

QUALITY-ASSURANCE DATA FOR ROUTINE WATER ANALYSIS IN THE
LABORATORIES OF THE U.S. GEOLOGICAL SURVEY:
1981 ANNUAL REPORT

By Dale B. Peart and Nancy Thomas

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 83-4090



Denver, Colorado

1983

UNITED STATES DEPARTMENT OF THE INTERIOR

JAMES G. WATT, Secretary

GEOLOGICAL SURVEY

Dallas L. Peck, Director

For additional information write to:

Dale B. Peart
U.S. Geological Survey
Water Resources Division, CR
Box 25046, Mail Stop 407
Denver Federal Center
Denver, Colorado 80225

Copies of this report can be purchased from:

Open-File Services Section
Western Distribution Branch
U.S. Geological Survey
Box 25425, Federal Center
Denver, Colorado 80225
Telephone: (303) 234-5888

CONTENTS

	<u>Page</u>
Abstract	1
Introduction	2
Program description	2
Statistical evaluation	3
Results and discussion	7
Precision	7
Bias	11
Chlorophyll α	15
Organic substances	16
Summary and conclusions	16
References	17
Supplemental data	19

ILLUSTRATIONS

Figures 1-184. Graphs showing:

1. Alkalinity, dissolved, data from the Atlanta Laboratory	21
2. Alkalinity, dissolved, data from the Denver Laboratory	21
3. Aluminum, dissolved, data from the Atlanta Laboratory	22
4. Aluminum, dissolved, data from the Denver Laboratory	22
5. Antimony, dissolved, data from the Atlanta Laboratory	23
6. Antimony, dissolved, data from the Denver Laboratory	23
7. Arsenic, dissolved, data from the Atlanta Laboratory	24
8. Arsenic, dissolved, data from the Denver Laboratory	24
9. Barium, dissolved, data from the Atlanta Laboratory	25
10. Barium, dissolved, data from the Denver Laboratory	25
11. Barium, total recoverable, data from the Atlanta Laboratory	26
12. Barium, total recoverable, data from the Denver Laboratory	26
13. Beryllium, dissolved, data from the Atlanta Laboratory	27
14. Beryllium, dissolved, data from the Denver Laboratory	27
15. Boron, dissolved, data from the Atlanta Laboratory	28
16. Boron, dissolved, data from the Denver Laboratory	28
17. Cadmium, dissolved, data from the Atlanta Laboratory	29
18. Cadmium, dissolved, data from the Denver Laboratory	29
19. Cadmium, total recoverable, data from the Atlanta Laboratory	30
20. Cadmium, total recoverable, data from the Denver Laboratory	30
21. Calcium, dissolved, data from the Atlanta Laboratory	31
22. Calcium, dissolved, data from the Denver Laboratory	31
23. Chloride, dissolved, data from the Atlanta Laboratory	32
24. Chloride, dissolved, data from the Denver Laboratory	32
25. Chromium, dissolved, data from the Atlanta Laboratory	33
26. Chromium, dissolved, data from the Denver Laboratory	33
27. Chromium, total recoverable, data from the Atlanta Laboratory	34
28. Chromium, total recoverable, data from the Denver Laboratory	34

ILLUSTRATIONS—Continued

	<u>Page</u>
Figure 29. Cobalt, dissolved, data from the Atlanta Laboratory	35
30. Cobalt, dissolved, data from the Denver Laboratory	35
31. Cobalt, total recoverable, data from the Atlanta Laboratory	36
32. Cobalt, total recoverable, data from the Denver Laboratory	36
33. Copper, dissolved, data from the Atlanta Laboratory	37
34. Copper, dissolved, data from the Denver Laboratory	37
35. Copper, total recoverable, data from the Atlanta Laboratory	38
36. Copper, total recoverable, data from the Denver Laboratory	38
37. Dissolved solids, data from the Atlanta Laboratory	39
38. Dissolved solids, data from the Denver Laboratory	39
39. Fluoride, dissolved, data from the Atlanta Laboratory	40
40. Fluoride, dissolved, data from the Denver Laboratory	40
41. Iron, dissolved, data from the Atlanta Laboratory	41
42. Iron, dissolved, data from the Denver Laboratory	41
43. Iron, total recoverable, data from the Atlanta Laboratory	42
44. Iron, total recoverable, data from the Denver Laboratory	42
45. Lead, dissolved, data from the Atlanta Laboratory	43
46. Lead, dissolved, data from the Denver Laboratory	43
47. Lead, total recoverable, data from the Atlanta Laboratory	44
48. Lead, total recoverable, data from the Denver Laboratory	44
49. Lithium, dissolved, data from the Atlanta Laboratory	45
50. Lithium, dissolved, data from the Denver Laboratory	45
51. Magnesium, dissolved, data from the Atlanta Laboratory	46
52. Magnesium, dissolved, data from the Denver Laboratory	46
53. Manganese, dissolved, data from the Atlanta Laboratory	47
54. Manganese, dissolved, data from the Denver Laboratory	47
55. Manganese, total recoverable, data from the Atlanta Laboratory	48
56. Manganese, total recoverable, data from the Denver Laboratory	48
57. Mercury, dissolved, data from the Atlanta Laboratory	49
58. Mercury, dissolved, data from the Denver Laboratory	49
59. Molybdenum, dissolved, data from the Atlanta Laboratory	50
60. Molybdenum, dissolved, data from the Denver Laboratory	50
61. Nickel, dissolved, data from the Atlanta Laboratory	51
62. Nickel, dissolved, data from the Denver Laboratory	51
63. Nickel, total recoverable, data from the Atlanta Laboratory	52
64. Nickel, total recoverable, data from the Denver Laboratory	52
65. Nitrate plus nitrite-nitrogen, dissolved, data from the Atlanta Laboratory	53
66. Nitrate plus nitrite-nitrogen, dissolved, data from the Denver Laboratory	53
67. Nitrite-nitrogen, dissolved, data from the Atlanta Laboratory	54
68. Nitrite-nitrogen, dissolved, data from the Denver Laboratory	54
69. Phosphorus, dissolved, data from the Atlanta Laboratory	55
70. Phosphorus, dissolved, data from the Denver Laboratory	55
71. Potassium, dissolved, data from the Atlanta Laboratory	56
72. Potassium, dissolved, data from the Denver Laboratory	56
73. Selenium, dissolved, data from the Atlanta Laboratory	57

ILLUSTRATIONS—Continued

	<u>Page</u>
Figure 74. Selenium, dissolved, data from the Denver Laboratory	57
75. Silica, dissolved, data from the Atlanta Laboratory	58
76. Silica, dissolved, data from the Denver Laboratory	58
77. Silver, dissolved, data from the Atlanta Laboratory	59
78. Silver, dissolved, data from the Denver Laboratory	59
79. Silver, total recoverable, data from the Atlanta Laboratory.	60
80. Silver, total recoverable, data from the Denver Laboratory	60
81. Sodium, dissolved, data from the Atlanta Laboratory.	61
82. Sodium, dissolved, data from the Denver Laboratory	61
83. Specific conductance, data from the Atlanta Laboratory	62
84. Specific conductance, data from the Denver Laboratory	62
85. Strontium, dissolved, data from the Atlanta Laboratory	63
86. Strontium, dissolved, data from the Denver Laboratory.	63
87. Sulfate, dissolved, data from the Atlanta Laboratory.	64
88. Sulfate, dissolved, data from the Denver Laboratory	64
89. Zinc, dissolved, data from the Atlanta Laboratory	65
90. Zinc, dissolved, data from the Denver Laboratory	65
91. Zinc, total recoverable, data from the Atlanta Laboratory	66
92. Zinc, total recoverable, data from the Denver Laboratory	66
93. Precision data for alkalinity at the Atlanta Laboratory	67
94. Precision data for alkalinity at the Denver Laboratory	67
95. Precision data for aluminum at the Atlanta Laboratory.	68
96. Precision data for aluminum at the Denver Laboratory	68
97. Precision data for antimony at the Atlanta Laboratory	69
98. Precision data for antimony at the Denver Laboratory	69
99. Precision data for arsenic at the Atlanta Laboratory	70
100. Precision data for arsenic at the Denver Laboratory	70
101. Precision data for barium at the Atlanta Laboratory	71
102. Precision data for barium at the Denver Laboratory	71
103. Precision data for barium, total recoverable, at the Atlanta Laboratory	72
104. Precision data for barium, total recoverable, at the Denver Laboratory	72
105. Precision data for beryllium at the Atlanta Laboratory.	73
106. Precision data for beryllium at the Denver Laboratory	73
107. Precision data for boron at the Atlanta Laboratory	74
108. Precision data for boron at the Denver Laboratory.	74
109. Precision data for cadmium at the Atlanta Laboratory	75
110. Precision data for cadmium at the Denver Laboratory	75
111. Precision data for cadmium, total recoverable, at the Atlanta Laboratory	76
112. Precision data for cadmium, total recoverable, at the Denver Laboratory	76
113. Precision data for calcium at the Atlanta Laboratory	77
114. Precision data for calcium at the Denver Laboratory.	77

ILLUSTRATIONS—Continued

	<u>Page</u>
Figure 115. Precision data for chloride at the Atlanta Laboratory	78
116. Precision data for chloride at the Denver Laboratory	78
117. Precision data for chromium at the Atlanta Laboratory	79
118. Precision data for chromium at the Denver Laboratory	79
119. Precision data for chromium, total recoverable, at the Atlanta Laboratory	80
120. Precision data for chromium, total recoverable, at the Denver Laboratory	80
121. Precision data for cobalt at the Atlanta Laboratory	81
122. Precision data for cobalt at the Denver Laboratory	81
123. Precision data for cobalt, total recoverable, at the Atlanta Laboratory	82
124. Precision data for cobalt, total recoverable, at the Denver Laboratory	82
125. Precision data for copper at the Atlanta Laboratory	83
126. Precision data for copper at the Denver Laboratory	83
127. Precision data for copper, total recoverable, at the Atlanta Laboratory	84
128. Precision data for copper, total recoverable, at the Denver Laboratory	84
129. Precision data for dissolved solids at the Atlanta Laboratory	85
130. Precision data for dissolved solids at the Denver Laboratory	85
131. Precision data for fluoride at the Atlanta Laboratory	86
132. Precision data for fluoride at the Denver Laboratory	86
133. Precision data for iron at the Atlanta Laboratory	87
134. Precision data for iron at the Denver Laboratory	87
135. Precision data for iron, total recoverable, at the Atlanta Laboratory	88
136. Precision data for iron, total recoverable, at the Denver Laboratory	88
137. Precision data for lead at the Atlanta Laboratory	89
138. Precision data for lead at the Denver Laboratory	89
139. Precision data for lead, total recoverable, at the Atlanta Laboratory	90
140. Precision data for lead, total recoverable, at the Denver Laboratory	90
141. Precision data for lithium at the Atlanta Laboratory	91
142. Precision data for lithium at the Denver laboratory	91
143. Precision data for magnesium at the Atlanta Laboratory	92
144. Precision data for magnesium at the Denver Laboratory	92
145. Precision data for manganese at the Atlanta Laboratory	93
146. Precision data for manganese at the Denver Laboratory	93
147. Precision data for manganese, total recoverable, at the Atlanta Laboratory	94
148. Precision data for manganese, total recoverable, at the Denver Laboratory	94

ILLUSTRATIONS—Continued

	<u>Page</u>
Figure 149. Precision data for mercury at the Atlanta Laboratory	95
150. Precision data for mercury at the Denver Laboratory	95
151. Precision data for molybdenum at the Atlanta Laboratory	96
152. Precision data for molybdenum at the Denver Laboratory.	96
153. Precision data for nickel at the Atlanta Laboratory	97
154. Precision data for nickel at the Denver Laboratory	97
155. Precision data for nickel, total recoverable, at the Atlanta Laboratory	98
156. Precision data for nickel, total recoverable, at the Denver Laboratory	98
157. Precision data for nitrate plus nitrite-nitrogen at the Atlanta Laboratory	99
158. Precision data for nitrate plus nitrite-nitrogen at the Denver Laboratory	99
159. Precision data for nitrite-nitrogen at the Atlanta Laboratory	100
160. Precision data for nitrite-nitrogen at the Denver Laboratory	100
161. Precision data for phosphorus at the Atlanta Laboratory	101
162. Precision data for phosphorus at the Denver Laboratory	101
163. Precision data for potassium at the Atlanta Laboratory	102
164. Precision data for potassium at the Denver Laboratory.	102
165. Precision data for selenium at the Atlanta Laboratory	103
166. Precision data for selenium at the Denver Laboratory	103
167. Precision data for silica at the Atlanta Laboratory	104
168. Precision data for silica at the Denver Laboratory.	104
169. Precision data for silver at the Atlanta Laboratory	105
170. Precision data for silver at the Denver Laboratory.	105
171. Precision data for silver, total recoverable, at the Atlanta Laboratory	106
172. Precision data for silver, total recoverable, at the Denver Laboratory	106
173. Precision data for sodium at the Atlanta Laboratory	107
174. Precision data for sodium at the Denver Laboratory	107
175. Precision data for specific conductance at the Atlanta Laboratory	108
176. Precision data for specific conductance at the Denver Laboratory	108
177. Precision data for strontium at the Atlanta Laboratory.	109
178. Precision data for strontium at the Denver Laboratory	109
179. Precision data for sulfate at the Atlanta Laboratory	110
180. Precision data for sulfate at the Denver Laboratory	110
181. Precision data for zinc at the Atlanta Laboratory	111
182. Precision data for zinc at the Denver Laboratory	111
183. Precision data for zinc, total recoverable, at the Atlanta Laboratory	112
184. Precision data for zinc, total recoverable, at the Denver Laboratory	112

TABLES

		<u>Page</u>
Table 1.	Comparison of mean analyzed value with the most probable value from specific conductance	5
2.	Results of statistical testing from lack of precision in data from the Atlanta Laboratory: inorganic constituents and specific conductance	8
3.	Results of statistical testing from lack of precision in data from the Denver Laboratory: inorganic constituents and specific conductance	10
4.	Results of statistical testing from bias in data from the Atlanta Laboratory: inorganic constituents and specific conductance . . .	12
5.	Results of statistical testing from bias in data from the Denver Laboratory: inorganic constituents and specific conductance . . .	14

QUALITY-ASSURANCE DATA FROM ROUTINE WATER ANALYSIS
IN THE LABORATORIES OF THE
U.S. GEOLOGICAL SURVEY: 1981 ANNUAL REPORT

By Dale B. Peart and Nancy Thomas

ABSTRACT

The U.S. Geological Survey maintains a quality-assurance program based on the analysis of reference samples for its two water-analysis laboratories located in Atlanta, Georgia, and Denver, Colorado. Reference samples containing inorganic constituents are prepared at the U.S. Geological Survey's Ocala, Florida, office and disguised as routine samples, and sent daily to each laboratory through other U.S. Geological Survey offices. The results are permanently stored in the National Water Data Storage and Retrieval System (WATSTORE), the U.S. Geological Survey's data base for all water data. These data are analyzed statistically for precision and bias. The results of these statistical analyses are presented for data collected during the 1981 calendar year. In addition, one sample containing known concentrations of trihalomethanes and samples containing unknown concentrations chlorophyll *a* were analyzed in both laboratories, and these results also are presented.

INTRODUCTION

During the first months of 1981, a revised quality-assurance program was instituted for monitoring the quality of the work performed by the water-quality laboratories of the U.S. Geological Survey. The revision included permanent storage of the quality-assurance data, preparation of the quality-assurance samples outside of either laboratory, and a large increase in the frequency that samples were submitted to the laboratories. The laboratories, located in Atlanta, Georgia, and Denver, Colorado, routinely analyze water, suspended sediments, stream- and lake-bed materials for inorganic constituents, many organic substances including common pesticides, priority pollutants, and some physical properties. During 1981, only the following constituents 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), fluoride, iron, lead, lithium, manganese, magnesium, molybdenum, nickel, nitrate plus nitrite, nitrite, phosphorous, potassium, selenium, silica, silver, sodium, strontium, sulfate, and zinc.

Organic substances--known concentrations of chloroform, bromodichloromethane, dibromochloromethane, and bromoform.

Biological--unknown concentrations of chlorophyll *a*.

Physical properties--specific conductance.

Program Description

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

In addition to the SRWS, ampuls obtained from the U.S. Environmental Protection Agency that contain known concentrations of various constituents, and synthetic samples made from reagent grade chemicals are used in preparing reference samples. All samples are prepared in the U.S. Geological Survey's Ocala, Florida, office, and are made to appear as much like real samples as possible. This effort is coordinated with the offices that will be shipping the samples during any given calendar month. When the samples are prepared and the appropriate forms are completed, assuring proper analysis for the sample, they are shipped to selected offices across the country. These offices then ship the quality-assurance samples to the laboratories daily, along with their regular samples.

The analyses requested reflect the frequency of analyses for each chemical constituent in the laboratory. The program goal is to have at least one quality-assurance sample analyzed daily for those constituents that are analyzed daily and, similarly, an appropriate number of quality-assurance samples for those constituents analyzed less frequently.

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

The quality-assurance samples pass through each laboratory as routine samples including the application of laboratory quality-control and quality-assurance procedures. The data are then stored in the U.S Geological Survey's National Water Data Storage and Retrieval System (WATSTORE). Having passed through the laboratories in this manner, these quality-assurance samples should reflect the quality of the analytical data for environmental samples that the laboratories produce. Laboratory errors other than those related to analytical chemistry also will be reflected in these data. These may include errors in logging the sample into the laboratory, transcription errors by the analyst, and keypunching errors. No effort is made to correct nonanalytical errors of this type even when it is quite obvious which corrective measures were appropriate. This is to preserve the laboratories' data as they produce it, regardless of the source of error. Thus, if a data user is capable of detecting errors of this type, he can increase the quality of his data compared to that presented in this report.

Statistical Evaluation

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

For non-SRWS based samples, for example, ampuls provided by the U.S. Environmental Protection Agency, "true" or "most probable" values were supplied by the respective agency along with corresponding standard deviations. These values were used in determining whether or not the data from the Geological Survey laboratories was acceptable.

Initially, the appropriateness of using the mean of two specific-conductance values for an MPV in the case of mixed solution samples was questioned. However, because all of the SRWS have specific conductances less than 2,100 (micromhos per centimeter at 25° Celsius), it was believed that the departure from linearity would not be significant. A comparison of the means of the analyzed specific-conductance values and the MPVs for all the mixtures is presented in table 1. A paired-t test on the raw data showed a

significant difference between the two at the 95-percent confidence level. However, a closer examination of the raw data showed that results from three mixes (mixes 5, 9, and 23) were consistently greater than the MPV. The intramix precision for each of the three mixes is very good, with the exception of one outlier in mix 5. All three mixes were combinations of two solutions whose specific conductances differ approximately one order of magnitude. When these three mixtures are excluded from the paired-t test, no significant difference is found. This indicates that the linearity hypothesis holds true except where the parent samples have widely divergent specific conductances.

A bias test (Grant and Leavenworth, 1974) also was applied to the data in table 1 using the binomial-distribution probability. It was determined that no statistically significant bias existed, where the probability of assuming bias where there is none, is less than 1 percent.

Standard deviations were determined using linear least-squares equations developed by regressing the standard deviations achieved in the multilaboratory, multimethod analyses of all the SRWS for which we have data, against the corresponding mean values (MPVs) for those samples. This method allowed us to estimate a most probable standard deviation (MPSD) for each constituent on a sample-by-sample basis to determine whether that analysis was in or out of control. An individual reported value was considered acceptable if it was within two standard deviations of the MPV. This was generally a liberal criterion because the MPSDs were based on multilaboratory, multimethod data.

In certain situations, the above criterion was impossible to meet. This was true for all chromium, molybdenum, and zinc, as well as copper with values exceeding 99 (micrograms per liter). These constituents were reported to the nearest 10 $\mu\text{g/L}$. The regression equations were developed from data reported to the nearest 1 $\mu\text{g/L}$ resulting in standard deviations so small that no values reported by the laboratories were acceptable. A minimum standard deviation of 7.5 $\mu\text{g/L}$ was established to allow at least one reportable value on each side of the MPV to be accepted.

The number of standard deviations each constituent deviates from the theoretical value (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 accuracy (bias). This result for each laboratory and constituent is displayed in figures 1 through 92 in the Supplemental Data section at the back of this report. Three symbols are used on the figures to display results from the lower (+), middle (x), and upper (o) thirds of the potential analytical range tested in this program. This range does not necessarily correspond with the analytical capabilities of the laboratory instrumentation or methods, but rather the analytical range we are capable of testing with the available SRWS or other reference samples used. The three parts of this range are based on the MPV of the quality-assurance samples and not the reporting policy; thus, a sample may have a maximum MPV of 28 $\mu\text{g/L}$ chromium (figures 25 and 26) and still be reported to the nearest 10 $\mu\text{g/L}$ (that is, 30 $\mu\text{g/L}$). Not all figures will have all three parts of the analytical range displayed because some flexibility is given to the Ocala, Florida, office in sample selection. In addition, miscommunication between ourselves and the shipping offices resulted in many less samples than expected being shipped to the two laboratories during some parts of the year. Points outside the range of the plots are forced to plot at the limit (± 6) with the number of standard deviations indicated adjacent to the point.

