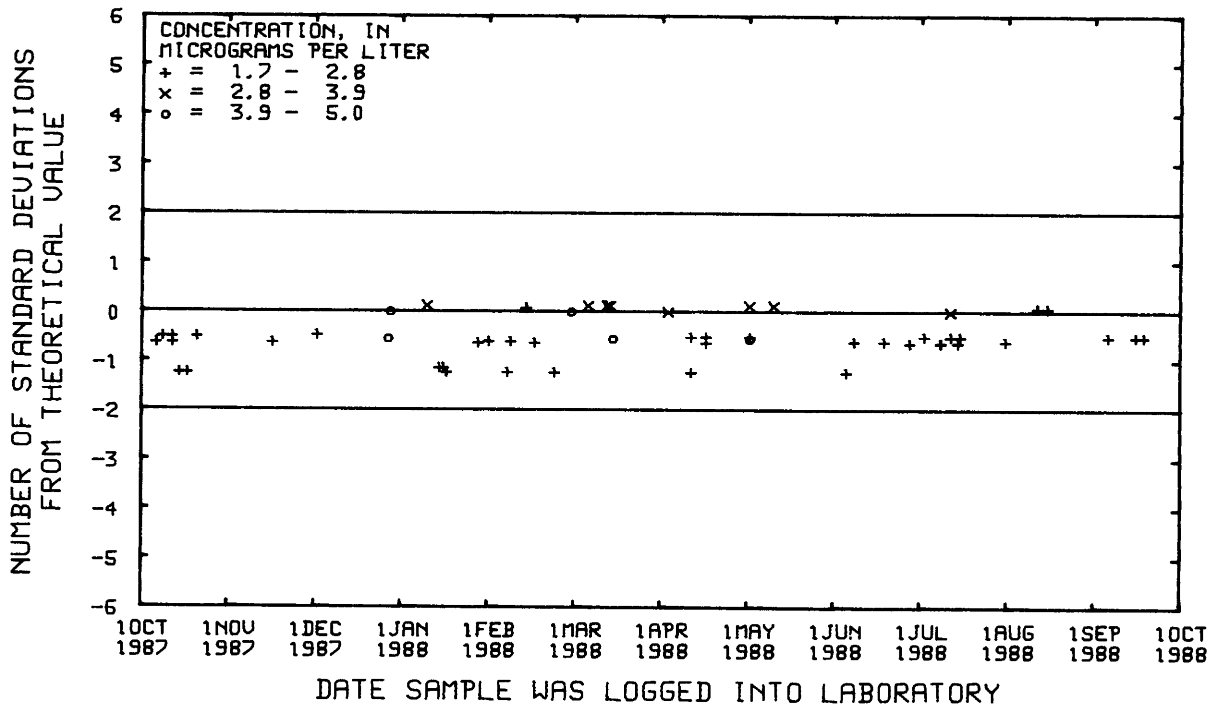

Figure 53.--Silver, total recoverable, data from the National Water Quality Laboratory.

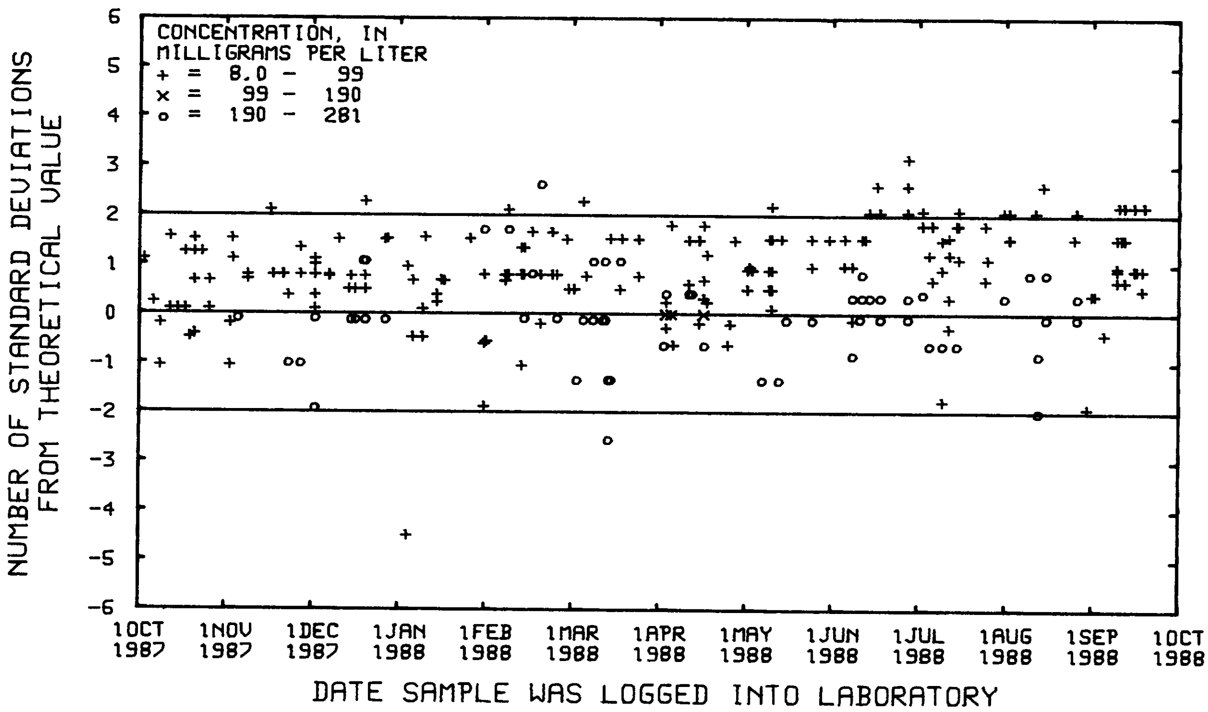

Figure 54.--Sodium, dissolved, (inductively coupled plasma emission spectrometry) data from the National Water Quality Laboratory.

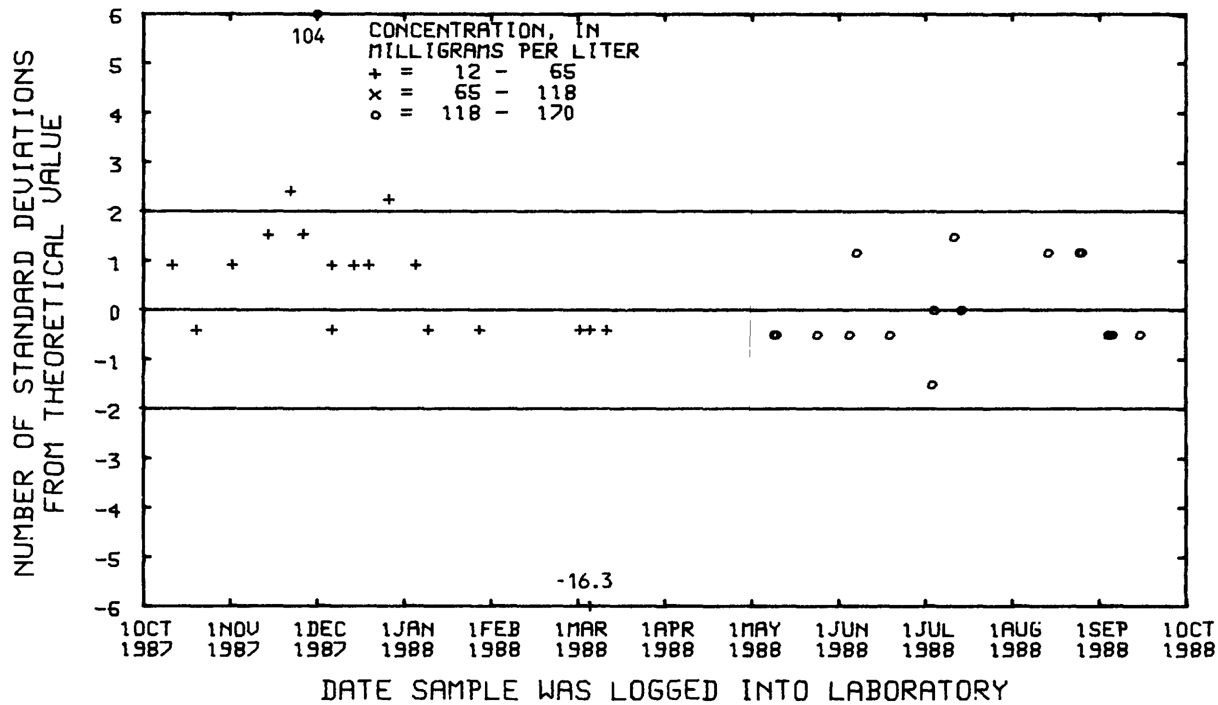

Figure 55.--Sodium, dissolved, (atomic absorption spectrometry) data from the National Water Quality Laboratory.

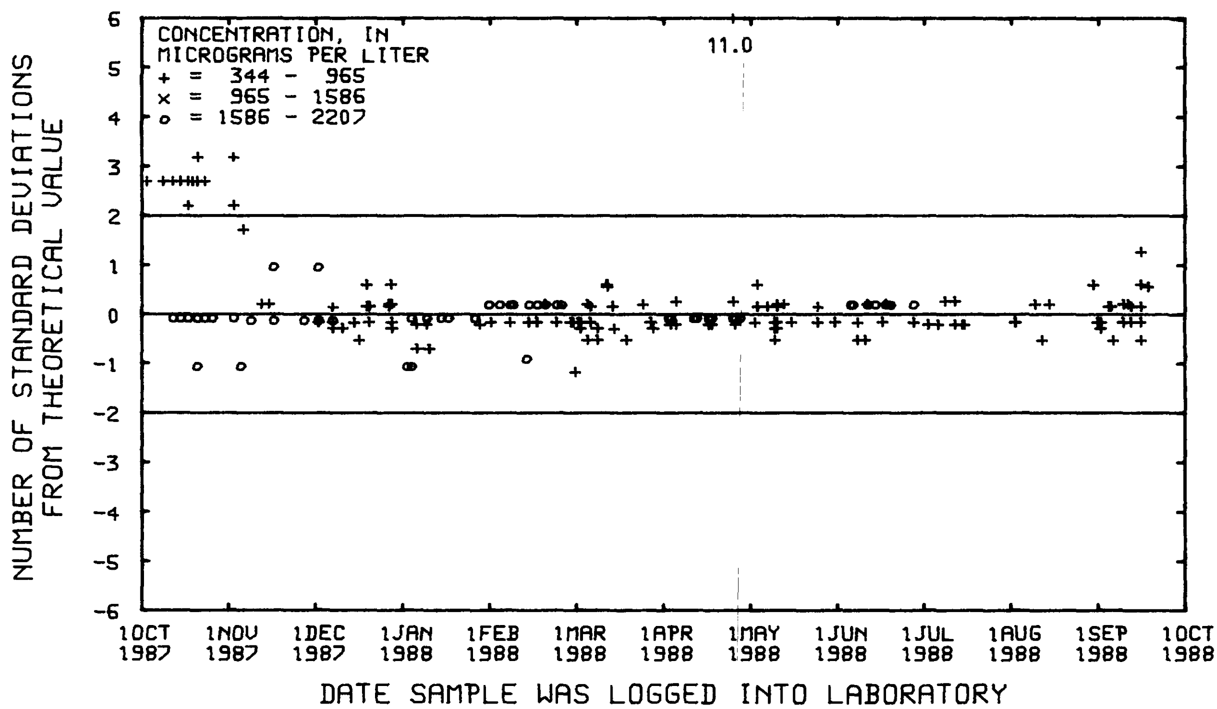

Figure 56.--Strontium, dissolved, data from the National Water Quality Laboratory.

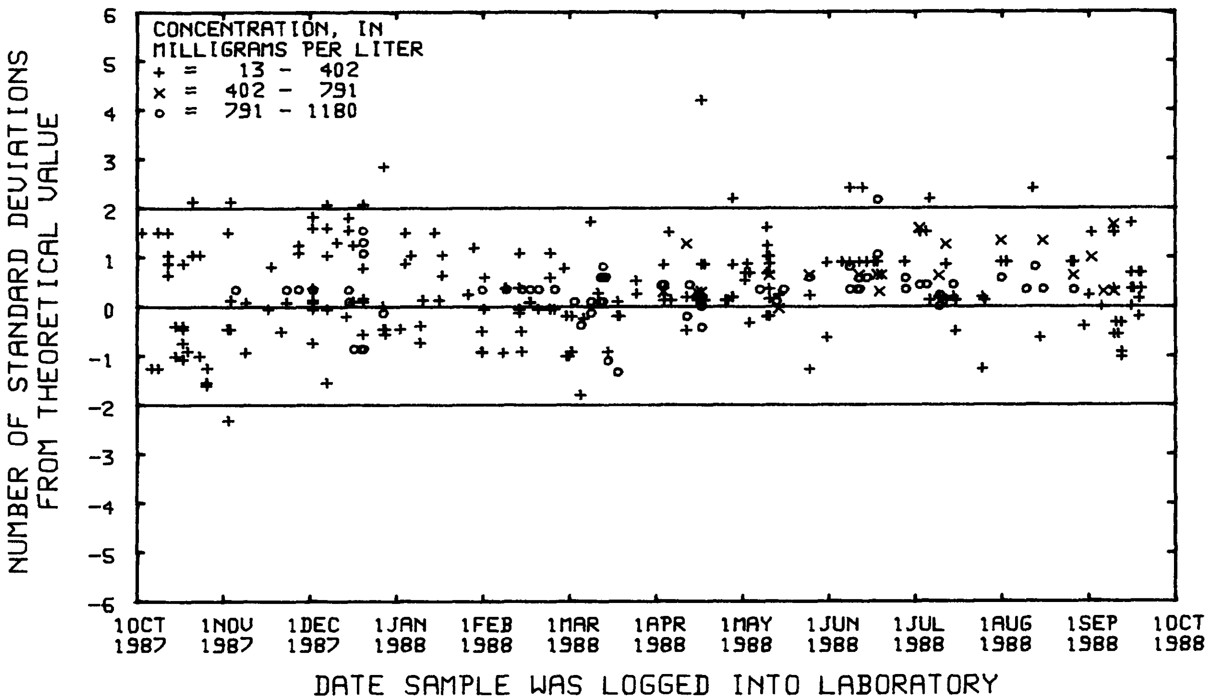

Figure 57.--Sulfate, dissolved, data from the National Water Quality Laboratory.

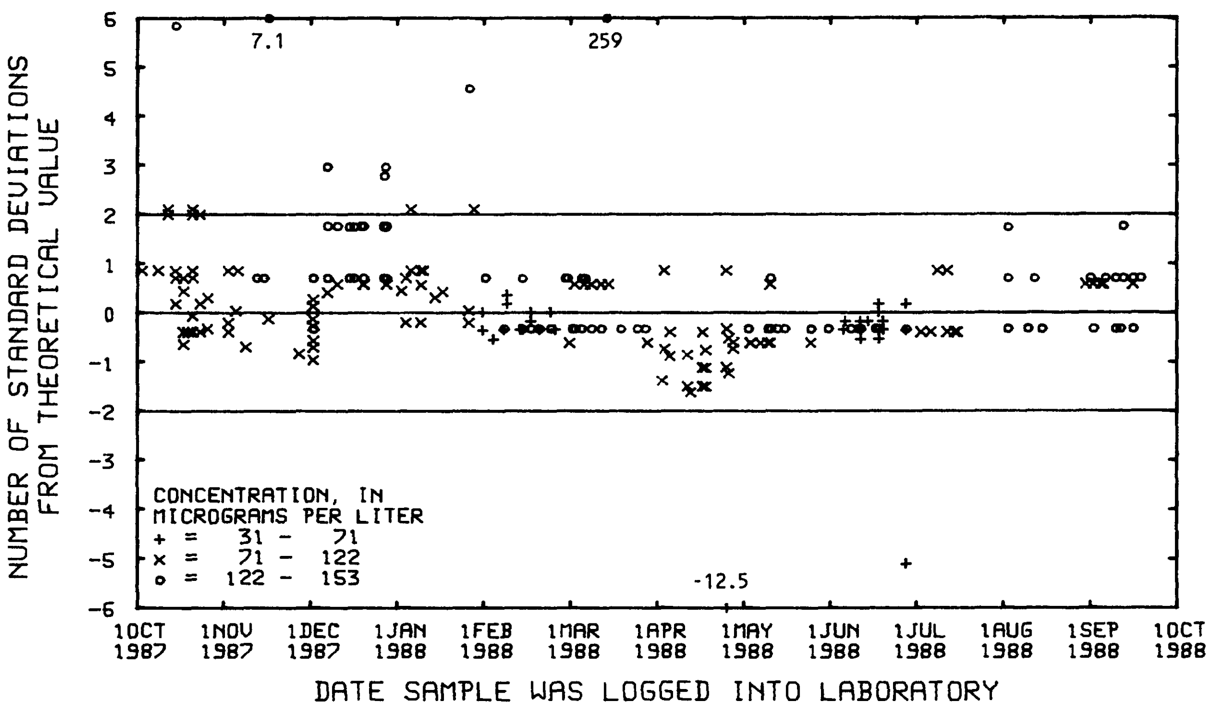

Figure 58.--Zinc, dissolved, (inductively coupled plasma emission spectrometry) data from the National Water Quality Laboratory.

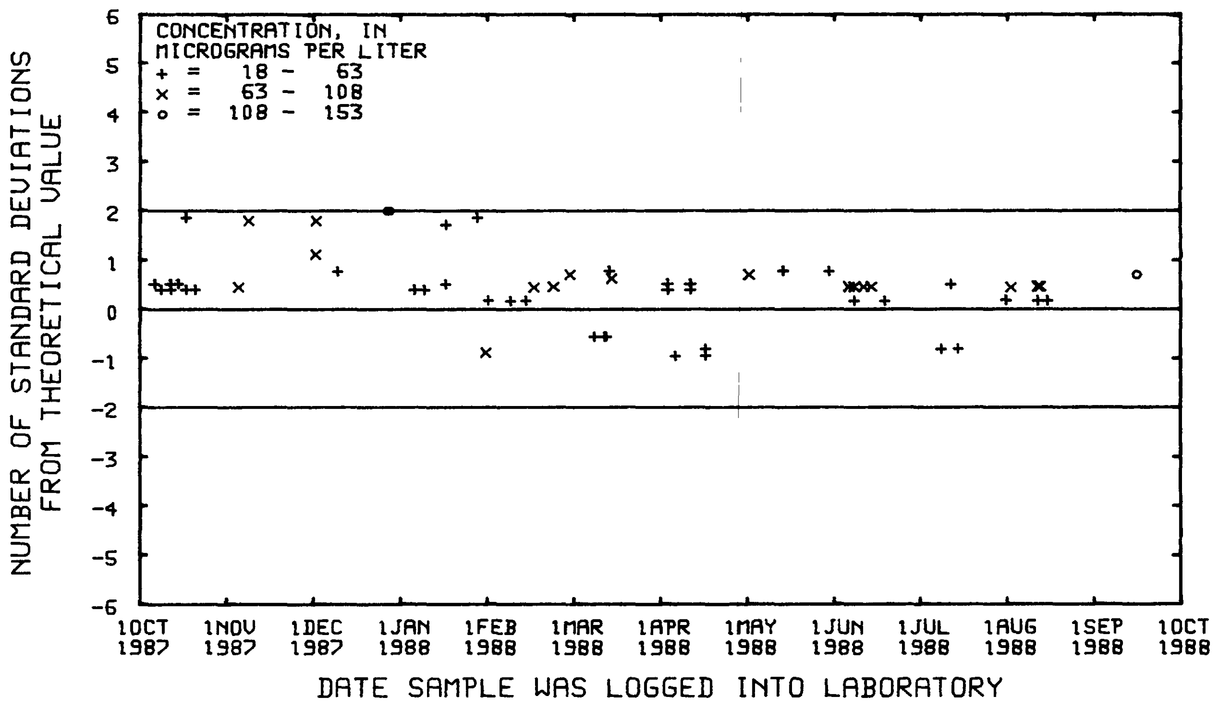

Figure 59.--Zinc, dissolved, (atomic absorption spectrometry) data from the National Water Quality Laboratory.

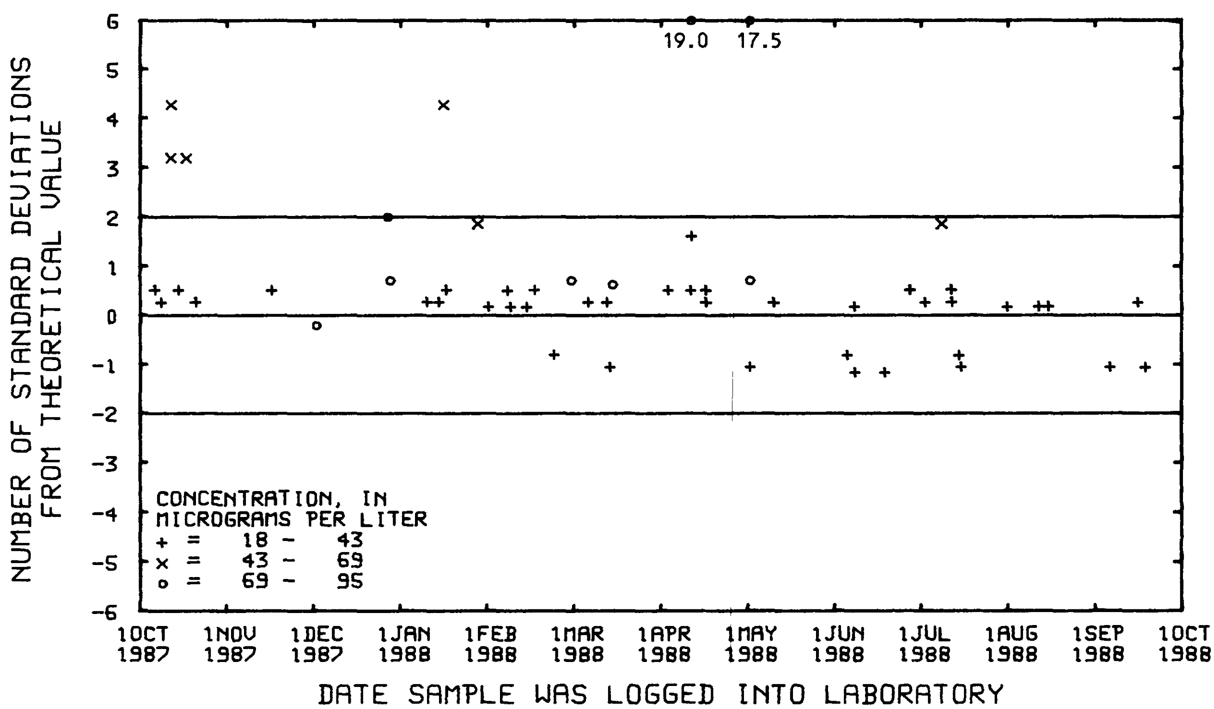

Figure 60.--Zinc, total recoverable, data from the National Water Quality Laboratory.

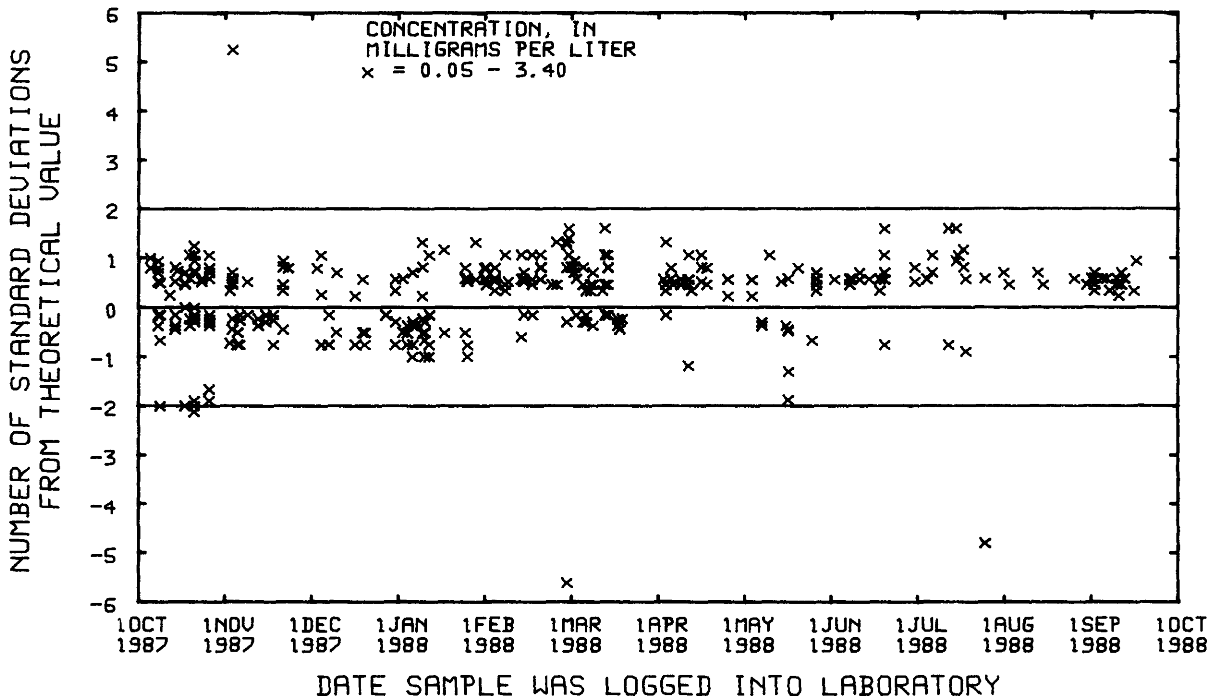

Figure 61.--Ammonia nitrogen as N, dissolved, data from the National Water Quality Laboratory.

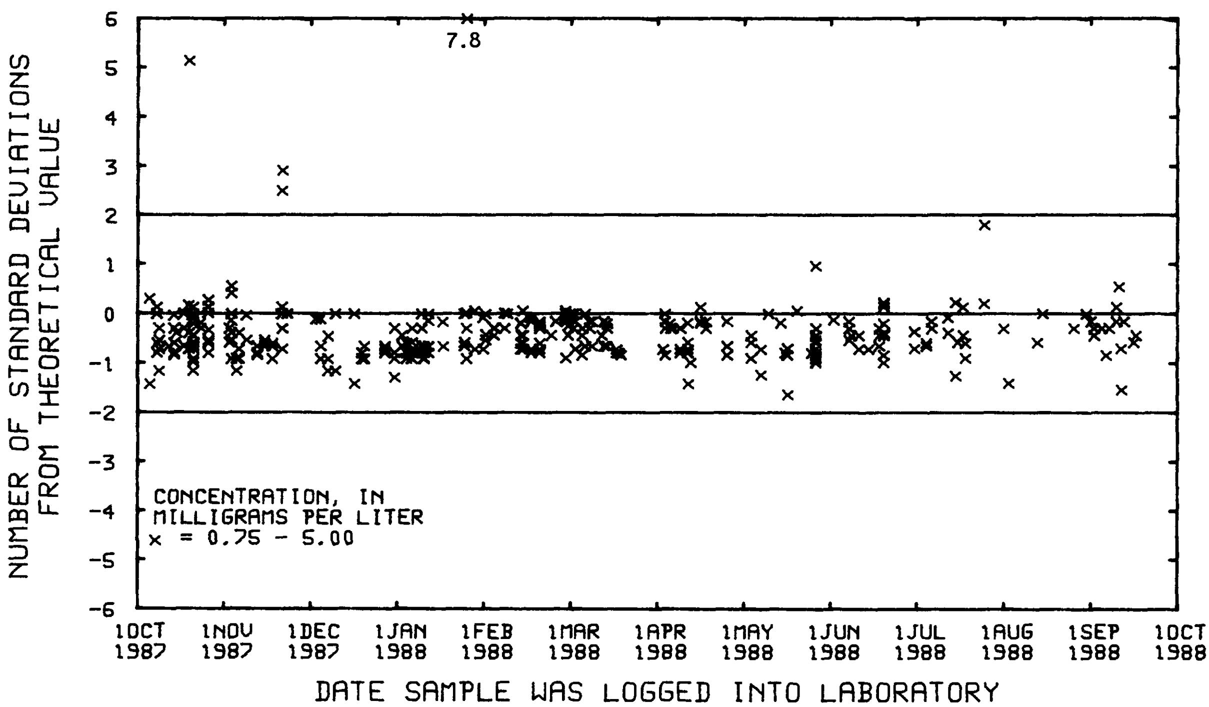

Figure 62.--Ammonia + organic nitrogen as N, dissolved, data from the National Water Quality Laboratory.

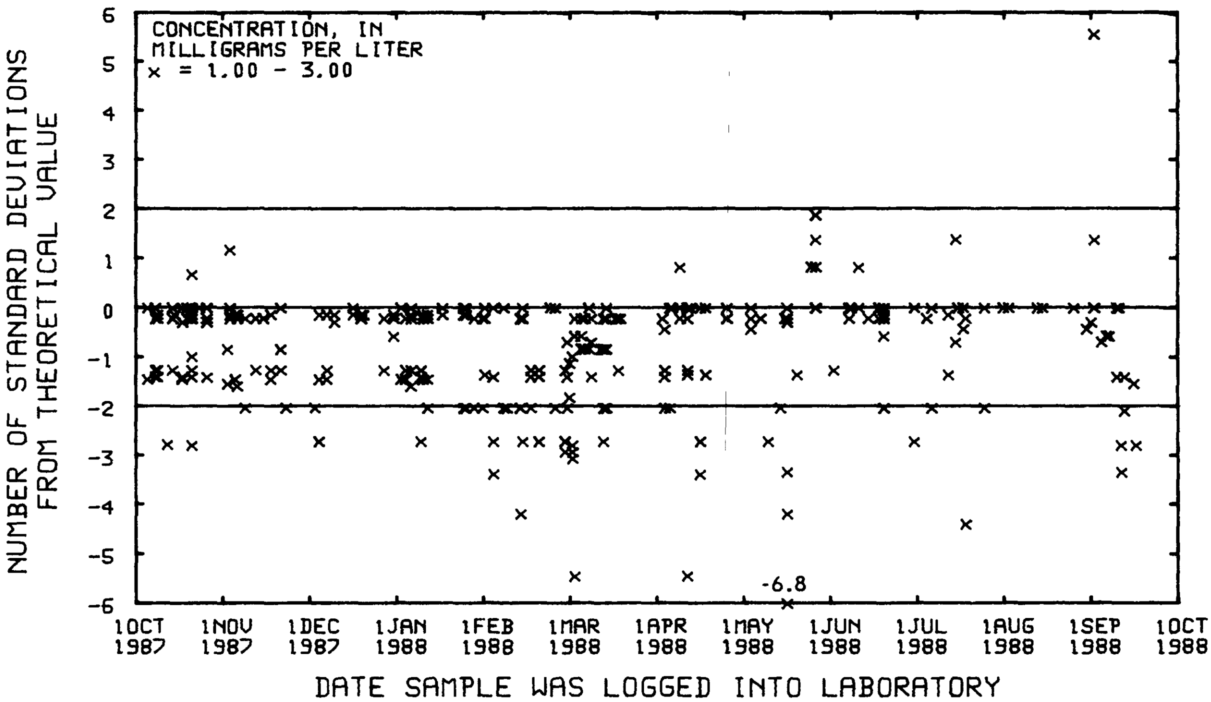

Figure 63.--Nitrate + nitrite nitrogen as N, dissolved, data from the National Water Quality Laboratory.

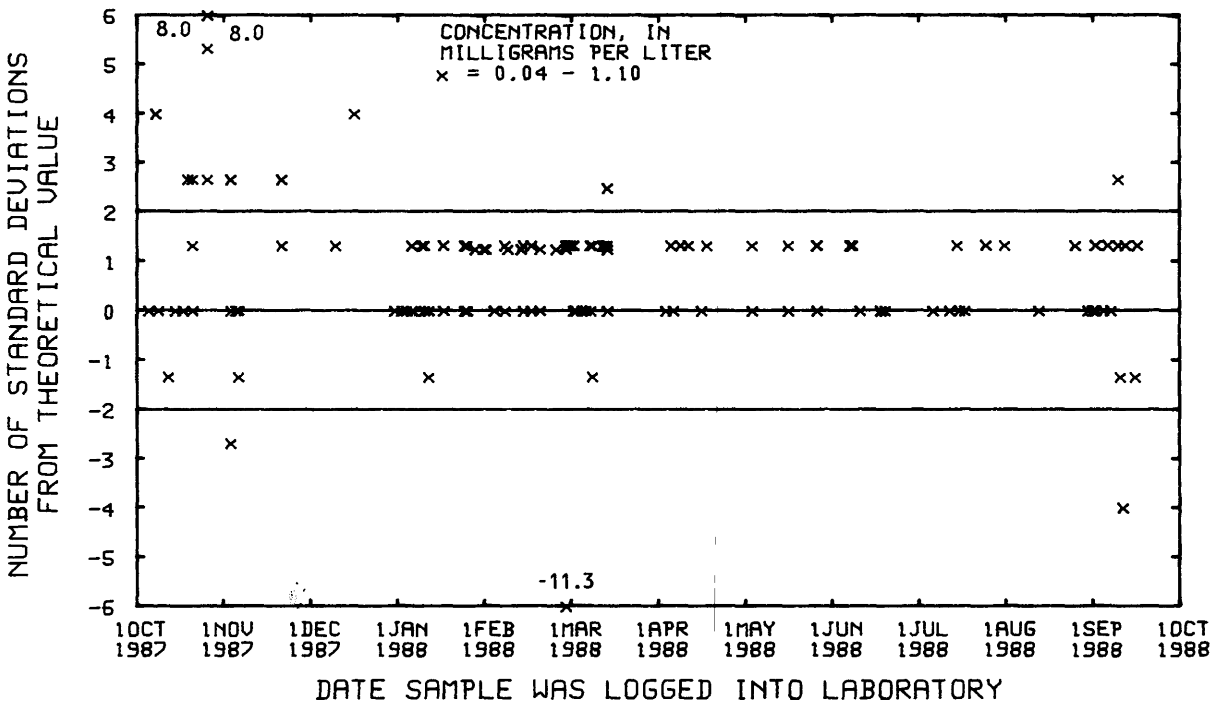

Figure 64.--Nitrite nitrogen as N, dissolved, data from the National Water Quality Laboratory.

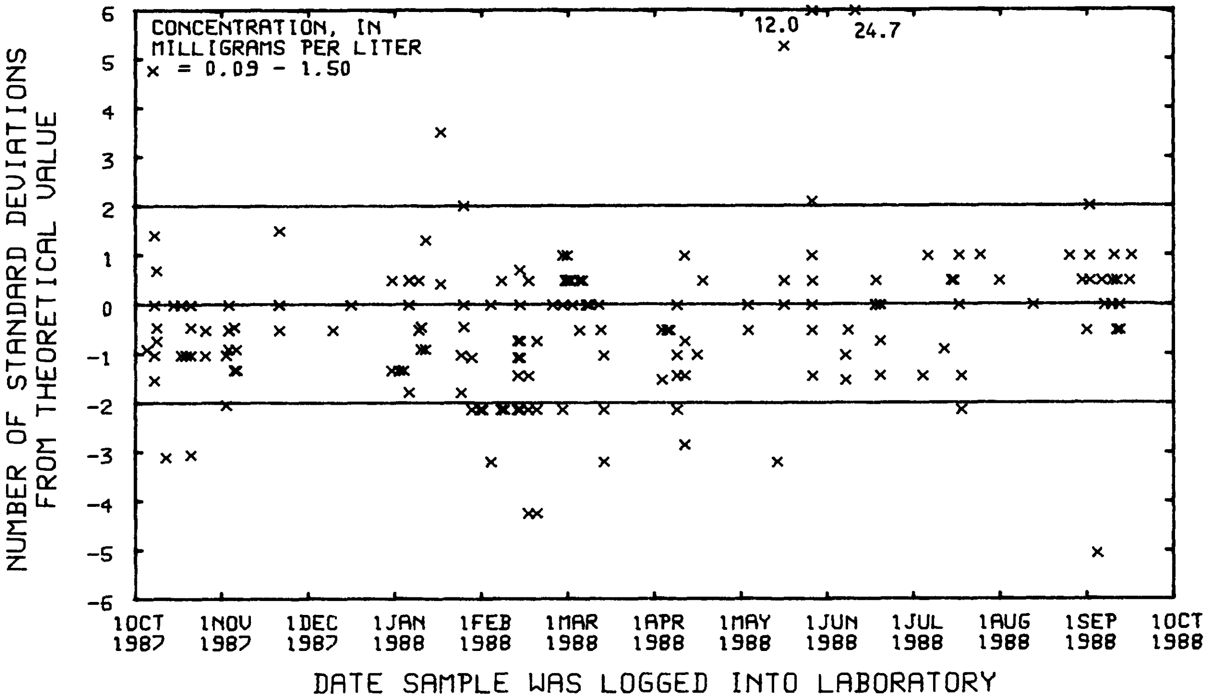

Figure 65.--Orthophosphate phosphorus as P, dissolved, data from the National Water Quality Laboratory.

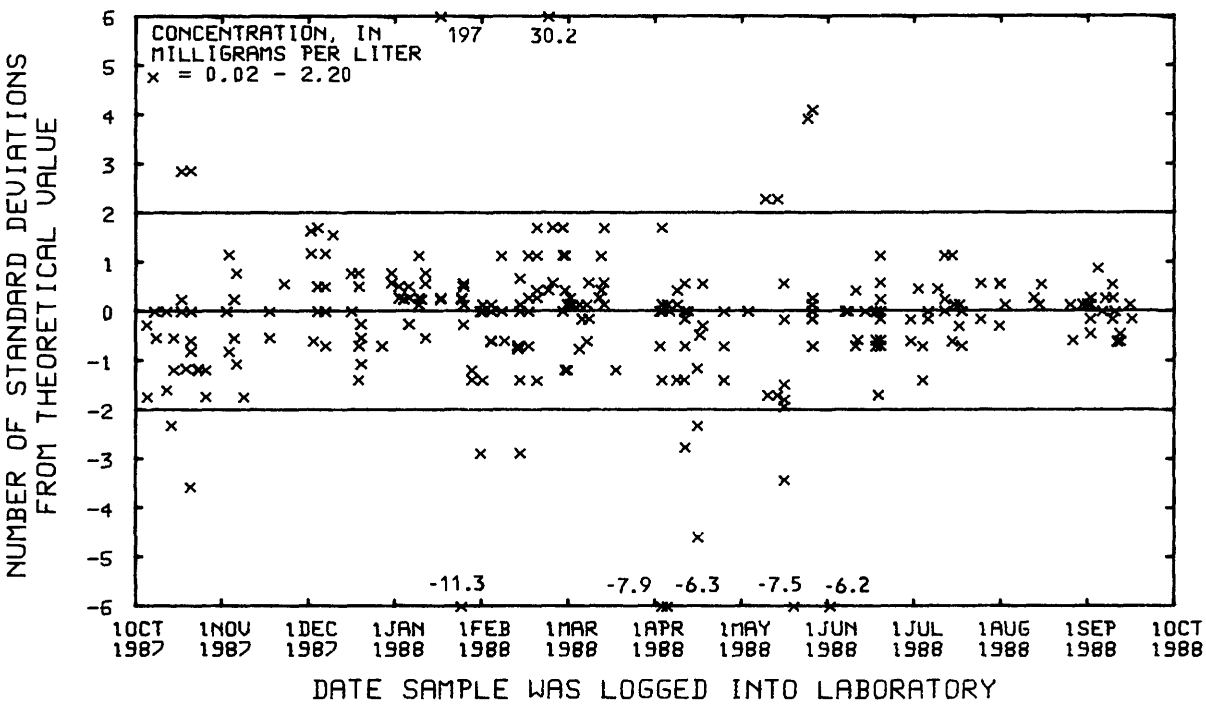

Figure 66.--Phosphorus as P, dissolved, data from the National Water Quality Laboratory.

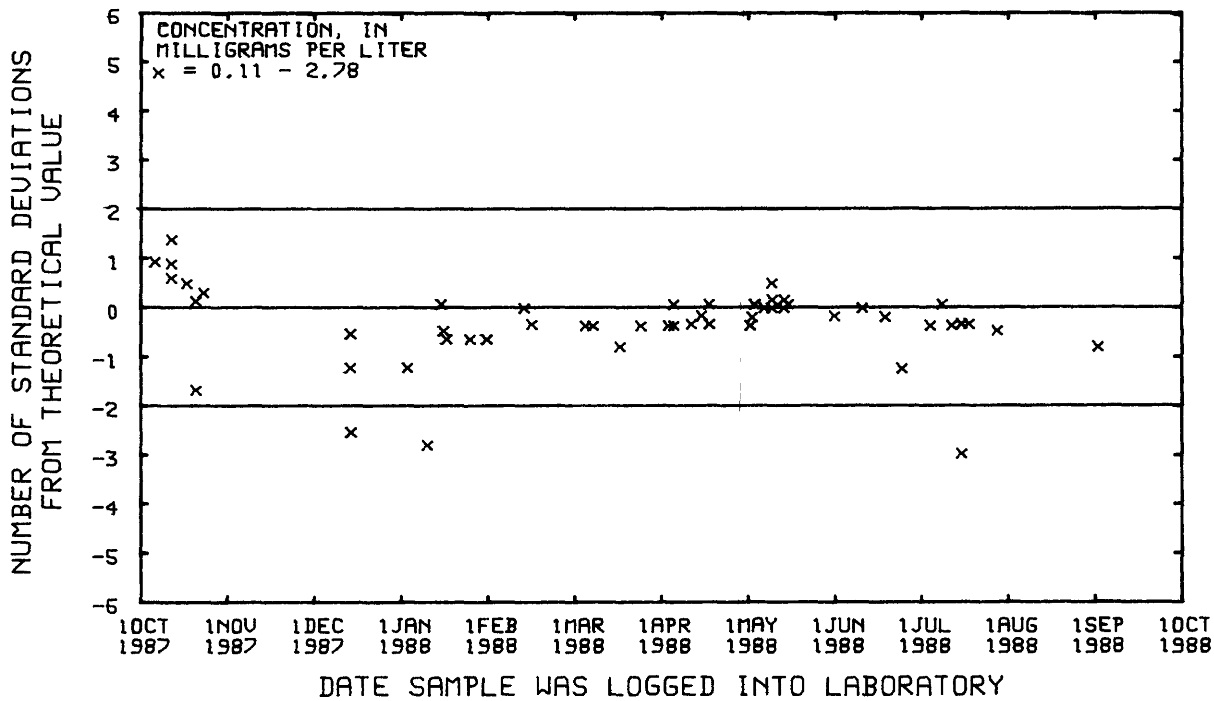

Figure 67.--Calcium, dissolved, (precipitation) data from the National Water Quality Laboratory.

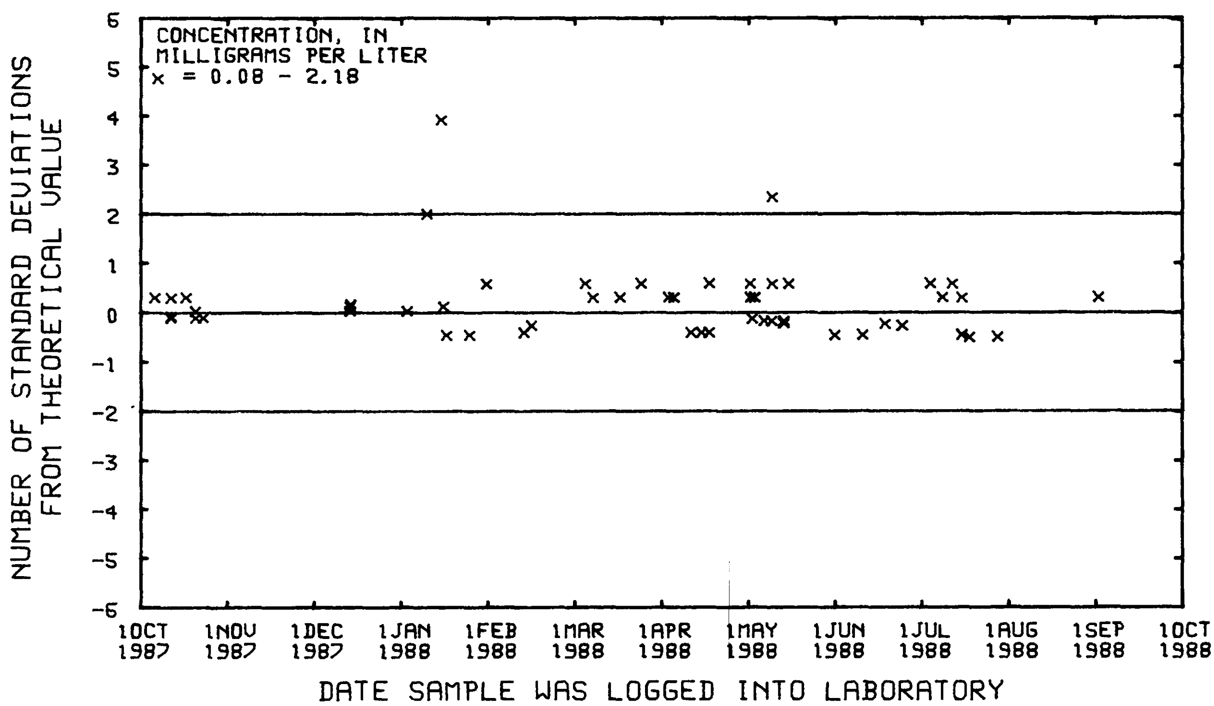

Figure 68.--Chloride, dissolved, (precipitation) data from the National Water Quality Laboratory.

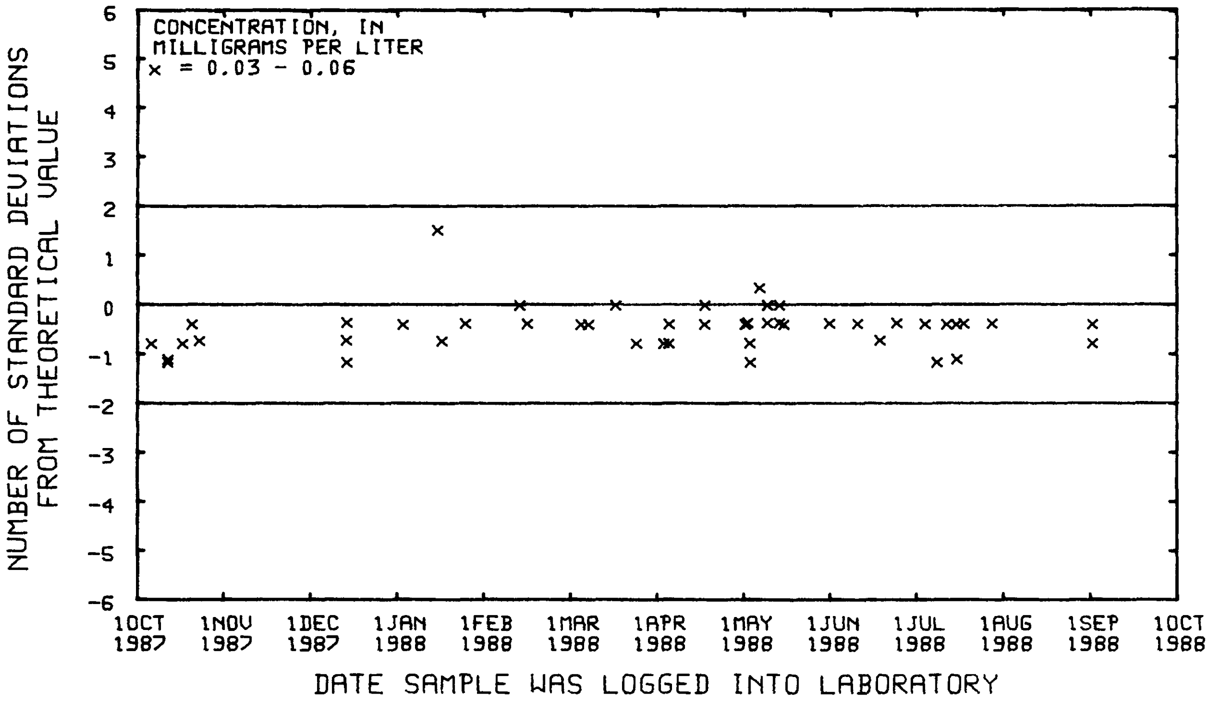

Figure 69.--Fluoride, dissolved, (precipitation) data from the National Water Quality Laboratory.

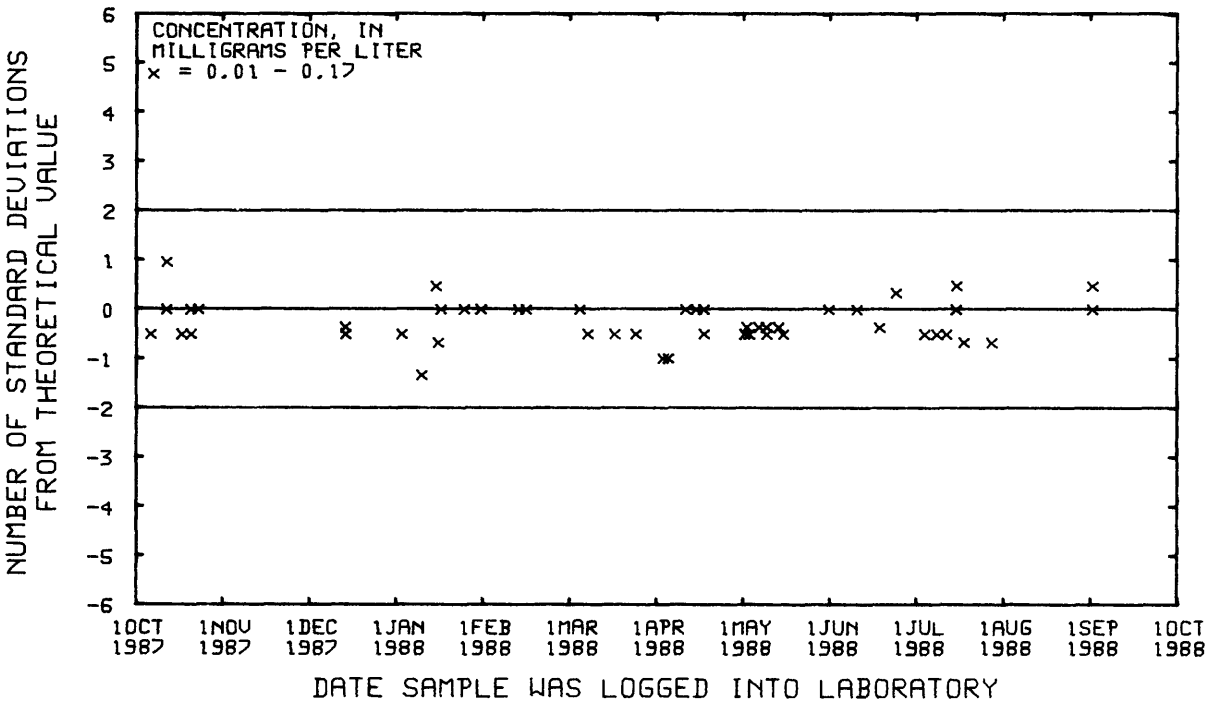

Figure 70.--Magnesium, dissolved, (precipitation) data from the National Water Quality Laboratory.

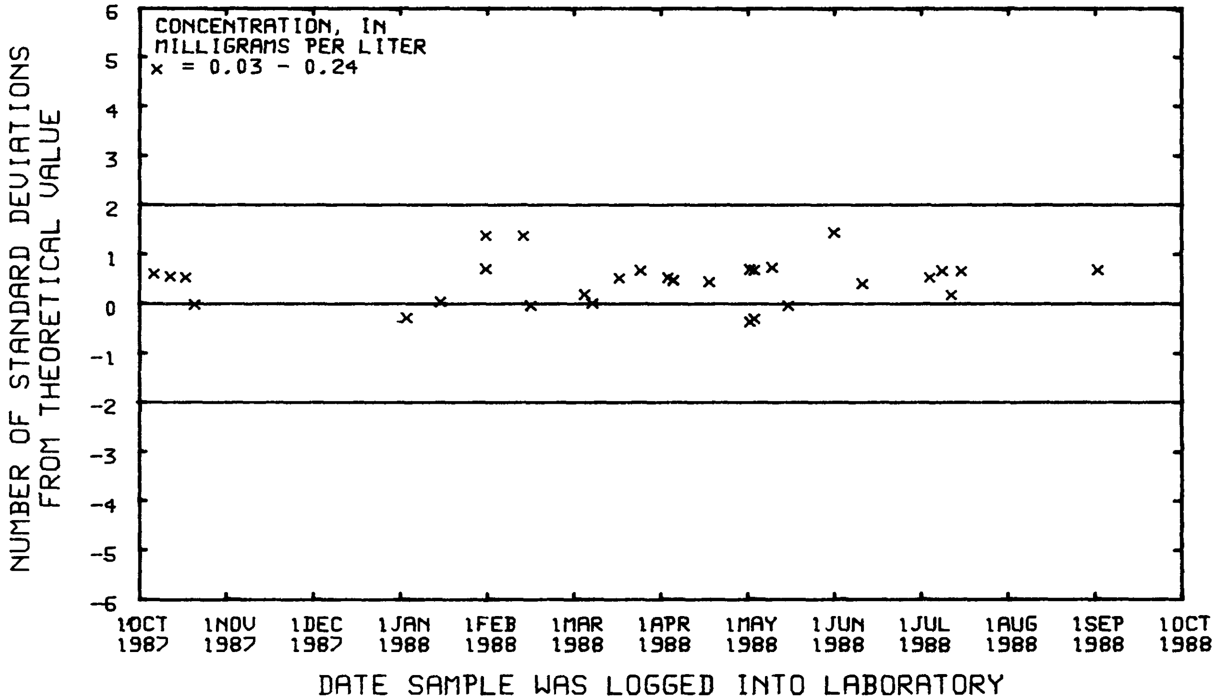

Figure 71.--Ammonia nitrogen as N, dissolved, (precipitation) data from the National Water Quality Laboratory.

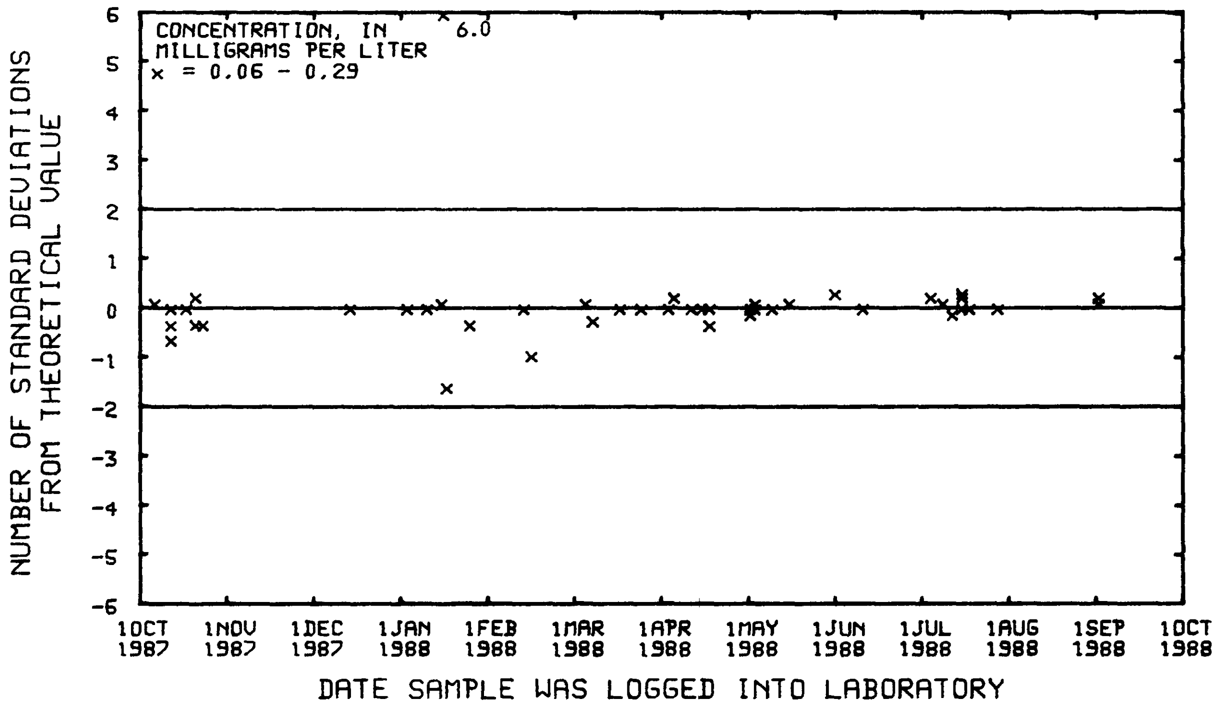

Figure 72.--Nitrate nitrogen as N, dissolved, (precipitation) data from the National Water Quality Laboratory.

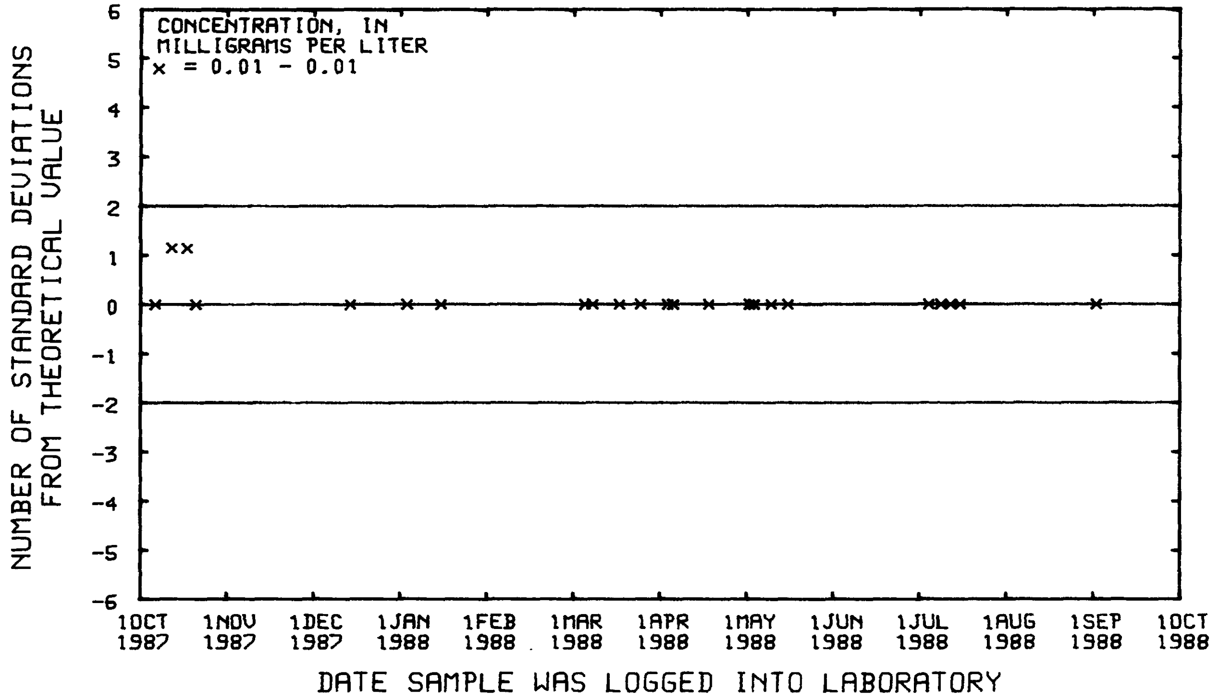

Figure 73.--Orthophosphate phosphorus as P, dissolved, (precipitation) data from the National Water Quality Laboratory.

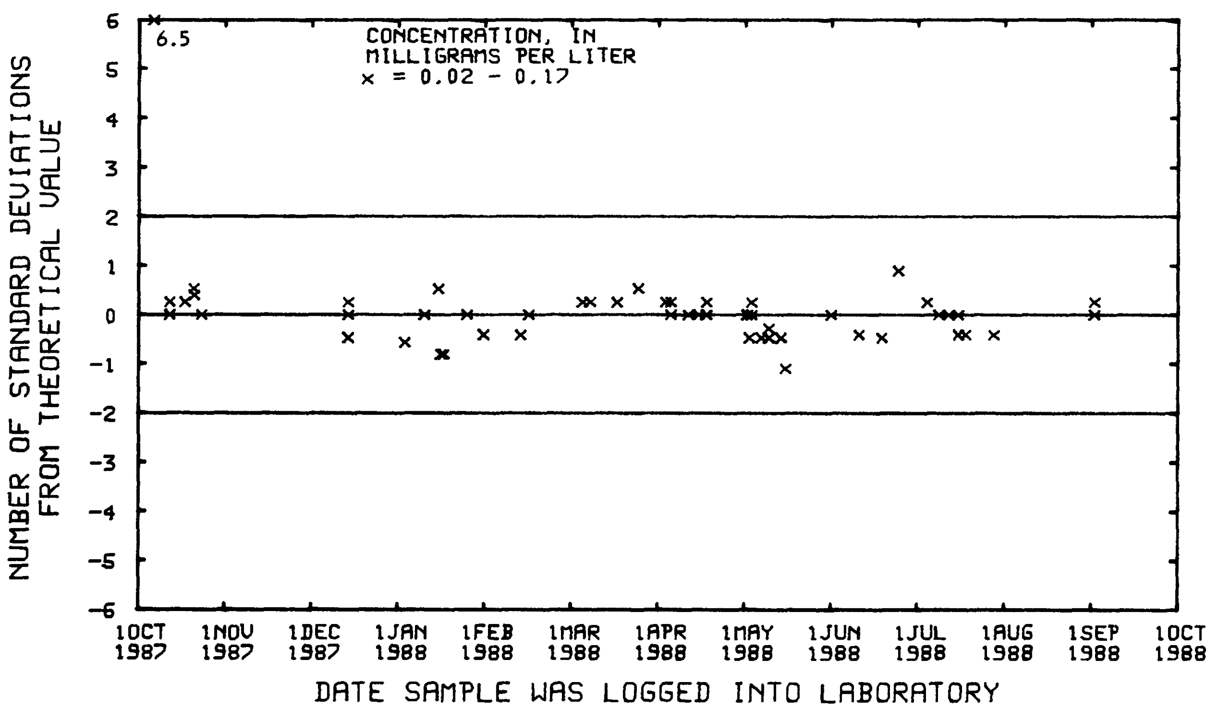

Figure 74.--Potassium, dissolved, (precipitation) data from the National Water Quality Laboratory.

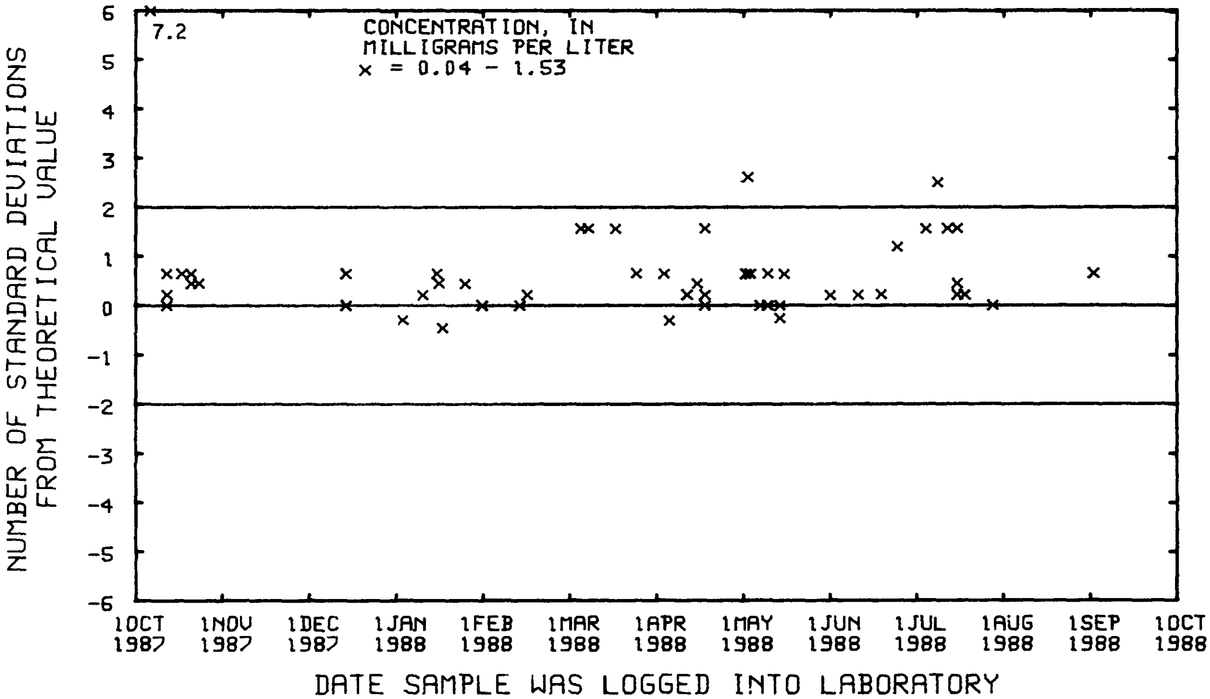

Figure 75.--Sodium, dissolved, (precipitation) data from the National Water Quality Laboratory.

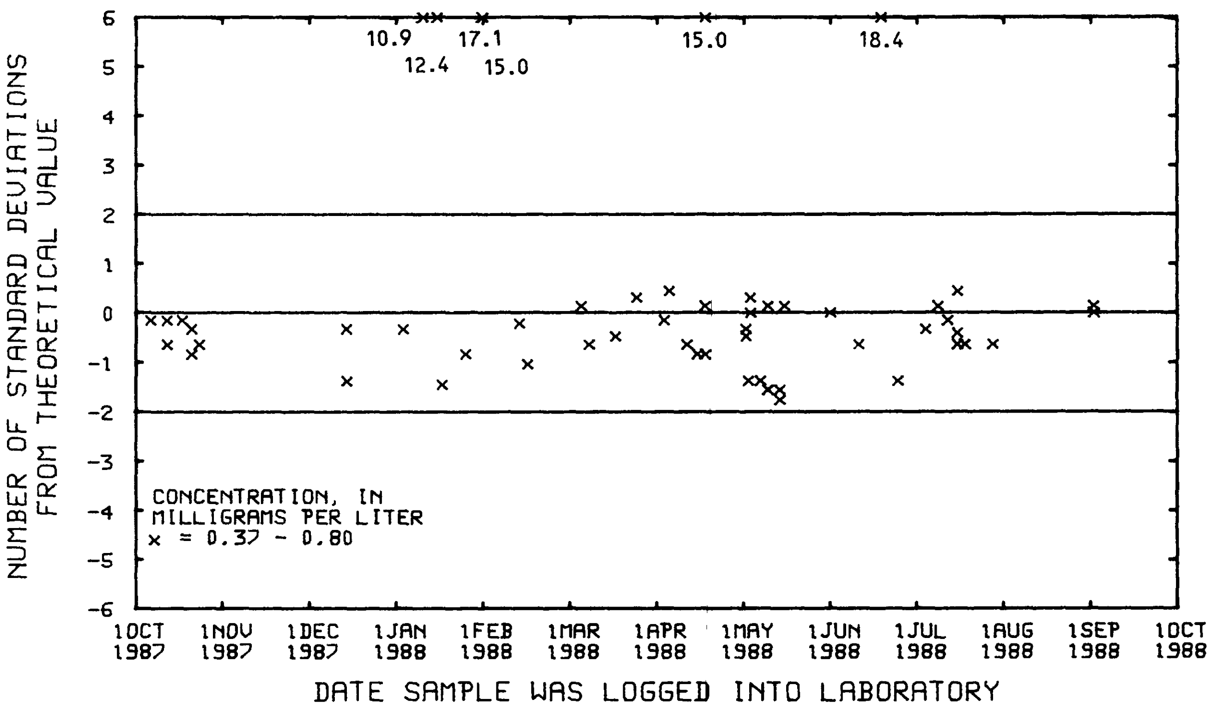

Figure 76.--Sulfate, dissolved, (precipitation) data from the National Water Quality Laboratory.

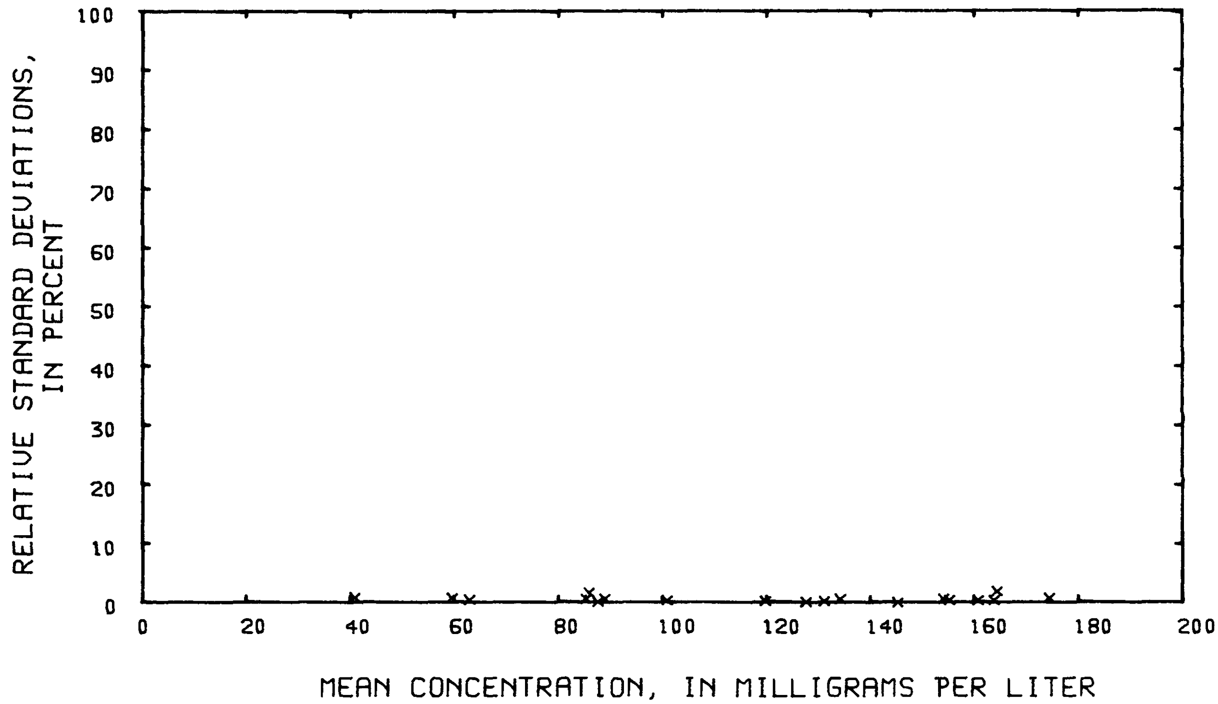

Figure 77.--Precision data for alkalinity, dissolved, at the National Water Quality Laboratory.