Table 1.--Comparison of mean analyzed value with the most probable value
for specific conductance

[Data from both laboratories combined]

Mix	Number of analyses	Micromhos per centimeter at 25° Celsius		
		Mean	Standard deviation	Most probable value
1	4	446	29.8	430
2	7	161	11.6	168
3	12	570	11.6	569
4	16	1385	39.2	1351
5	27	615	59.7	569
6	24	1004	24.4	970
7	11	610	17.6	612
8	22	804	24.3	785
9	18	419	10.7	369
10	11	520	11.6	524
11	8	1599	30.0	1601
12	6	526	38.2	519
13	22	262	16.5	257
14	24	254	5.6	242
15	19	1790	146.7	1735
16	17	121	3.6	119
17	8	919	62.4	878
18	4	1510	11.5	1536
19	8	1108	81.7	1014
20	24	309	9.7	298
21	10	557	7.5	566
22	12	294	16.0	288
23	8	647	19.8	584
24	11	390	10.4	381
25	14	463	12.2	473
26	32	1126	187.8	1167
27	39	125	8.6	124
28	33	669	65.0	658
29	34	105	5.5	103
30	7	2063	144.8	2094

Bias is determined by counting the number of points on either side of the zero line (line representing the MPV) and applying a binomial-probability-distribution equation (Grant and Leavenworth, 1974):

$$P(x) = 2 \left\{ \sum_{i=x}^N \frac{N!}{i!(N-i)!} (0.50)^i (0.50)^{N-i} \right\} \quad (1)$$

where

- $P(x)$ = the probability of having x or more points in the same side of the zero line,
 N = the number of successive points, and
 i = the number of points on the same side of the zero line.

If $P(x)$ is less than 1 percent then bias is considered to exist, that is, there is less than 1 percent probability of assuming bias where none exists.

Similarly, a binomial-distribution equation is used to determine if statistically significant lack of precision exists at the 95-percent confidence level.

$$P(x) = \left\{ \sum_{i=x}^N \frac{N!}{i!(N-i)!} (0.05)^i (0.95)^{N-i} \right\} \quad (2)$$

where

- $P(x)$ = probability of having x or more points greater than two standard deviations,
 N = number of successive points, and
 i = number of points greater than two standard deviations.

$P(x)$ is chosen at less than 1 percent here as well so that our probability of assuming lack of precision where none exists is less than 1 percent. An example: for $N = 70$ and $i = 9$, $P(x)$ is less than 1 percent; therefore, the overall precision of the determination is considered unacceptable; for $N = 70$ and $i = 8$ however $P(x)$ is greater than 1 percent so no lack of precision is assumed.

When precision is determined as stated previously, it contains an element of accuracy as well, because the MPVs rather than the analyzed means are used as the basis for determining the number of standard deviations each sample deviates from that value. Thus, in this analysis, precision is based on whether or not the analytical process was in or out of control, and the figures represent control charts.

Traditional determinations of precision (calculation of means and standard deviations) were done for this report. Because standard deviations may vary with concentration in chemical analyses, these determinations were done separately on individual sample mixtures and, therefore, do not give overall appraisals of the analytical processes. Relative standard deviations were calculated and plotted against concentrations in figures 93 through 184 in the Supplemental Data section at the back of this report. These plots will allow a data reviewer to estimate the error at any concentration for all constituents.

RESULTS AND DISCUSSION

Initially, 1981 data were presented statistically in three unpublished reports for the following periods: February 1 - June 30, July 1 - September 30, and October 1 - December 31. The linear least-squares equations used to calculate the MPSD changed for each of the periods because of data from newly developed SRWS. Data presented in this report were reanalyzed using the latest set of equations in order to provide uniform criteria throughout the year. Therefore, data presented in this report may not always correspond to that in the unpublished reports. Results of the binomial-distribution tests for these three periods, as well as the overall results for the year are shown in tables 2 through 5. In general, if a constituent showed significant lack of precision or bias during one part of the year, the yearly result was the same.

Precision

Precision data for each inorganic constituent is presented in tables 2 and 3. For each constituent, these tables indicate significant lack of precision (by LOP) when it occurred as well as all acceptable results (by a plus).

Almost all of the individual aluminum analyses showing lack of precision (LOP) were associated with SRWS 73, which had an initially reported range of values from 70 to 1,100 µg/L. The resulting mean value appears to be disproportionately large based on subsequent analyses of this sample. This caused consistent rejection of these analyses. Apart from these samples, aluminum has consistently failed to show significant lack of precision.

Beginning in July and continuing through December, the quality-assurance samples were contaminated with iron. Thus, the test for lack of precision for iron and iron, total recoverable, was not made during this period. At times other than during the period of contamination, iron has failed to show significant lack of precision.

Mercury consistently had a lack of precision in the data presented in the unpublished reports. Part of the reason seems to be associated with possible contamination of some samples of SRWS 73. Most mercury analyses that were outside the two standard deviation criteria and associated with SRWS 73 generally had values considerably greater than the MPV. When these data are removed, the results are as they appear in the tables and figures. Another partial explanation may result from the use of nitric acid as the singular preservation agent used by the Survey. Several investigators have shown that nitric acid alone is insufficient for the preservation of mercury in dilute solutions (El-Awady, Miller and Carter, 1976; Feldman, 1974). Most samples failing the precision test and not containing SRWS 73 had values that were less than the MPV. Data users need to consider these items when interpreting mercury data.

Silver also showed a lack of precision. Marvin J. Fishman (U.S. Geological Survey, oral communication, 1981) states that earlier investigations have shown that samples containing small silver concentrations need to be preserved at a pH of less than 1 in order to prevent loss of this element.

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

[LOP, significant lack of precision; *, too few analyses to determine;
+, acceptable results; †, samples contaminated with iron during preparation,
all iron data has been deleted for this period]

Constituent (dissolved except as indicated)	Feb. - June 1981	July - Sept. 1981	Oct. - Dec. 1981	Summary Feb. - Dec. 1981
Alkalinity	+	+	+	+
Aluminum	+	+	+	LOP
Antimony	+	LOP	+	LOP
Arsenic	LOP	+	+	LOP
Barium	+	+	+	+
Beryllium	+	+	+	+
Boron	+	+	+	+
Cadmium	+	LOP	+	LOP
Cadmium, total recoverable	LOP	+	+	LOP
Calcium	+	+	+	+
Chloride	+	+	+	+
Chromium	+	+	+	+
Chromium, total recoverable	+	+	+	+
Cobalt	+	+	+	+
Cobalt, total recoverable	+	+	+	+
Copper	+	+	+	+
Copper, total recoverable	+	+	+	+
Dissolved solids	+	+	+	+
Fluoride	+	+	+	+
Iron	+	*†	*†	+
Iron, total recoverable	+	*†	*†	+
Lead	+	+	+	+
Lead, total recoverable	+	+	+	+
Lithium	+	+	+	+
Magnesium	+	+	LOP	LOP
Manganese	LOP	+	+	LOP
Manganese, total recoverable	+	+	+	+
Mercury	+	+	LOP	LOP
Molybdenum	+	+	+	+
Nickel	+	+	+	+
Nickel, total recoverable	+	+	+	+

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

[LOP, significant lack of precision; *, too few analyses to determine;
+, acceptable results; †, samples contaminated with iron during preparation,
all iron data has been deleted for this period]

Constituent (dissolved except as indicated)	Feb. - June 1981	July - Sept. 1981	Oct. - Dec. 1981	Summary Feb. - Dec. 1981
Nitrate plus nitrite	+	+	+	+
Nitrite	+	+	*	+
Phosphorus	+	+	+	+
Potassium	+	+	+	+
Selenium	+	+	+	+
Silica	+	+	LOP	+
Silver	+	LOP	LOP	LOP
Silver, total recoverable	+	+	LOP	LOP
Sodium	+	LOP	LOP	LOP
Specific conductance	LOP	+	LOP	LOP
Strontium	+	+	+	+
Sulfate	+	+	LOP	LOP
Zinc	LOP	+	LOP	LOP
Zinc, total recoverable	LOP	LOP	LOP	LOP

Specific conductance was discussed somewhat in the statistical evaluations section; however, it too has almost always failed the precision criteria. Apart from the discussion in the previous section, the reasons for the LOP determinations appear to be mostly due to random errors.

Zinc only failed to have lack of precision during July to September in the Atlanta Laboratory and during February to June in the Denver Laboratory. These periods of LOP appear to be due to consistently high results and some occasional random errors.

Other constituents failing the precision criteria at one time or another during the year may have done so because of a combination of factors. These factors include random errors, samples misidentified during the log-in process, and keypunch errors.

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

[LOP, significant lack of precision; *, too few analyses to determine
+, acceptable results; †, samples contaminated with iron during preparation,
all iron data has been deleted for this period]

Constituent (dissolved except as indicated)	Feb. - June 1981	July - Sept. 1981	Oct. - Dec. 1981	Summary Feb. - Dec. 1981
Alkalinity	+	+	+	+
Aluminum	LOP	+	+	LOP
Antimony	+	+	+	+
Arsenic	+	+	+	+
Barium	+	+	+	+
Beryllium	+	+	+	+
Boron	+	+	+	+
Cadmium	+	+	+	+
Cadmium, total recoverable	+	+	+	+
Calcium	+	+	+	+
Chloride	LOP	+	LOP	LOP
Chromium	+	+	+	+
Chromium, total recoverable	+	+	+	+
Cobalt	+	+	+	+
Cobalt, total recoverable	+	+	LOP	LOP
Copper	+	+	+	+
Copper, total recoverable	LOP	+	+	LOP
Dissolved solids	+	+	+	+
Fluoride	+	+	+	+
Iron	+	*†	*†	+
Iron, total recoverable	+	*†	*†	+
Lead	+	+	+	+
Lead, total recoverable	+	+	+	+
Lithium	+	+	+	+
Magnesium	+	+	+	+
Manganese	+	+	+	+
Manganese, total recoverable	+	+	+	+

Table 3.--Results of statistical testing for lack of precision in data
from the Denver Laboratory:
inorganic constituents and specific conductance—Continued

[LOP, significant lack of precision; *, too few analyses to determine
+, acceptable results; †, samples contaminated with iron during preparation,
all iron data has been deleted for this period]

Constituent (dissolved except as indicated)	Feb. - June 1981	July - Sept. 1981	Oct. - Dec. 1981	Summary Feb. - Dec. 1981
Mercury	LOP	+	LOP	LOP
Molybdenum	+	+	+	+
Nickel	+	+	+	+
Nickel, total recoverable	+	+	+	+
Nitrate plus nitrite	+	+	+	+
Nitrite	+	+	*	+
Phosphorus	LOP	LOP	+	LOP
Potassium	+	+	+	+
Selenium	LOP	+	+	+
Silica	+	+	+	+
Silver	LOP	+	+	LOP
Silver, total recoverable	LOP	+	+	LOP
Sodium	+	+	+	+
Specific conductance	LOP	LOP	LOP	LOP
Strontium	+	+	+	+
Sulfate	LOP	+	+	LOP
Zinc	+	LOP	LOP	LOP
Zinc, total recoverable	LOP	LOP	+	LOP

Bias

Results of the statistical tests for bias are shown in tables 4 and 5. Using the method described previously, it is not possible to determine bias where results from less than eight samples were available. This situation occurred from July through December for many constituents as noted in the tables.

Results from boron analyses obtained from different analytical methods do not correlate well (Marvin J. Fishman, U.S. Geological Survey, oral communication, 1981). This may explain the consistent negative bias indicated for boron. The negative bias indicated for by silver resulted from the preservation problem discussed in the Precision section.

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

[N, negative; P, positive; *, too few analyses to determine
+, acceptable results; †, samples contaminated with iron during preparation,
all iron data has been deleted for this period]

Constituent (dissolved except as indicated)	Feb. - June 1981	July - Sept. 1981	Oct. - Dec. 1981	Summary Feb. - Dec. 1981
Alkalinity	+	+	+	+
Aluminum	+	+	+	+
Antimony	+	+	+	+
Arsenic	+	P	+	P
Barium	N	N	+	N
Barium, total recoverable	+	*	*	+
Beryllium	N	+	+	N
Boron	N	N	*	N
Cadmium	+	+	+	+
Cadmium, total recoverable	+	*	*	+
Calcium	N	+	+	N
Chloride	+	+	+	+
Chromium	+	P	+	+
Chromium, total recoverable	+	*	*	P
Cobalt	+	+	+	+
Cobalt, total recoverable	+	*	*	N
Copper	+	+	+	+
Copper, total recoverable	+	*	*	+
Dissolved solids	+	P	+	+
Fluoride	P	+	P	P
Iron	+	*†	*†	+
Iron, total recoverable	+	*†	*†	+
Lead	+	+	+	+
Lead, total recoverable	+	*	*	+
Lithium	+	+	+	+
Magnesium	+	+	+	+
Manganese	+	P	+	P
Manganese, total recoverable	+	*	*	+

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

[N, negative; P, positive; *, too few analyses to determine
+, acceptable results; †, samples contaminated with iron during preparation,
all iron data has been deleted for this period]

Constituent (dissolved except as indicated)	Feb. - June 1981	July - Sept. 1981	Oct. - Dec. 1981	Summary Feb. - Dec. 1981
Mercury	+	+	+	+
Molybdenum	+	+	N	N
Nickel	N	N	+	N
Nickel, total recoverable	+	*	*	+
Nitrate plus nitrite	N	N	+	N
Nitrite	*	*	*	+
Phosphorus	P	+	+	+
Potassium	+	+	N	N
Selenium	P	+	+	P
Silica	+	+	N	+
Silver	N	+	N	N
Silver, total recoverable	N	*	*	+
Sodium	+	+	+	+
Specific conductance	+	+	+	+
Sulfate	+	N	N	N
Strontium	N	+	+	N
Zinc	+	+	P	+
Zinc, total recoverable	+	*	*	P

The reasons for other constituents showing either consistent or occasional bias are not entirely clear. Several factors may be involved including bias inherent in the analytical method, 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 the mixing of two very different SRWS together, undetected contamination or, as mentioned above, inaccurate MPV resulting from a very large range of results during the initial analysis of a SRWS. In any case, where bias is statistically significant but precision is good, the bias may have little effect on data interpretation and, therefore, may be of little practical significance.

Table 5.--Results of statistical testing for bias in data
from the Denver Laboratory:
inorganic constituents and specific conductance

[N, negative; P, positive; *, too few analyses to determine
+, acceptable results; †, samples contaminated with iron during preparation,
all iron data has been deleted for this period]

Constituent (dissolved except as indicated)	Feb. - June 1981	July - Sept. 1981	Oct. - Dec. 1981	Summary Feb. - Dec. 1981
Alkalinity	N	+	+	+
Aluminum	N	N	N	N
Antimony	+	*	P	+
Arsenic	+	P	P	P
Barium	+	+	N	+
Barium, total recoverable	+	*	+	+
Beryllium	+	*	+	+
Boron	N	*	*	N
Cadmium	+	+	N	N
Cadmium, total recoverable	N	*	N	N
Calcium	+	+	+	+
Chloride	+	+	+	+
Chromium	+	+	+	+
Chromium, total recoverable	P	*	P	P
Cobalt	N	+	N	N
Cobalt, total recoverable	N	*	N	N
Copper	+	+	+	+
Copper, total recoverable	+	*	+	+
Dissolved solids	+	+	N	N
Fluoride	N	+	P	+
Iron	+	*†	*†	+
Iron, total recoverable	+	*†	*†	+
Lead	+	+	+	+
Lead, total recoverable	+	*	+	+
Lithium	+	*	+	+
Magnesium	+	+	P	P
Manganese	+	+	+	+
Manganese, total recoverable	+	*	+	+

Table 5.--Results of statistical testing for bias in data
from the Denver Laboratory:
inorganic constituents and specific conductance—Continued

[N, negative; P, positive; *, too few analyses to determine
+, acceptable results; +, samples contaminated with iron during preparation,
all iron data has been deleted for this period]

Constituent (dissolved except as indicated)	Feb. - June 1981	July - Sept. 1981	Oct. - Dec. 1981	Summary Feb. - Dec. 1981
Mercury	N	+	N	N
Molybdenum	P	+	N	+
Nickel	N	N	N	N
Nickel, total recoverable	N	*	N	N
Nitrate plus nitrite	+	+	N	N
Nitrite	+	*	*	+
Phosphorus	P	+	+	P
Potassium	+	+	+	+
Selenium	P	+	+	P
Silica	N	+	+	N
Silver	N	N	N	N
Silver, total recoverable	N	*	N	N
Sodium	P	+	P	P
Specific conductance	P	P	+	P
Strontium	+	*	+	+
Sulfate	P	+	P	P
Zinc	+	P	P	P
Zinc, total recoverable	+	*	P	P

Chlorophyll a

Nine chlorophyll a samples were divided between the two laboratories and the Potomac Estuary project that collected the samples. One of these samples was divided six ways to determine precision. All three laboratories showed excellent within-laboratory precision on this sample. Atlanta and Denver were using the same analytical method; the project laboratory used a different method. However, the concentration values reported by the Denver Laboratory were approximately one-third those of the other two laboratories. There was no significant difference between the results of the Atlanta Laboratory and those of the project laboratory.

The analyst feels that the results from the Denver Laboratory are a result of the very small sample size submitted (30 milliliters compared to the 1 liter requested). Subsequent analyses of known reference samples failed to identify anything in the analytical process to cause the stated results.

Organic Substances

Two ampuls provided by the U.S. Environmental Protection Agency that contained trihalomethanes were given to each laboratory for analysis. The Denver Laboratory correctly identified the only four compounds present in the sample: bromoform, dichlorobromomethane, chloroform, chlorodibromomethane. The Atlanta Laboratory also correctly identified these compounds as being present but identified benzene in addition. The quantitative results for both laboratories were within the 95-percent confidence limits of the true values for the four compounds. The benzene may have been identified as present because of contamination, since it is commonly used as a solvent in the laboratories.

SUMMARY AND CONCLUSIONS

Reference samples with known most probable values are disguised as regular samples and submitted with real samples by selected offices of the U.S. Geological Survey to the two water-quality laboratories operated by the Survey. The data generated are stored in the U.S. Geological Survey's National Water Data Storage and Retrieval System (WATSTORE). The data are then statistically analyzed for precision and bias using a binomial-probability-distribution equation.

Recurring problems with lack of precision existed in Atlanta for silver; sodium; specific conductance; zinc; and zinc, total recoverable; and in Denver for chloride; mercury; phosphorus; specific conductance; zinc; and zinc, total recoverable.

Significant bias recurred in Atlanta for barium; boron; fluoride; nickel; nitrate plus nitrite; silver and sulfate; and in Denver for aluminum; arsenic; cadmium, total recoverable; chromium, total recoverable; cobalt; cobalt, total recoverable; fluoride; mercury; molybdenum; nickel; nickel, total recoverable; silver; silver, total recoverable; sodium; specific conductance; sulfate; and zinc.

The quality-assurance samples were contaminated with iron during preparation beginning in July and continuing through December. Therefore, no evaluation of iron or iron, total-recoverable data was made for this period.

Chlorophyll *a* samples divided between the two laboratories showed good intra-laboratory precision but Denver's reported values were approximately one-third those of Atlanta's. The cause is not known, but is thought to be related to the inadequate sample volume submitted.

Results of analysis of ampuls provided by the U.S. Environmental Protection Agency containing four trihalomethanes each were acceptable in both laboratories, except that Atlanta also erroneously identified benzene, a common solvent used in the laboratory, as being present. This probably was a case of contamination.

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

1. Nonanalytical errors were not corrected by this project in order to preserve the data as the laboratory produced it. Thus, if the data reviewer in the U.S. Geological Survey's office that collected the sample initially, is familiar with the collection site or the historical data from that site, many errors of this type can be easily corrected. For example, if two samples from different sites are submitted to the laboratory on the same day and happen to get misidentified so that the analytical data are misreported for these samples, the collecting office very often can detect this situation and correct it, based on historical data from these sites.

2. No quality-assurance samples had any constituents reanalyzed except those requested by the laboratory quality-assurance group. U.S. Geological Survey data reviewers in the collecting offices are expected to scrutinize incoming new data for discrepancies and make requests for reanalysis; these requests may help to detect analytical and nonanalytical errors, and data quality will improve compared to that stated in this report.

3. Figures included in this report may be used to determine analytical conditions at any given time. Where they show that an analytical process may have been in control for the majority of the year and out of control for a short period, but long enough so that the statistical tests applied indicated lack of precision or significant bias results for the year, the data from that period when the analytical process was in control can be considered precise and unbiased.

REFERENCES

- American Society for Testing and Materials, 1980, Annual book of ASTM standards, part 41: Philadelphia, p. 206-232.
- El-Awady, A. A., Miller, R. B., and Carter, M. J., 1976, Automated method for the determination of total and inorganic mercury in water and wastewater samples: Analytical Chemistry, v. 48, no. 1, p. 110-116.
- Feldman, Cyrus, 1974, Preservation of dilute mercury solutions: Analytical Chemistry, v. 46, no. 1, p. 99-102.
- Grant, E. L., and Leavenworth, R. S., 1974, Statistical quality control (4th ed): New York, McGraw Hill, 694 p.
- Schroder, L. J., Fishman, M. J., Friedman, L. C., and Darlington, G. W., 1980, The use of standard reference water samples by the U.S. Geological Survey: U.S. Geological Survey Open-File Report 80-738, 11 p.
- Skougstad, M. W., and Fishman, M. J., 1975, Standard reference water samples: Proceedings, American Water Works Association Water Quality Technology Conference, December, 1974, American Water Works Association, p. XIX-1 - XIX-6.

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

SUPPLEMENTAL DATA

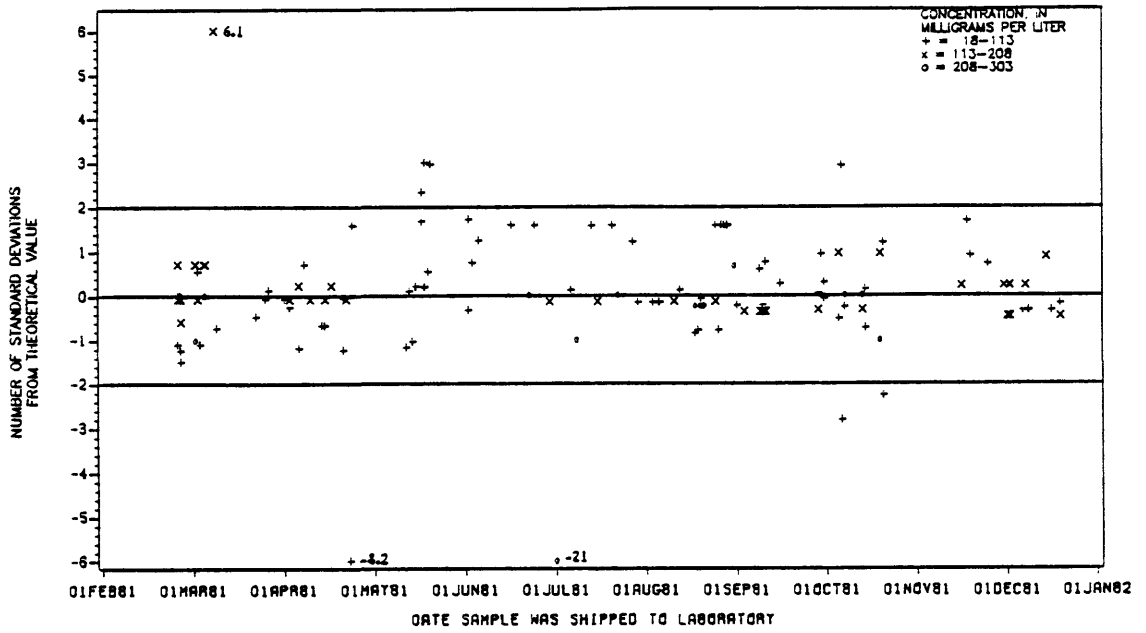


Figure 1.--Alkalinity, dissolved, data from the Atlanta laboratory.

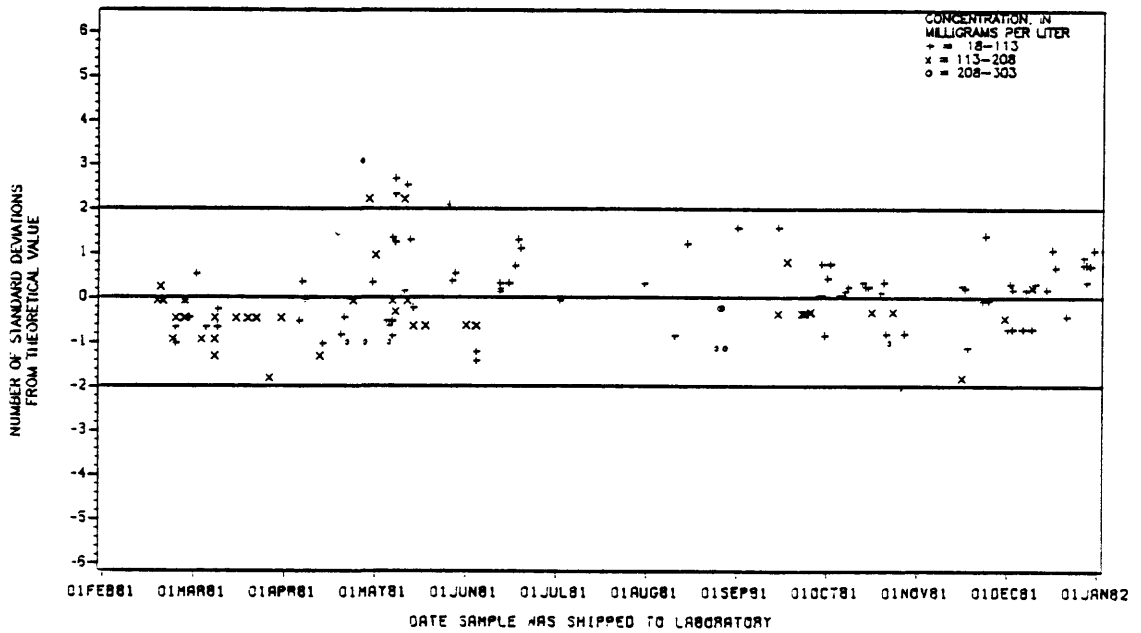


Figure 2.--Alkalinity, dissolved, data from the Denver laboratory.

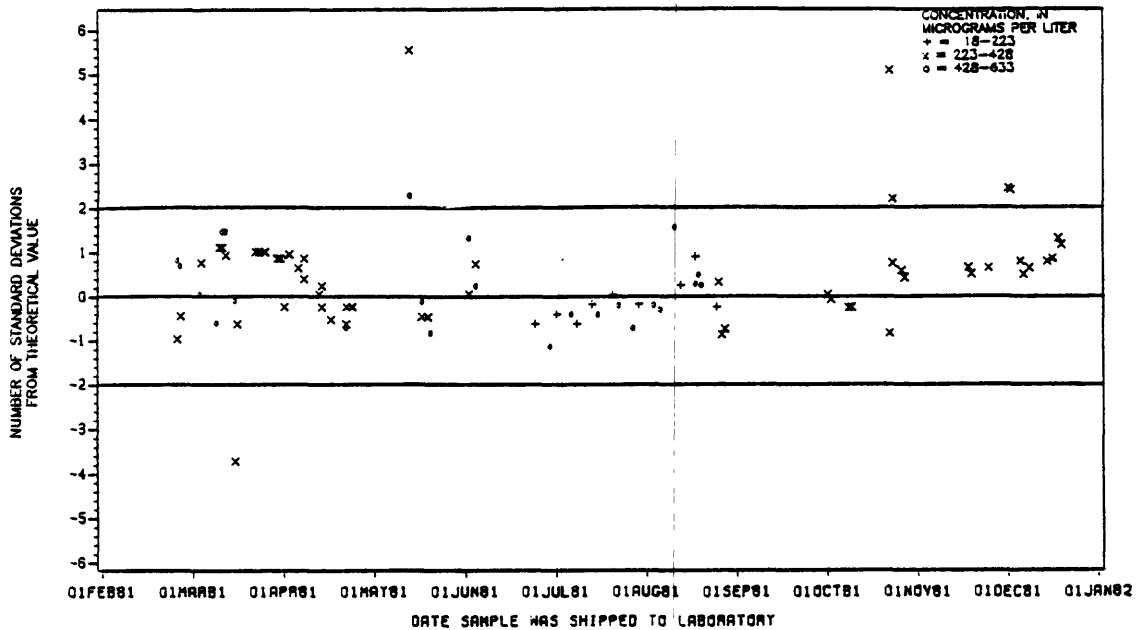


Figure 3.--Aluminum, dissolved, data from the Atlanta laboratory.

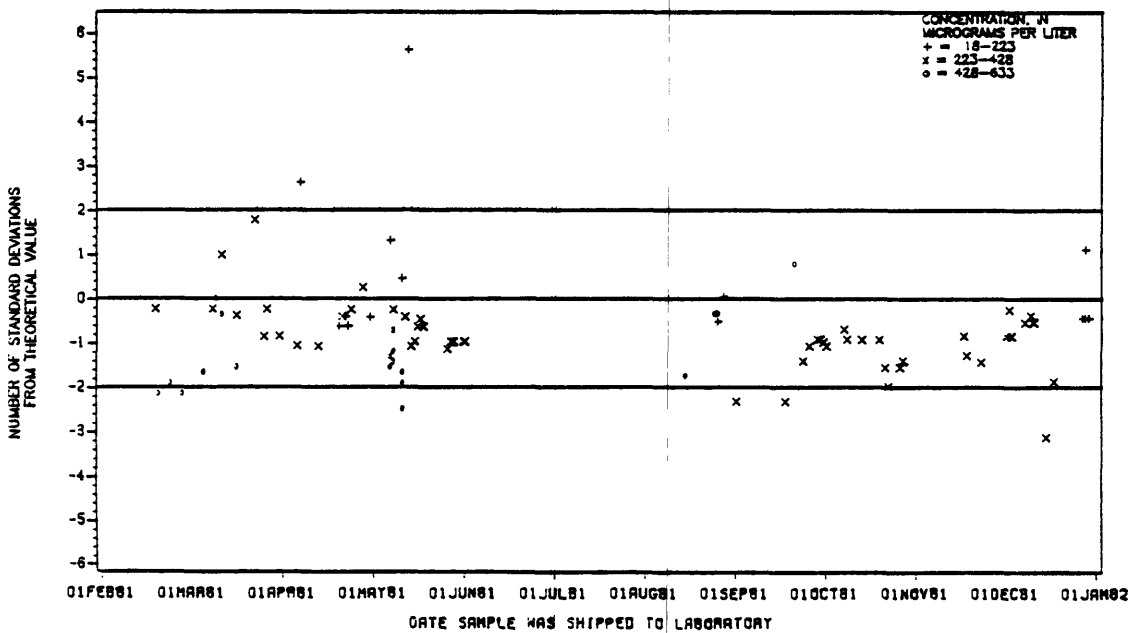


Figure 4.--Aluminum, dissolved, data from the Denver laboratory.

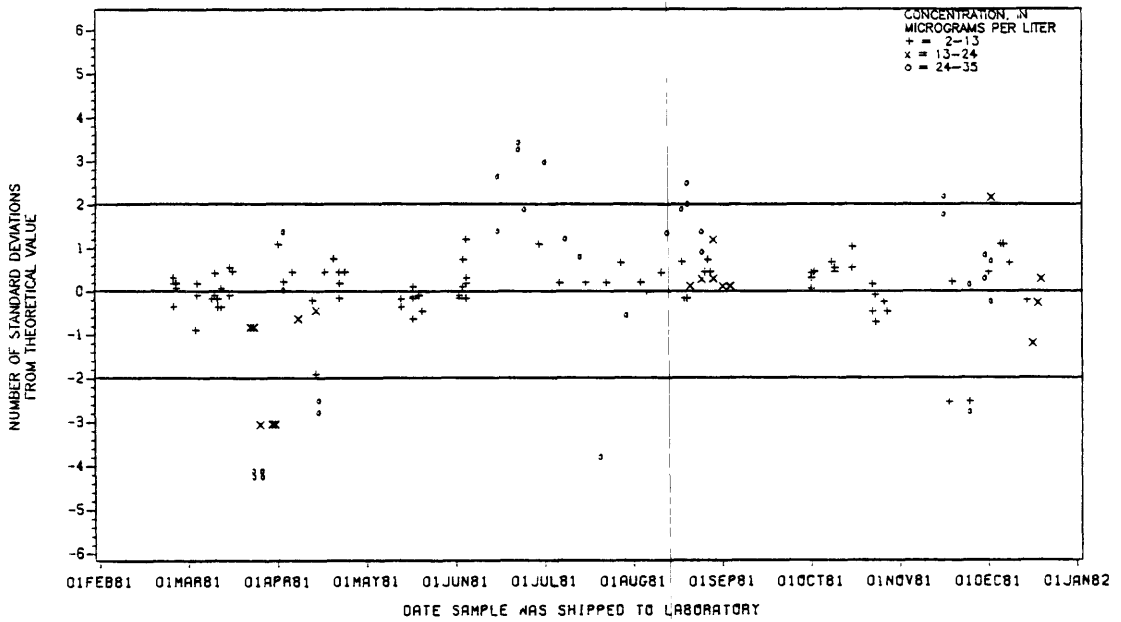


Figure 7.--Arsenic, dissolved, data from the Atlanta laboratory.

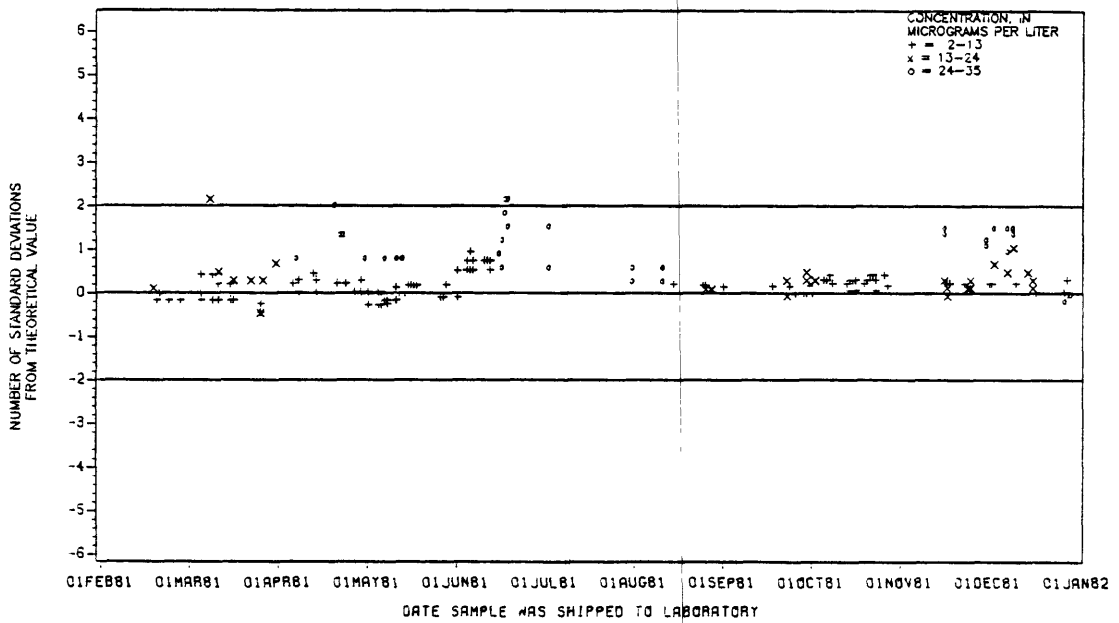


Figure 8.--Arsenic, dissolved, data from the Denver laboratory.

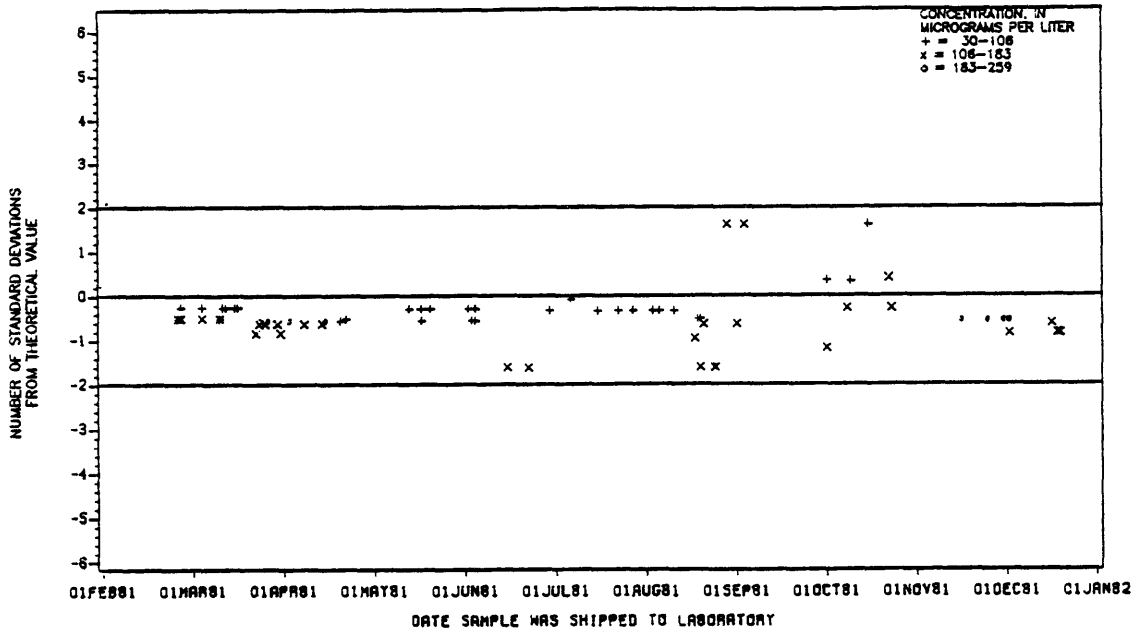


Figure 9.—Barium, dissolved, data from the Atlanta laboratory.

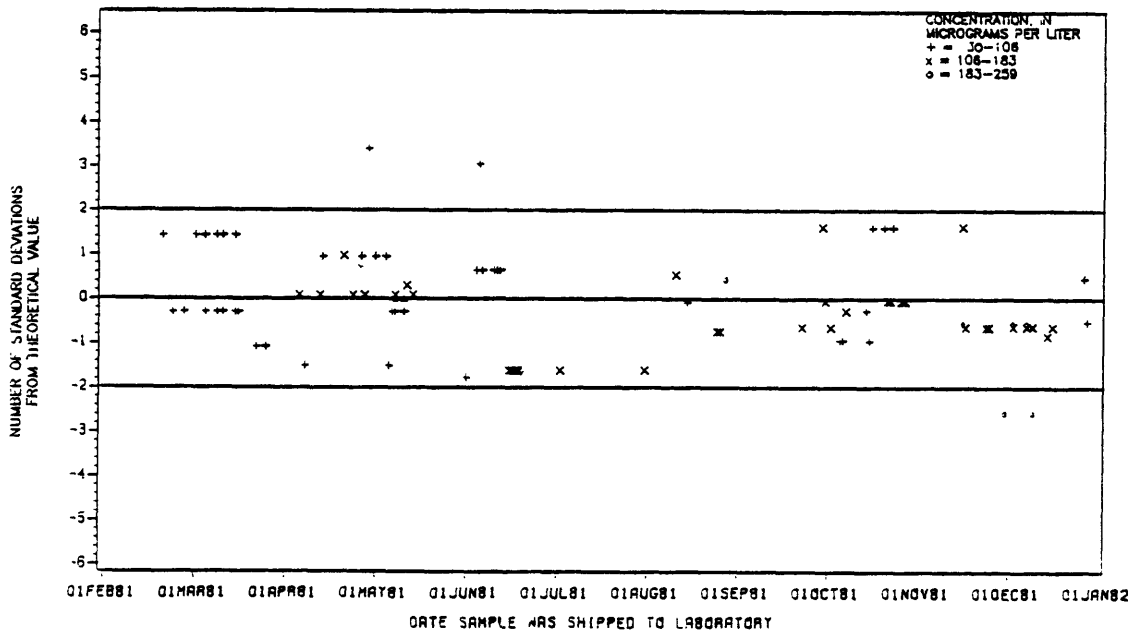


Figure 10.—Barium, dissolved, data from the Denver laboratory.