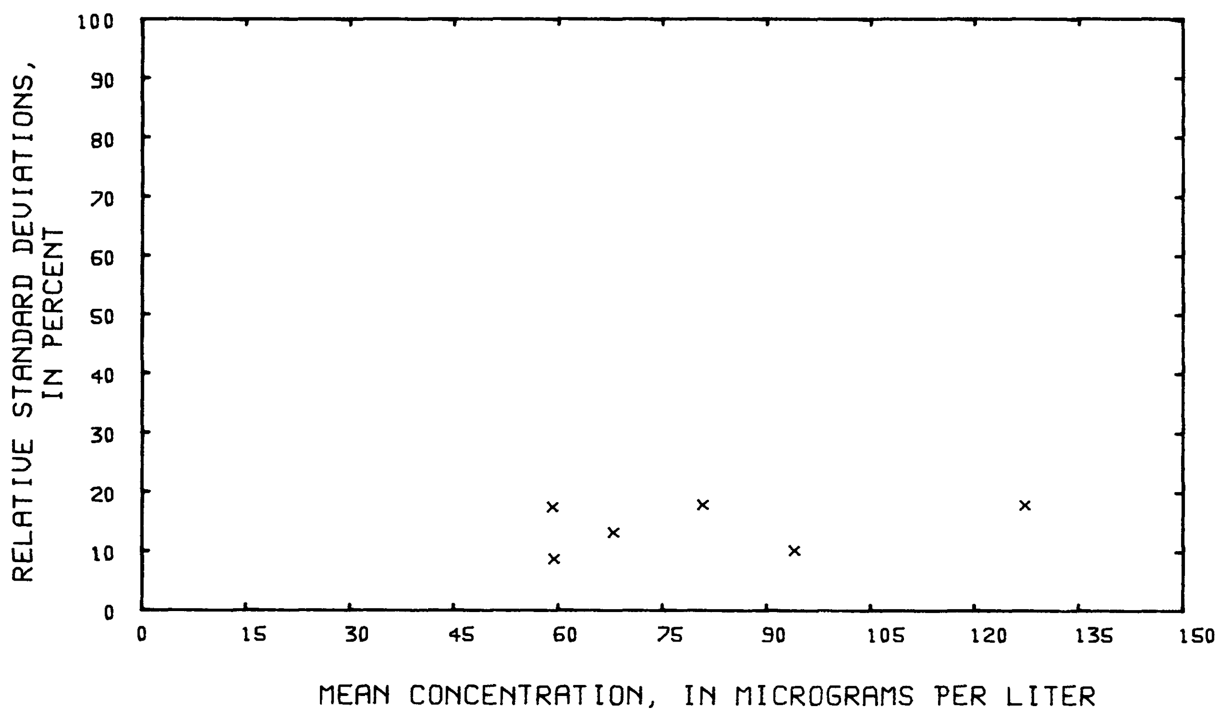

Figure 78.--Precision data for aluminum, dissolved, at the National Water Quality Laboratory.

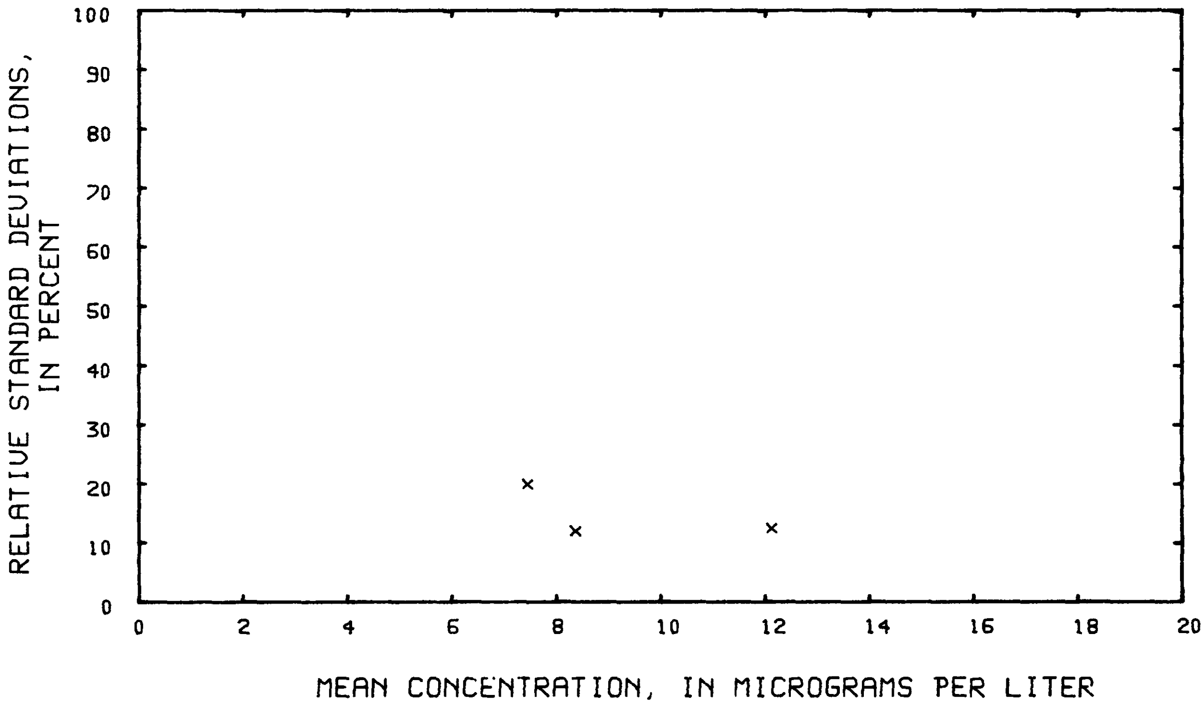

Figure 79.--Precision data for antimony, dissolved, at the National Water Quality Laboratory.

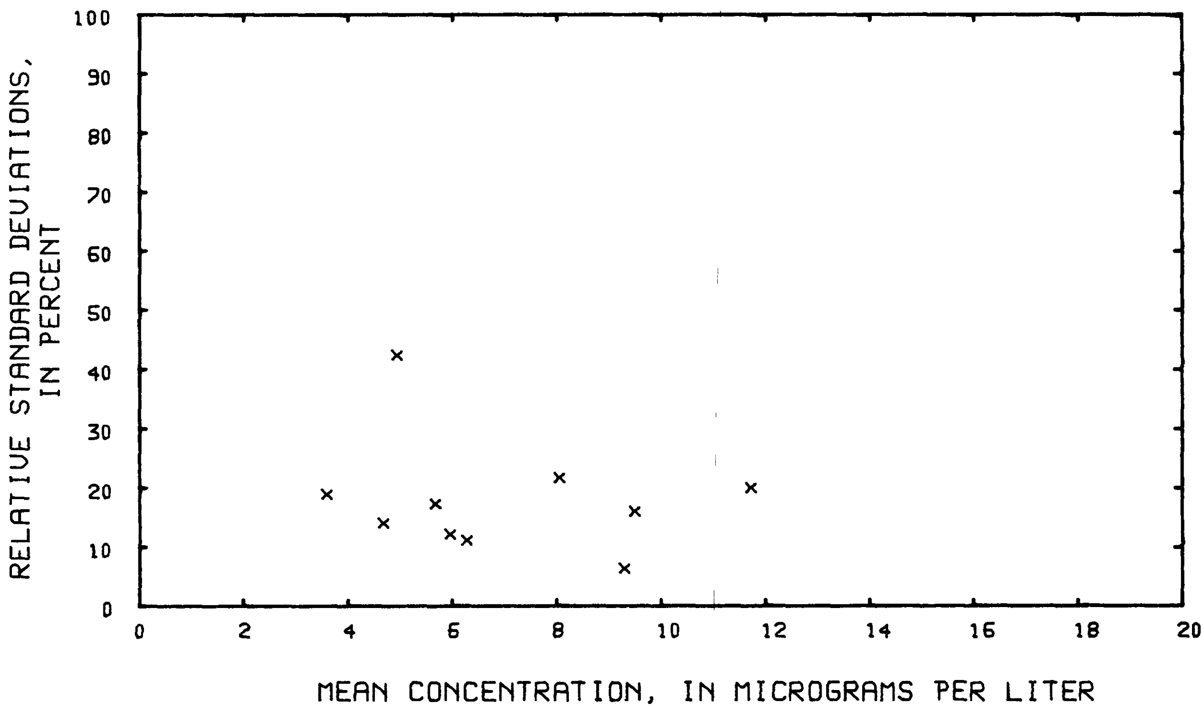

Figure 80.--Precision data for arsenic, dissolved, at the National Water Quality Laboratory.

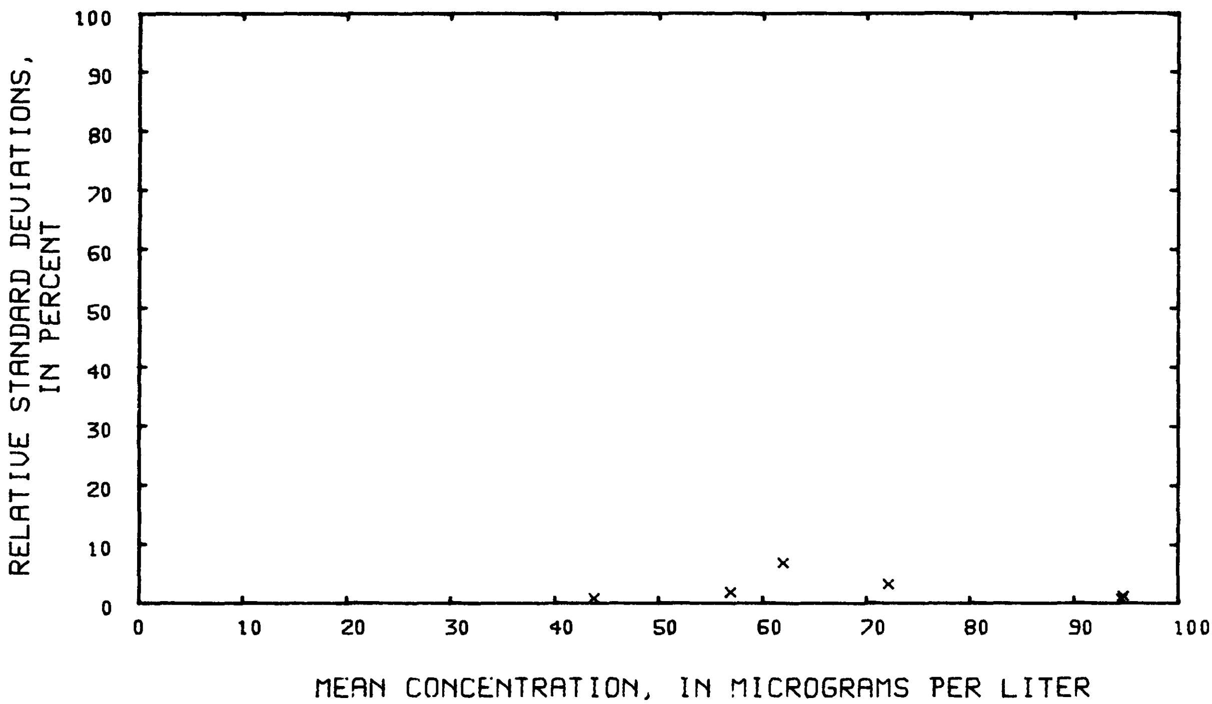

Figure 81.--Precision data for barium, dissolved, (inductively coupled plasma emission spectrometry) at the National Water Quality Laboratory.

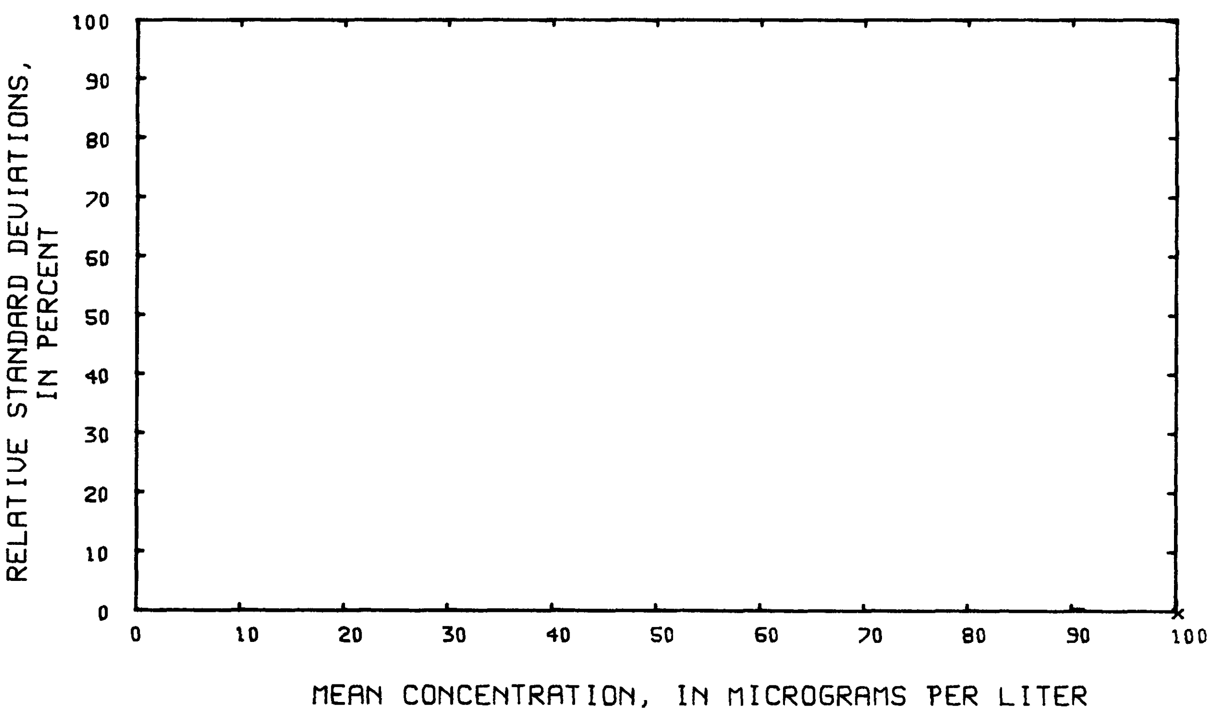

Figure 82.--Precision data for barium, dissolved, (atomic absorption spectrometry) at the National Water Quality Laboratory.

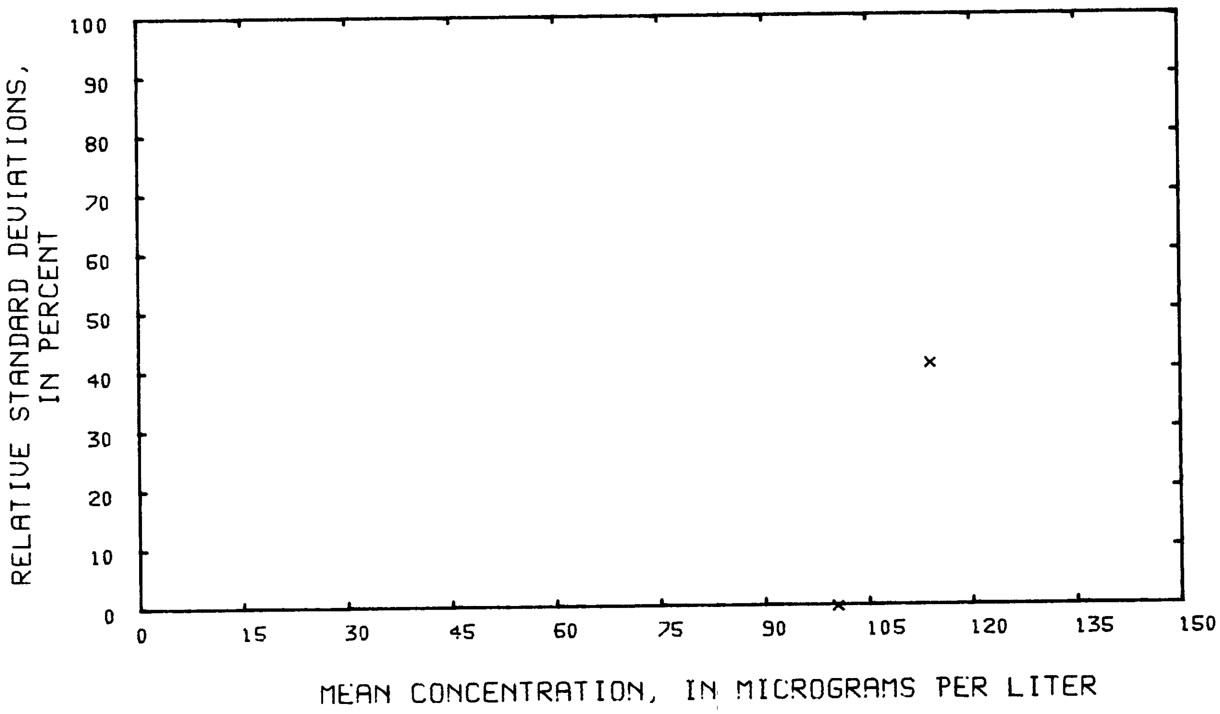

Figure 83.--Precision data for barium, total recoverable, at the National Water Quality Laboratory.

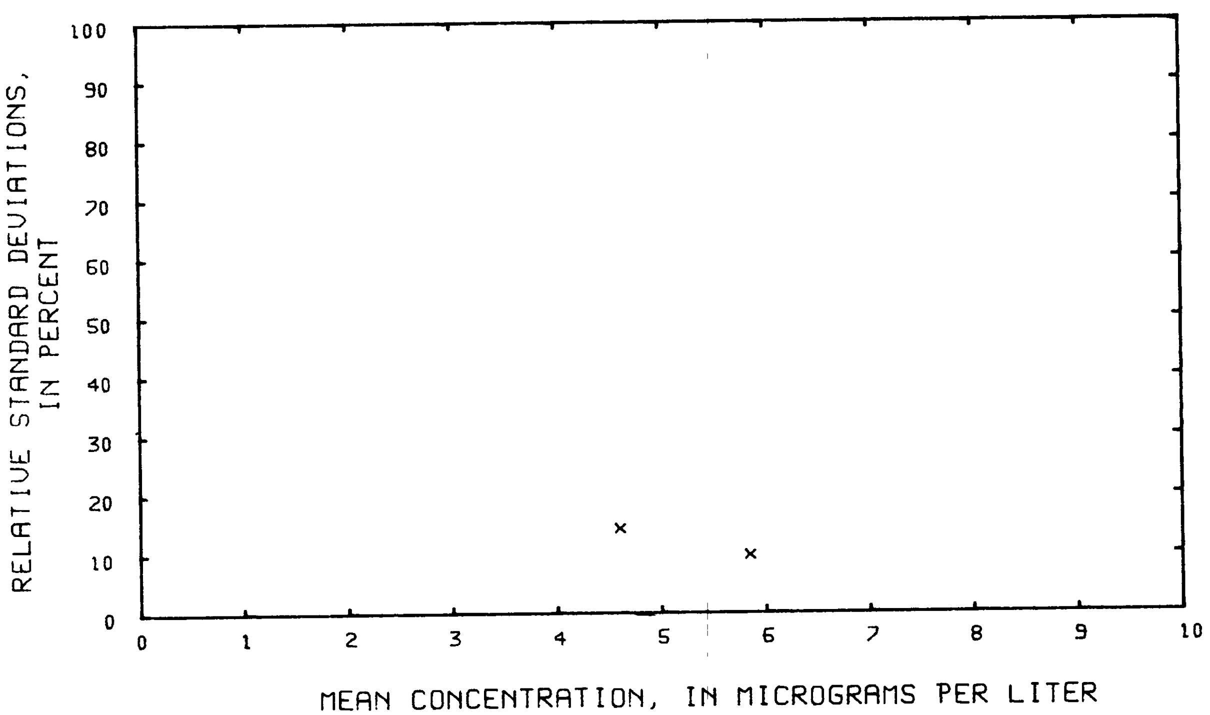

Figure 84.--Precision data for beryllium, dissolved, at the National Water Quality Laboratory.

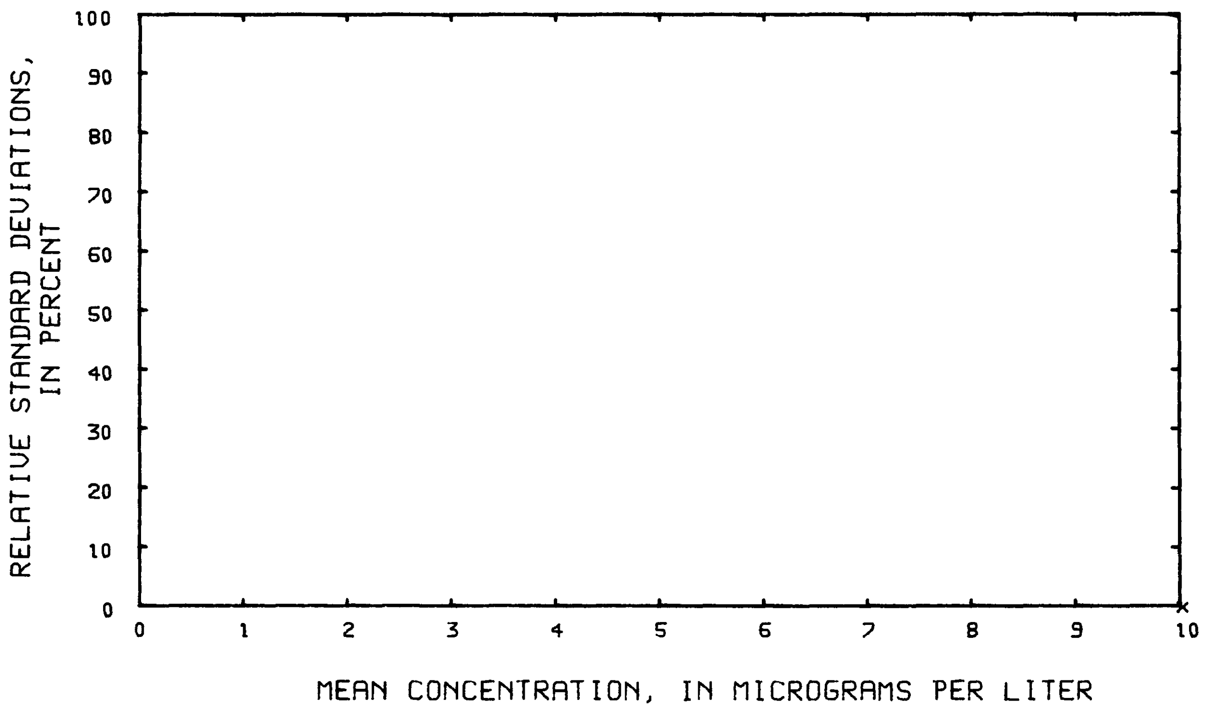

Figure 85.--Precision data for beryllium, total recoverable, at the National Water Quality Laboratory.

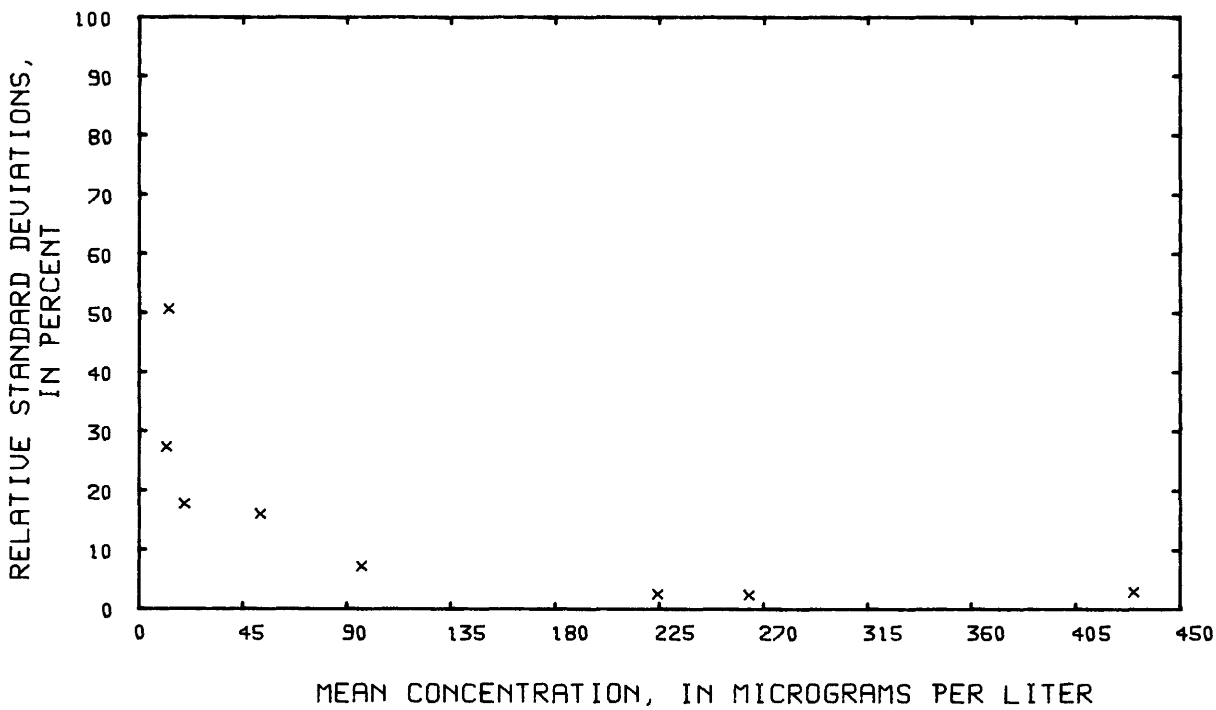

Figure 86.--Precision data for boron, dissolved, at the National Water Quality Laboratory.

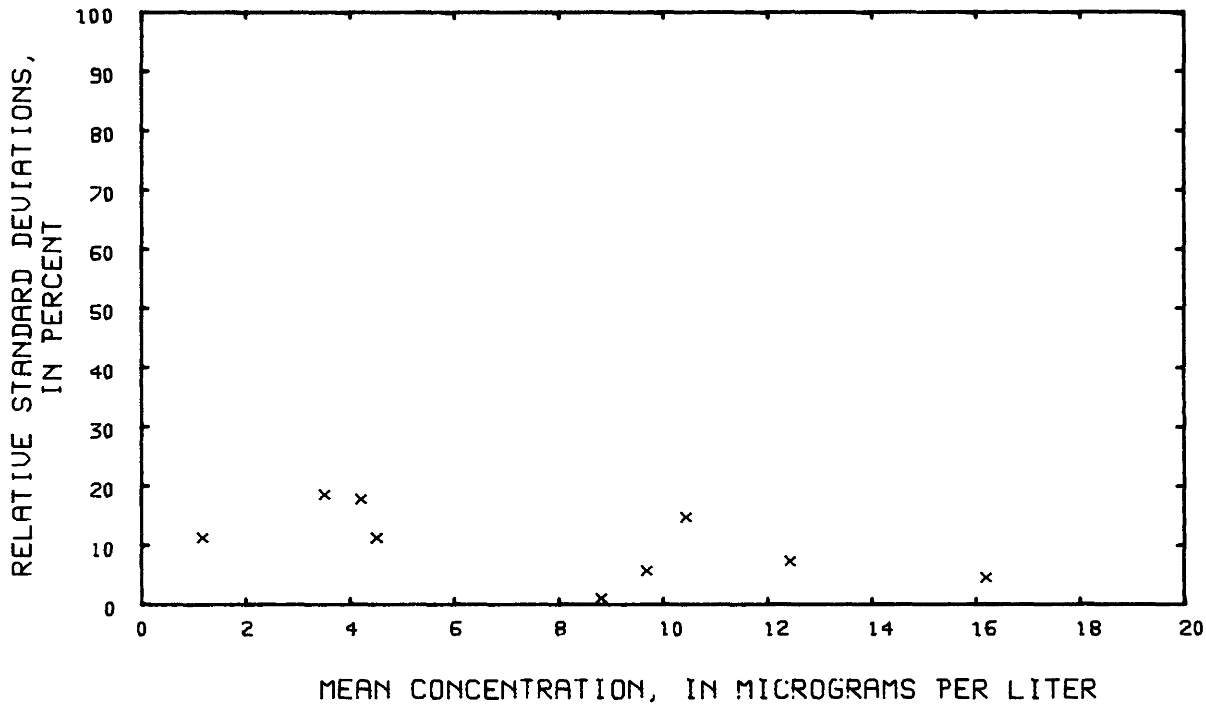

Figure 87.--Precision data for cadmium, dissolved, (inductively coupled plasma emission spectrometry) at the National Water Quality Laboratory.

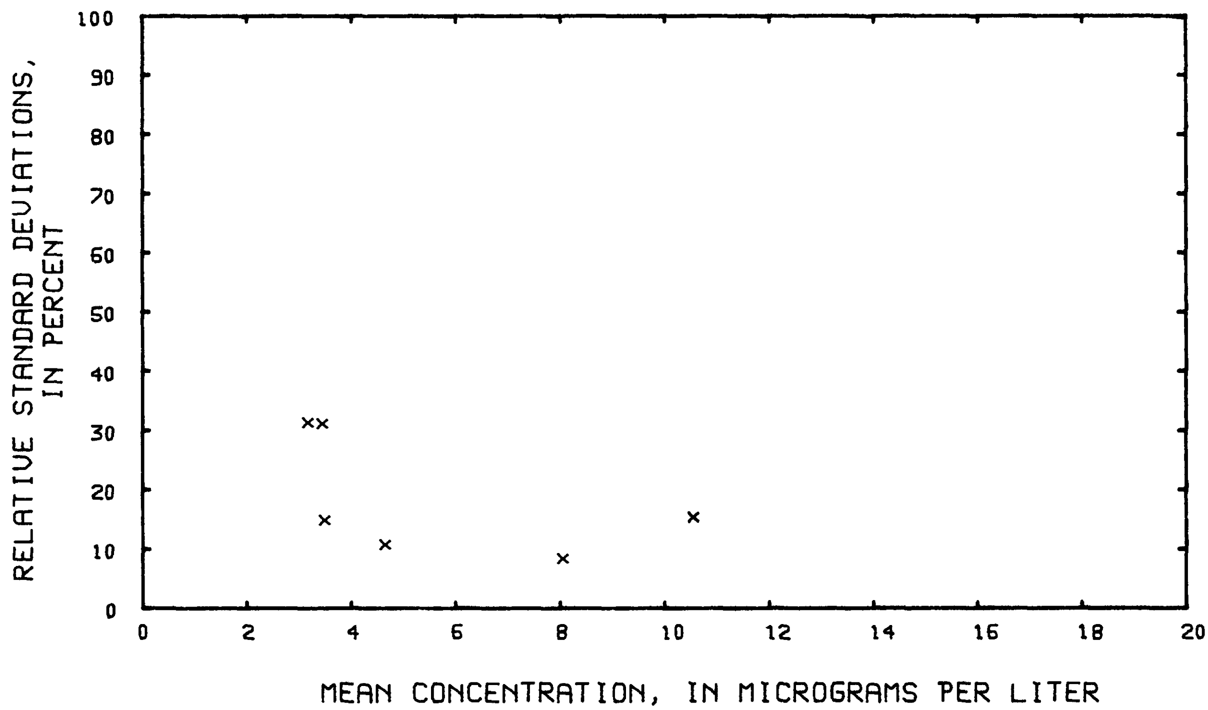

Figure 88.--Precision data for cadmium, dissolved, (atomic absorption spectrometry) at the National Water Quality Laboratory.

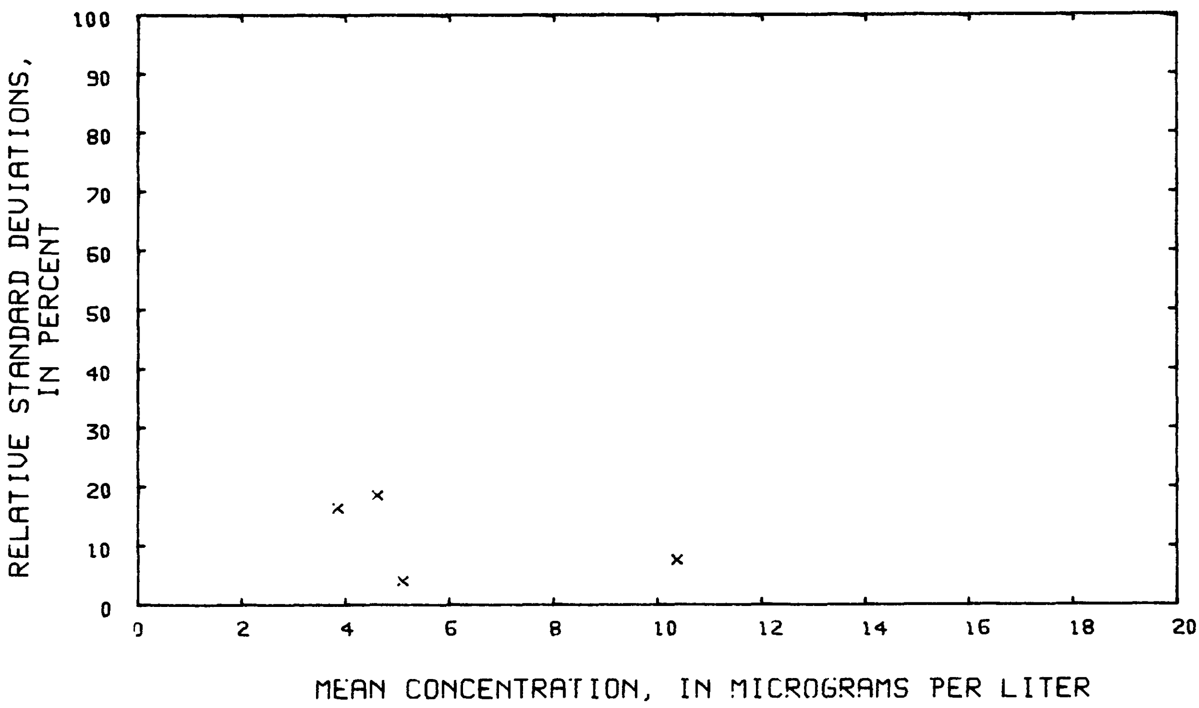

Figure 89.--Precision data for cadmium, total recoverable, at the National Water Quality Laboratory.

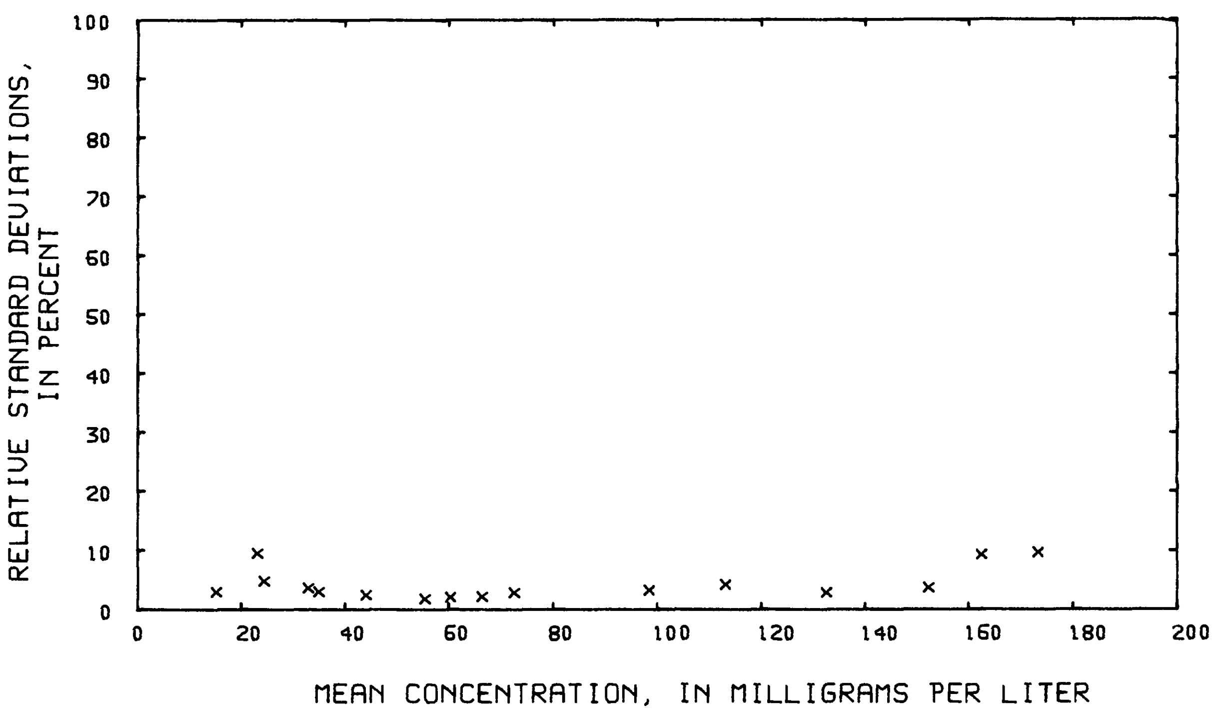

Figure 90.--Precision data for calcium, dissolved, (inductively coupled plasma emission spectrometry) at the National Water Quality Laboratory.

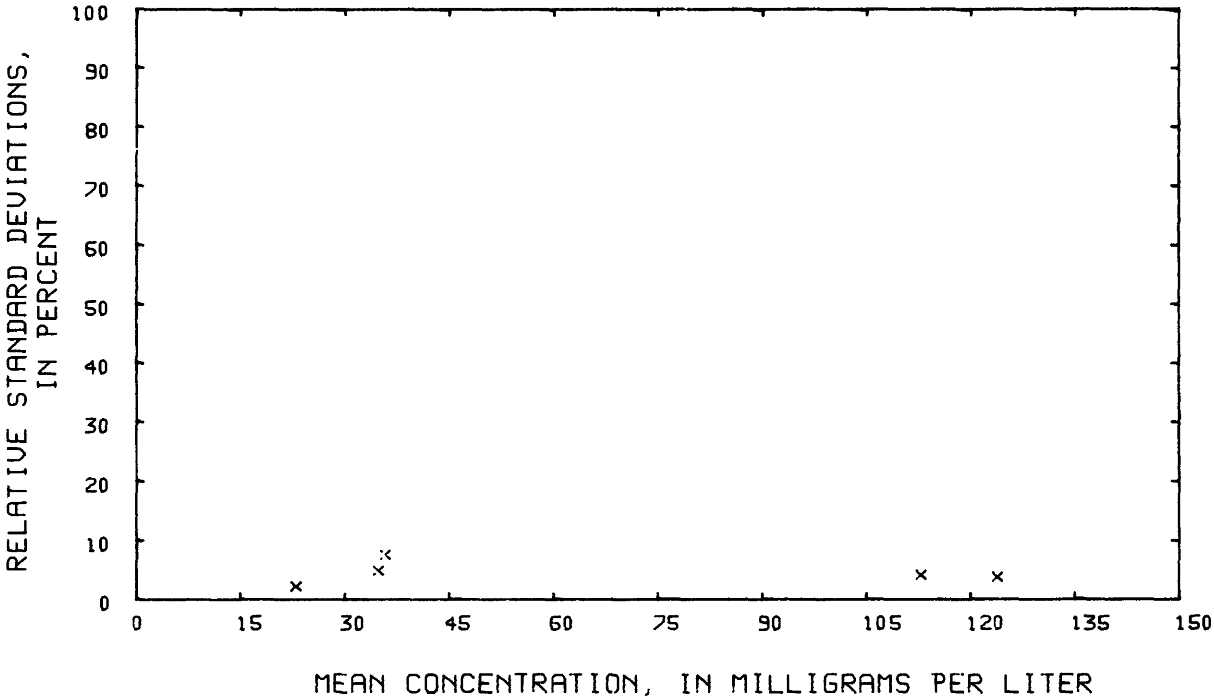

Figure 91.--Precision data for calcium, dissolved, (atomic absorption spectrometry) at the National Water Quality Laboratory.

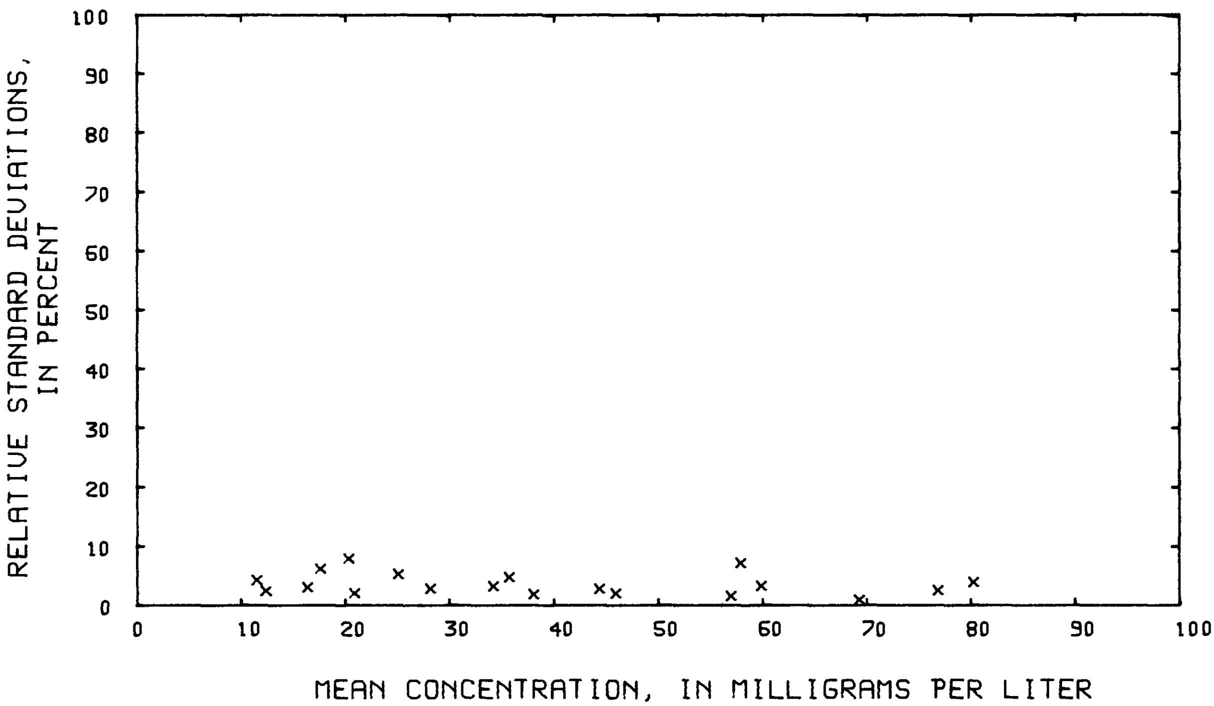

Figure 92.--Precision data for chloride, dissolved, at the National Water Quality Laboratory.

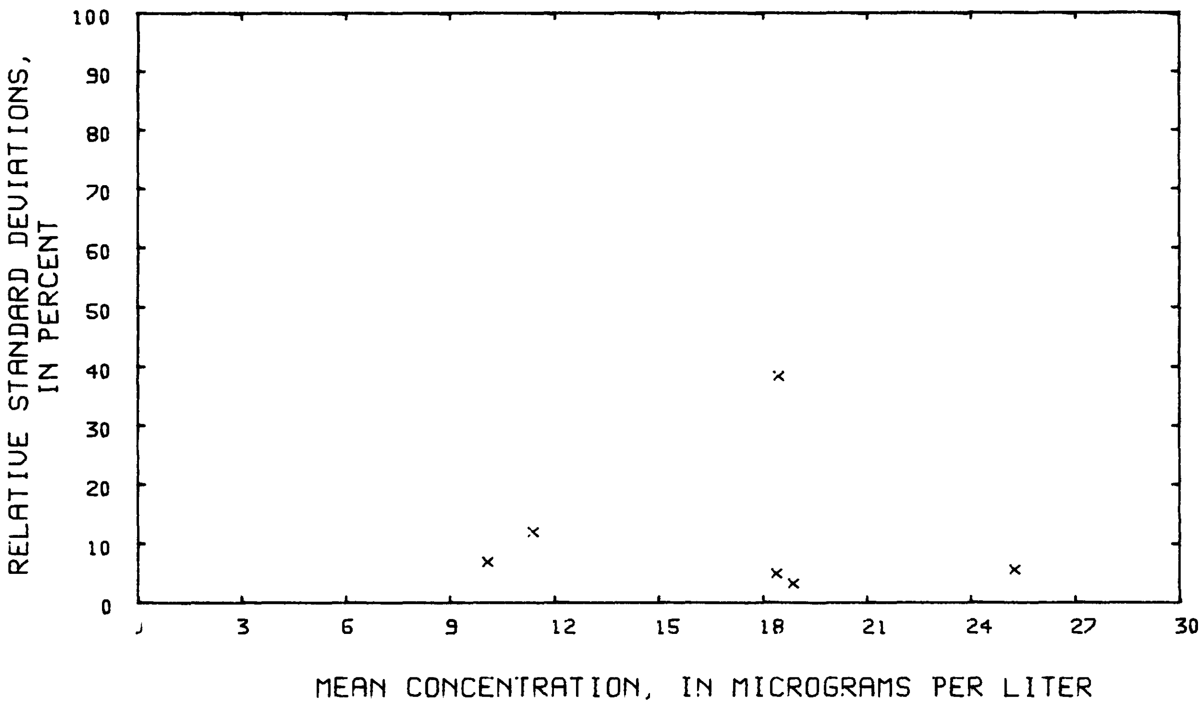

Figure 93.--Precision data for chromium, dissolved, (inductively coupled plasma emission spectrometry) at the National Water Quality Laboratory.

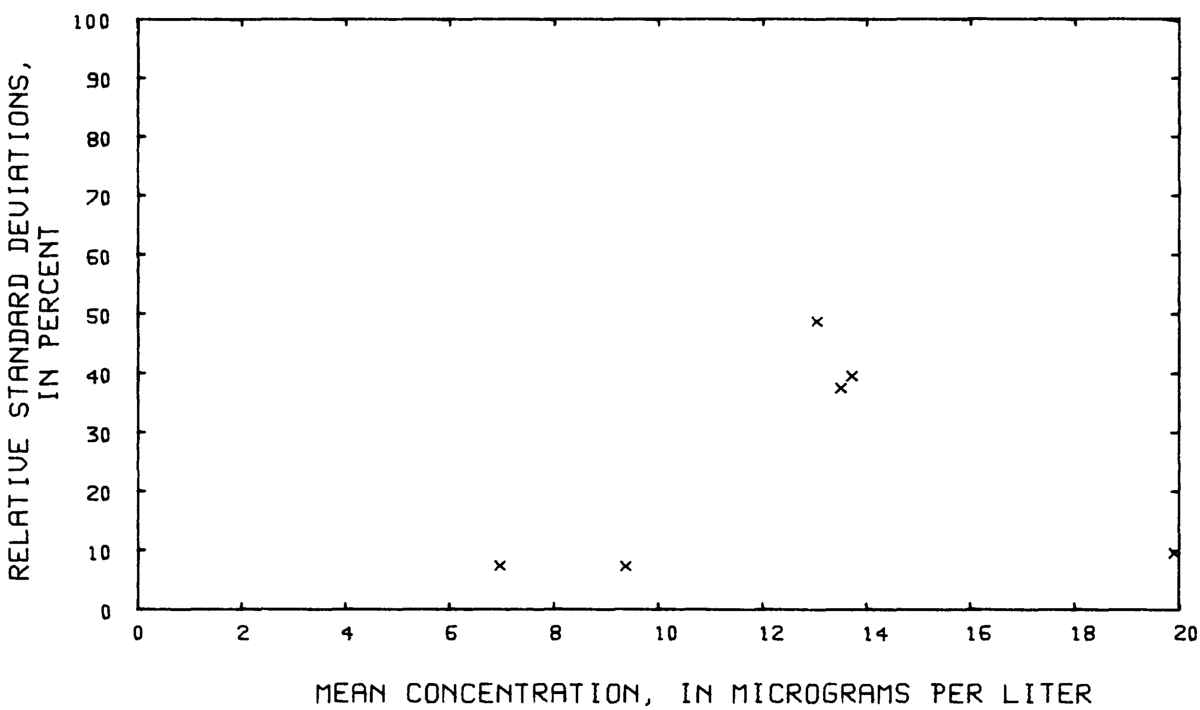

Figure 94.--Precision data for chromium, dissolved, (direct current plasma emission spectrometry) at the National Water Quality Laboratory.

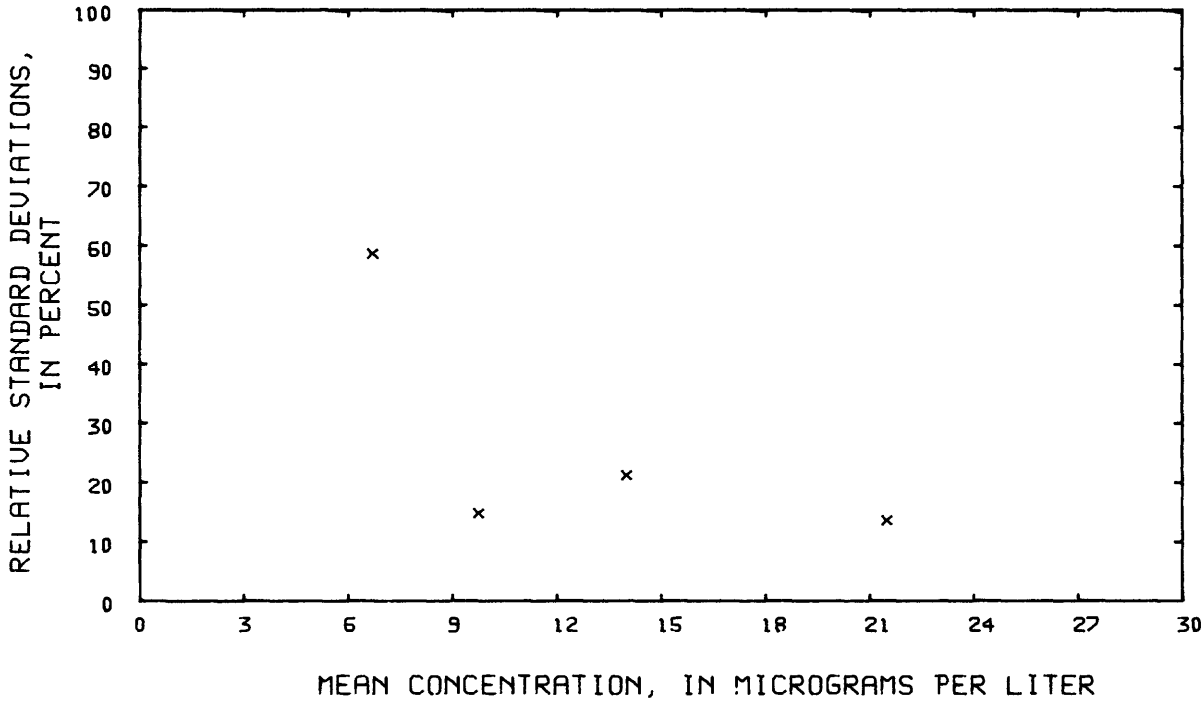

Figure 95.--Precision data for chromium, total recoverable, at the National Water Quality Laboratory.

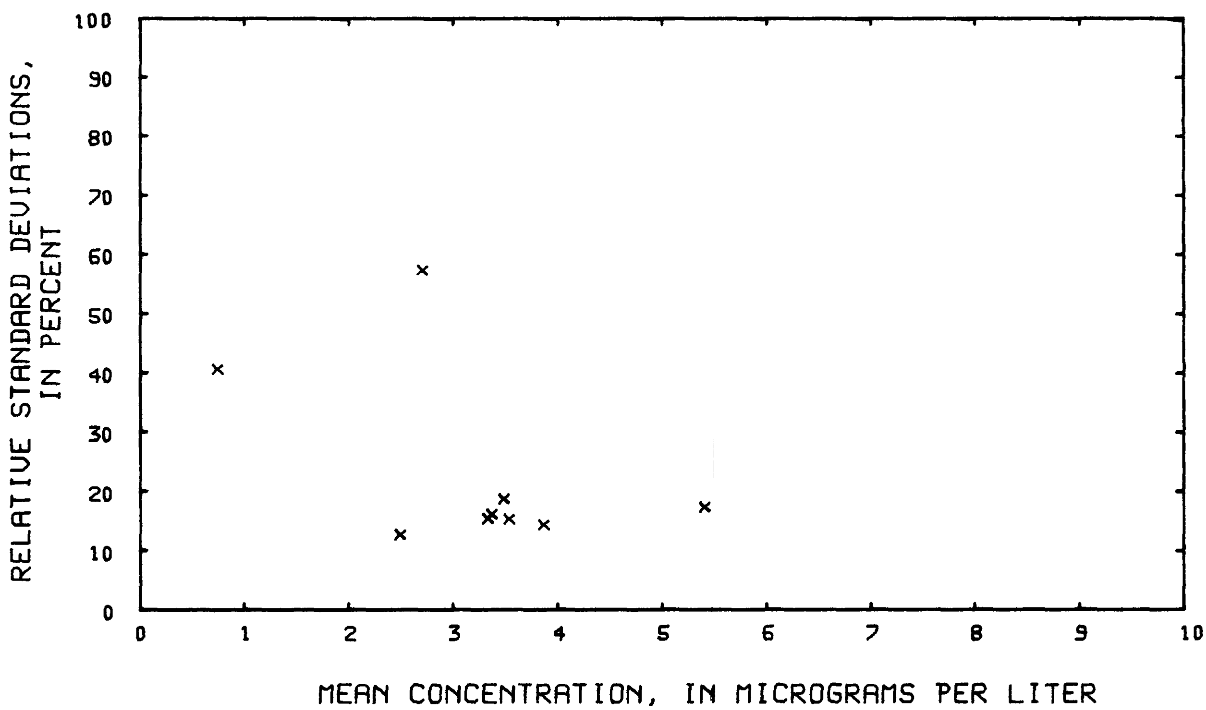

Figure 96.--Precision data for cobalt, dissolved, (inductively coupled plasma emission spectrometry) at the National Water Quality Laboratory.

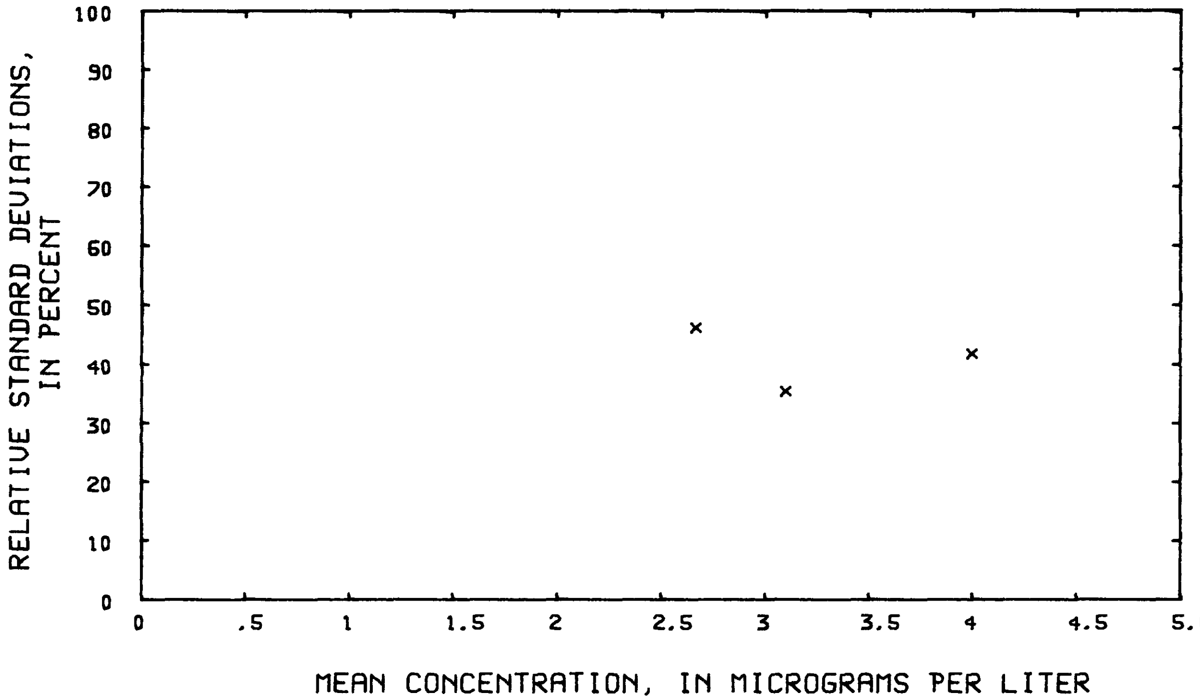

Figure 97.--Precision data for cobalt, dissolved, (atomic absorption spectrometry) at the National Water Quality Laboratory.

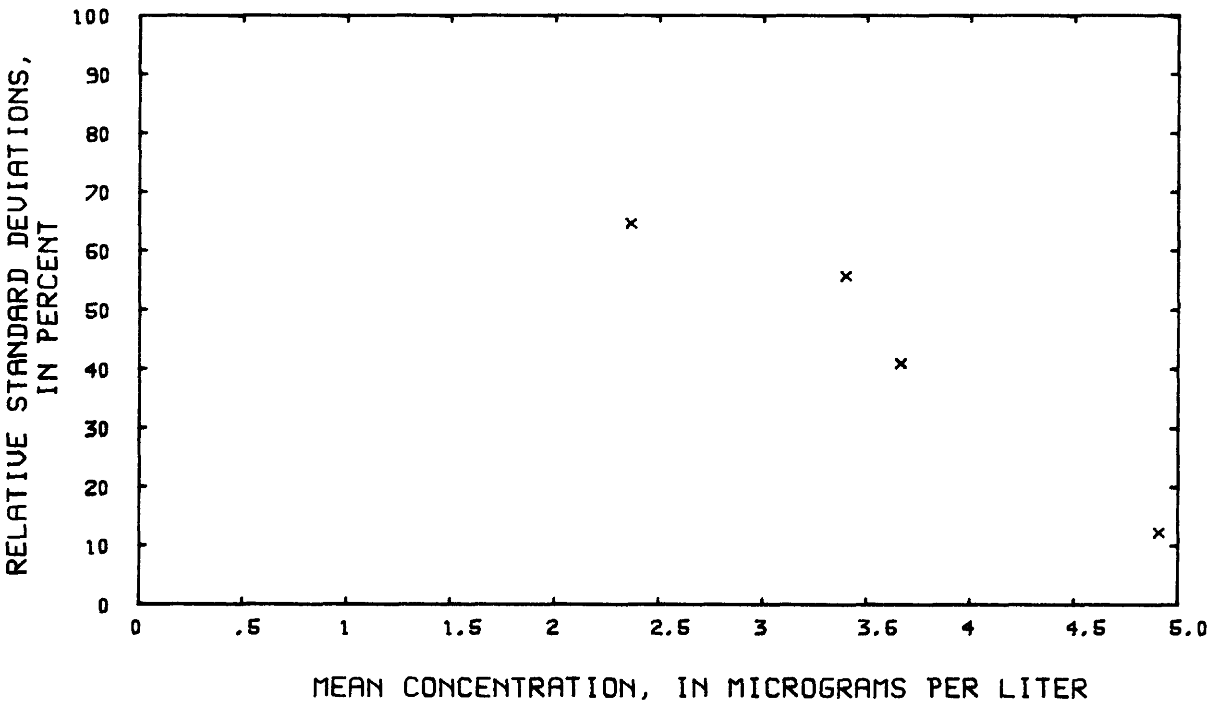

Figure 98.--Precision data for cobalt, total recoverable, at the National Water Quality Laboratory.

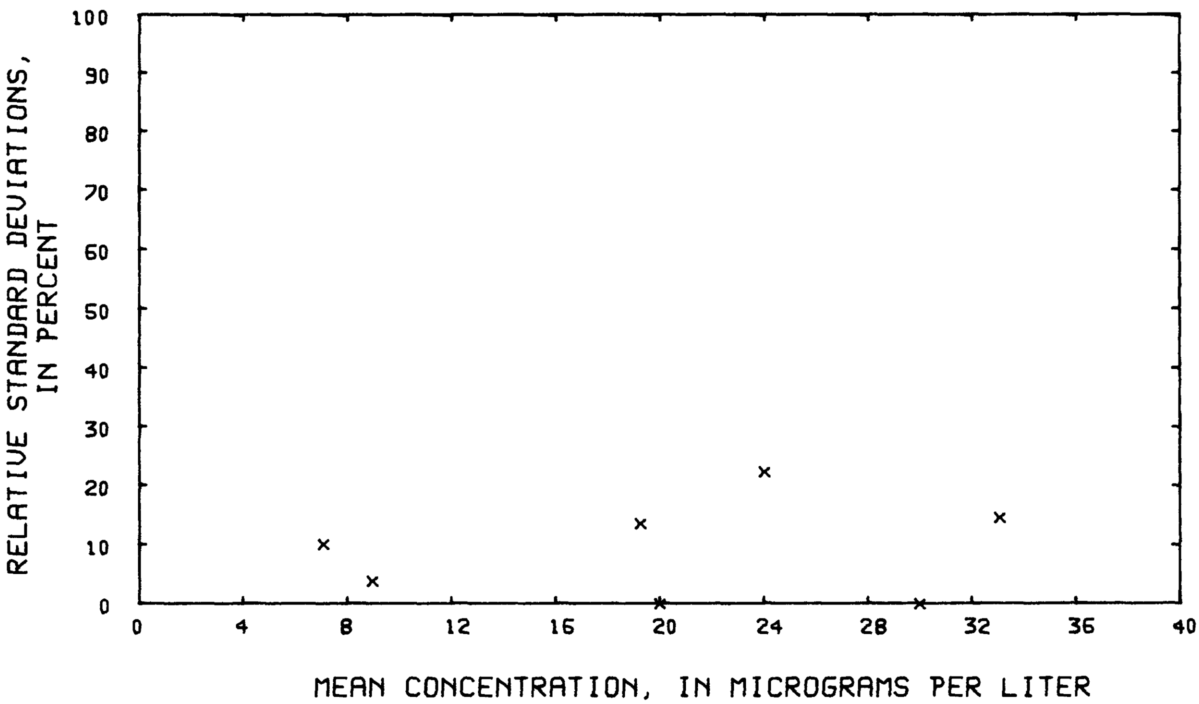

Figure 99.--Precision data for copper, dissolved, (inductively coupled plasma emission spectrometry) at the National Water Quality Laboratory.

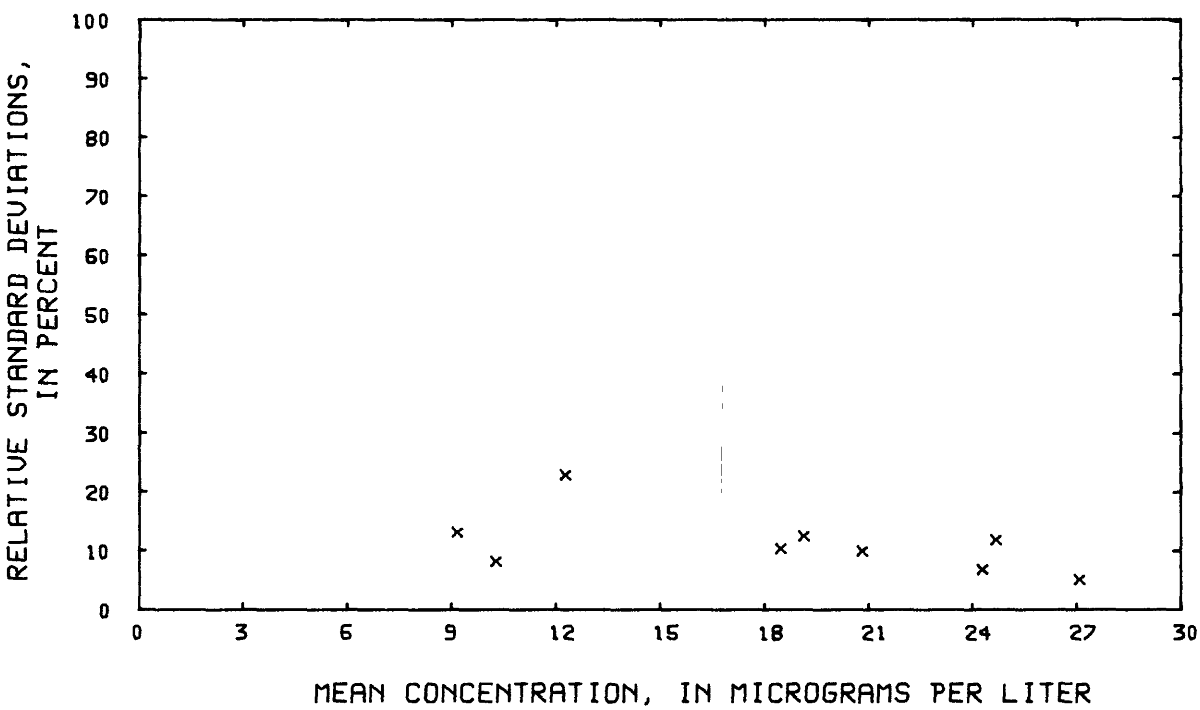

Figure 100.--Precision data for copper, dissolved, (atomic absorption spectrometry) at the National Water Quality Laboratory.

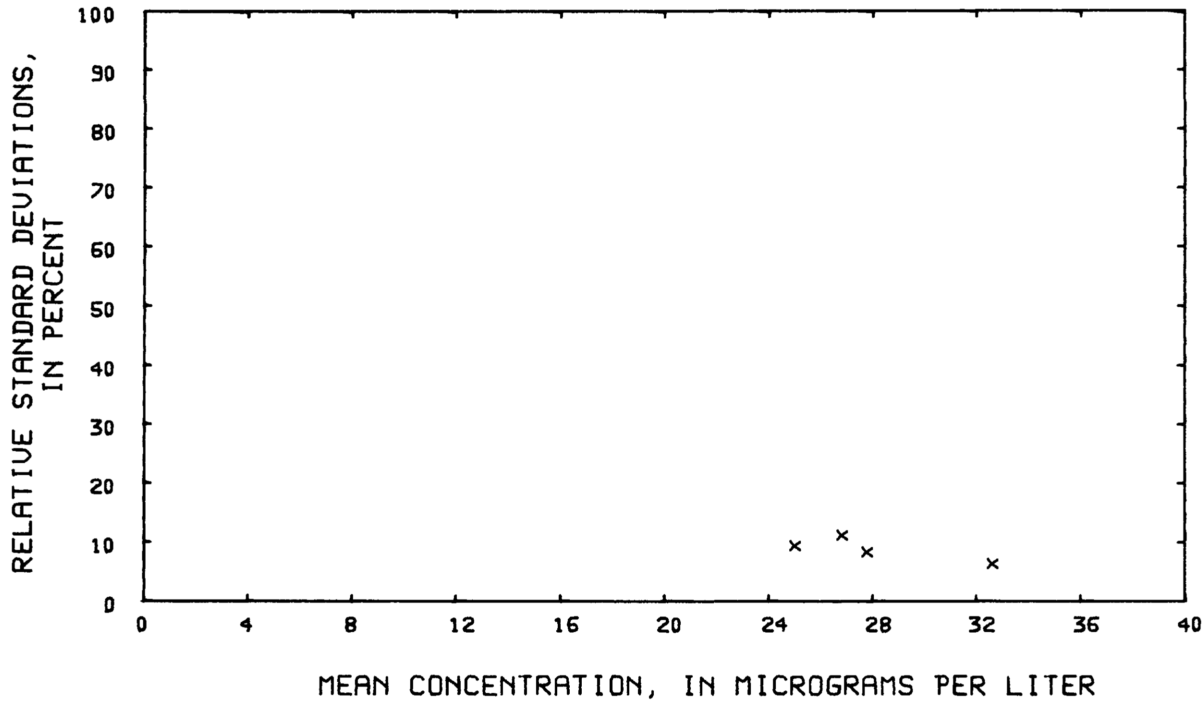

Figure 101.--Precision data for copper, total recoverable, at the National Water Quality Laboratory.

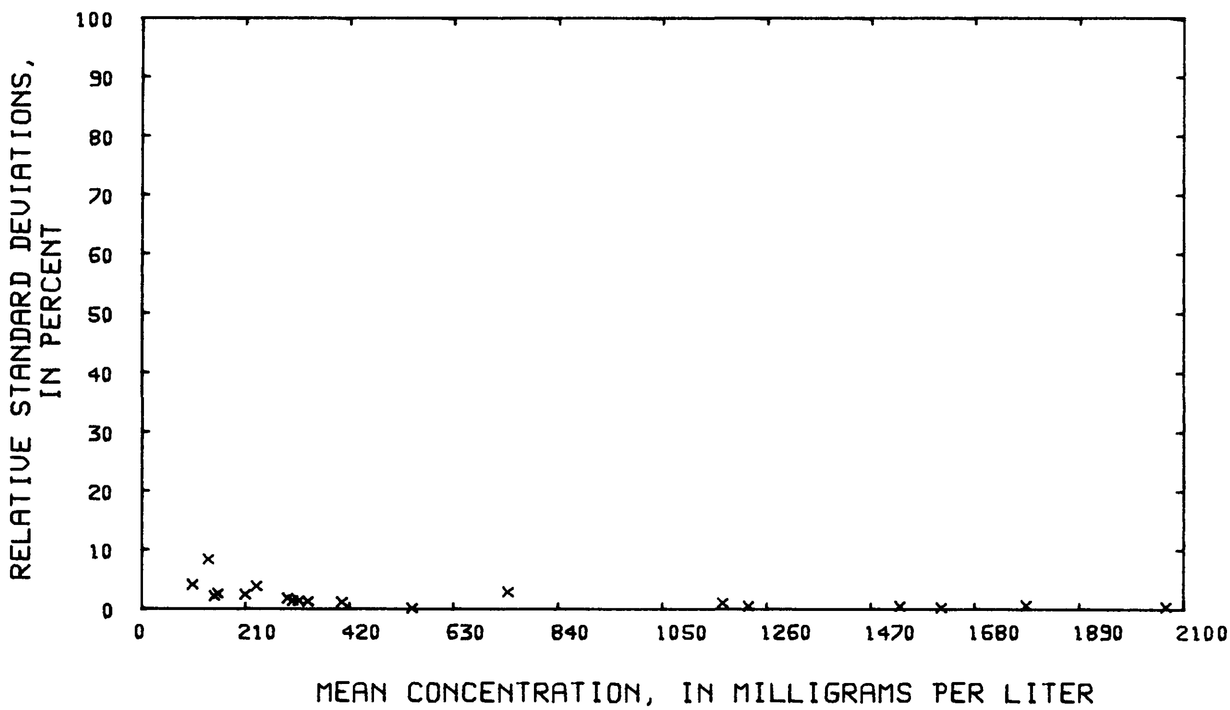

Figure 102.--Precision data for dissolved solids at the National Water Quality Laboratory.