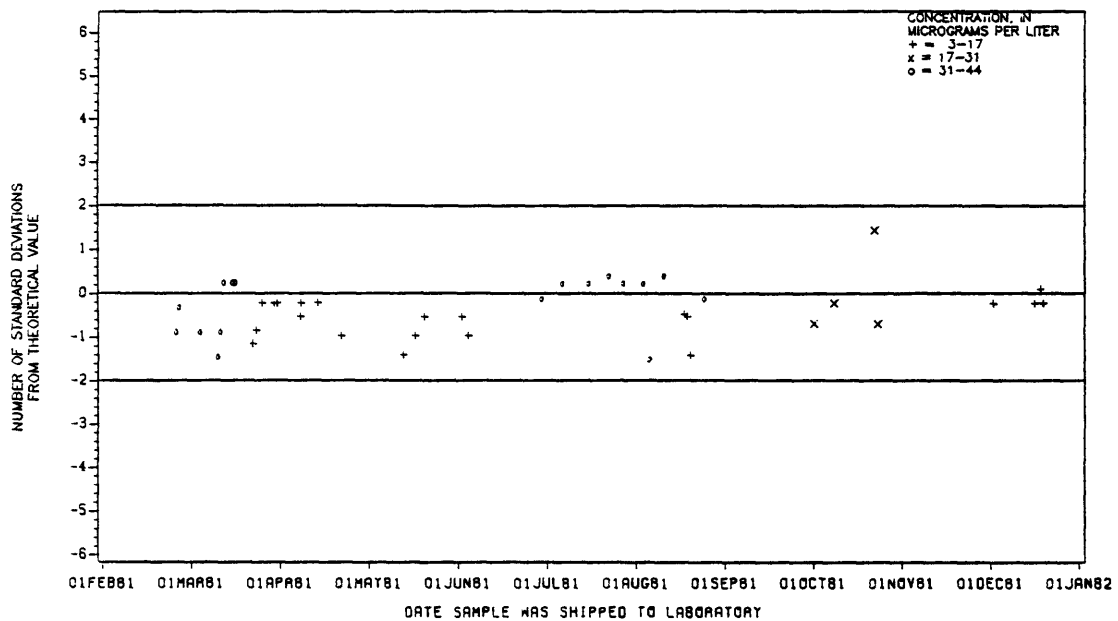


Figure 13.--Beryllium, dissolved, data from the Atlanta laboratory.

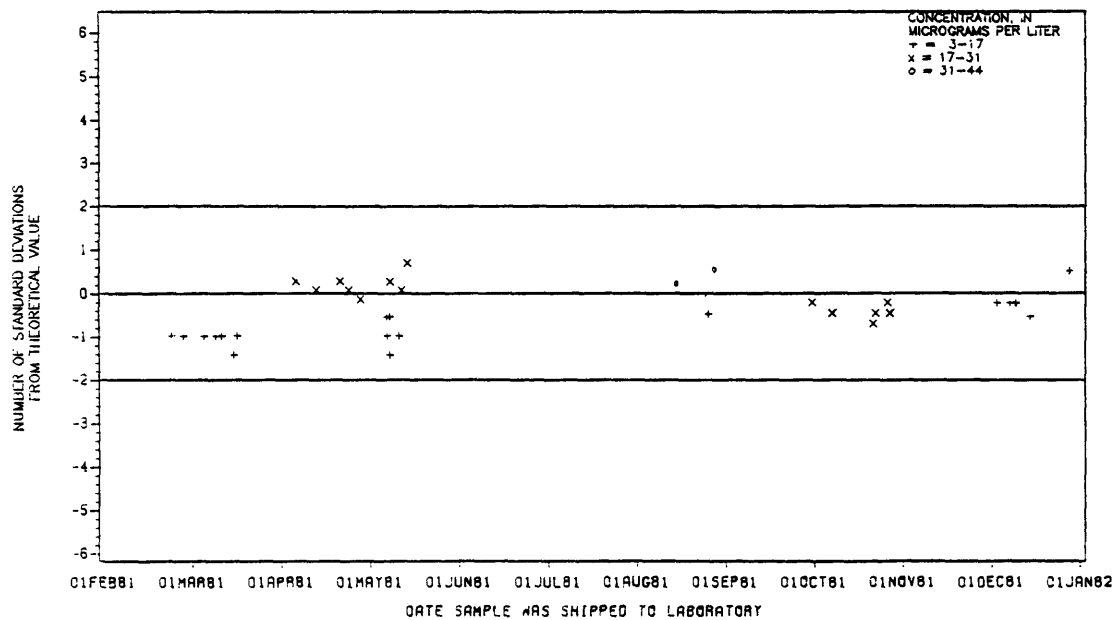


Figure 14.--Beryllium, dissolved, data from the Denver laboratory.

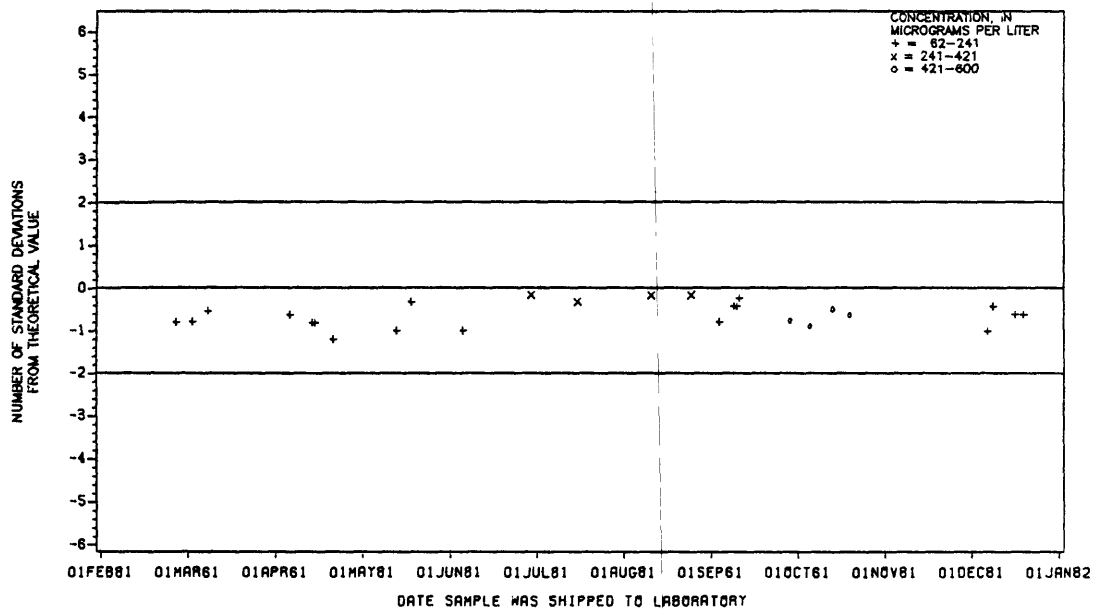


Figure 15.--Boron, dissolved, data from the Atlanta laboratory.

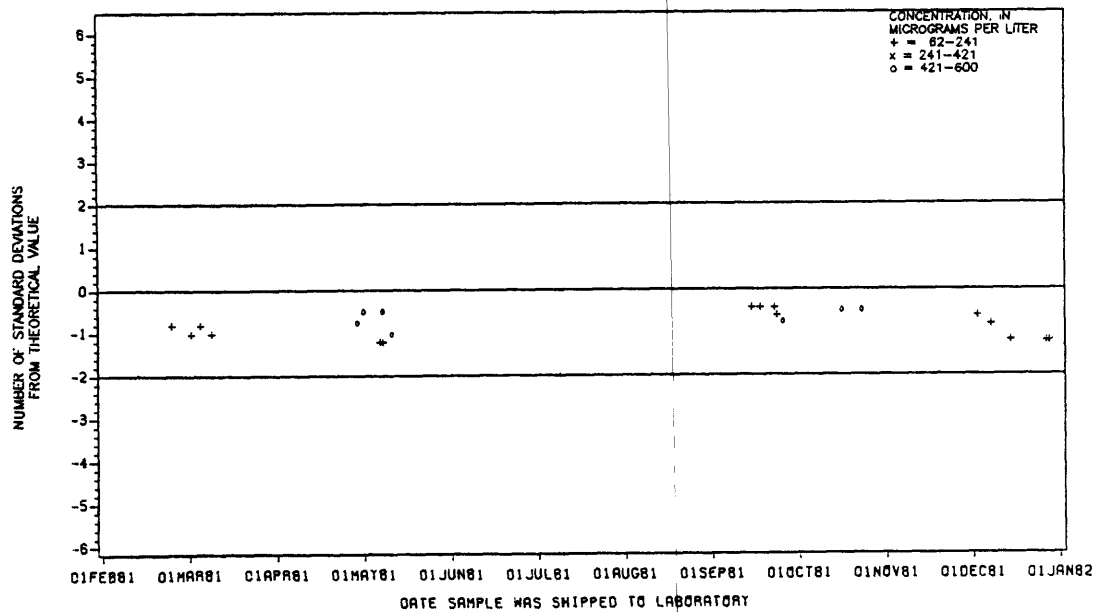


Figure 16.--Boron, dissolved, data from the Denver laboratory.

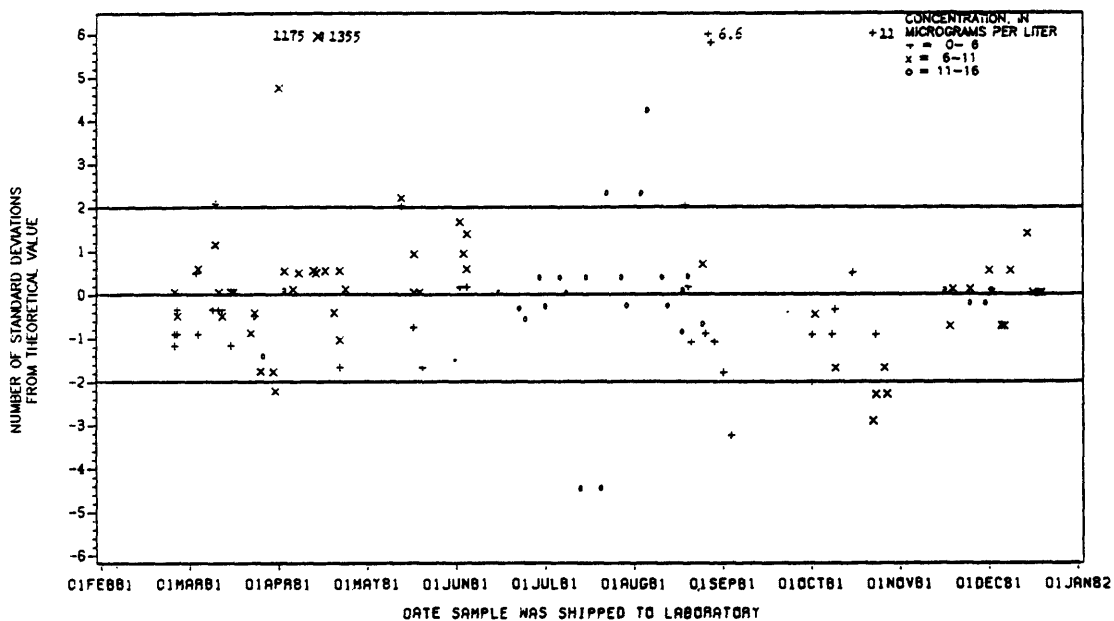


Figure 17.--Cadmium, dissolved, data from the Atlanta laboratory.

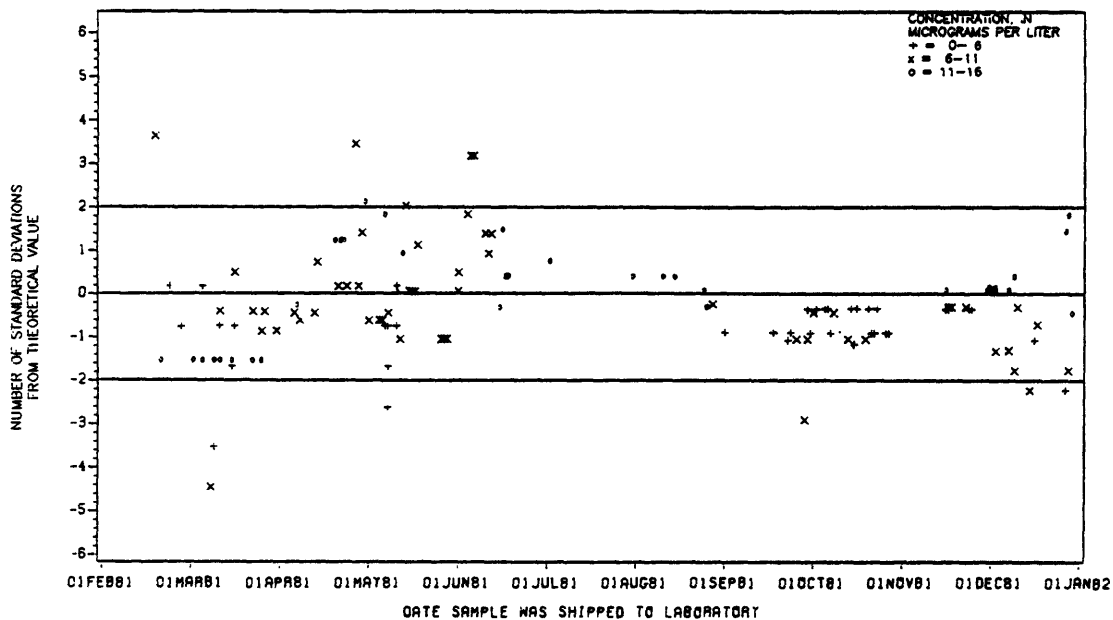


Figure 18.--Cadmium, dissolved, data from the Denver laboratory.

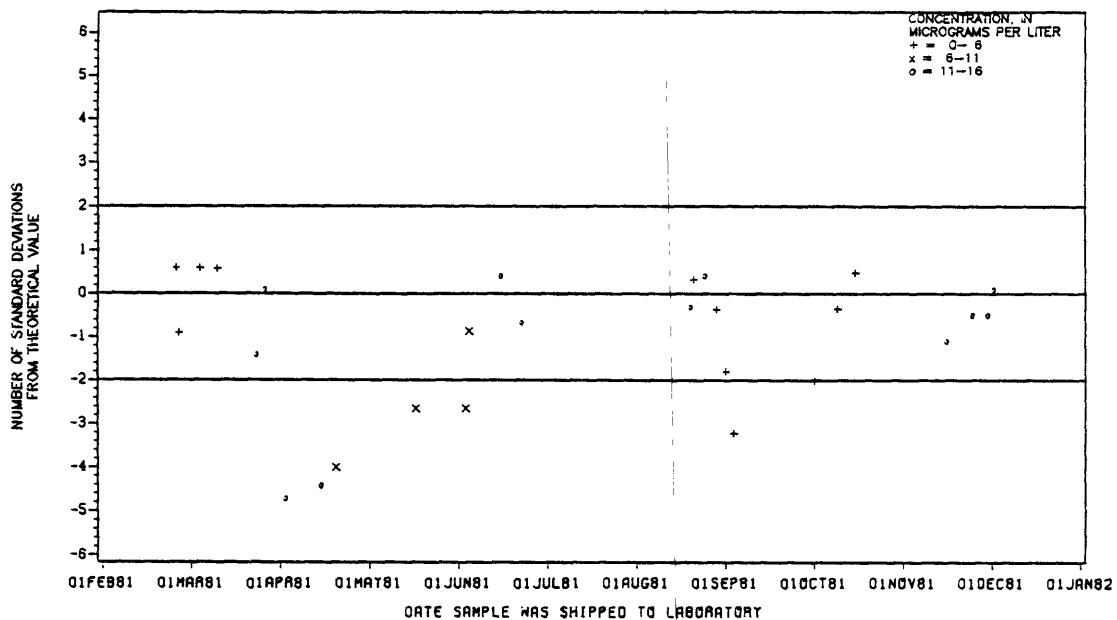


Figure 19.--Cadmium, total recoverable, data from the Atlanta laboratory.

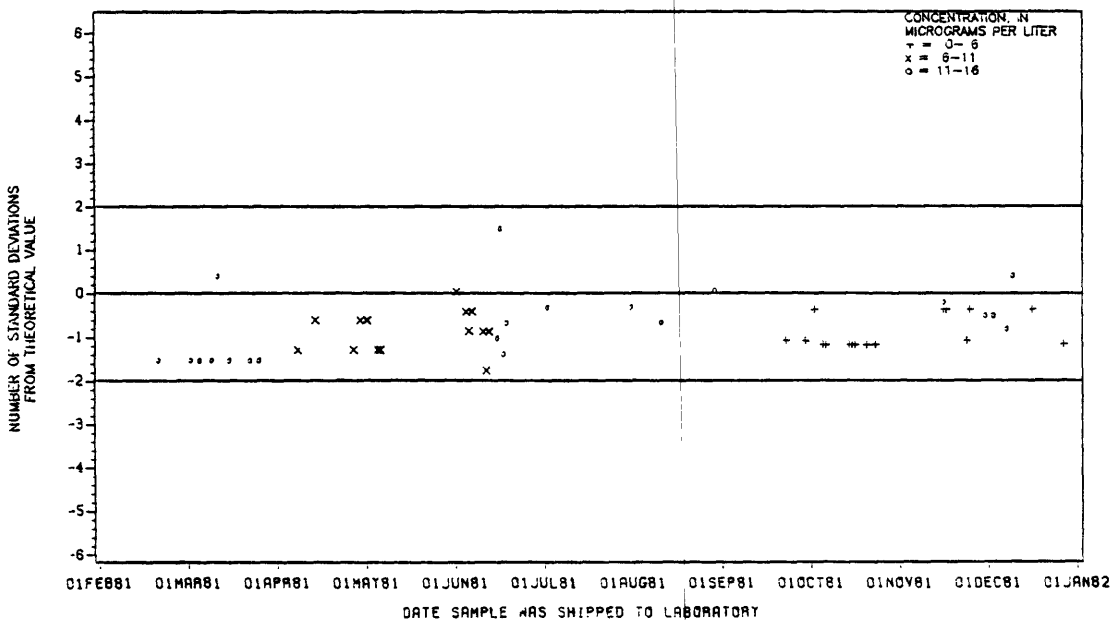


Figure 20.--Cadmium, total recoverable, data from the Denver laboratory.

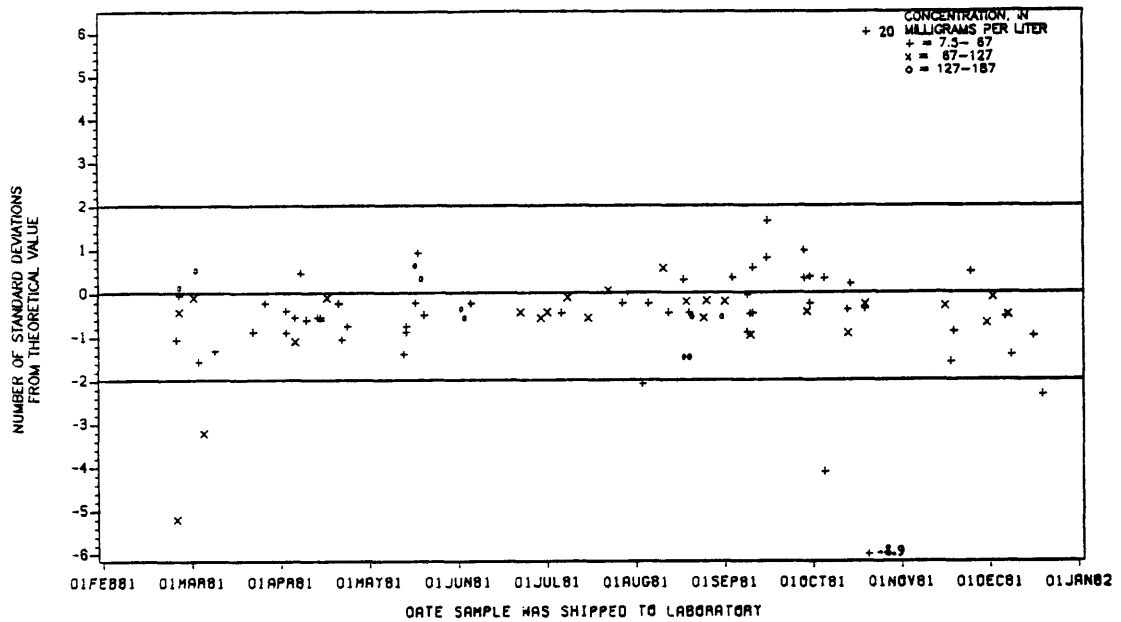


Figure 21.--Calcium, dissolved, data from the Atlanta laboratory.

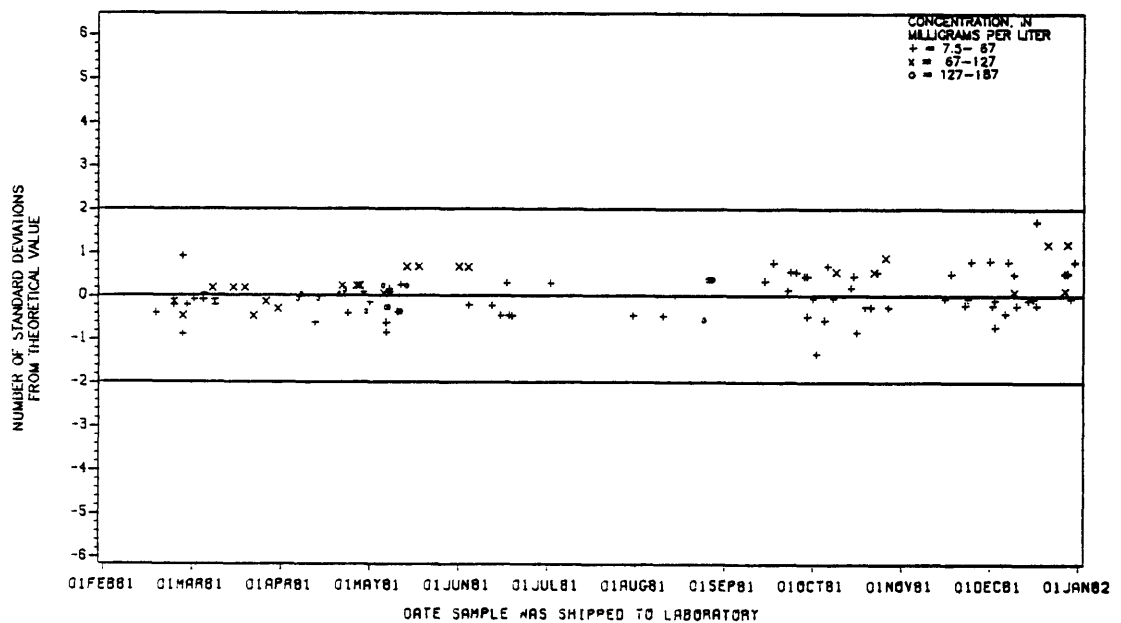


Figure 22.--Calcium, dissolved, data from the Denver laboratory.