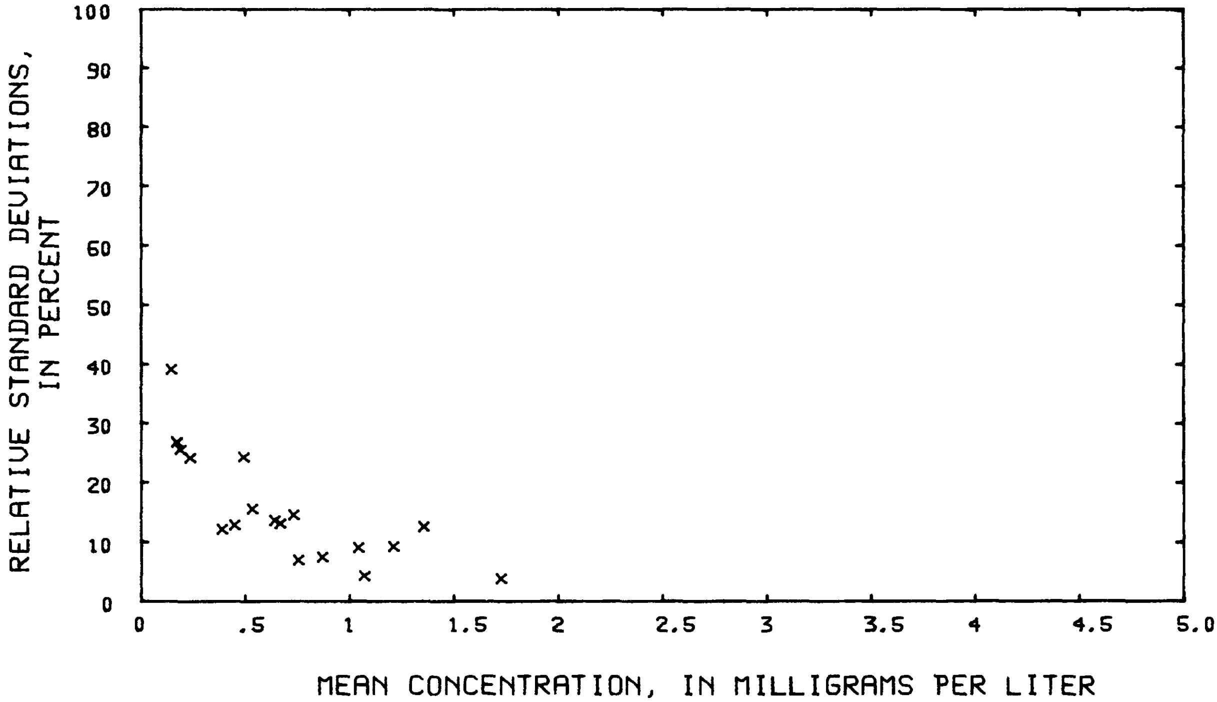

Figure 103.--Precision data for fluoride, dissolved, at the National Water Quality Laboratory.

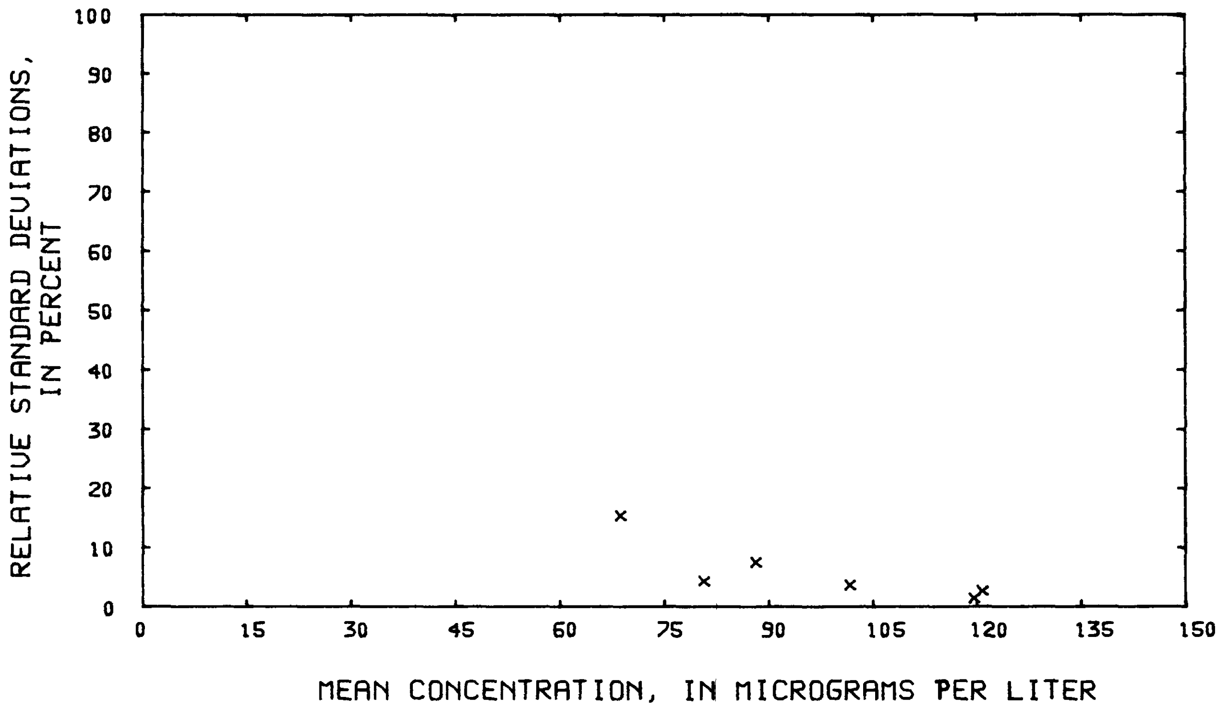

Figure 104.--Precision data for iron, dissolved, (inductively coupled plasma emission spectrometry) at the National Water Quality Laboratory.

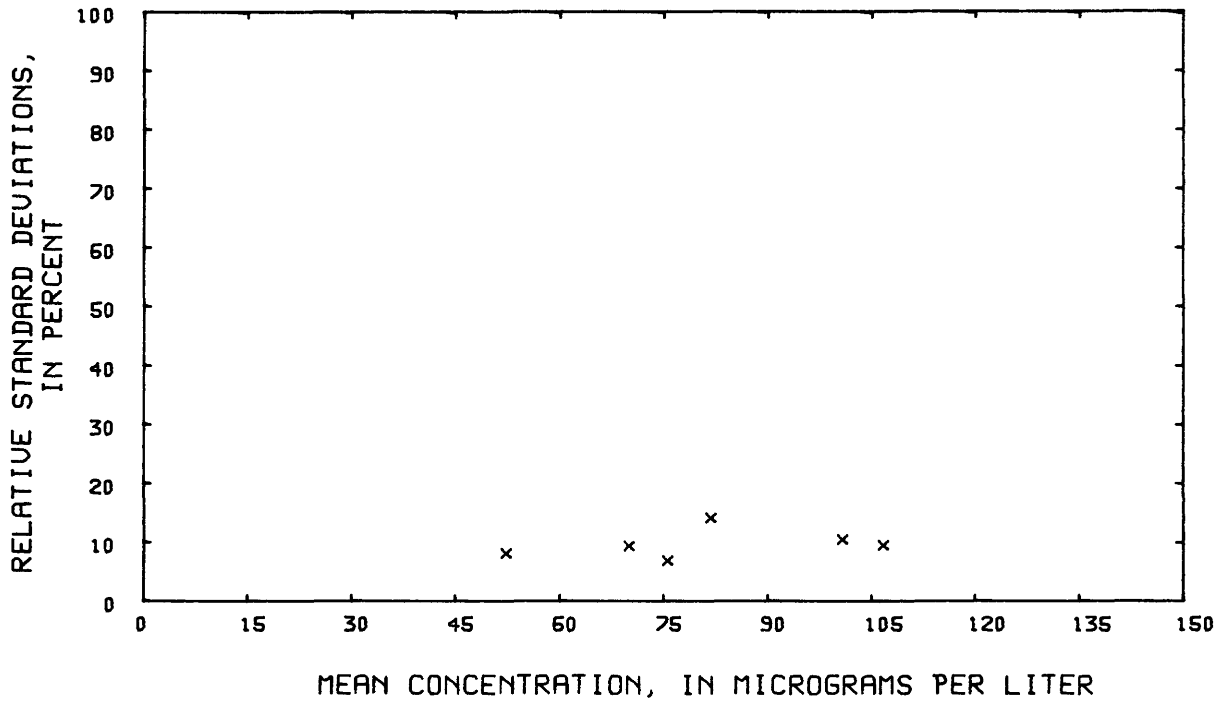

Figure 105.--Precision data for iron, dissolved, (atomic absorption spectrometry) at the National Water Quality Laboratory.

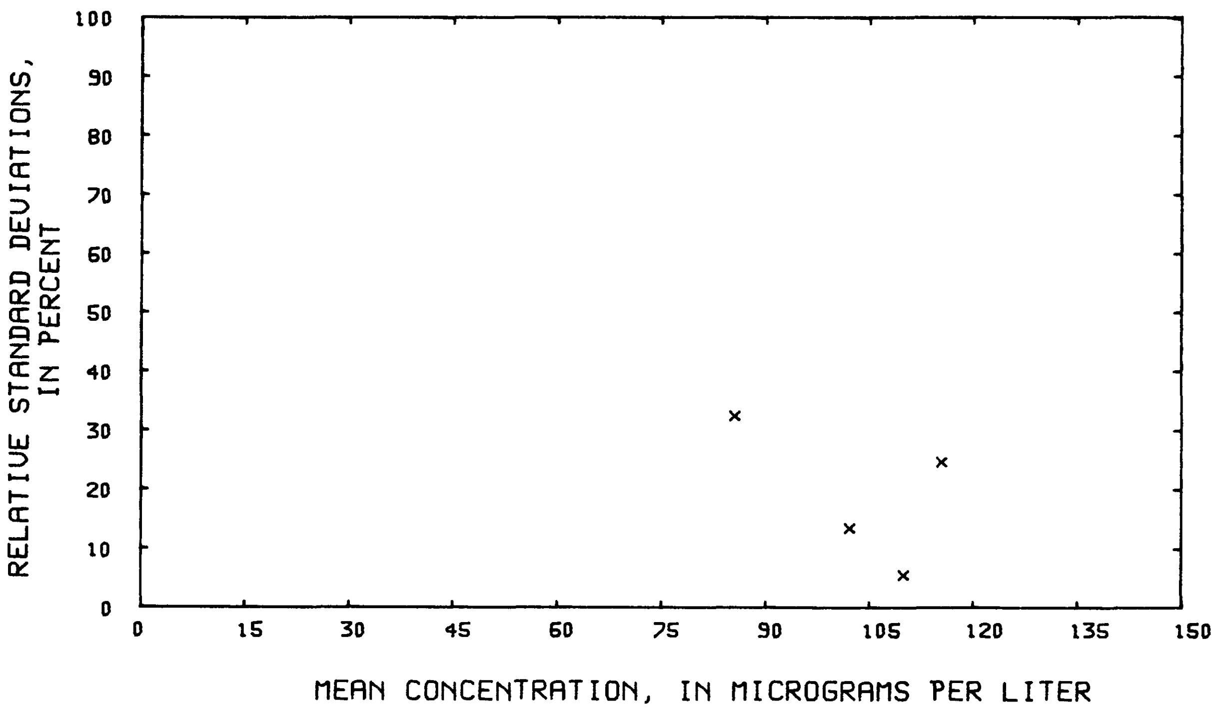

Figure 106.--Precision data for iron, total recoverable, at the National Water Quality Laboratory.

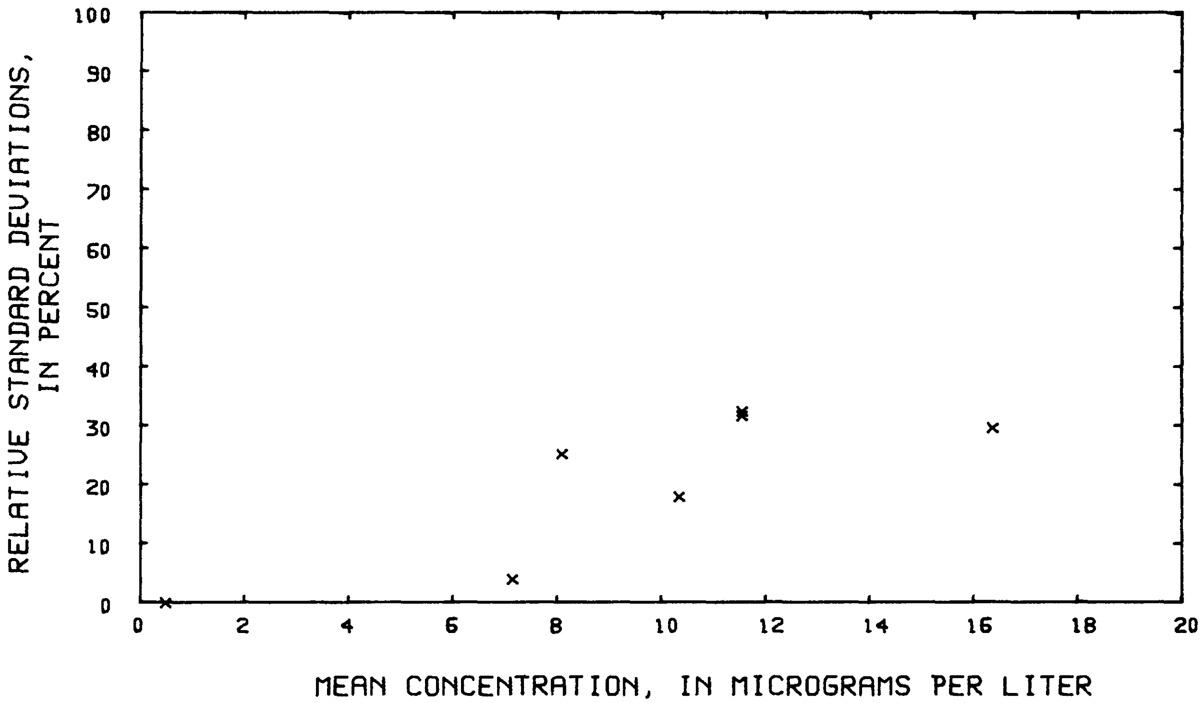

Figure 107.--Precision data for lead, dissolved, (inductively coupled plasma emission spectrometry) at the National Water Quality Laboratory.

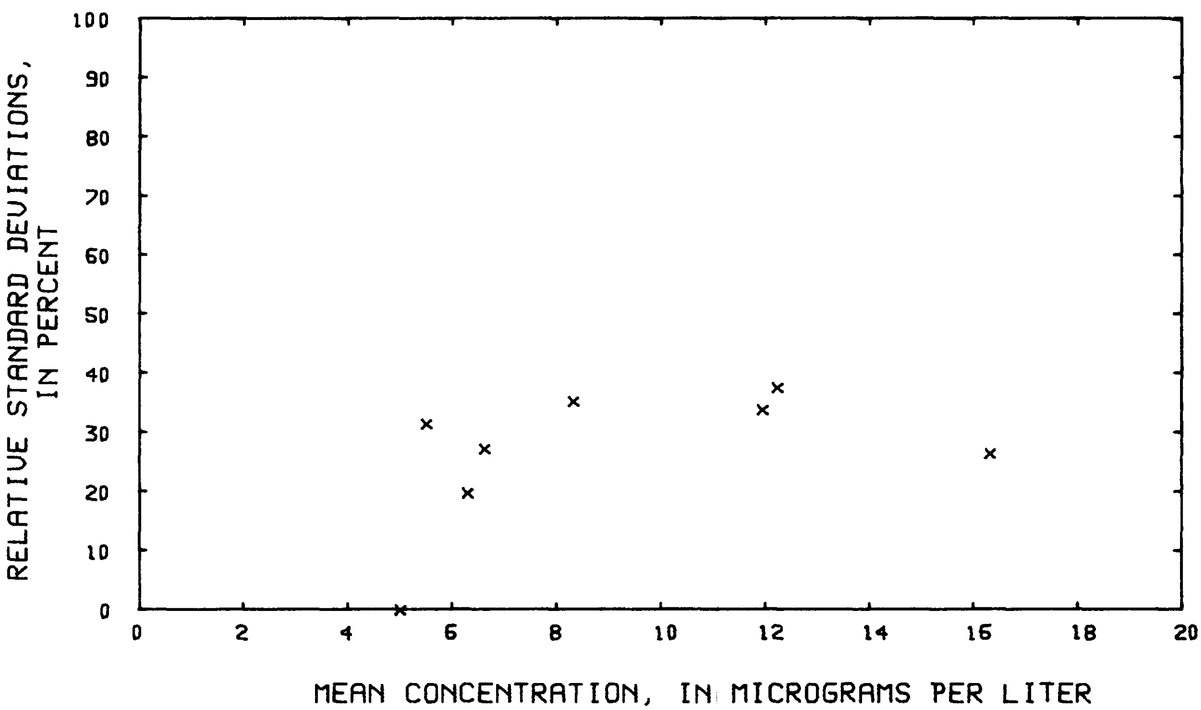

Figure 108.--Precision data for lead, dissolved, (atomic absorption spectrometry) at the National Water Quality Laboratory.

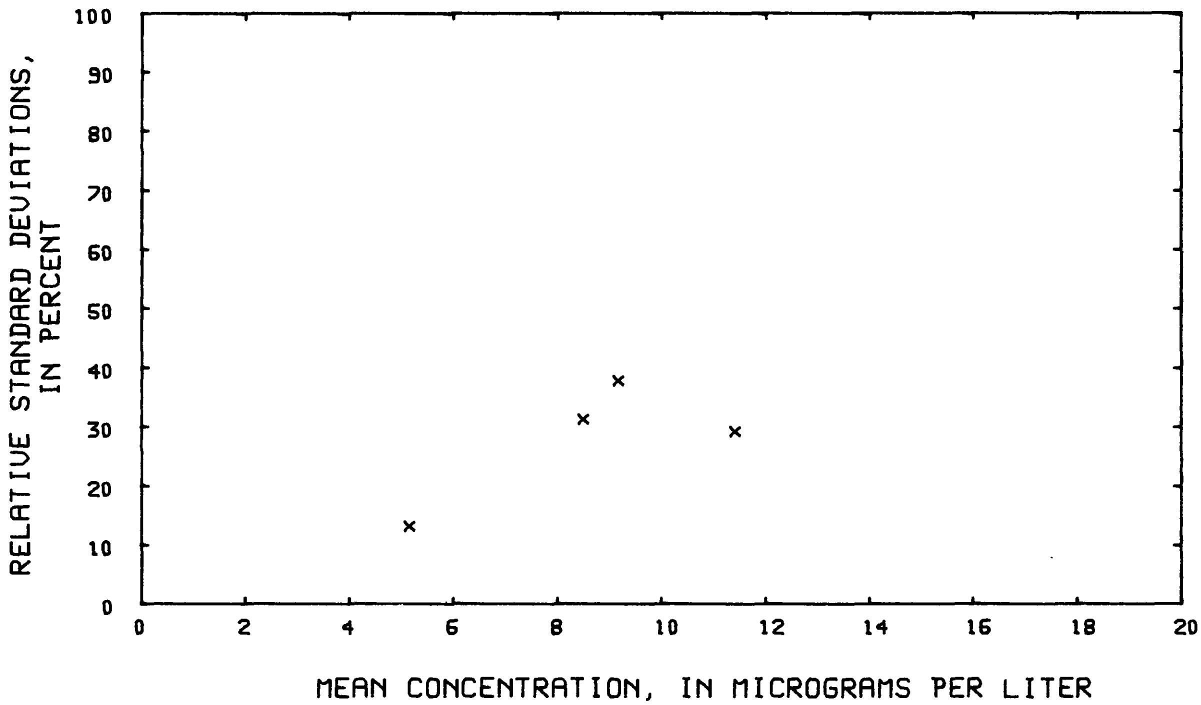

Figure 109.--Precision data for lead, total recoverable, at the National Water Quality Laboratory.

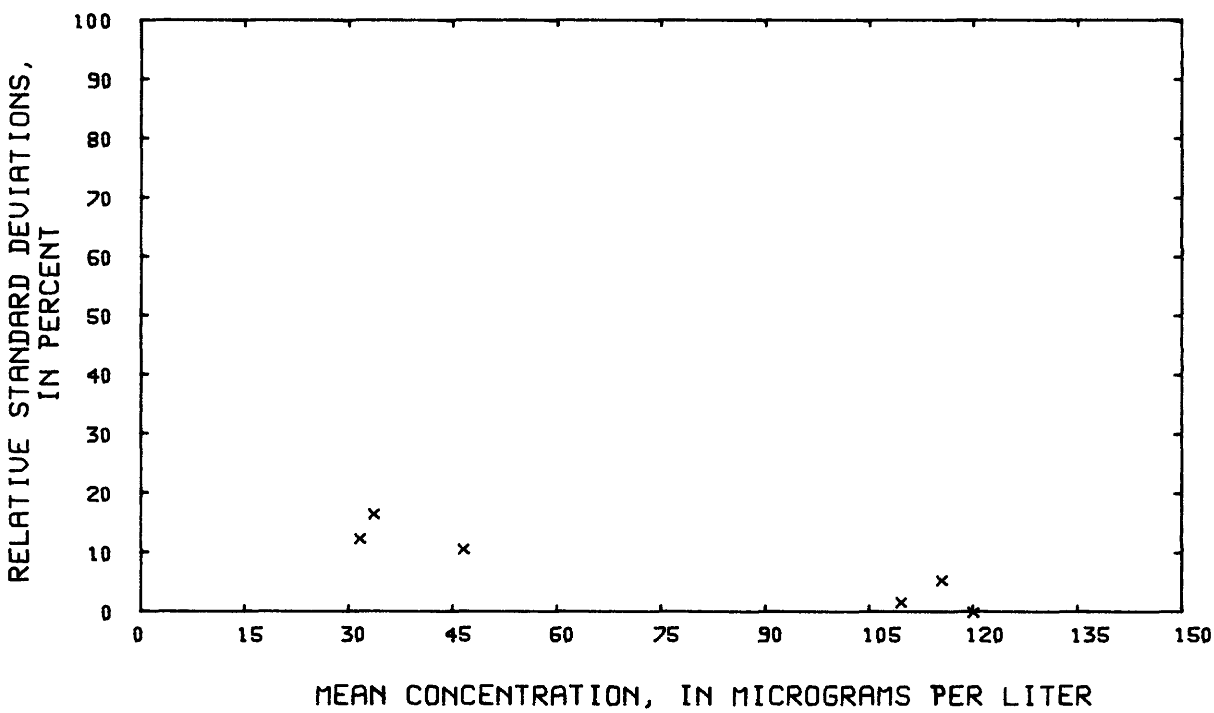

Figure 110.--Precision data for lithium, dissolved, at the National Water Quality Laboratory.

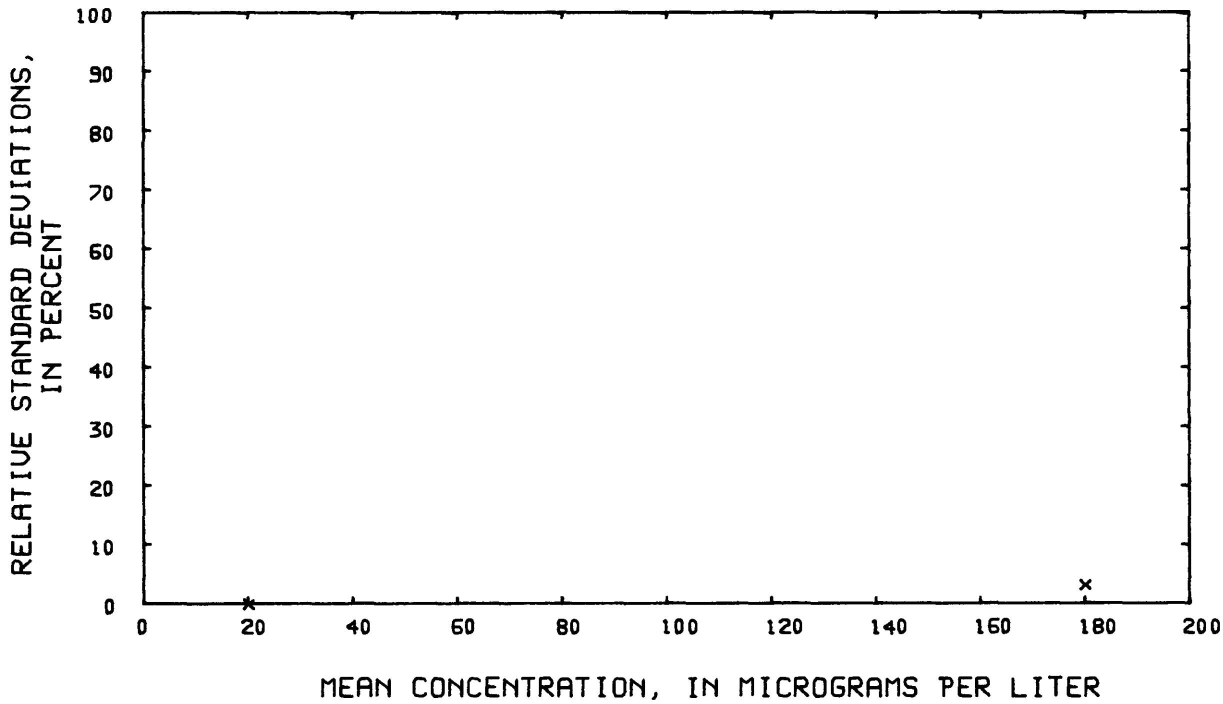

Figure 111.--Precision data for lithium, total recoverable, at the National Water Quality Laboratory.

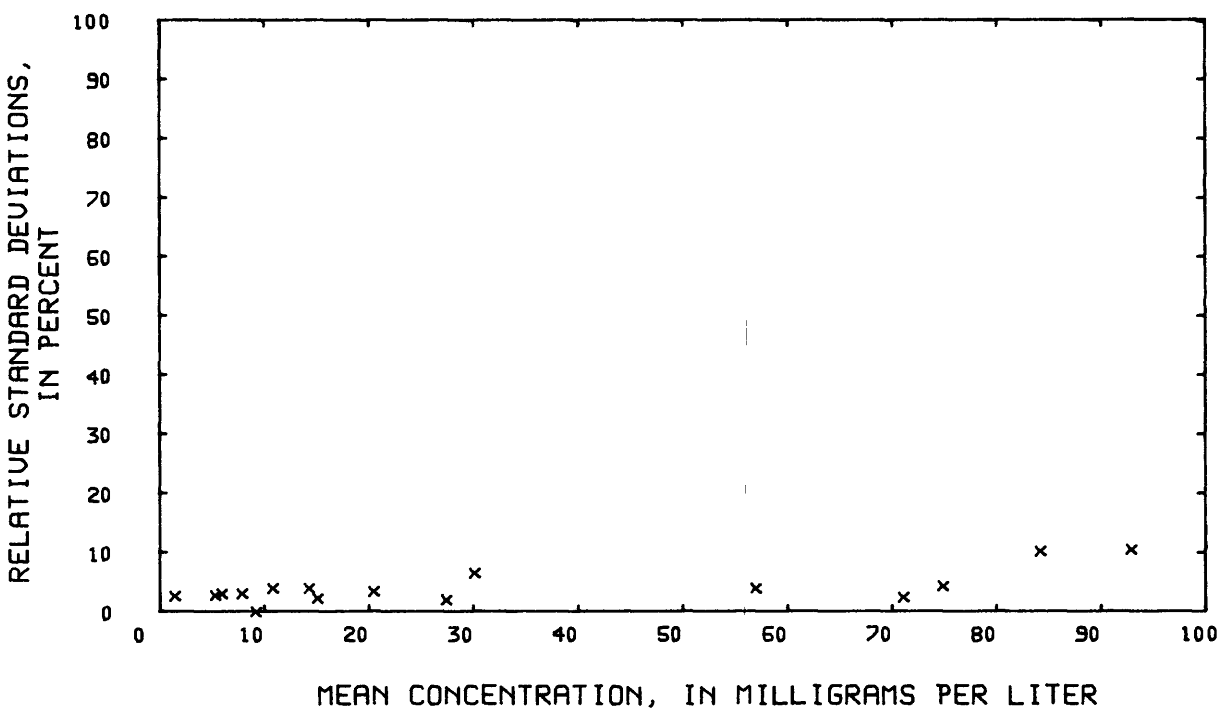

Figure 112.--Precision data for magnesium, dissolved, (inductively coupled plasma emission spectrometry) at the National Water Quality Laboratory.

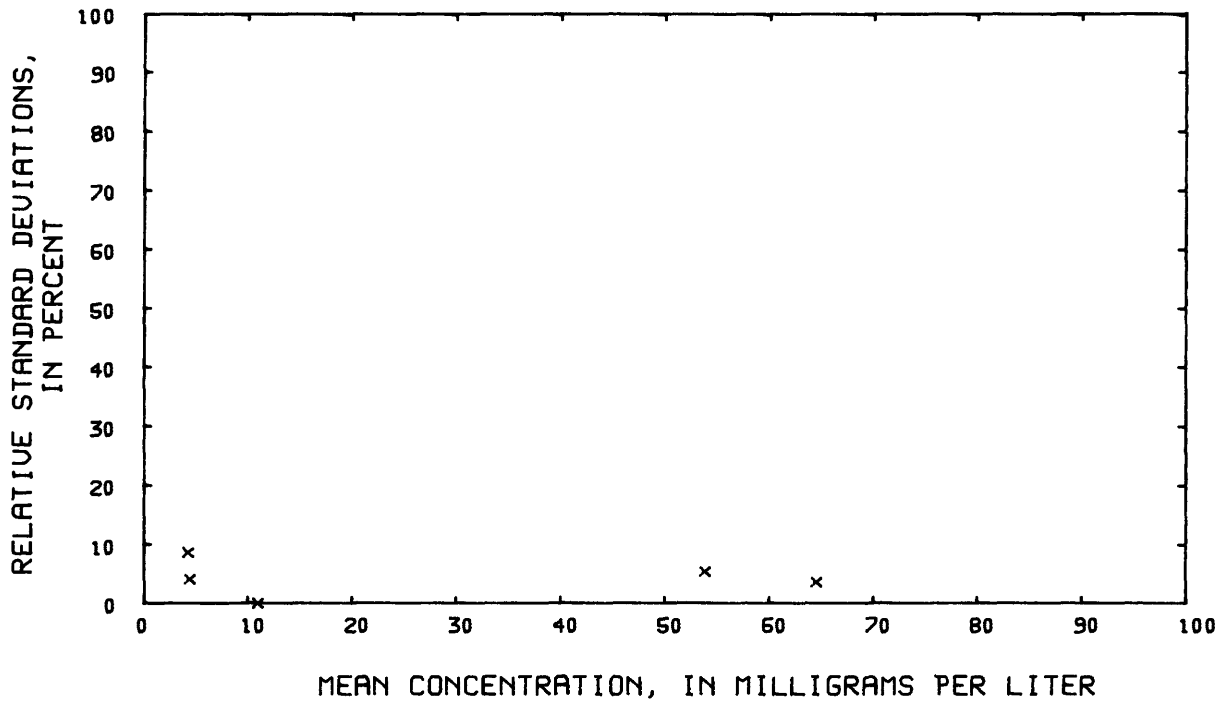

Figure 113.--Precision data for magnesium, dissolved, (atomic absorption spectrometry) at the National Water Quality Laboratory.

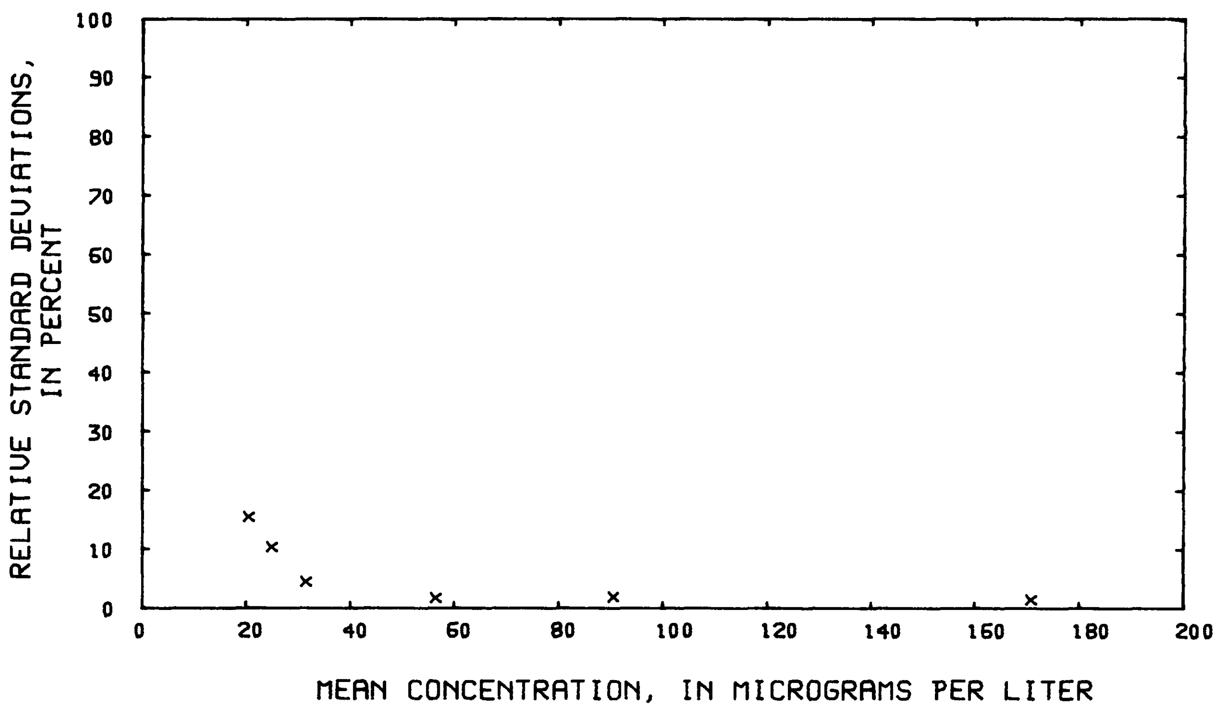

Figure 114.--Precision data for manganese, dissolved, at the National Water Quality Laboratory.