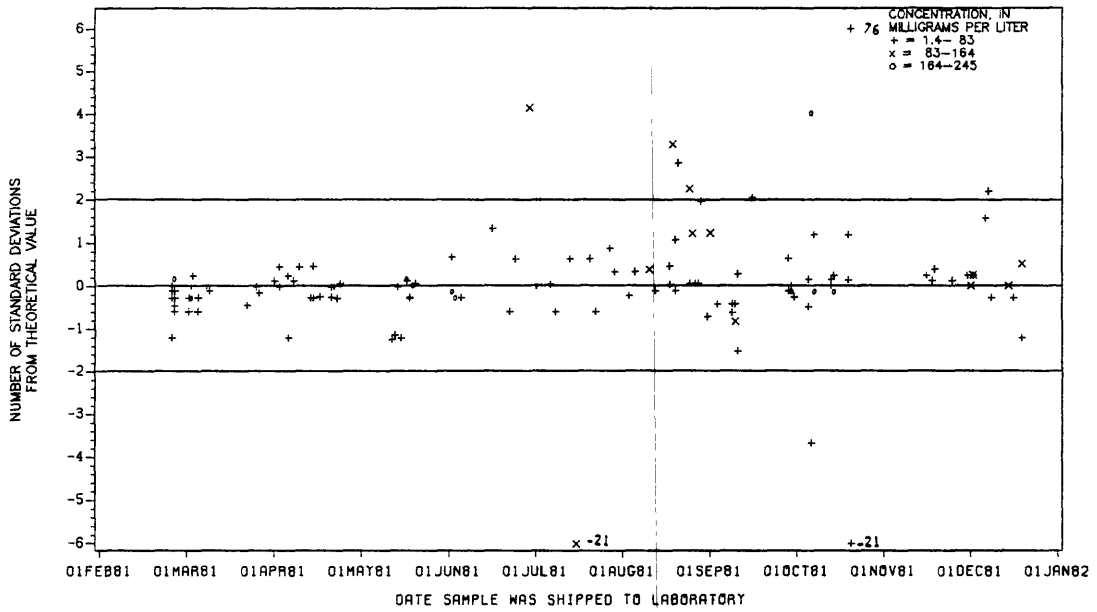


Figure 23.--Chloride, dissolved, data from the Atlanta laboratory.

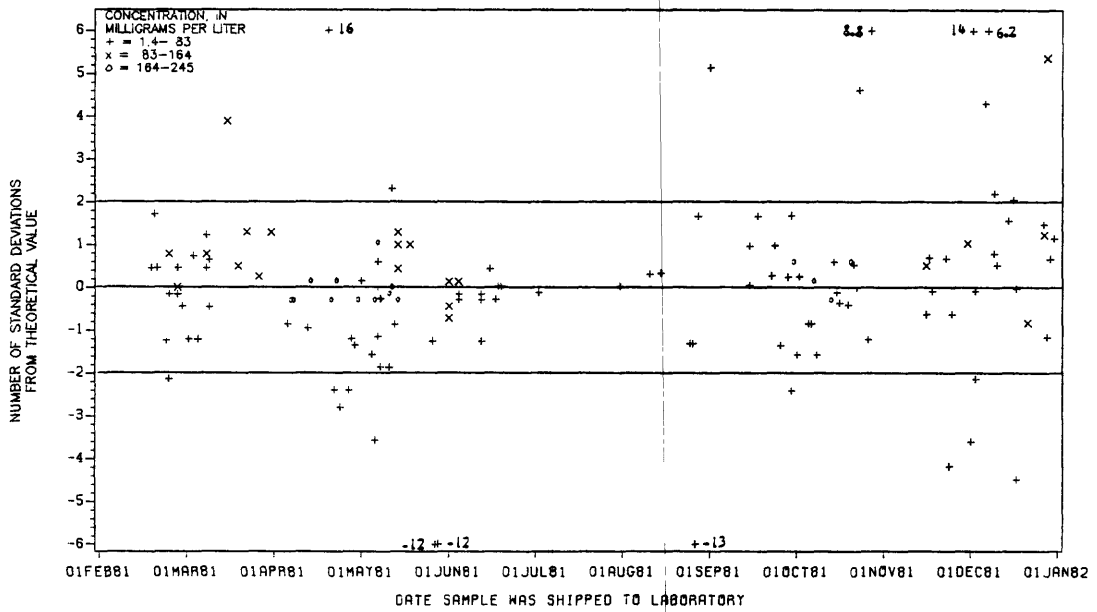


Figure 24.--Chloride, dissolved, data from the Denver laboratory.

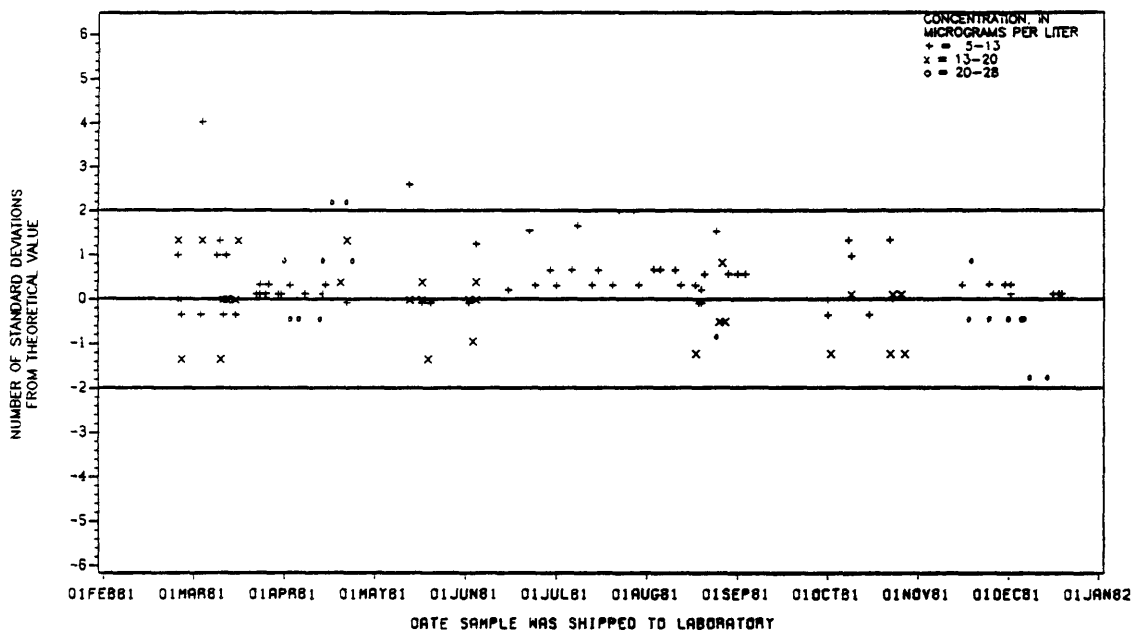


Figure 25.--Chromium, dissolved, data from the Atlanta laboratory.

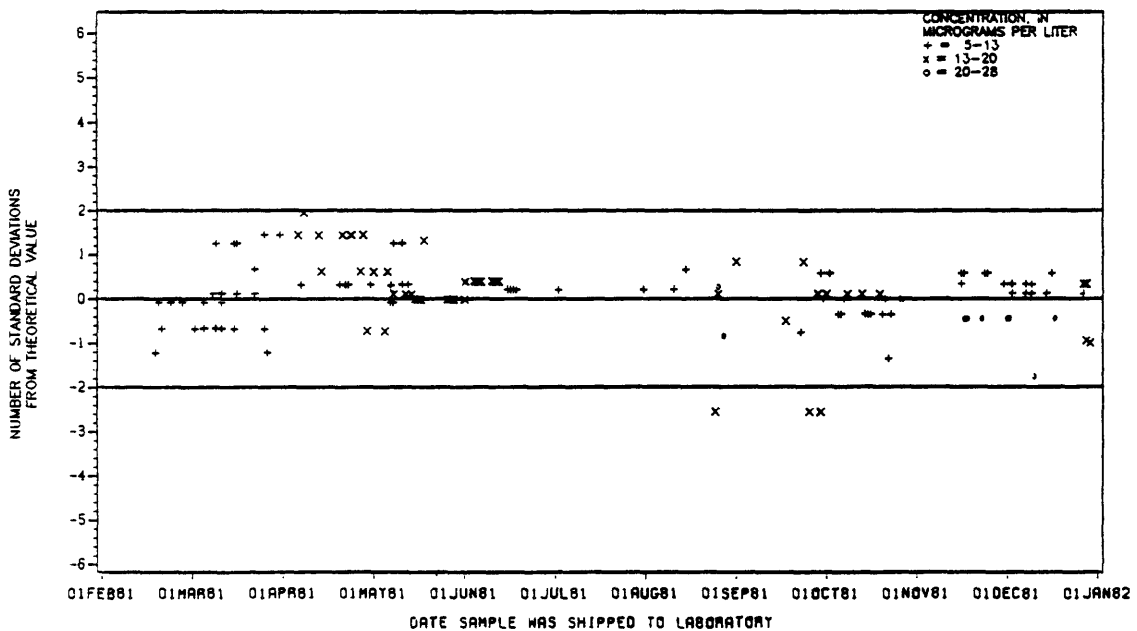


Figure 26.--Chromium, dissolved, data from the Denver laboratory.

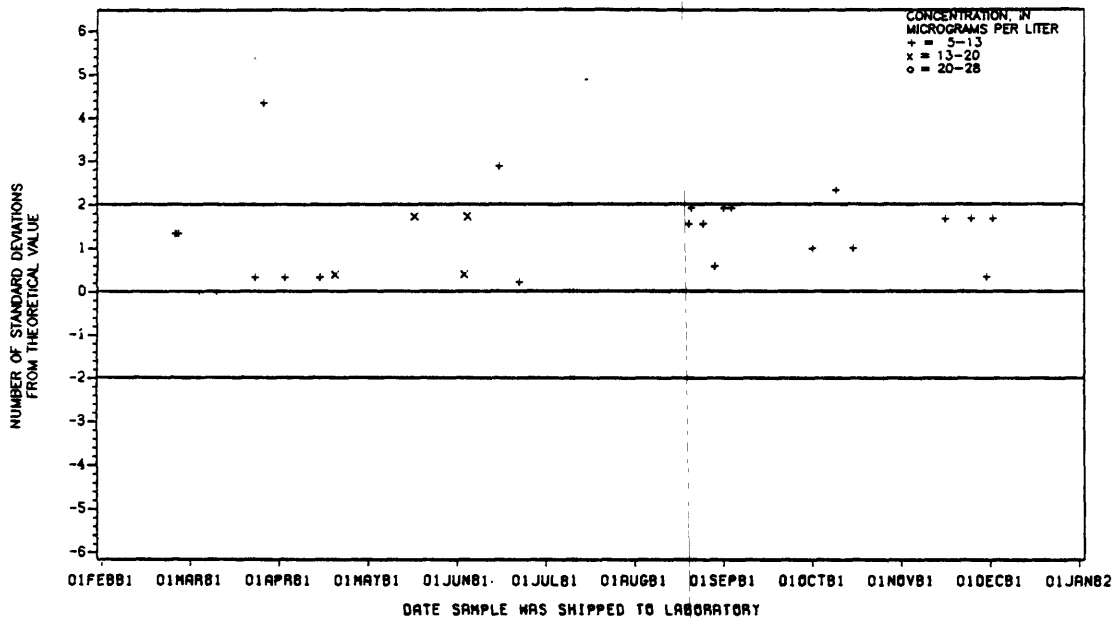


Figure 27.--Chromium, total recoverable, data from the Atlanta laboratory.

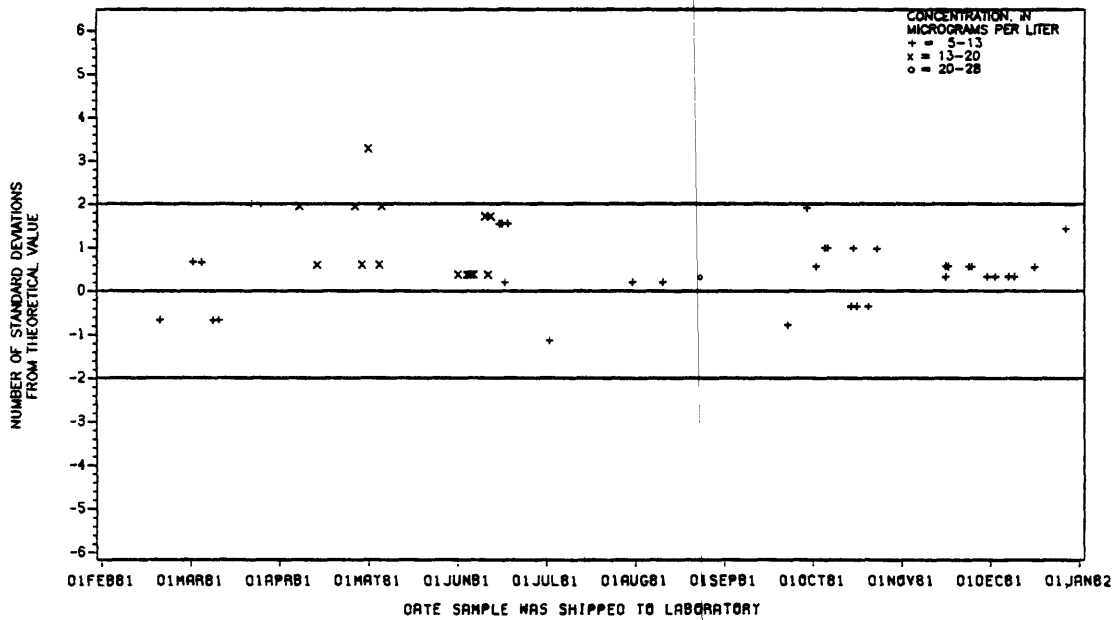


Figure 28.--Chromium, total recoverable, data from the Denver laboratory.

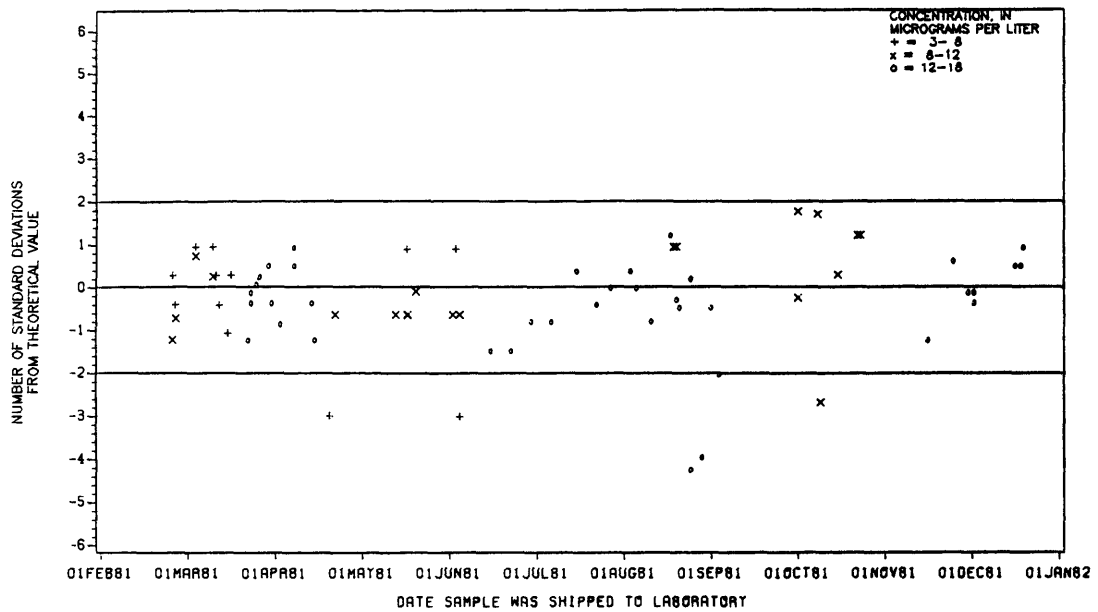


Figure 29.--Cobalt, dissolved, data from the Atlanta laboratory.

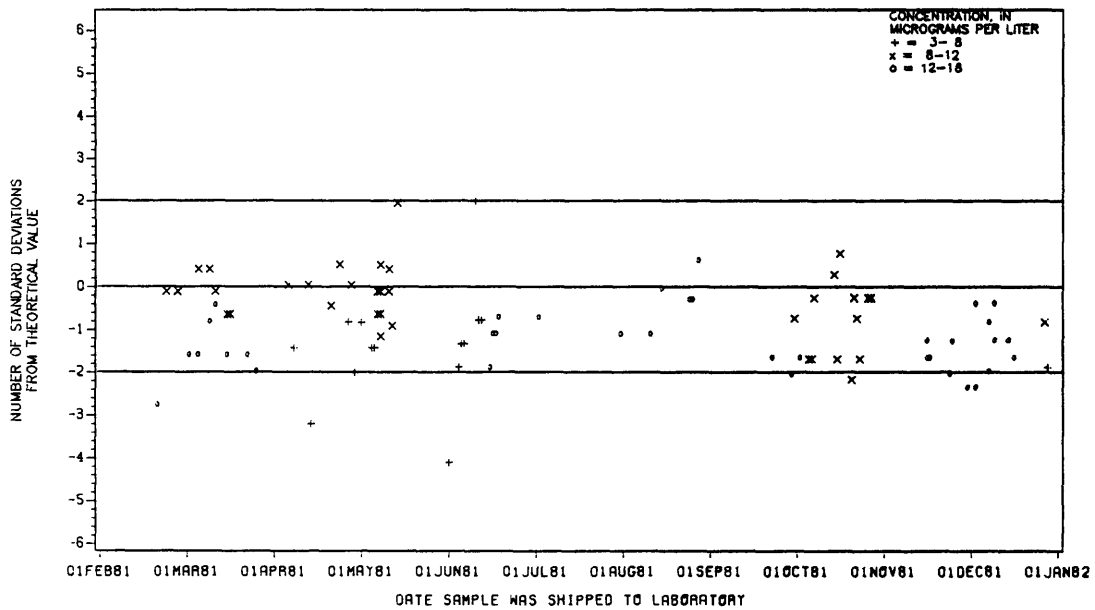


Figure 30.--Cobalt, dissolved, data from the Denver laboratory.

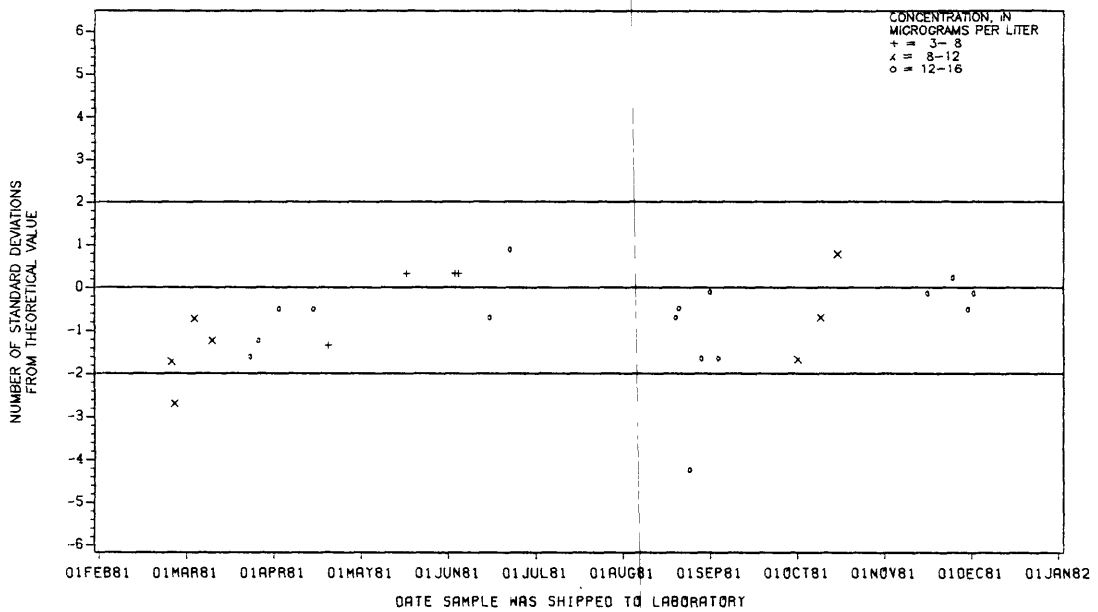


Figure 31.--Cobalt, total recoverable, data from the Atlanta laboratory.

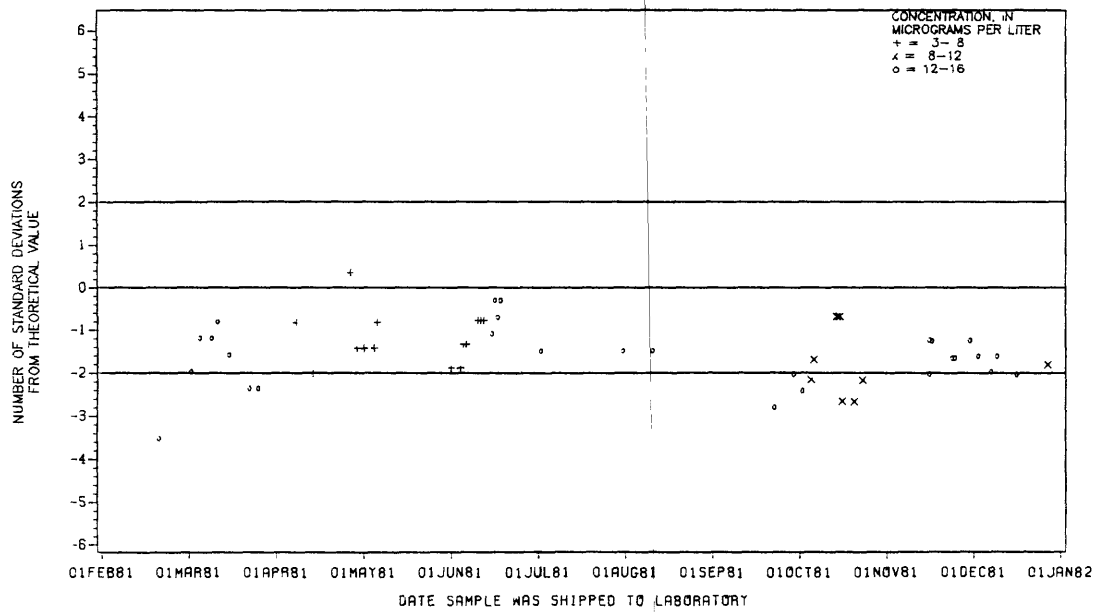


Figure 32.--Cobalt, total recoverable, data from the Denver laboratory.

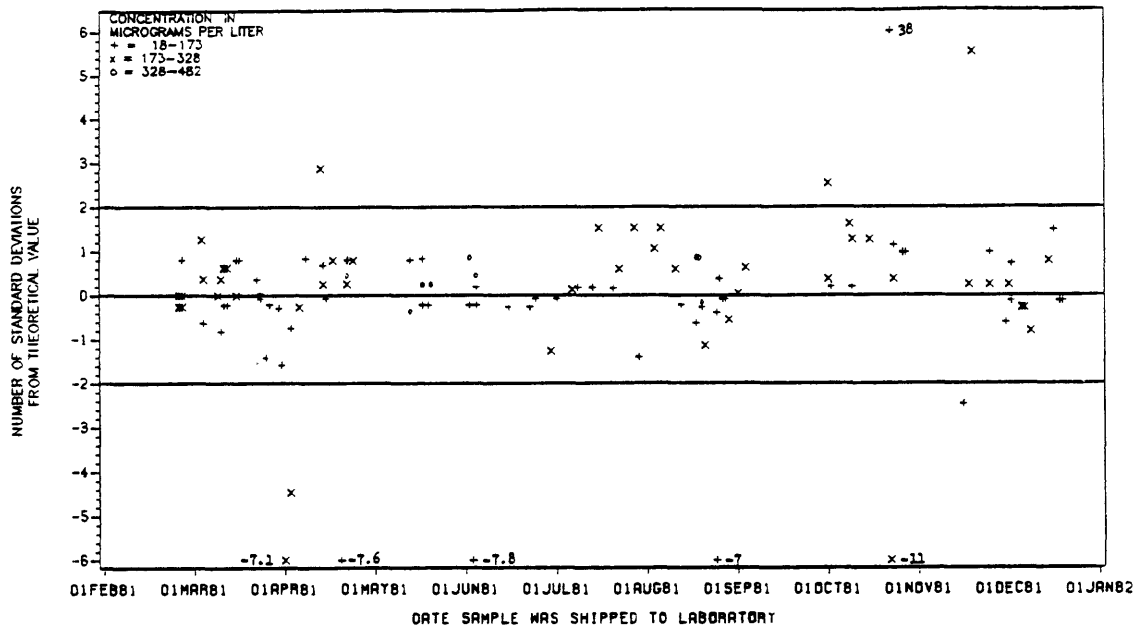


Figure 33.--Copper, dissolved, data from the Atonto laboratory.

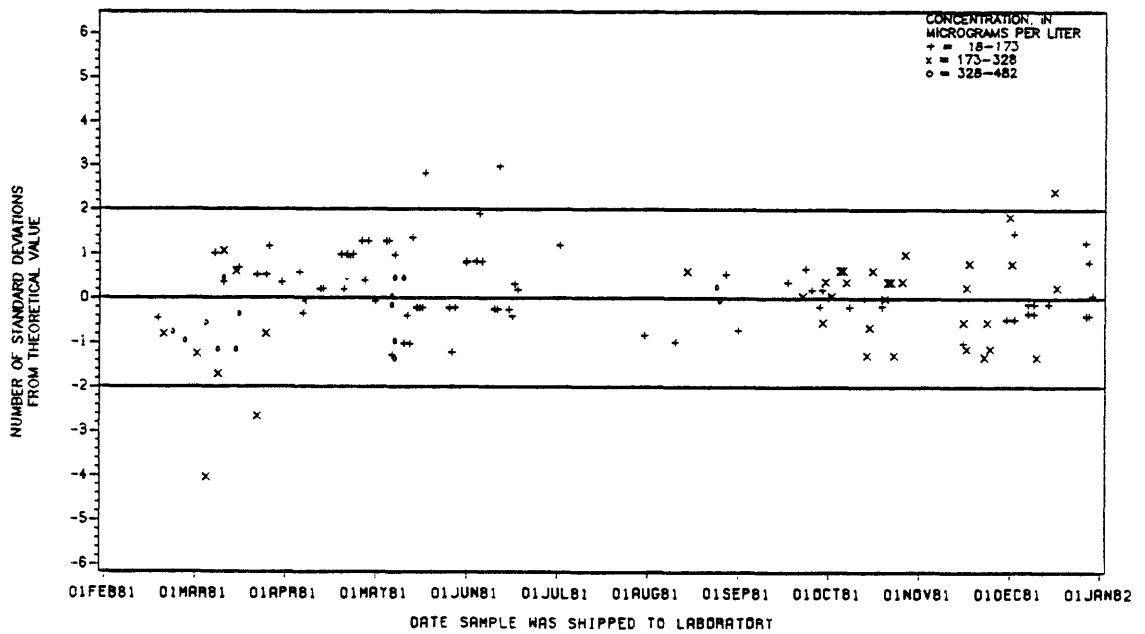


Figure 34.--Copper, dissolved, data from the Denver laboratory.

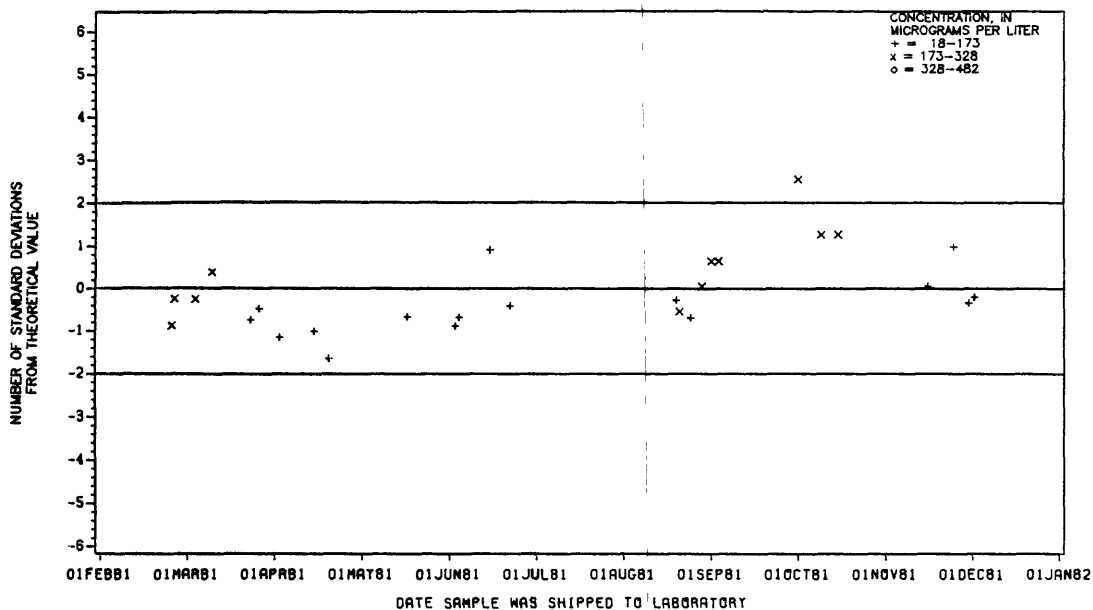


Figure 35.--Copper, total recoverable, data from the Atlanta laboratory.

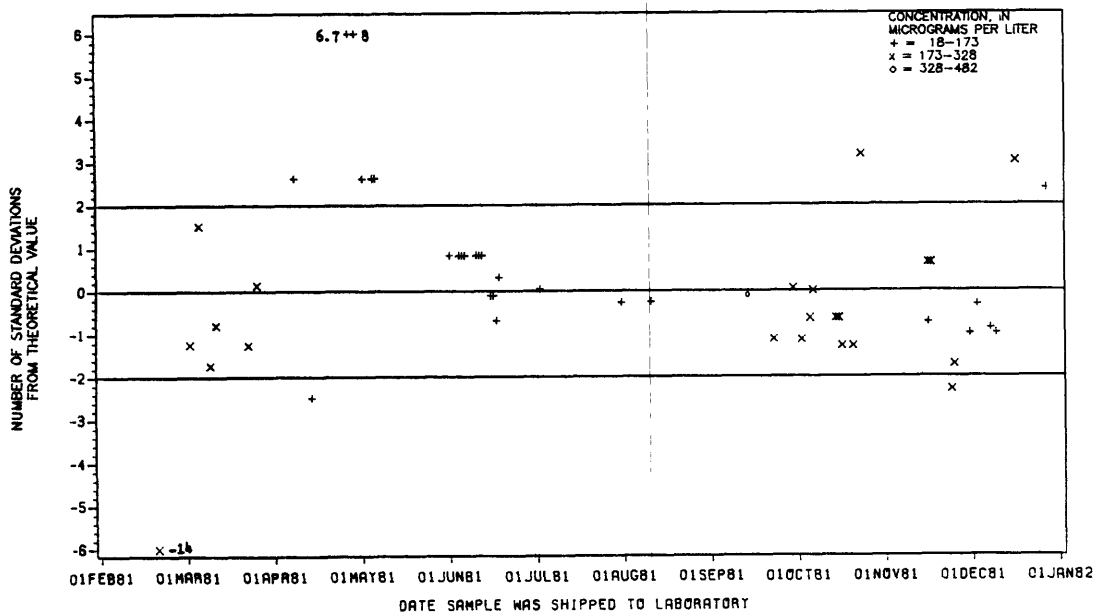


Figure 36.--Copper, total recoverable, data from the Denver laboratory.

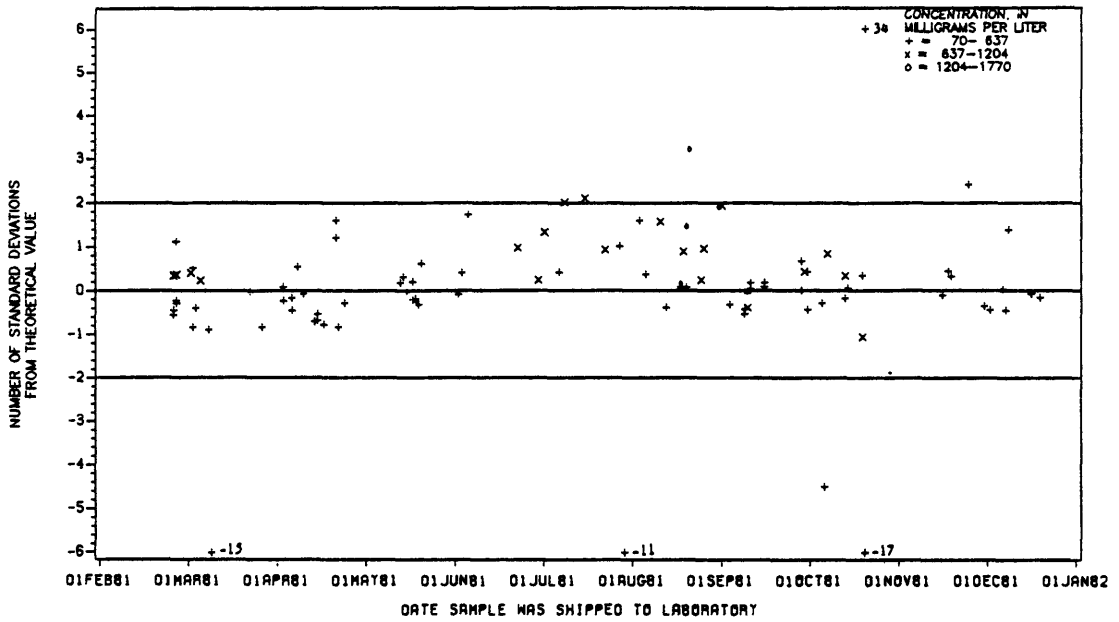


Figure 37.--Dissolved solids, data from the Atlanta laboratory.

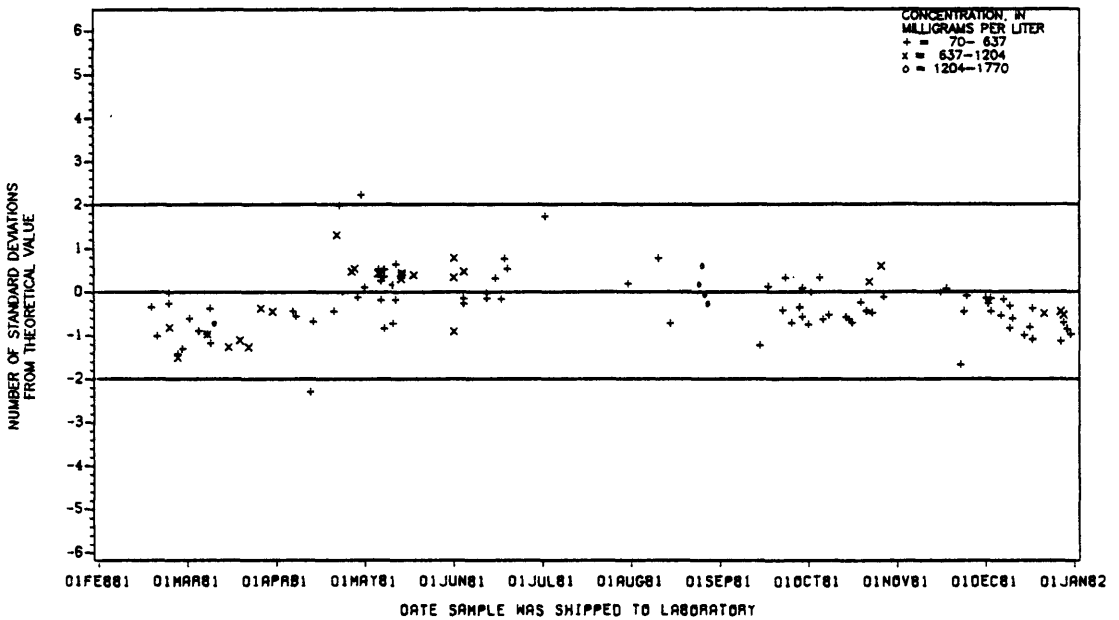


Figure 38.--Dissolved solids, data from the Denver laboratory.

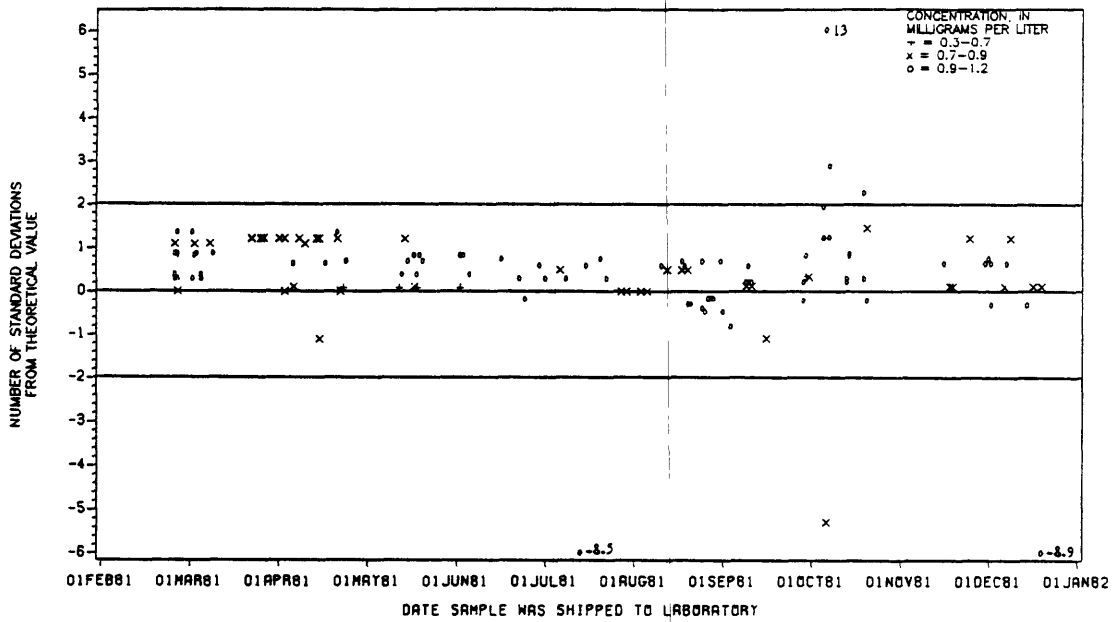


Figure 39.--Fluoride, dissolved, data from the Atlanta laboratory.

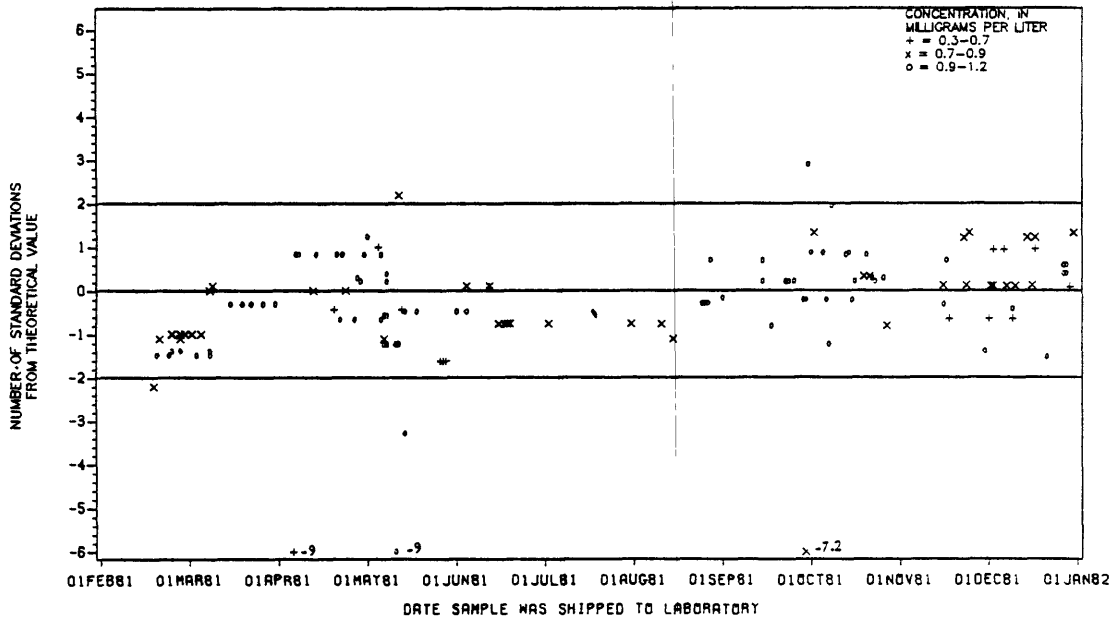


Figure 40.--Fluoride, dissolved, data from the Denver laboratory.