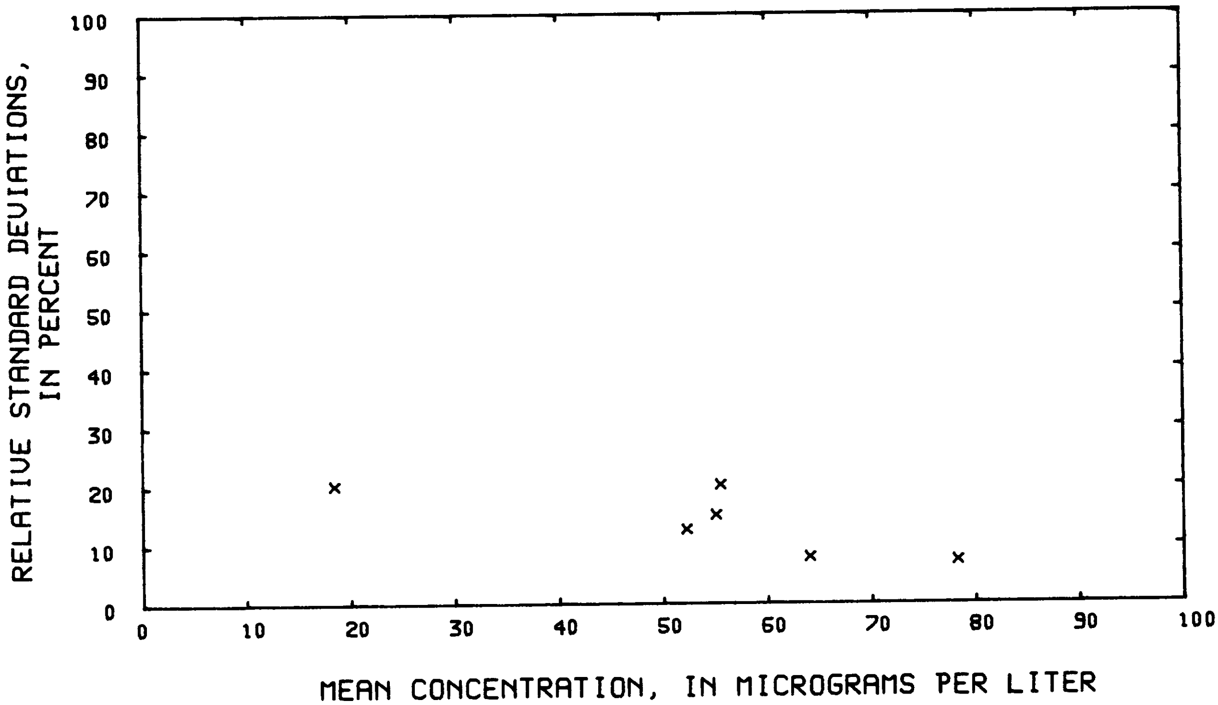

Figure 115.--Precision data for manganese, dissolved, (atomic absorption spectrometry) at the National Water Quality Laboratory.

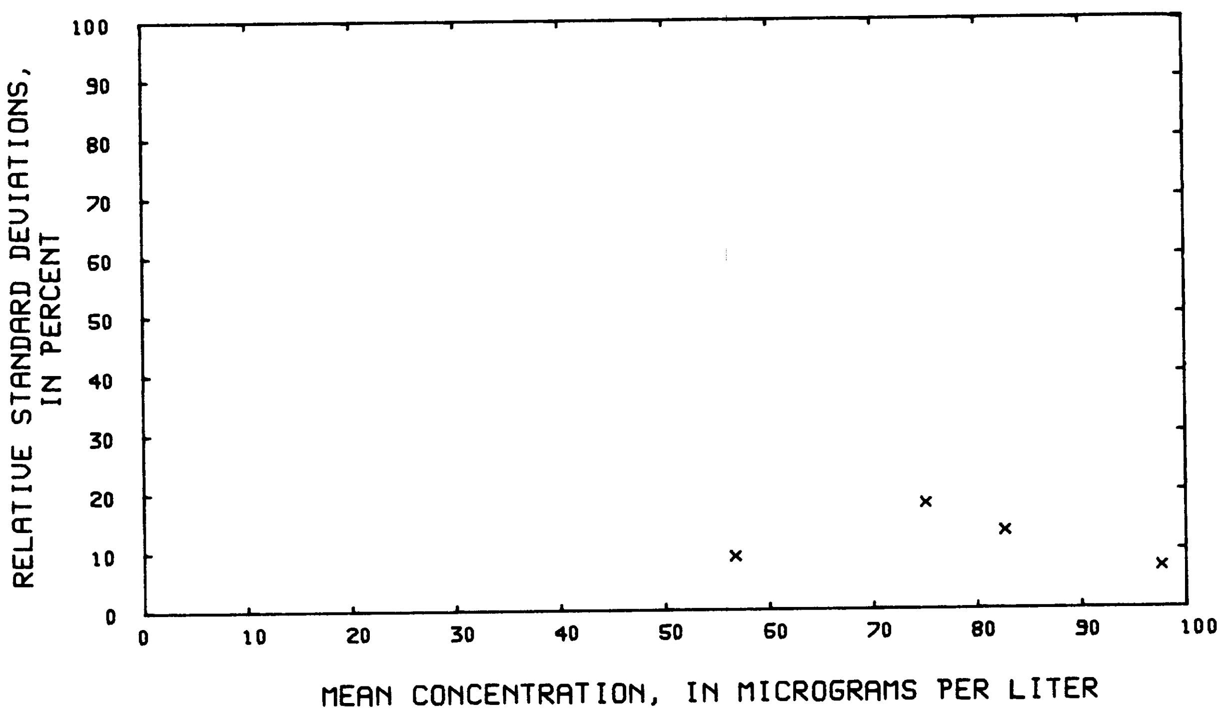

Figure 116.--Precision data for manganese, total recoverable, at the National Water Quality Laboratory.

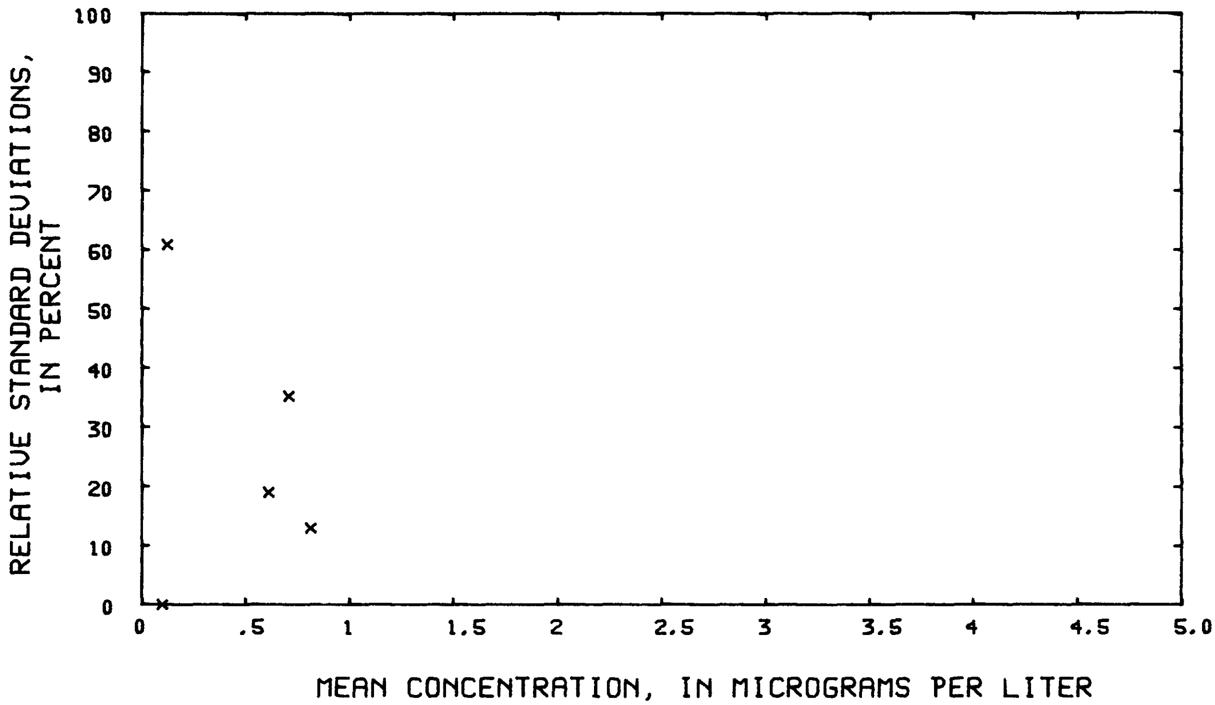

Figure 117.--Precision data for mercury, dissolved, at the National Water Quality Laboratory.

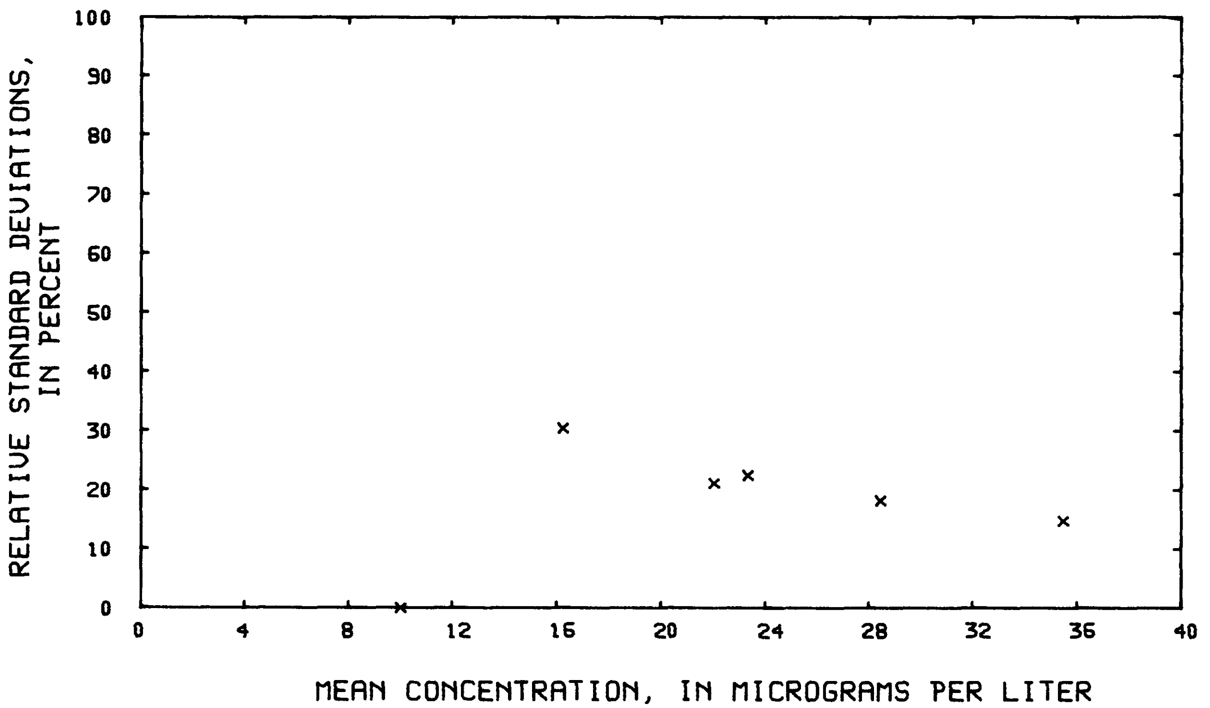

Figure 118.--Precision data for molybdenum, dissolved, (inductively coupled plasma emission spectrometry) at the National Water Quality Laboratory.

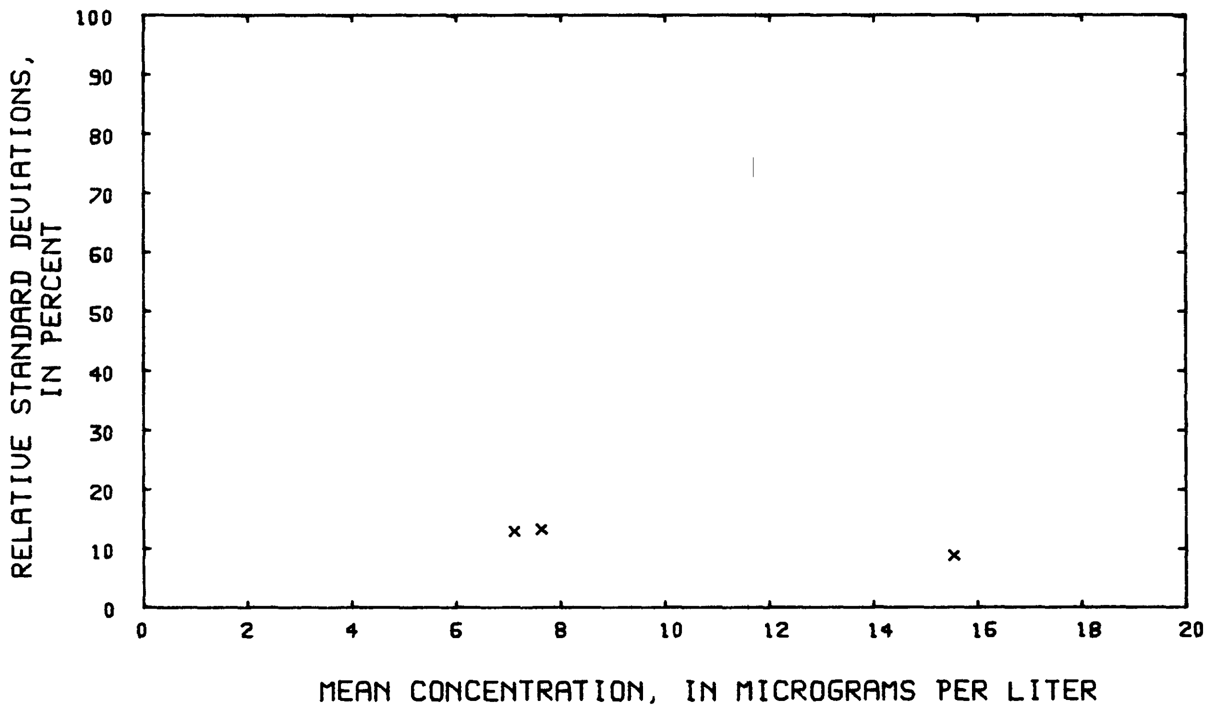

Figure 119.--Precision data for molybdenum, dissolved, (atomic absorption spectrometry) at the National Water Quality Laboratory.

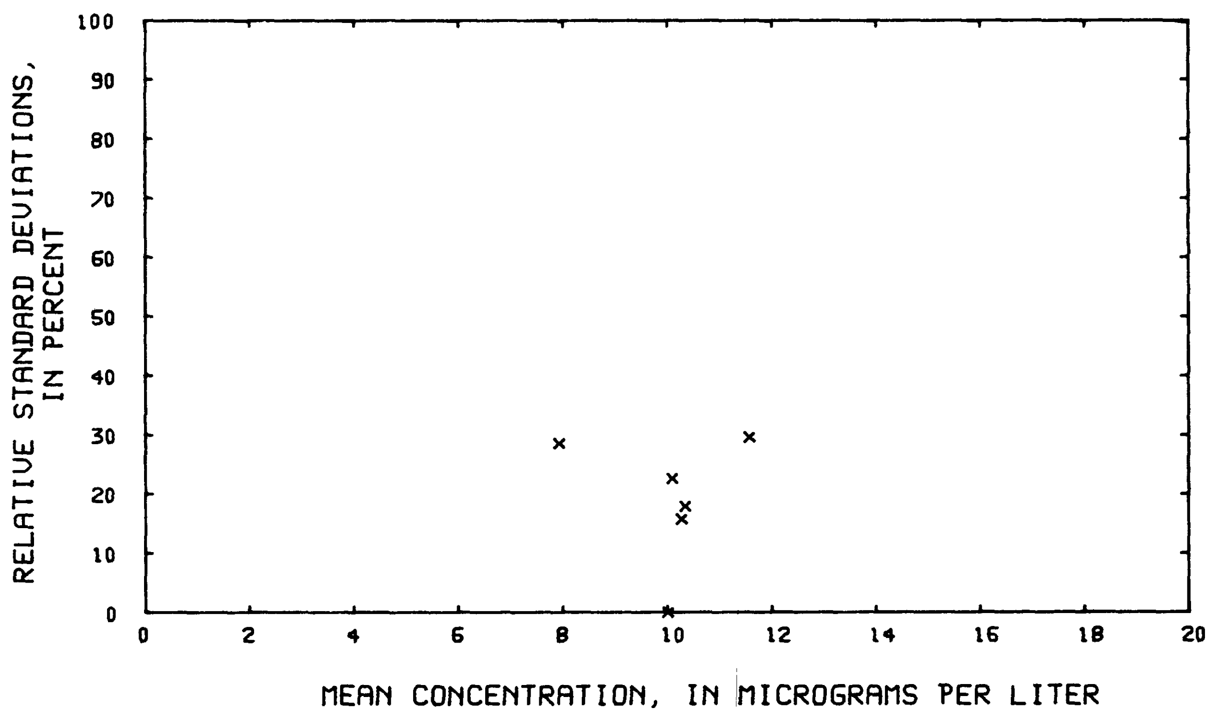

Figure 120.--Precision data for nickel, dissolved, (inductively coupled plasma emission spectrometry) at the National Water Quality Laboratory.

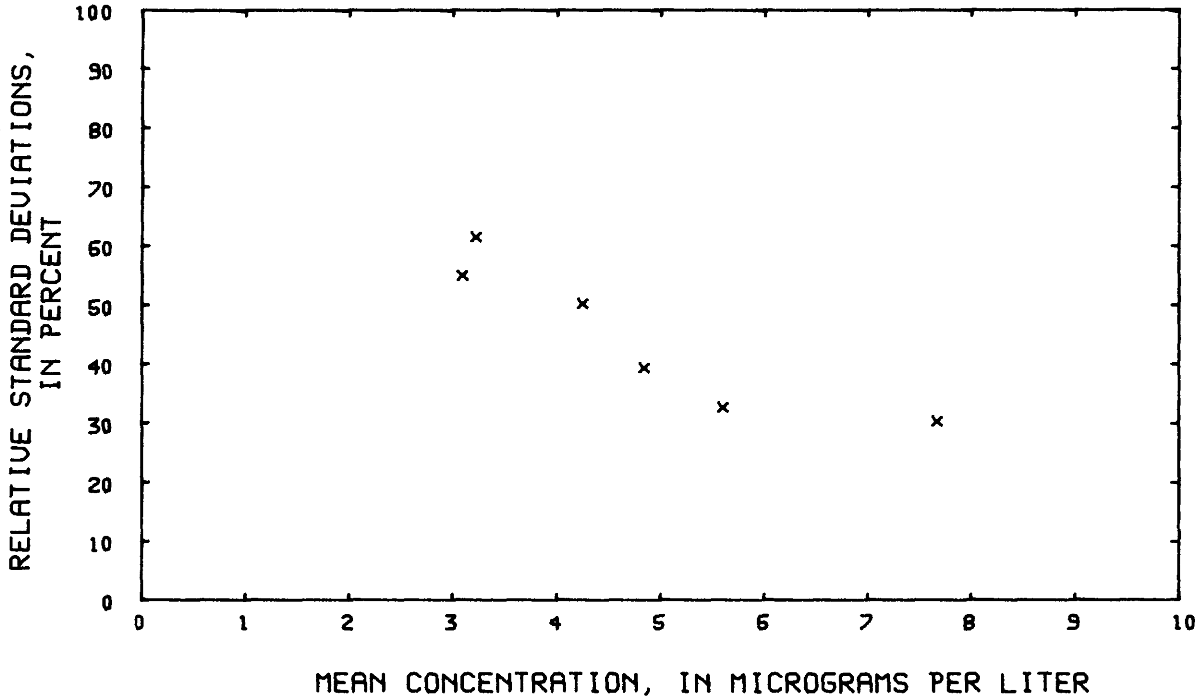

Figure 121.--Precision data for nickel, dissolved, (atomic absorption spectrometry) at the National Water Quality Laboratory.

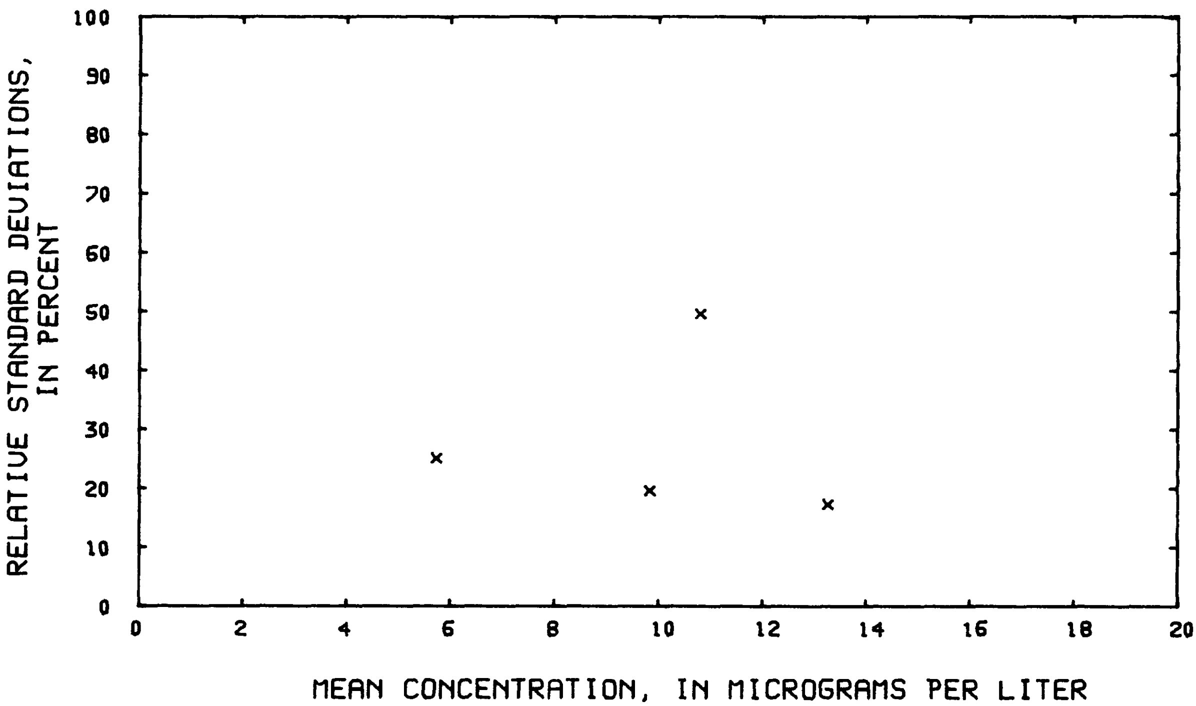

Figure 122.--Precision data for nickel, total recoverable, at the National Water Quality Laboratory.

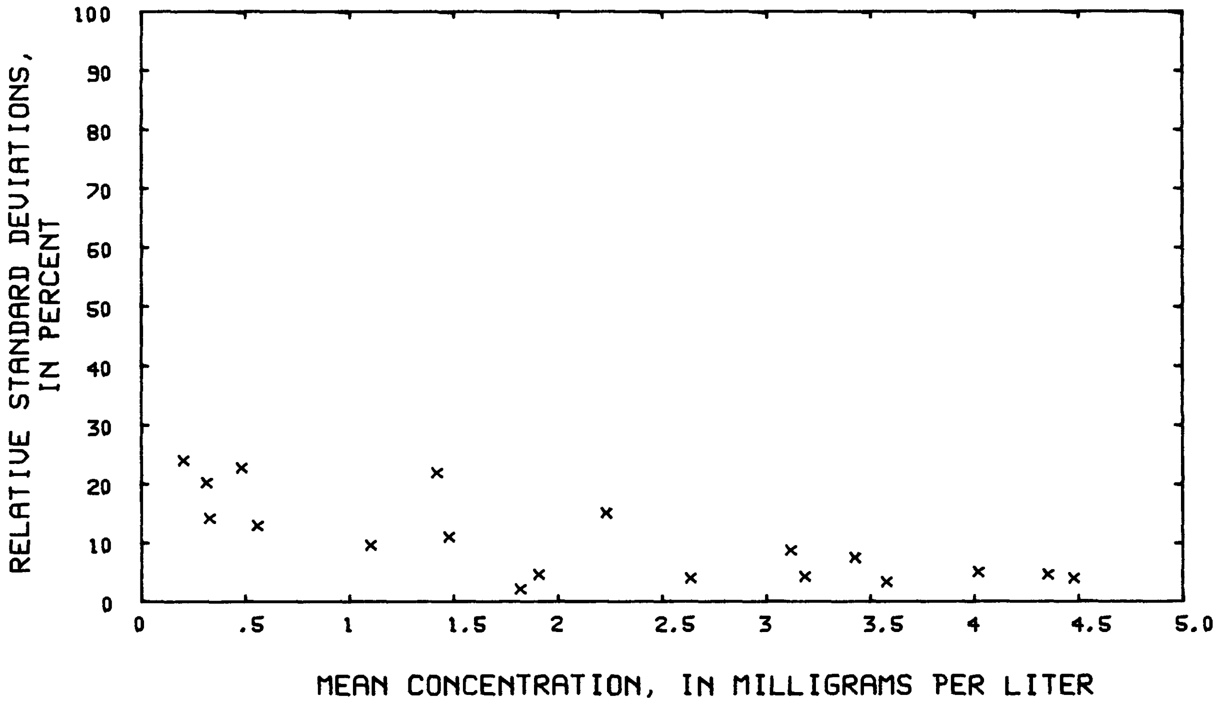

Figure 123.--Precision data for potassium, dissolved, at the National Water Quality Laboratory.

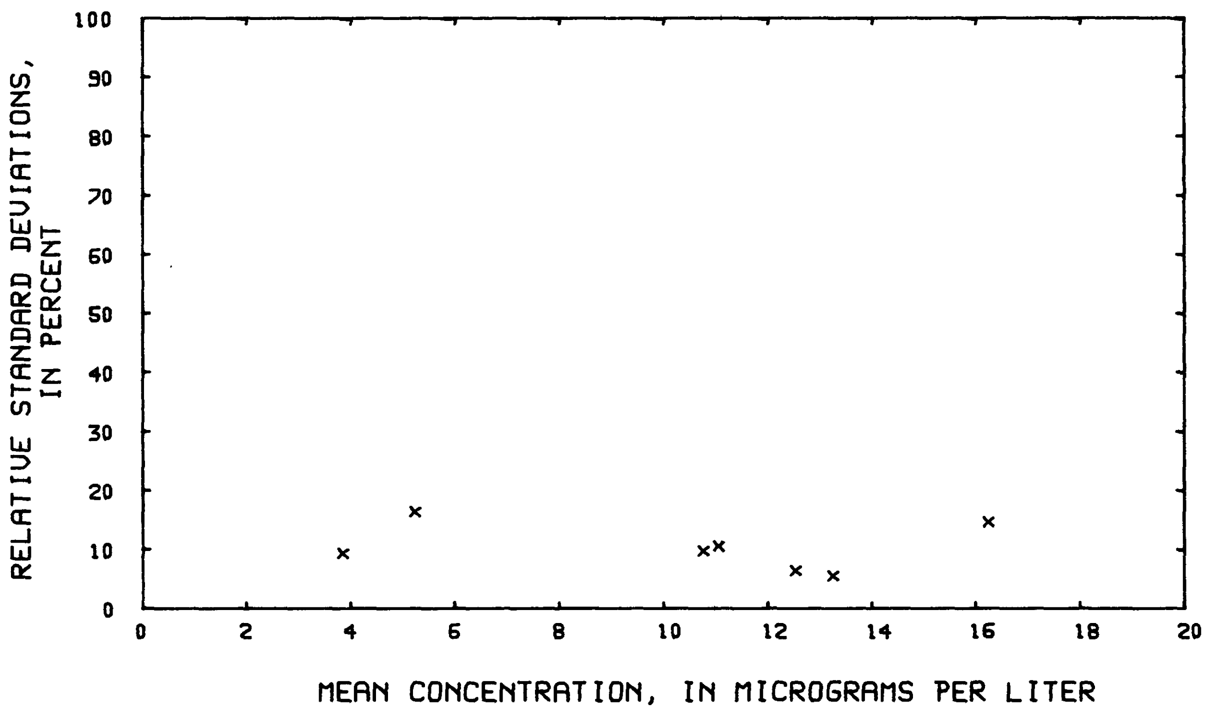

Figure 124.--Precision data for selenium, dissolved, at the National Water Quality Laboratory.

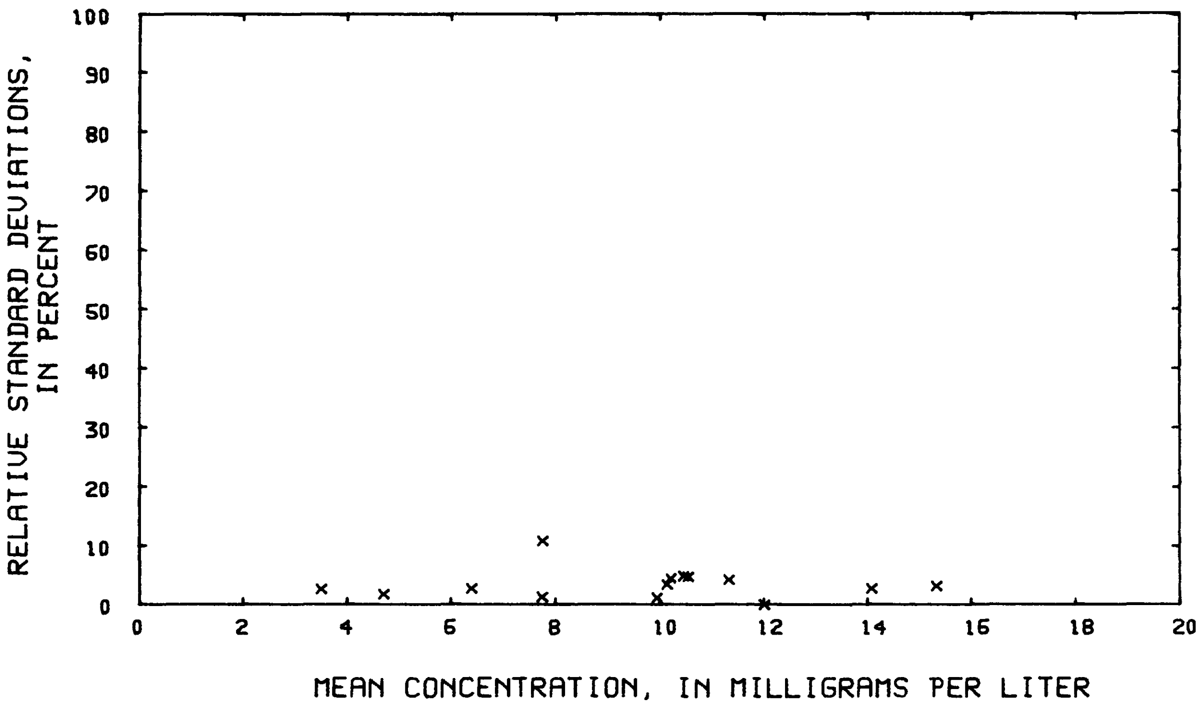

Figure 125.--Precision data for silica, dissolved, (inductively coupled plasma emission spectrometry) at the National Water Quality Laboratory.

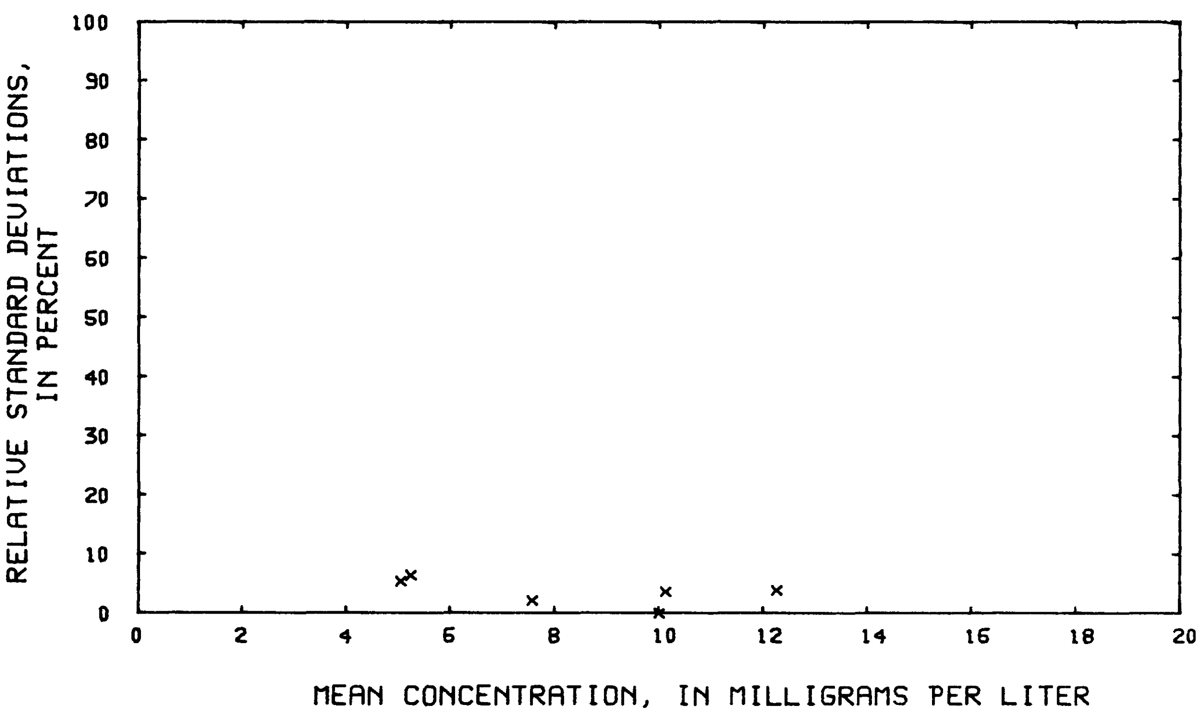

Figure 126.--Precision data for silica, dissolved, (colorimetry) at the National Water Quality Laboratory.

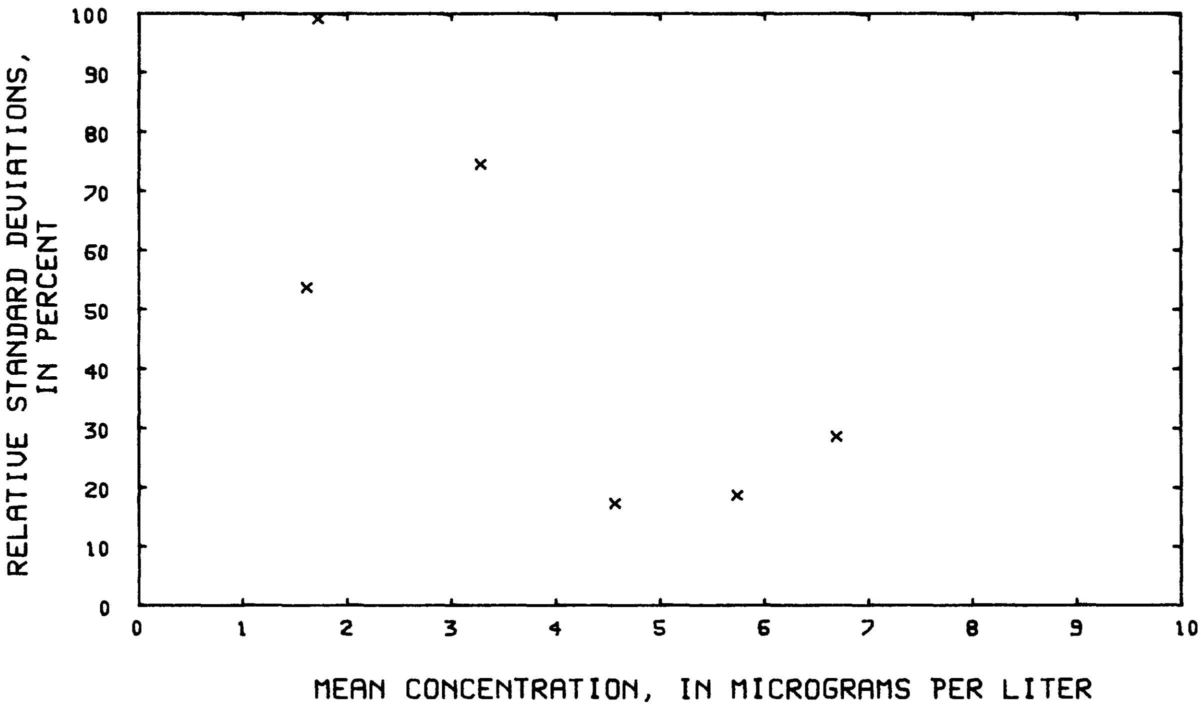

Figure 127.--Precision data for silver, dissolved, (inductively coupled plasma emission spectrometry) at the National Water Quality Laboratory.