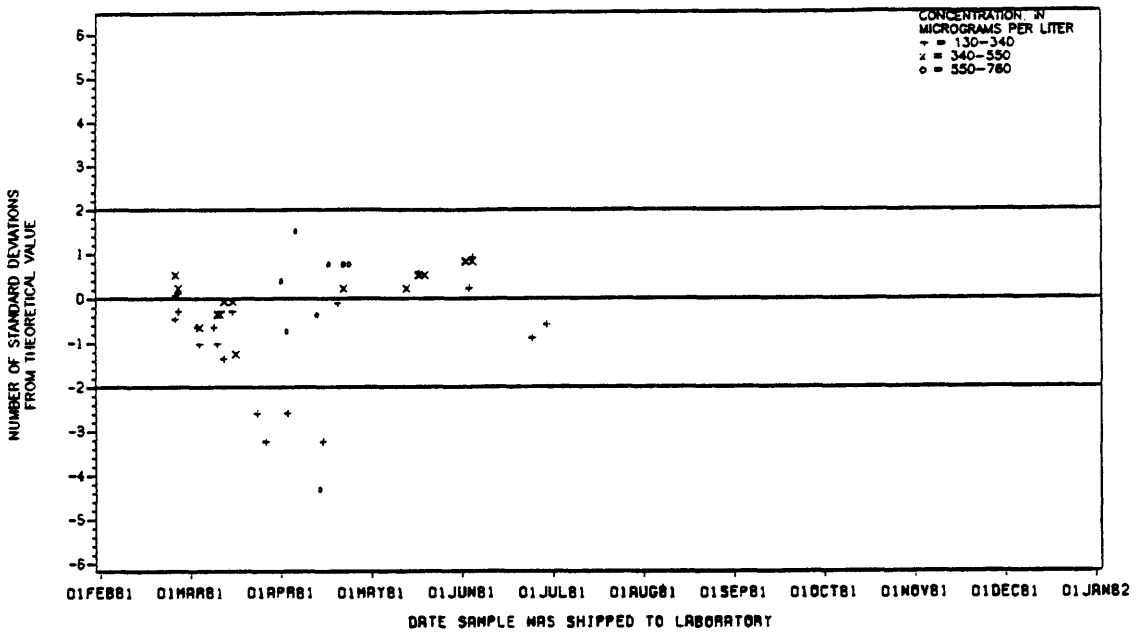


Figure 41.--Iron, dissolved, data from the Atlanta laboratory.

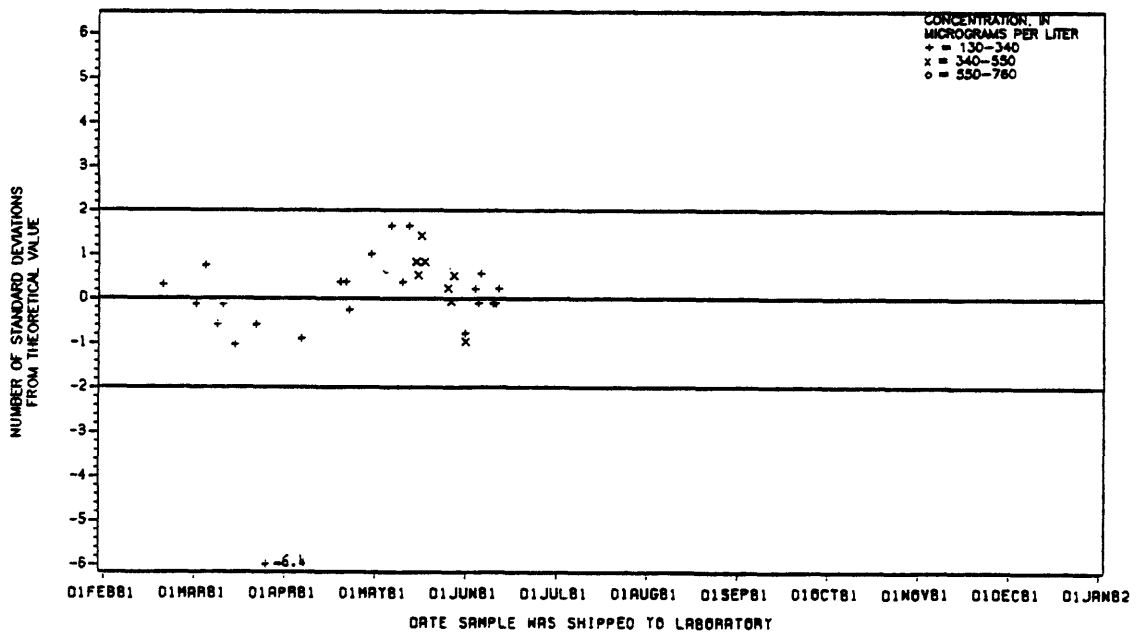


Figure 42.--Iron, dissolved, data from the Denver laboratory.

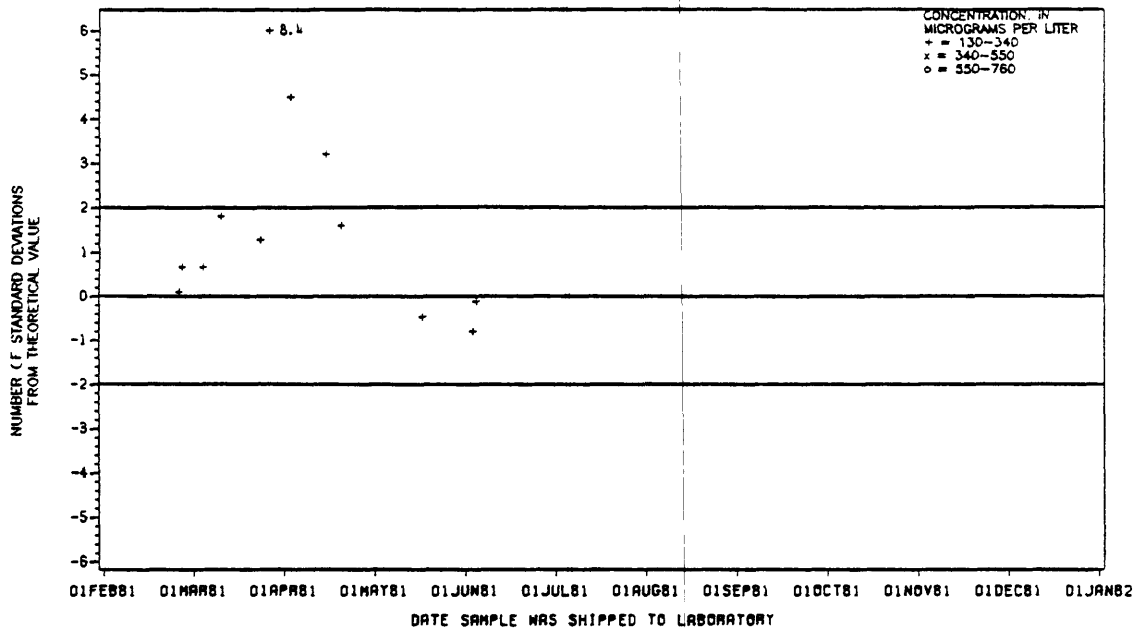


Figure 43.--Iron, total recoverable, data from the Atlanta laboratory.

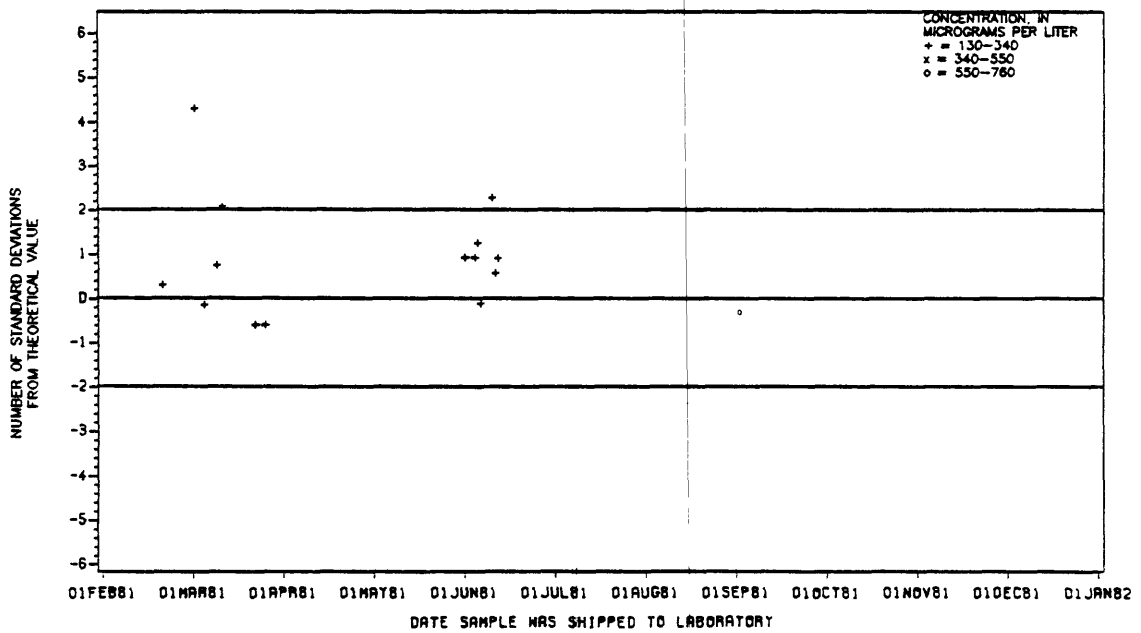


Figure 44.--Iron, total recoverable, data from the Denver laboratory.

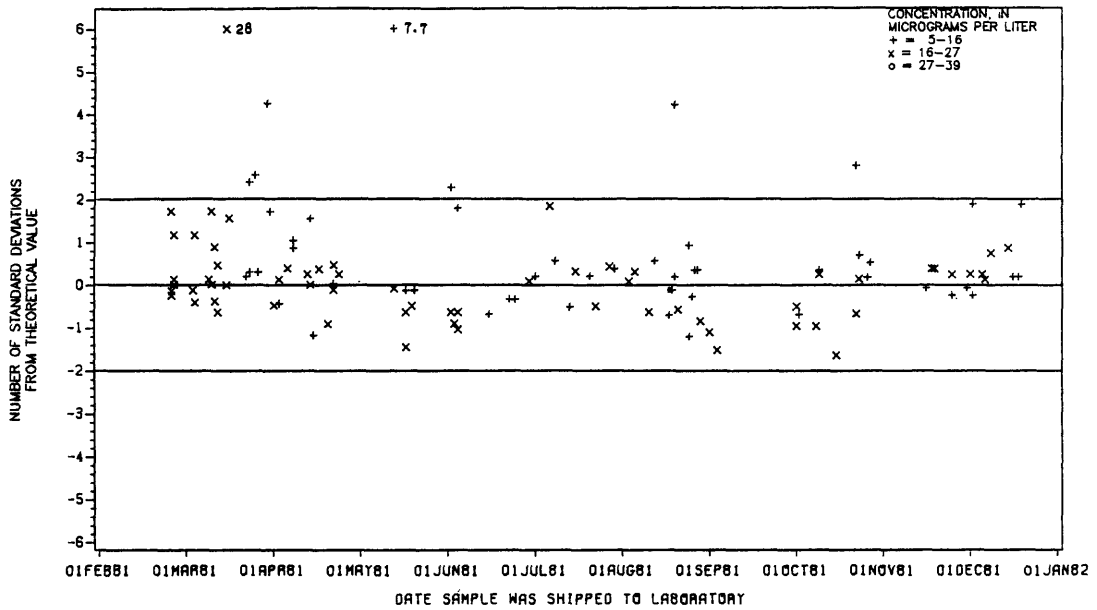


Figure 45.--Lead, dissolved, data from the Atlanta laboratory.

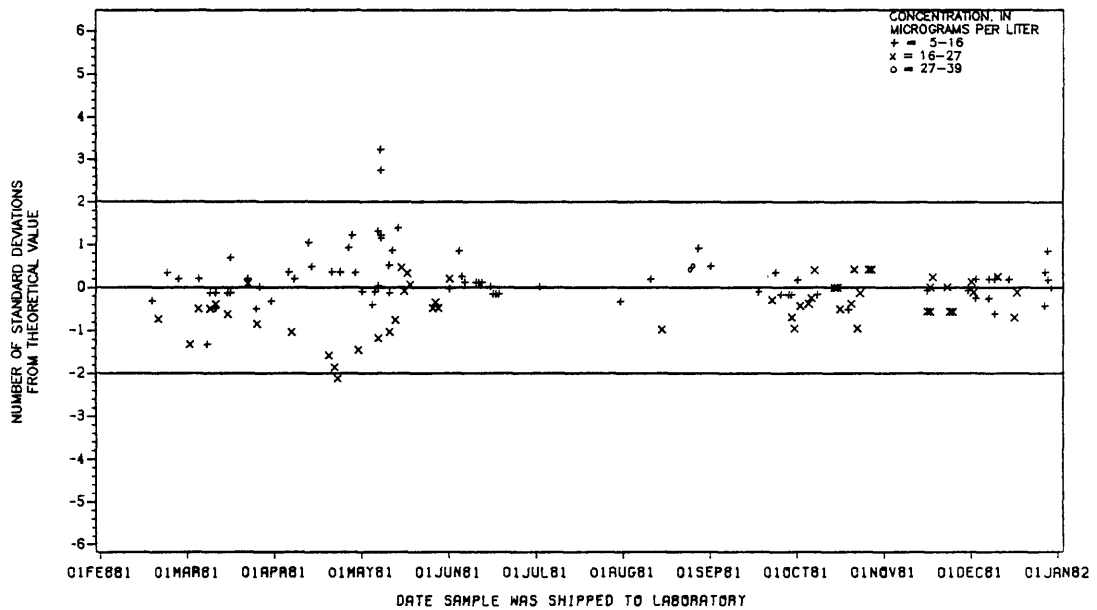


Figure 46.--Lead, dissolved, data from the Denver laboratory.

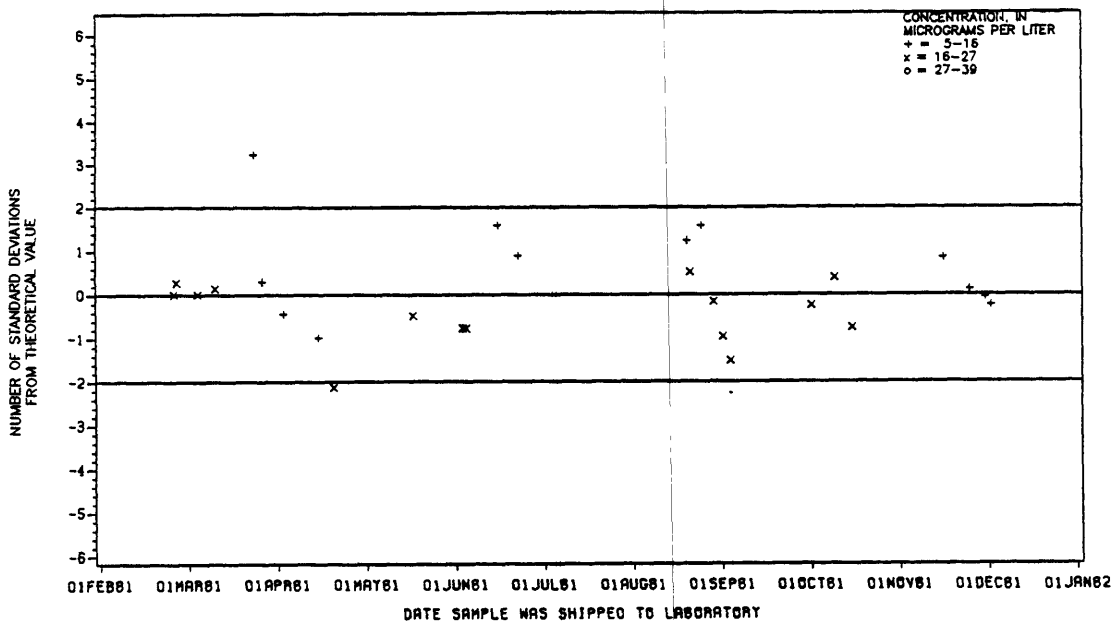


Figure 47.—Lead, total recoverable, data from the Atlanta laboratory.

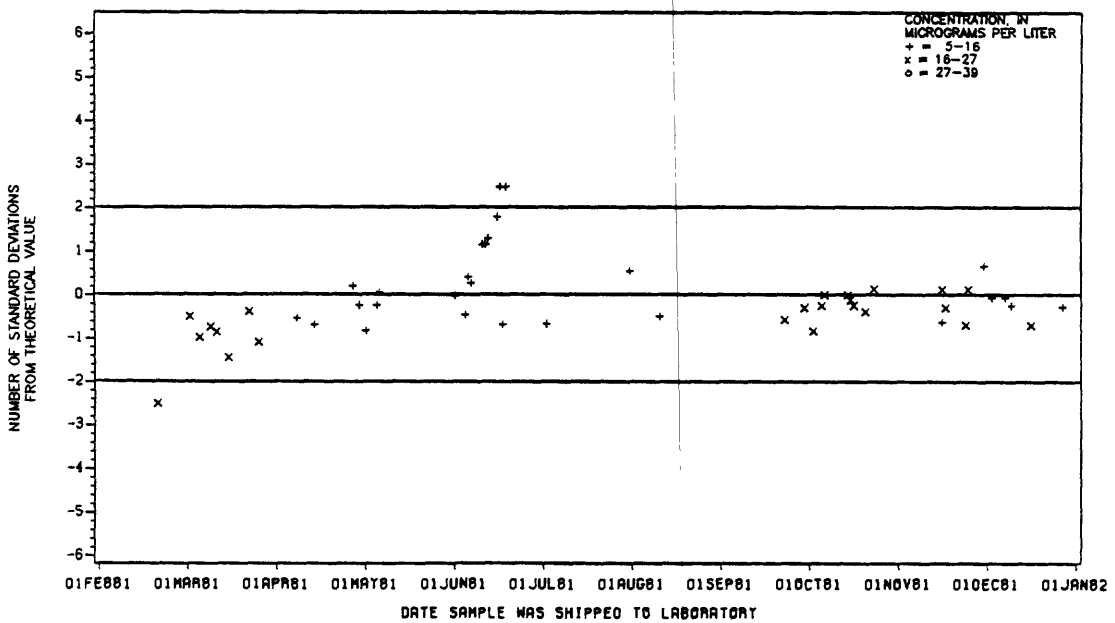


Figure 48.—Lead, total recoverable, data from the Denver laboratory.

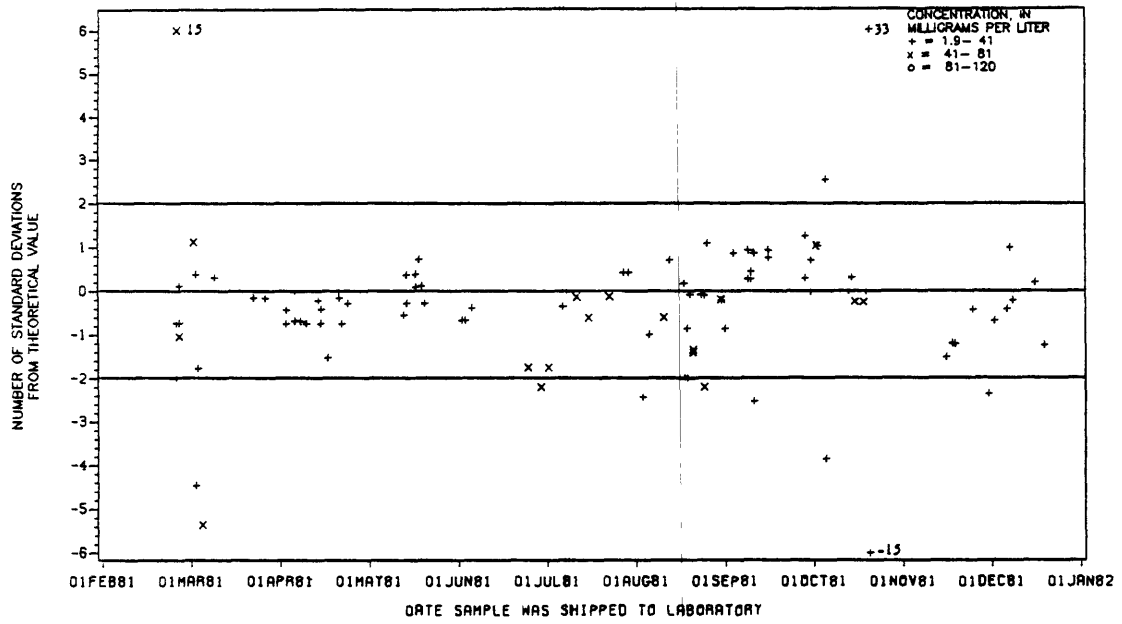


Figure 51.--Magnesium, dissolved, data from the Atlanta laboratory.