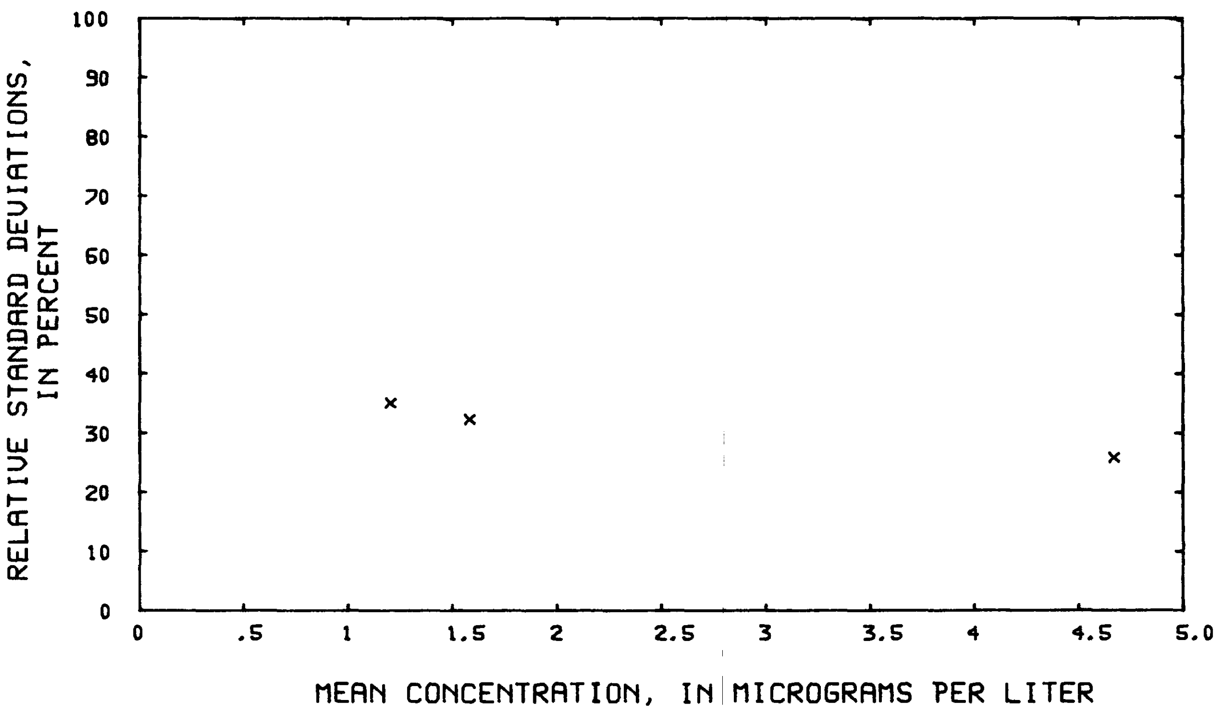

Figure 128.--Precision data for silver, dissolved, (atomic absorption spectrometry) at the National Water Quality Laboratory.

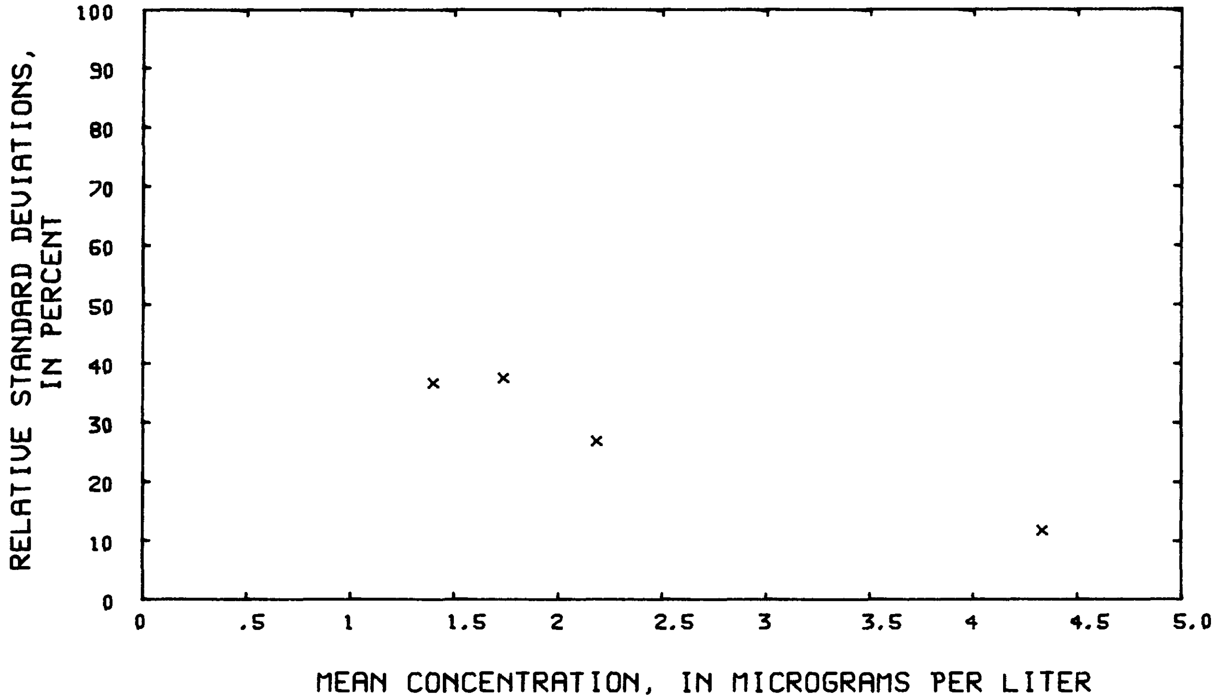

Figure 129.--Precision data for silver, total recoverable, at the National Water Quality Laboratory.

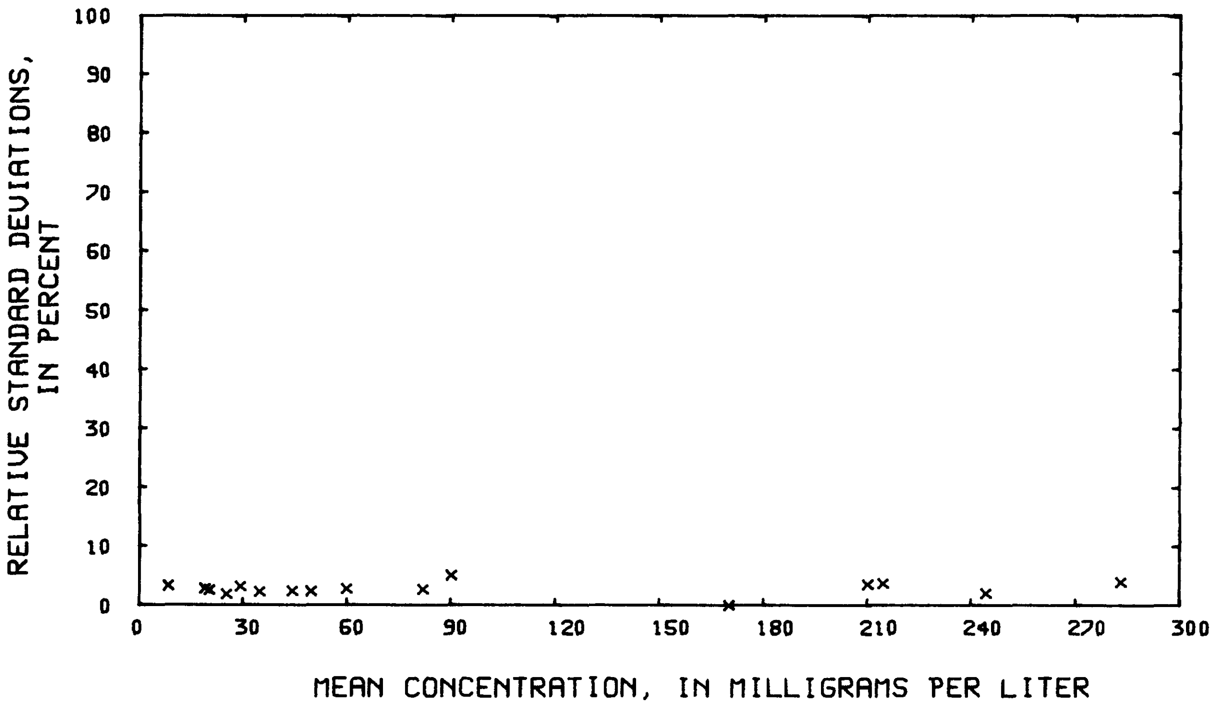

Figure 130.--Precision data for sodium, dissolved, (inductively coupled plasma emission spectrometry) at the National Water Quality Laboratory.

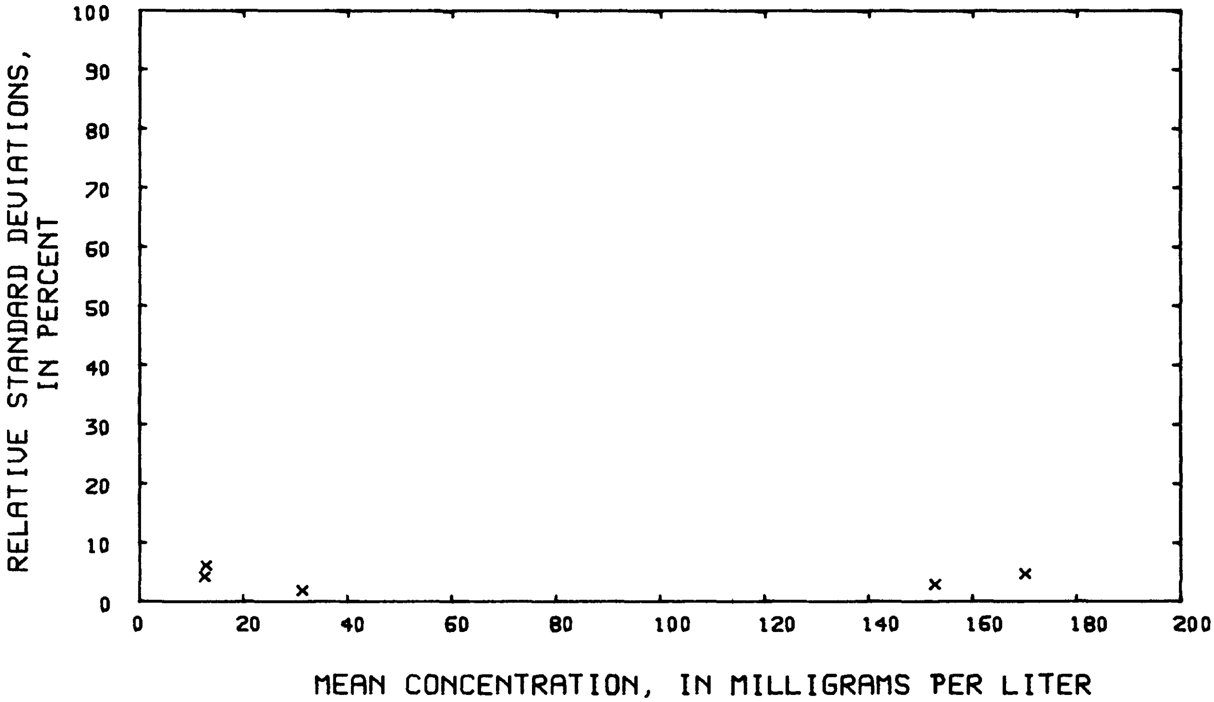

Figure 131.--Precision data for sodium, dissolved, (atomic absorption spectrometry) at the National Water Quality Laboratory.

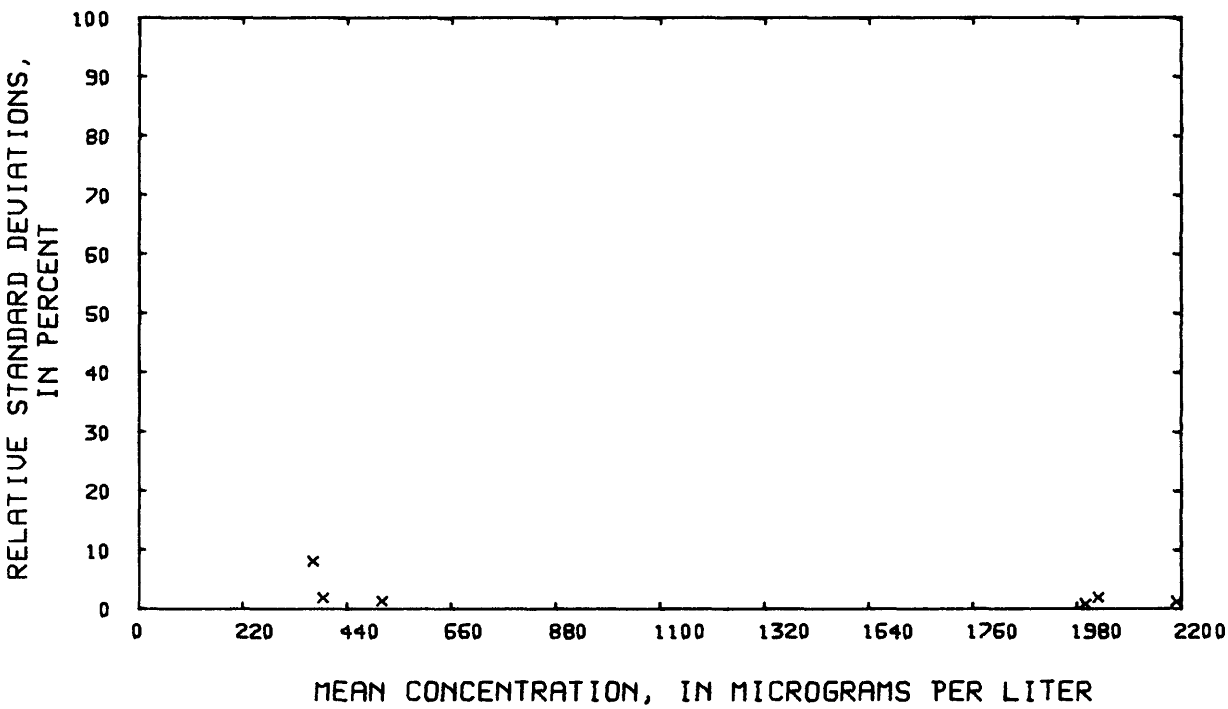

Figure 132.--Precision data for strontium, dissolved, at the National Water Quality Laboratory.

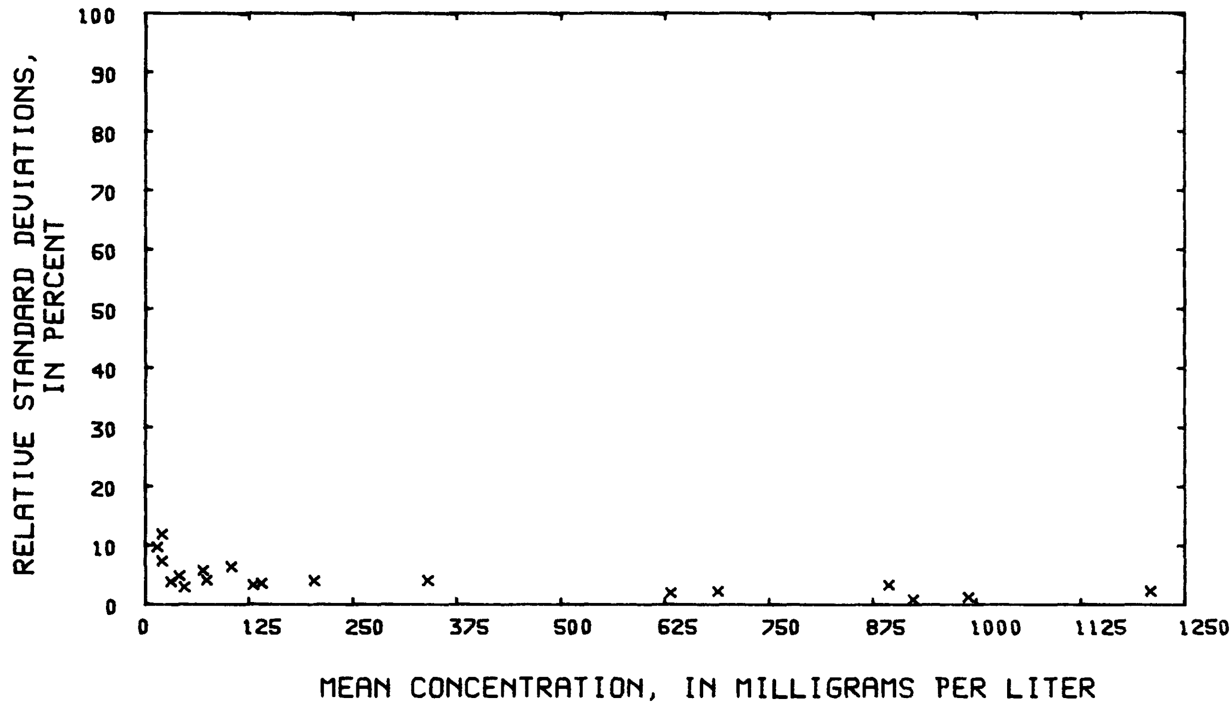

Figure 133.--Precision data for sulfate, dissolved, at the National Water Quality Laboratory.

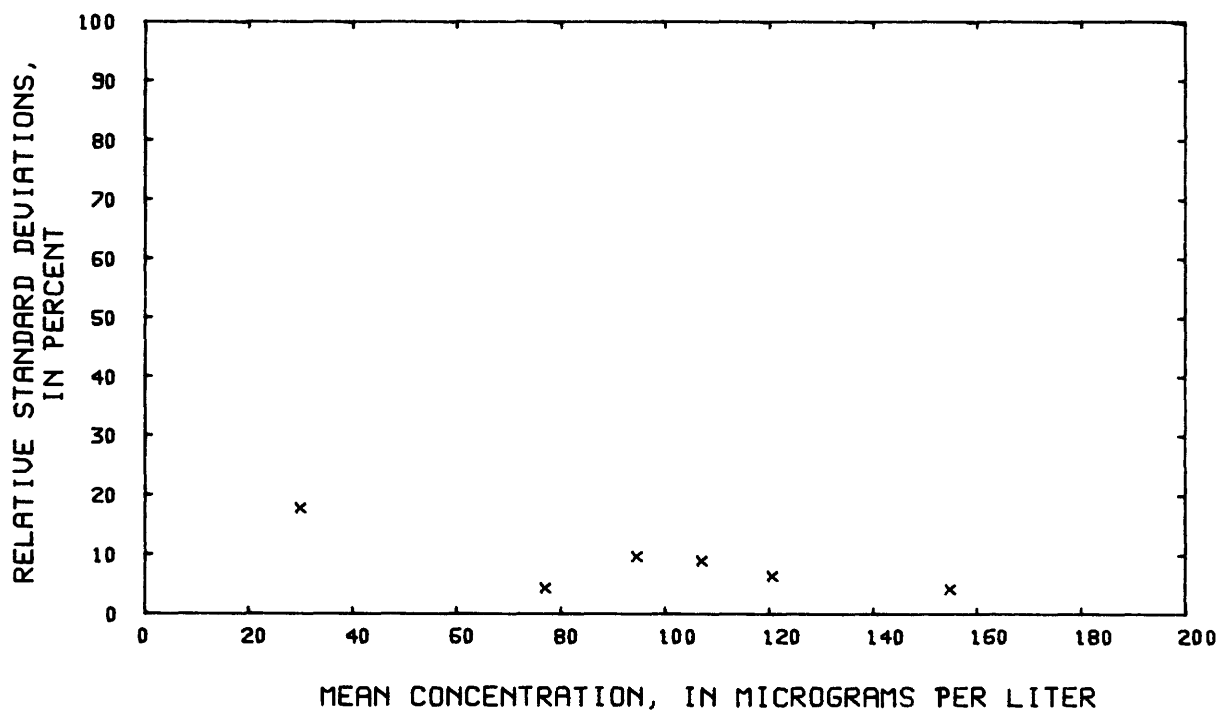

Figure 134.--Precision data for zinc, dissolved, (inductively coupled plasma emission spectrometry) at the National Water Quality Laboratory.

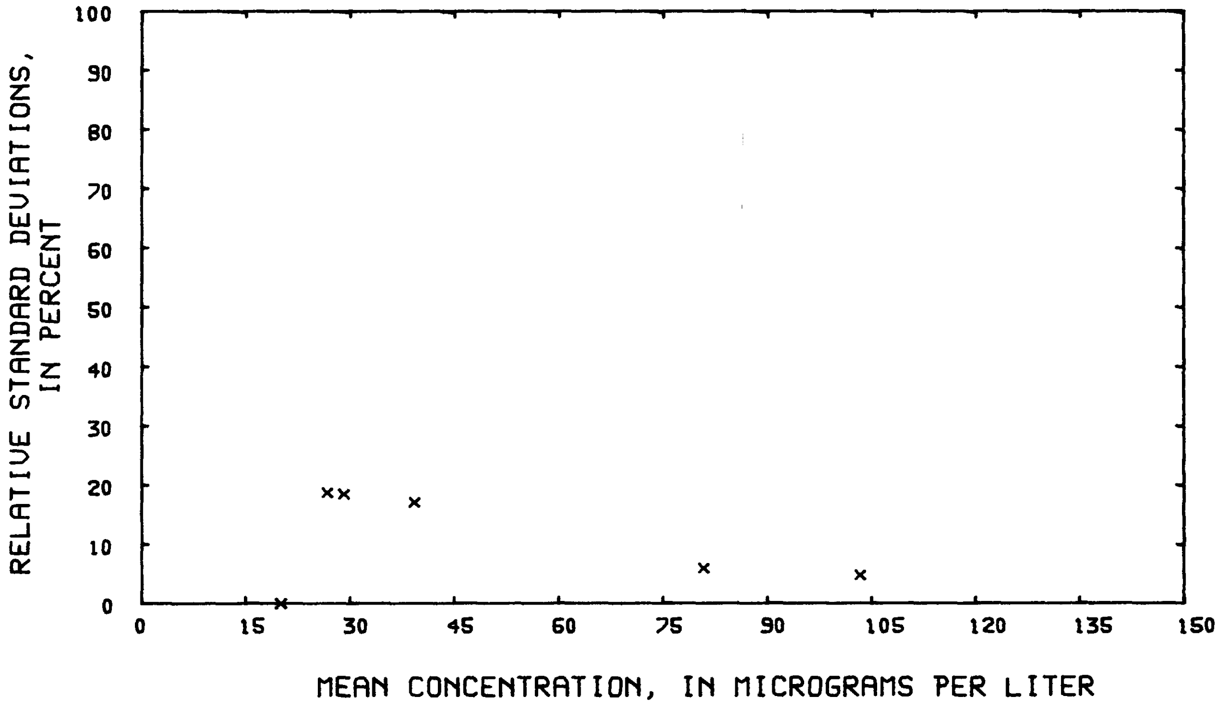

Figure 135.--Precision data for zinc, dissolved, (atomic absorption spectrometry) at the National Water Quality Laboratory.

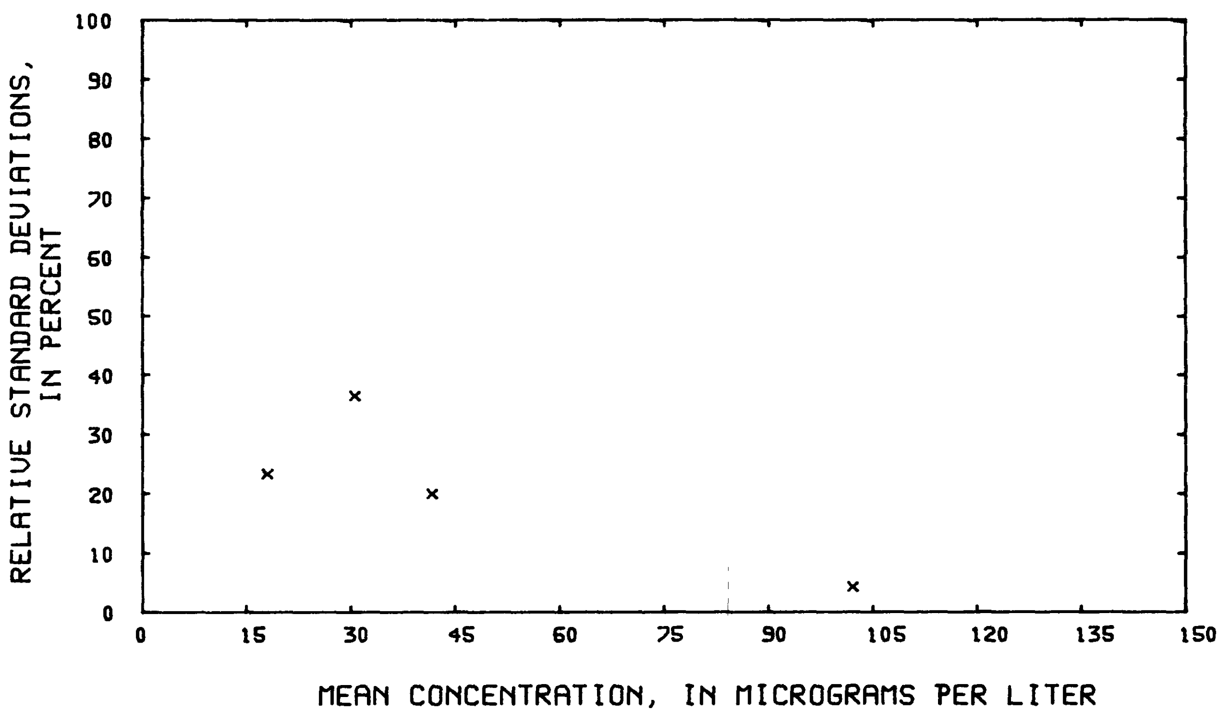

Figure 136.--Precision data for zinc, total recoverable, at the National Water Quality Laboratory.

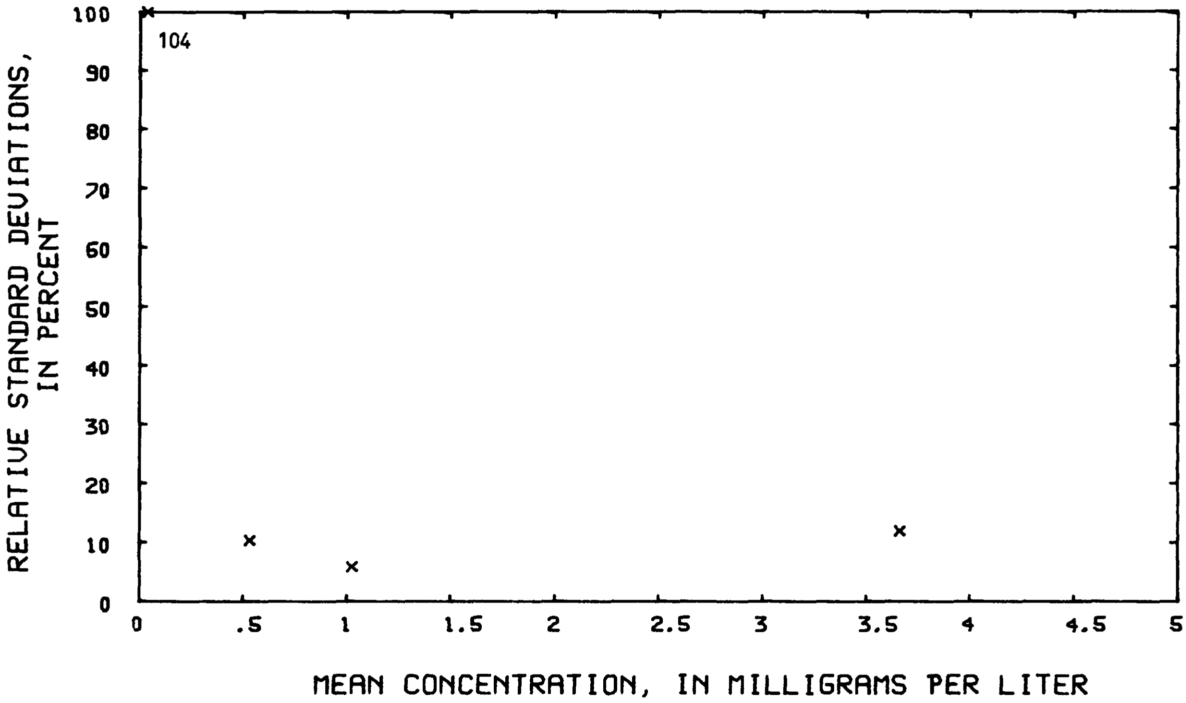

Figure 137.--Precision data for ammonia nitrogen as N, dissolved, at the National Water Quality Laboratory.

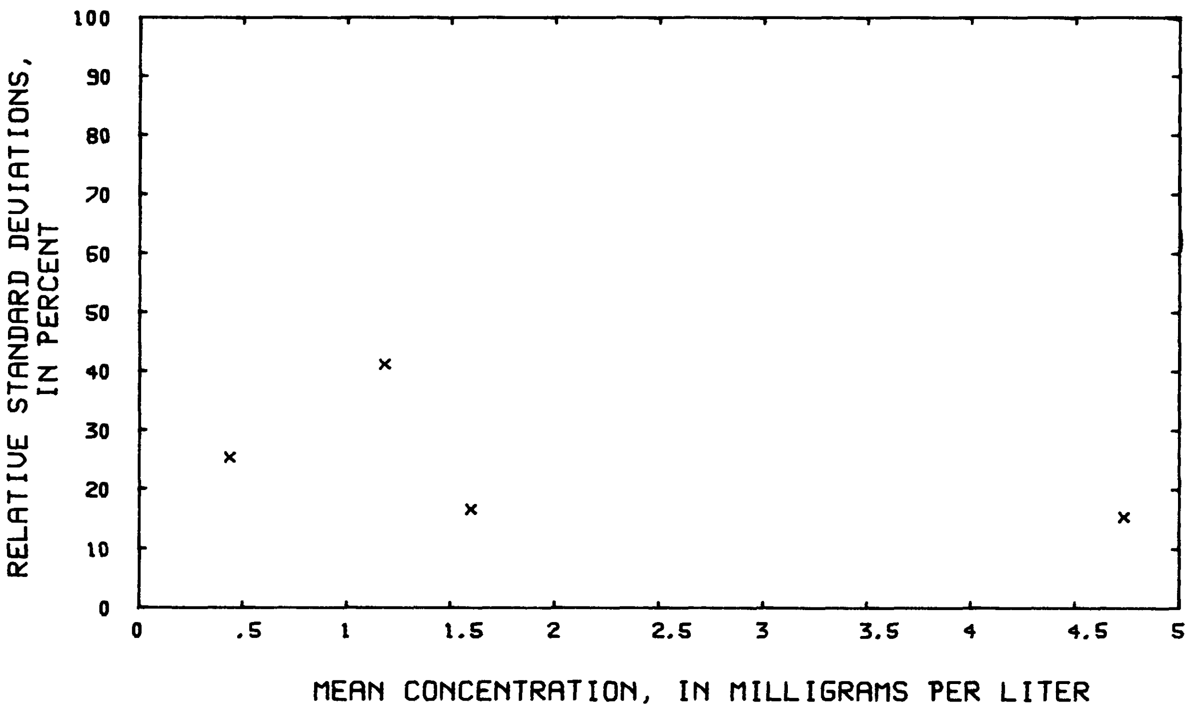

Figure 138.--Precision data for ammonia + organic nitrogen as N, dissolved, at the National Water Quality Laboratory.

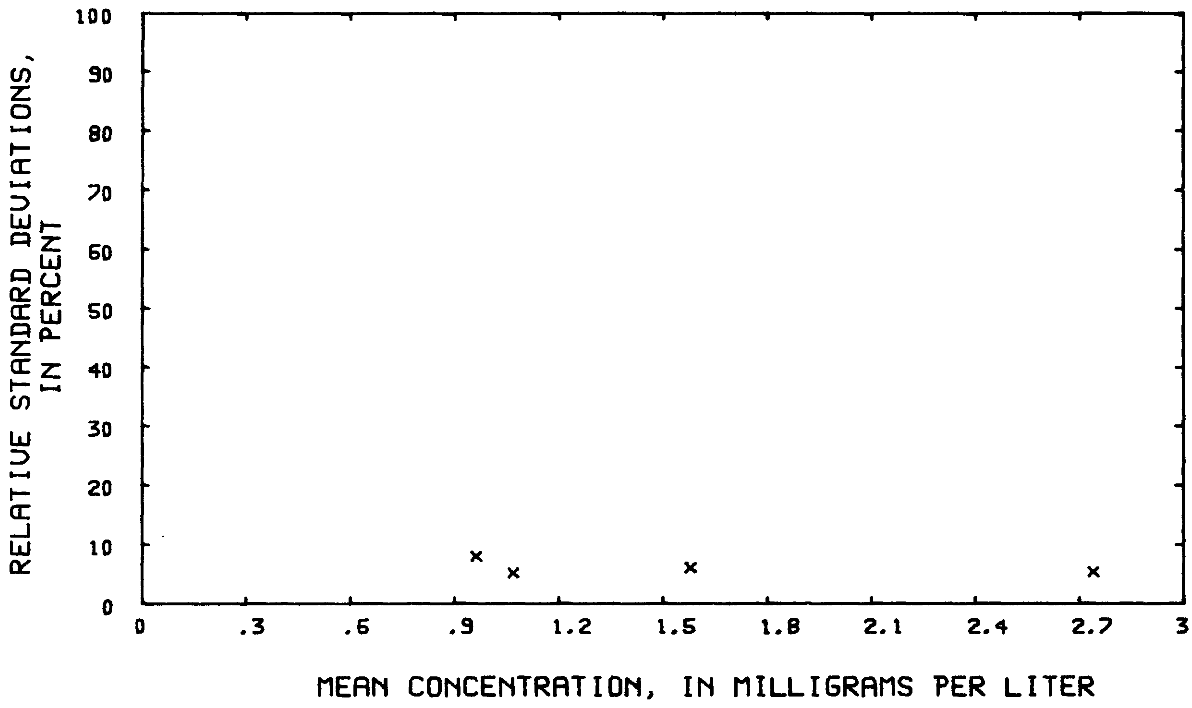

Figure 139.--Precision data for nitrate + nitrite nitrogen as N, dissolved, at the National Water Quality Laboratory.

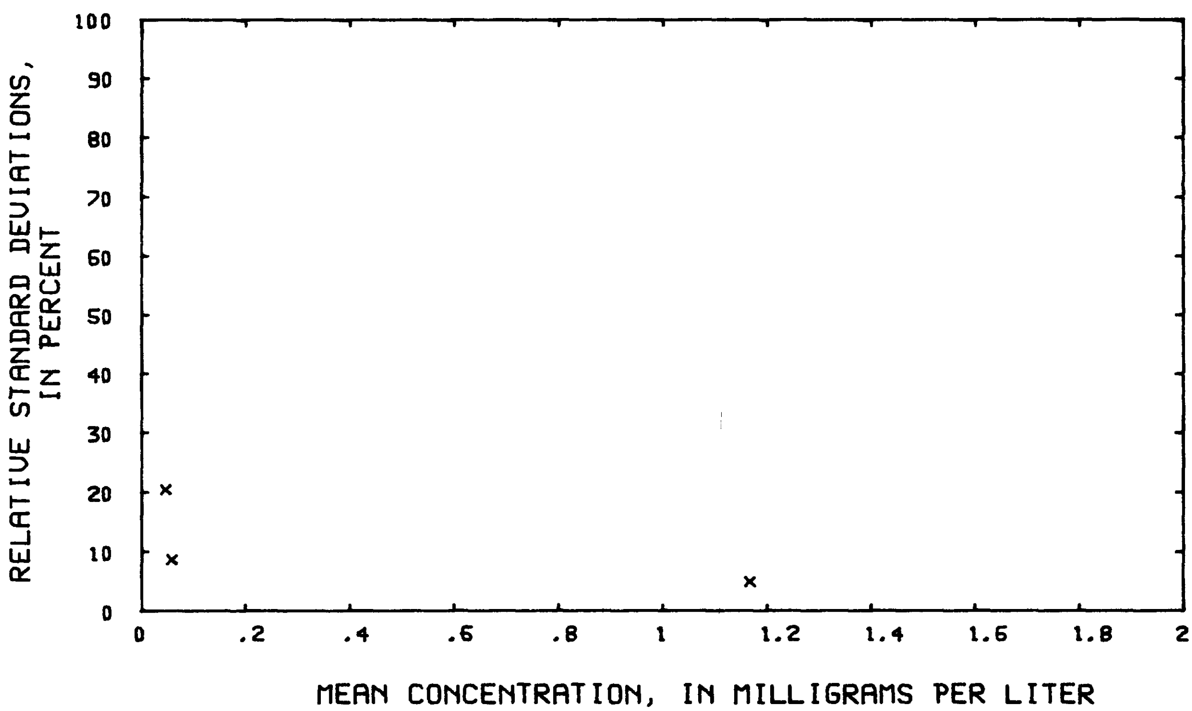

Figure 140.--Precision data for nitrite nitrogen as N, dissolved, at the National Water Quality Laboratory.

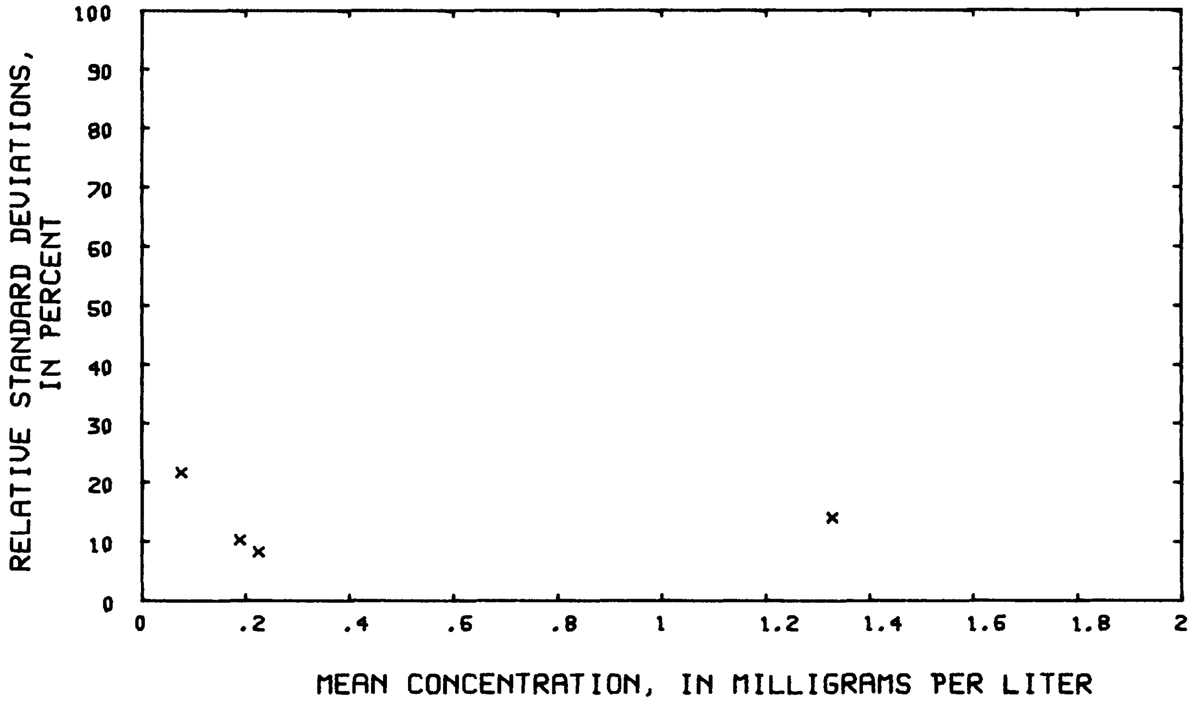

Figure 141.--Precision data for orthophosphate phosphorus as P, dissolved, at the National Water Quality Laboratory.

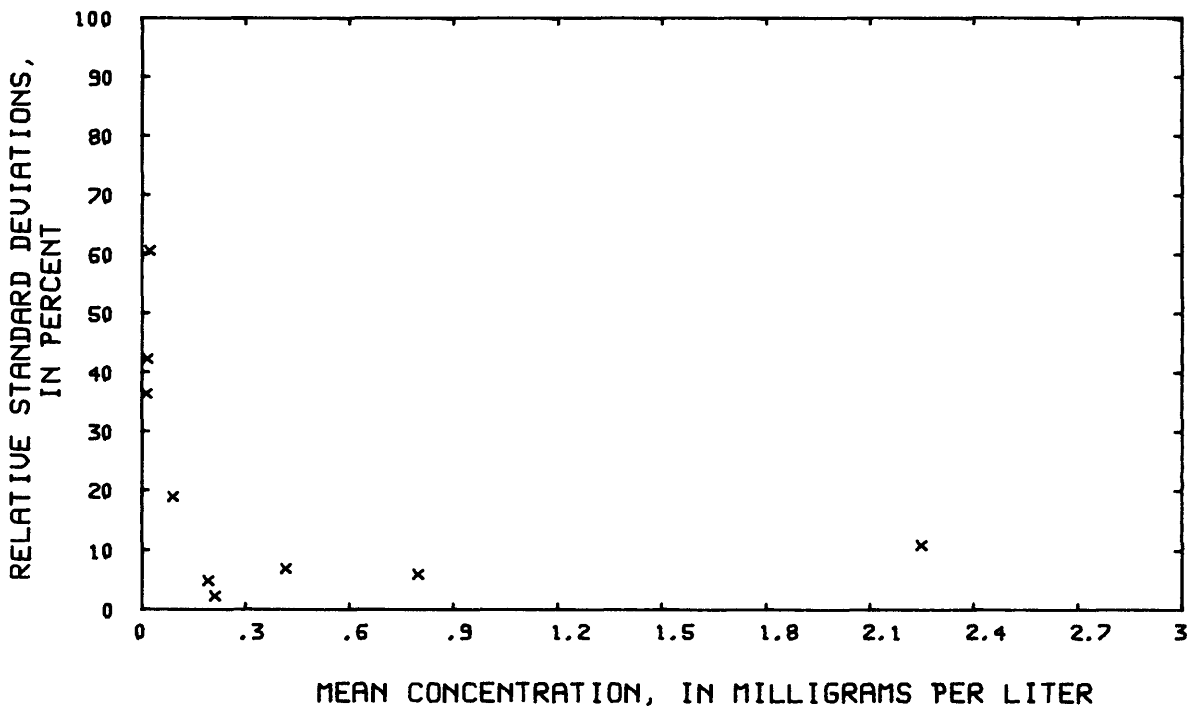

Figure 142.--Precision data for phosphorus as P, dissolved, at the National Water Quality Laboratory.

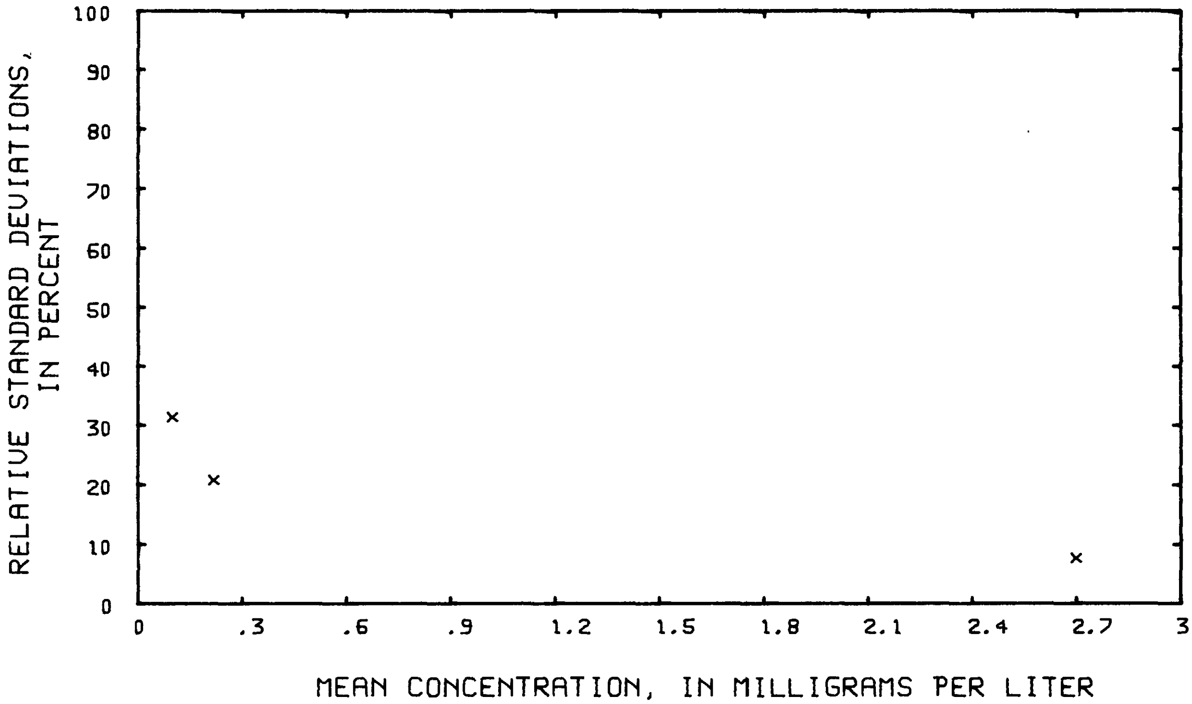

Figure 143.--Precision data for calcium, dissolved, (precipitation) at the National Water Quality Laboratory.

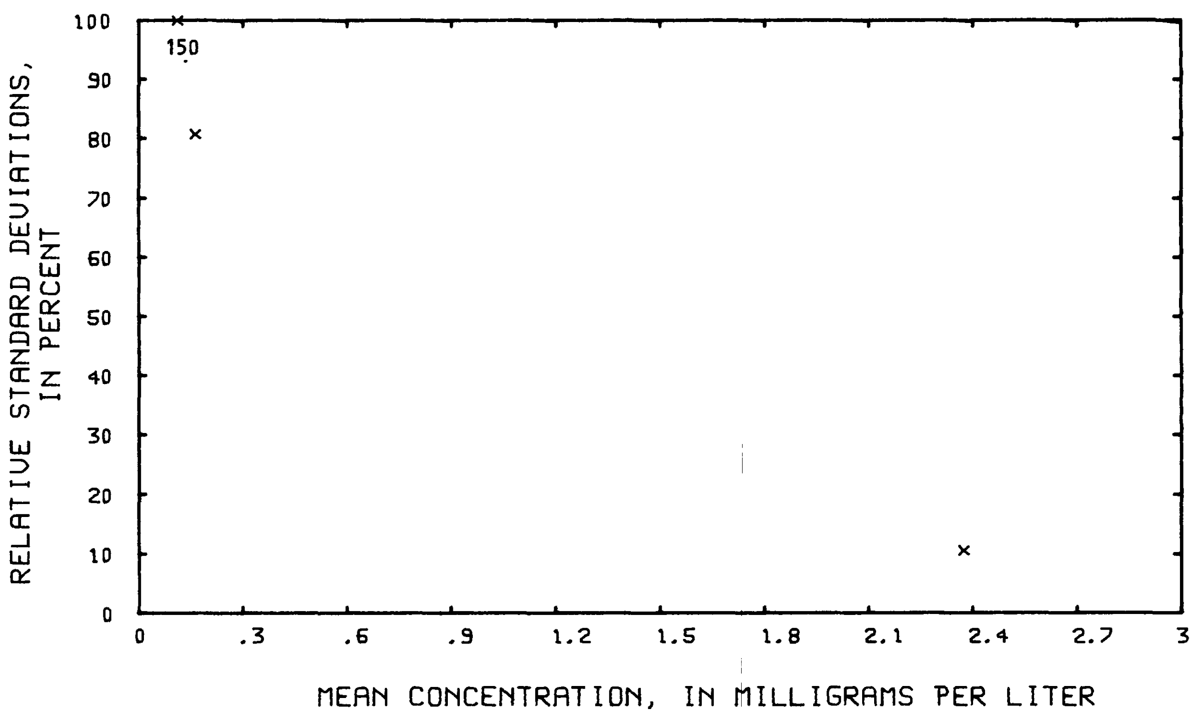

Figure 144.--Precision data for chloride, dissolved, (precipitation) at the National Water Quality Laboratory.

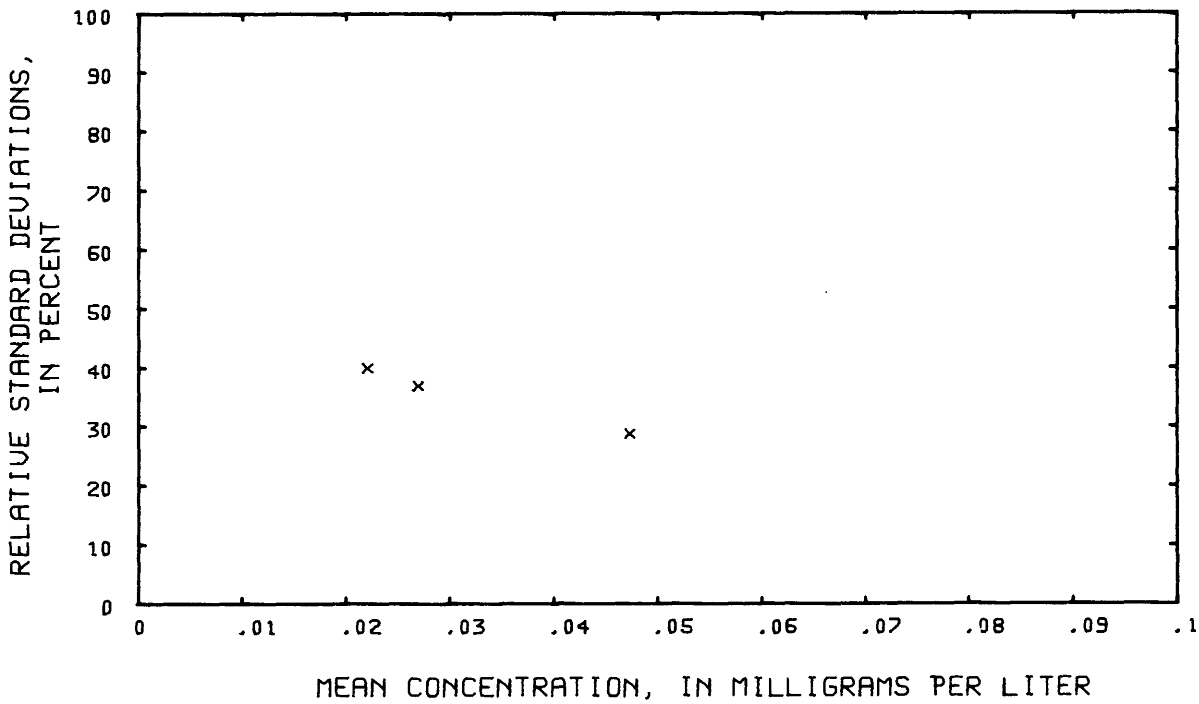

Figure 145.--Precision data for fluoride, dissolved, (precipitation) at the National Water Quality Laboratory.

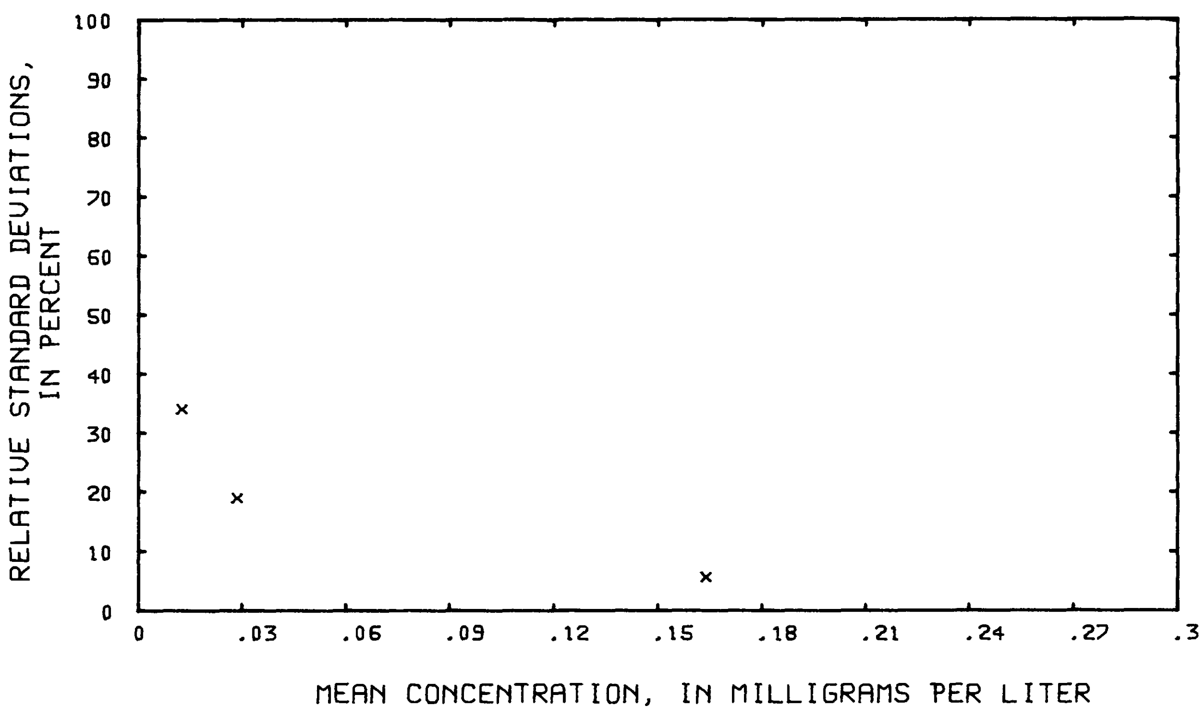

Figure 146.--Precision data for magnesium, dissolved, (precipitation) at the National Water Quality Laboratory.

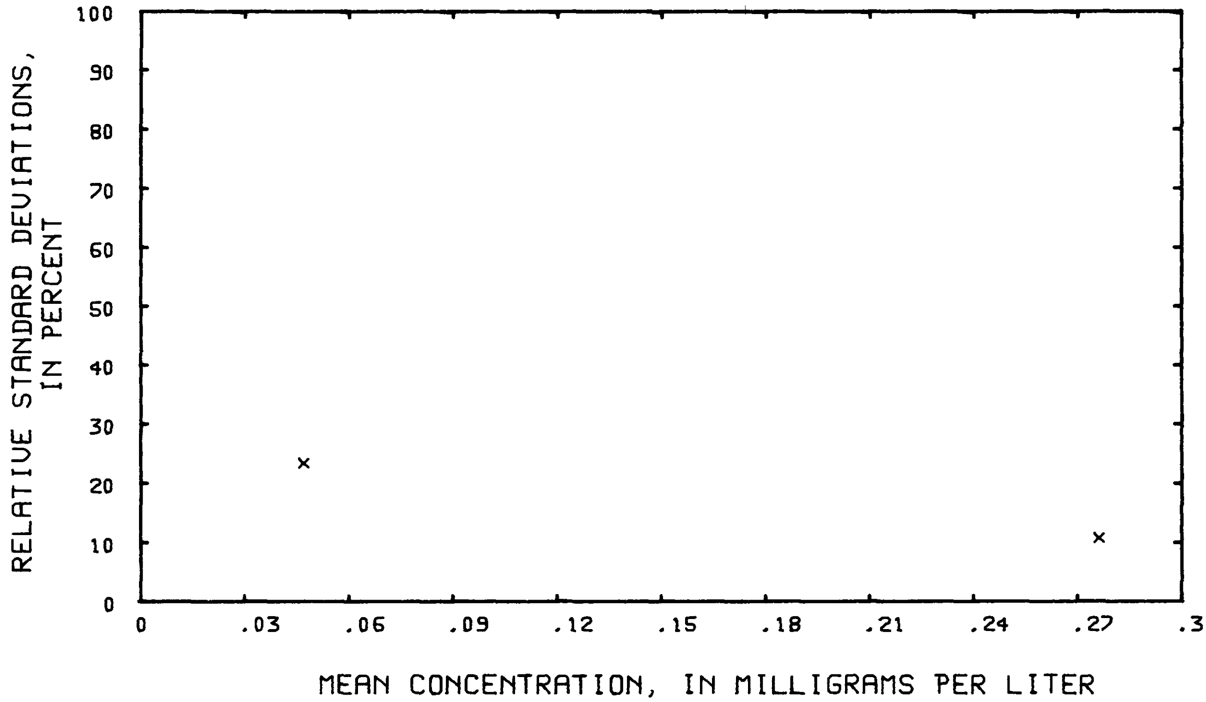

Figure 147.--Precision data for ammonia nitrogen as N, dissolved, (precipitation) at the National Water Quality Laboratory.

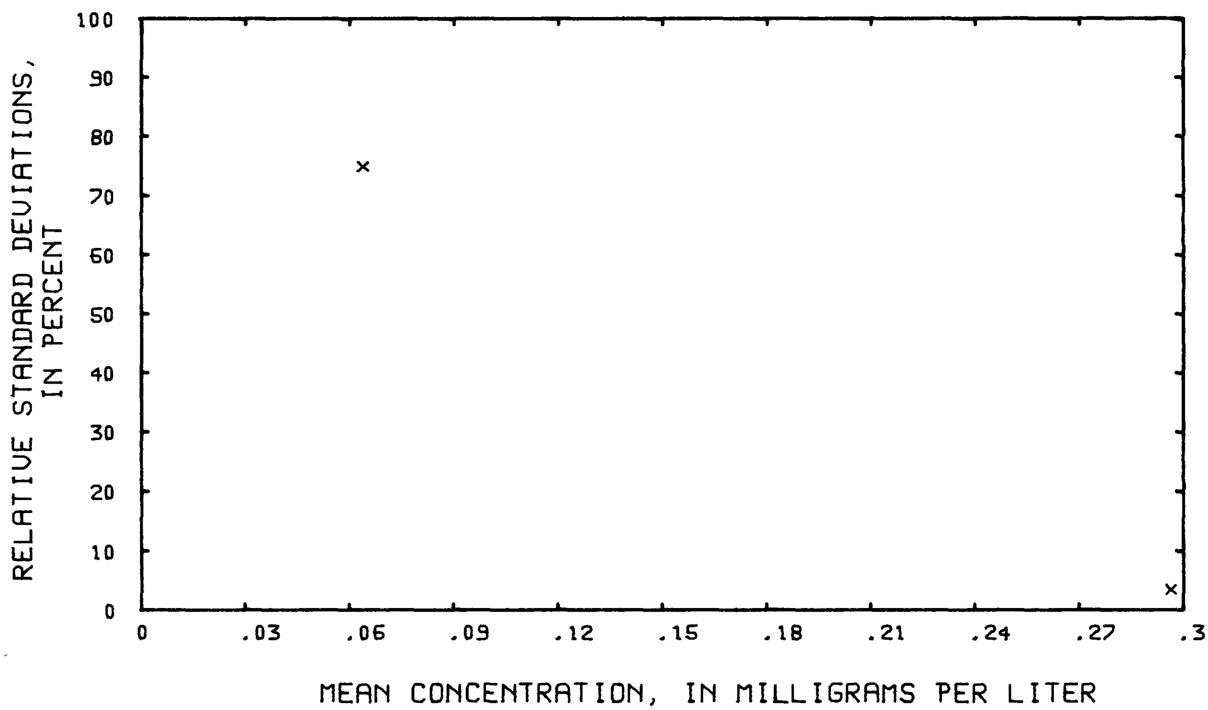

Figure 148.--Precision data for nitrate nitrogen as N, dissolved, (precipitation) at the National Water Quality Laboratory.

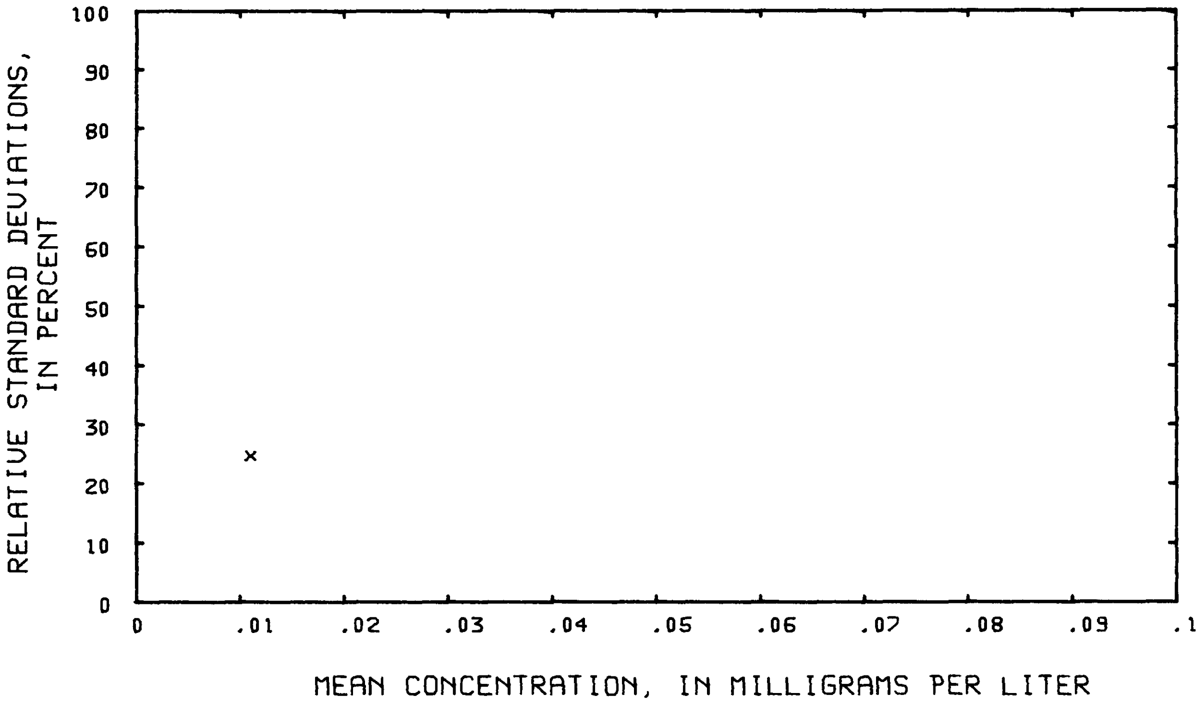

Figure 149.--Precision data for orthophosphate phosphorus as P, dissolved, (precipitation) at the National Water Quality Laboratory.

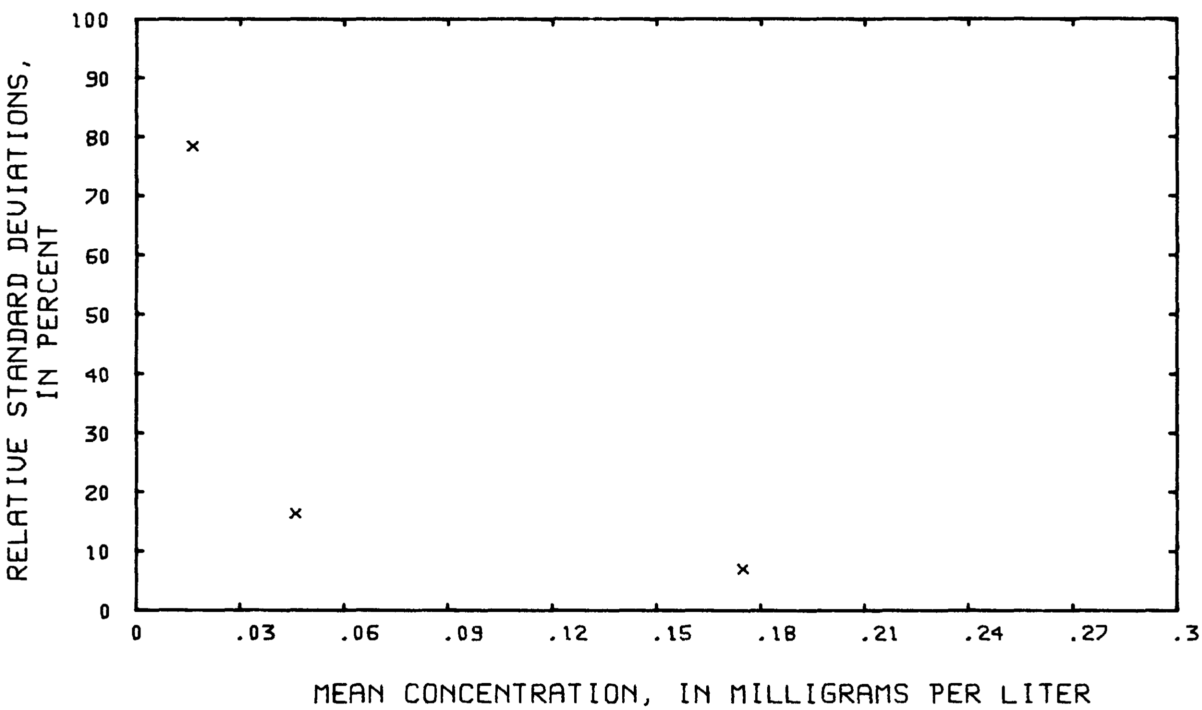

Figure 150.--Precision data for potassium, dissolved, (precipitation) at the National Water Quality Laboratory.

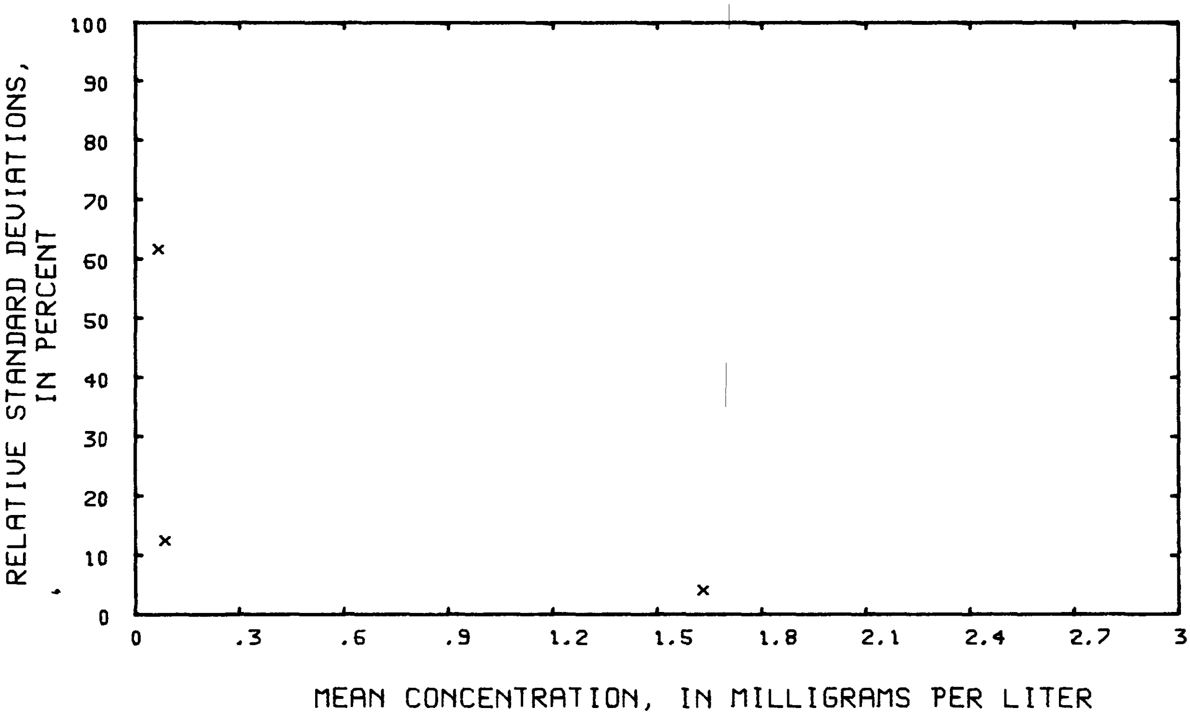

Figure 151.--Precision data for sodium, dissolved, (precipitation) at the National Water Quality Laboratory.

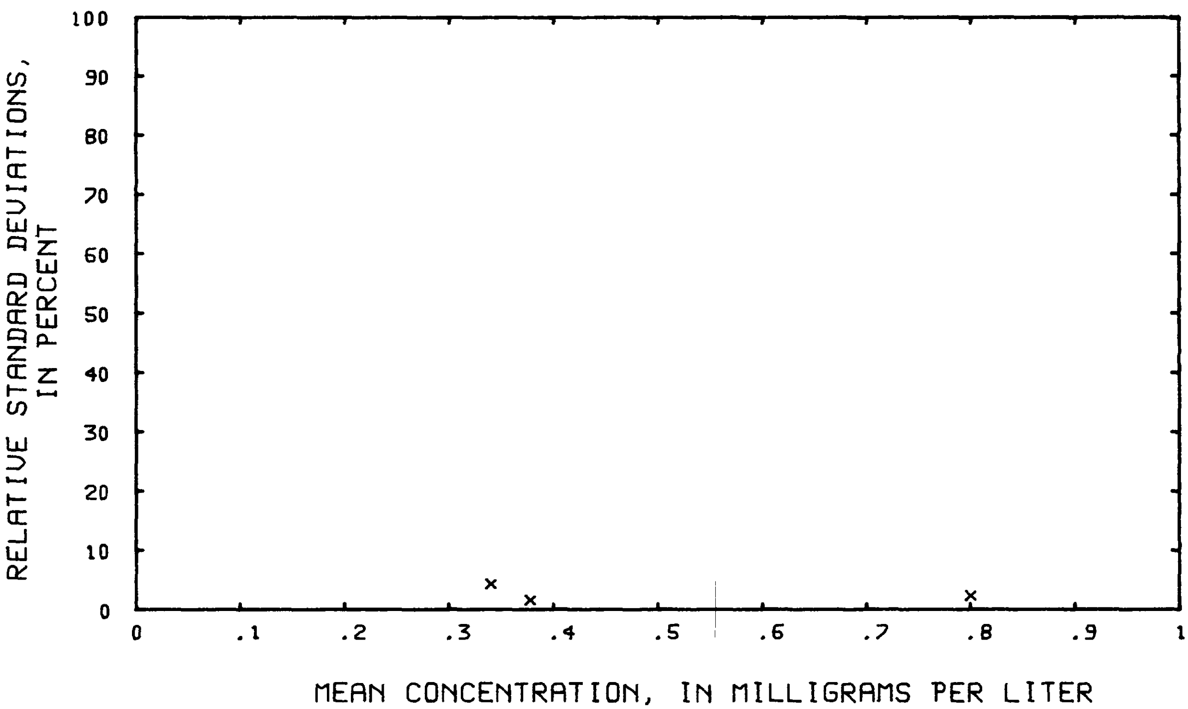

Figure 152.--Precision data for sulfate, dissolved, (precipitation) at the National Water Quality Laboratory.

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