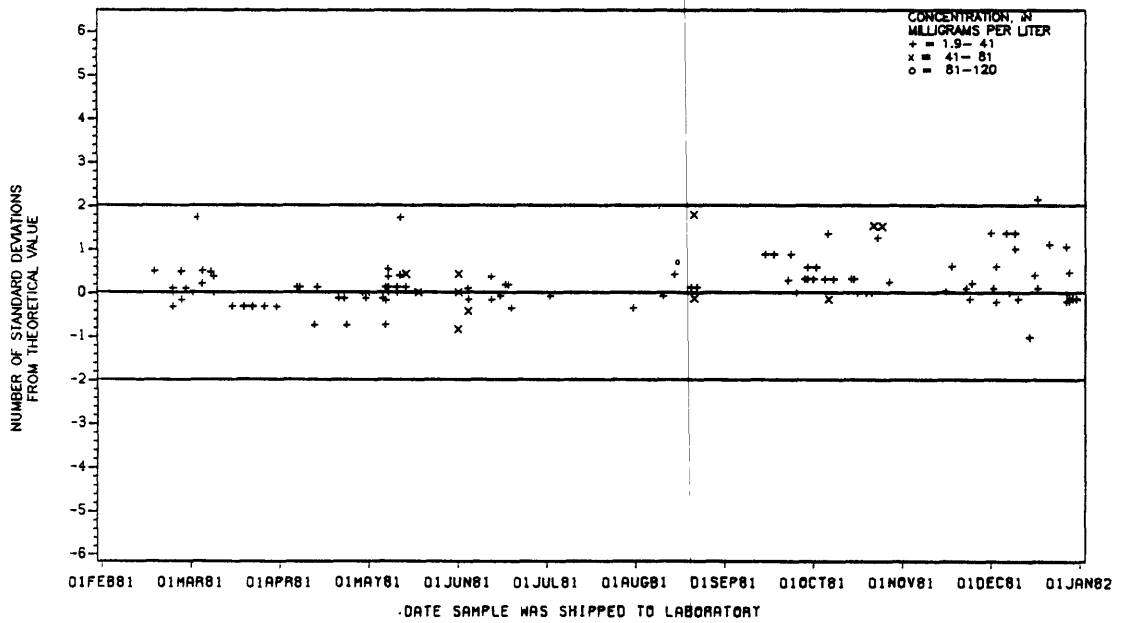


Figure 52.--Magnesium, dissolved, data from the Denver laboratory.

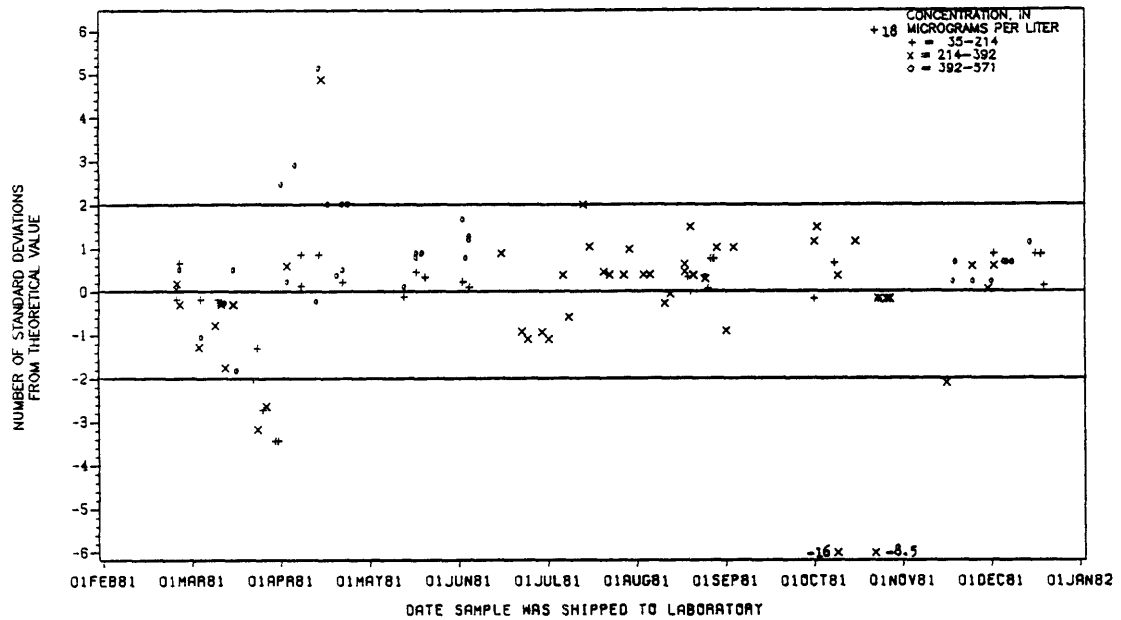


Figure 53.--Manganese, dissolved, data from the Atlanta laboratory.

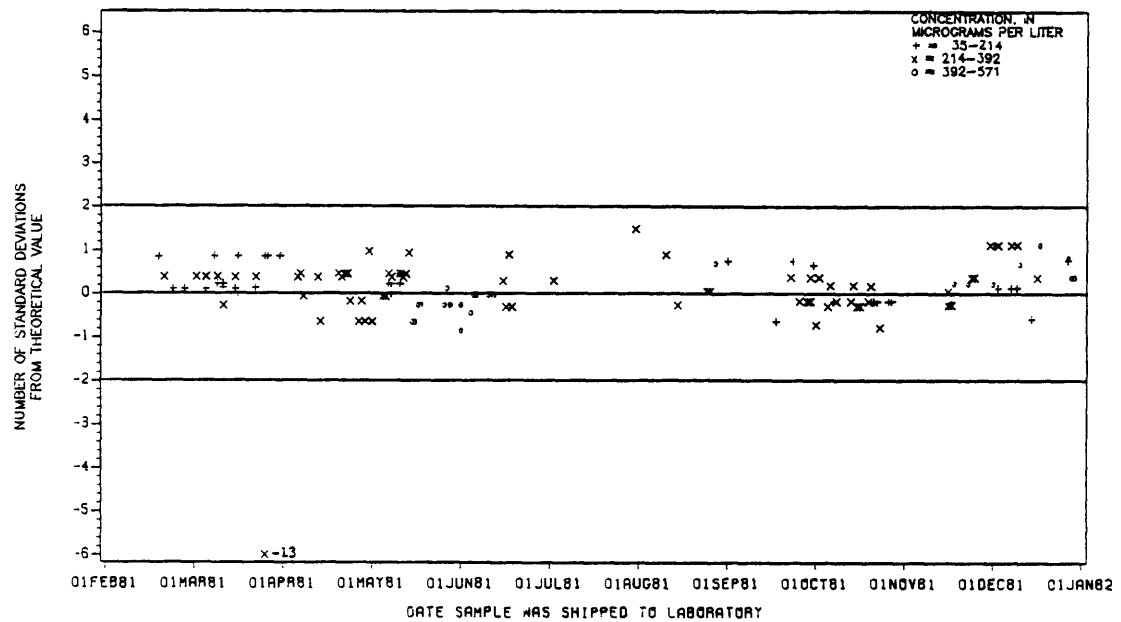


Figure 54.--Manganese, dissolved, data from the Denver laboratory.

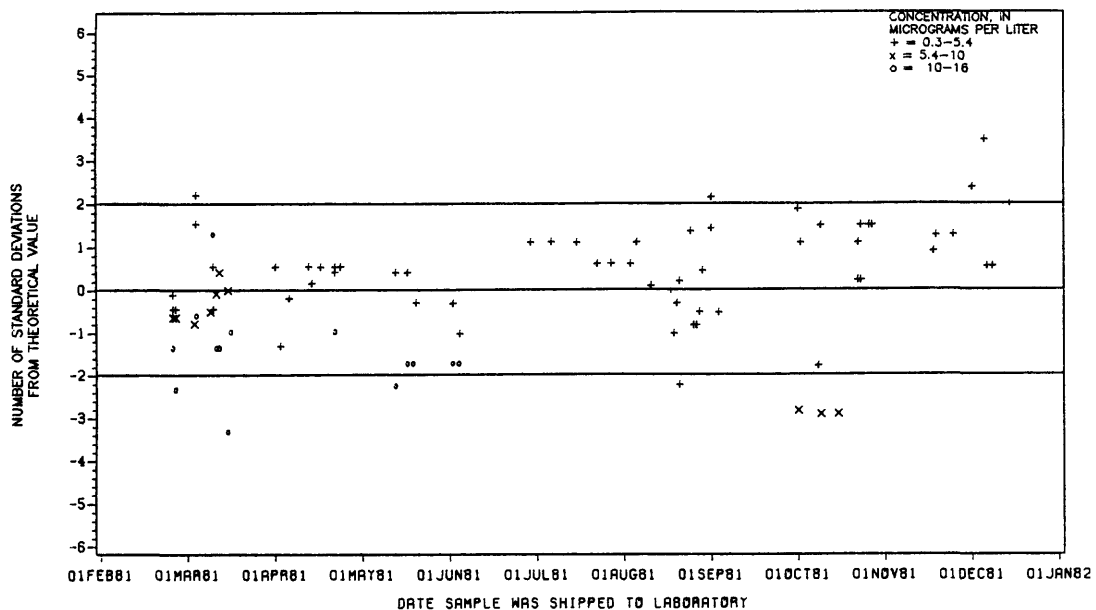


Figure 57.--Mercury, dissolved, data from the Atlanta laboratory.

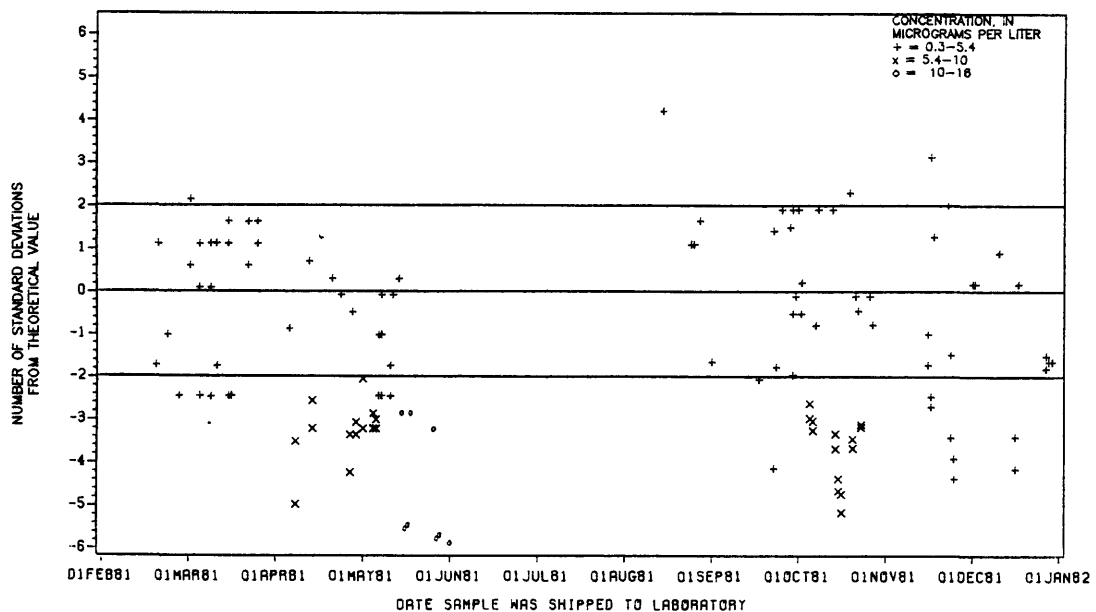


Figure 58.--Mercury, dissolved, data from the Denver laboratory.

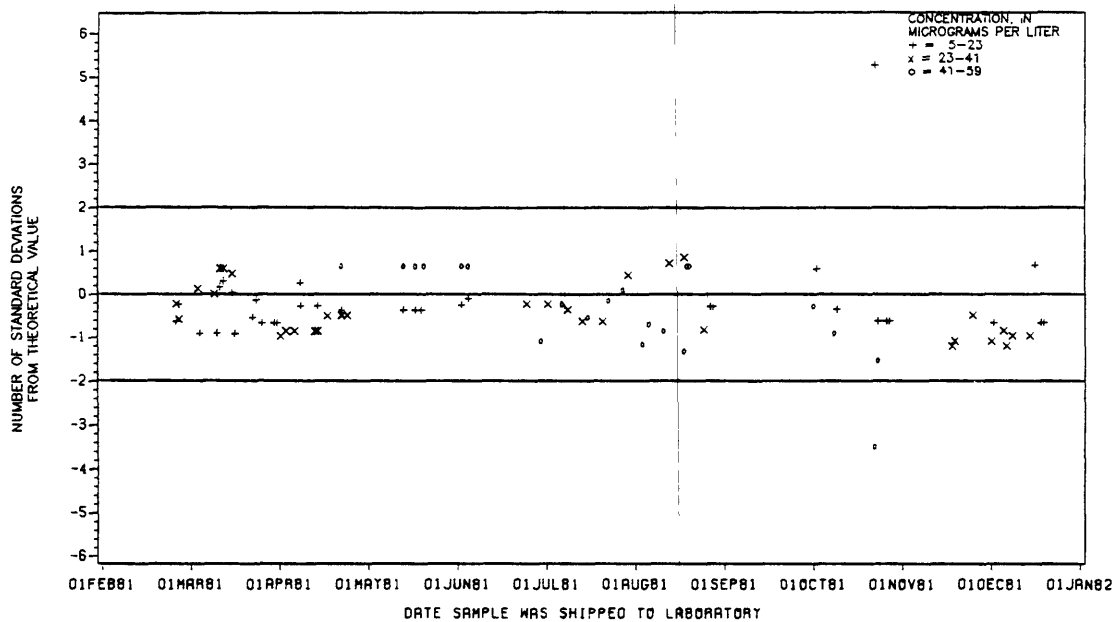


Figure 59.--Molybdenum, dissolved, data from the Atlanta laboratory.

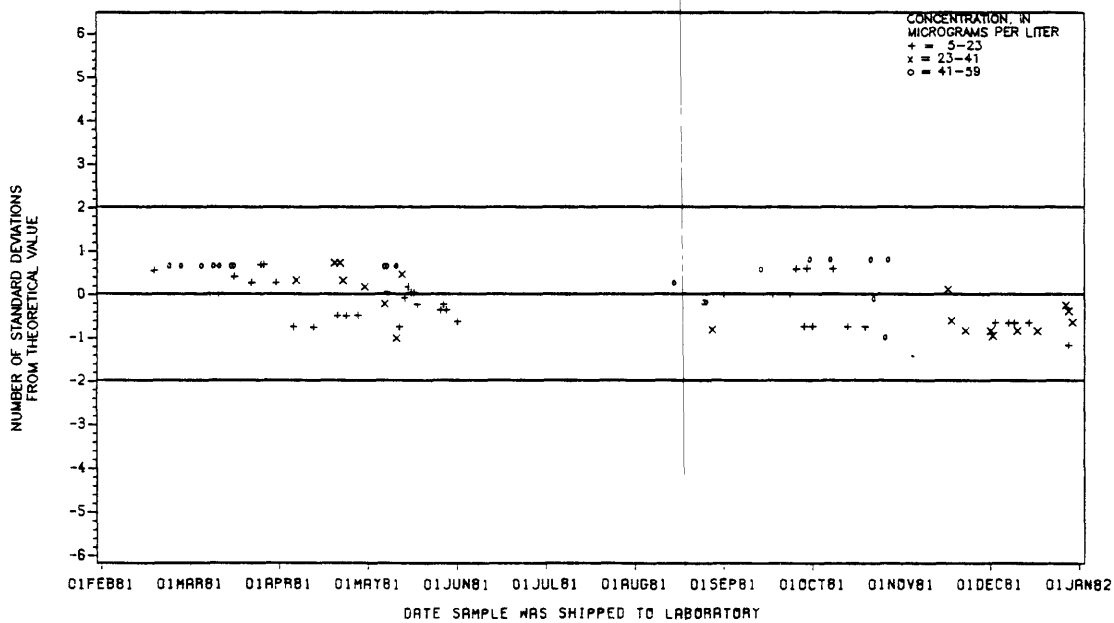


Figure 60.--Molybdenum, dissolved, data from the Denver laboratory.

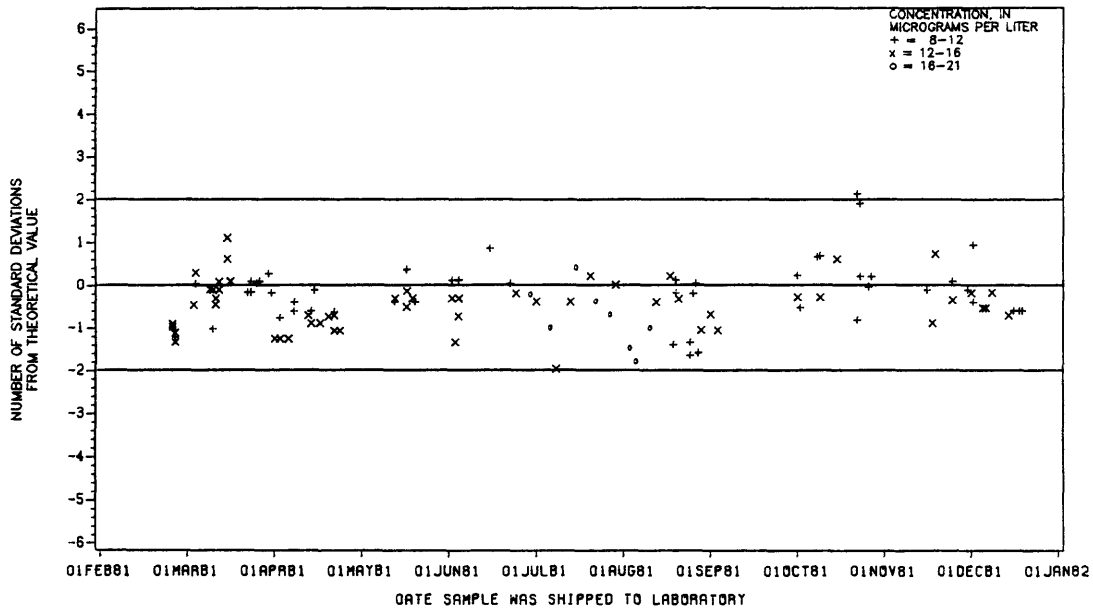


Figure 61.--Nickel, dissolved, data from the Atlanta laboratory.

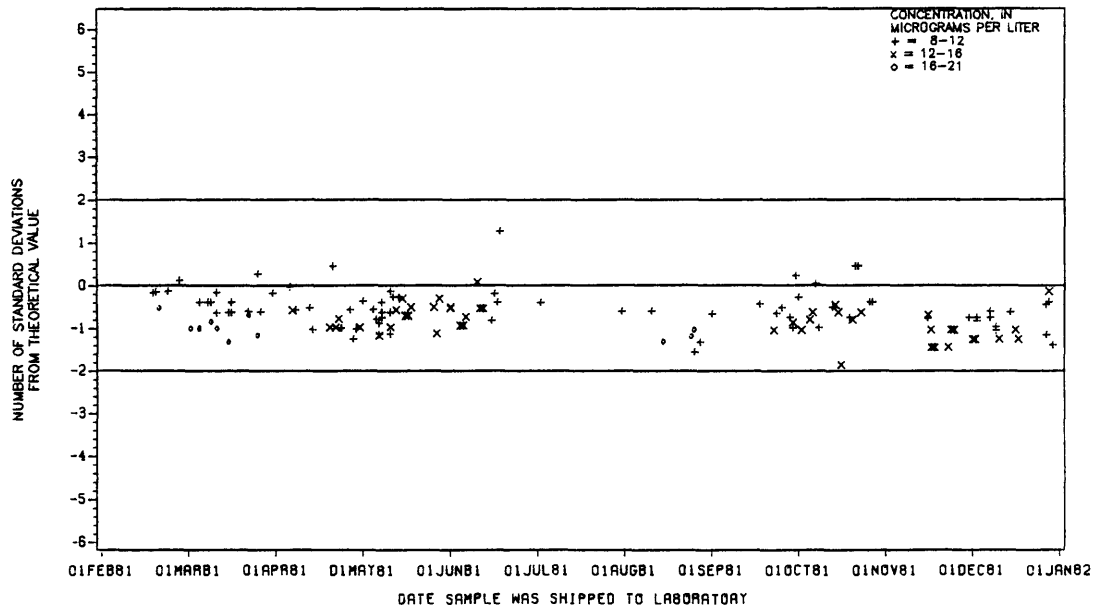


Figure 62.--Nickel, dissolved, data from the Denver laboratory.

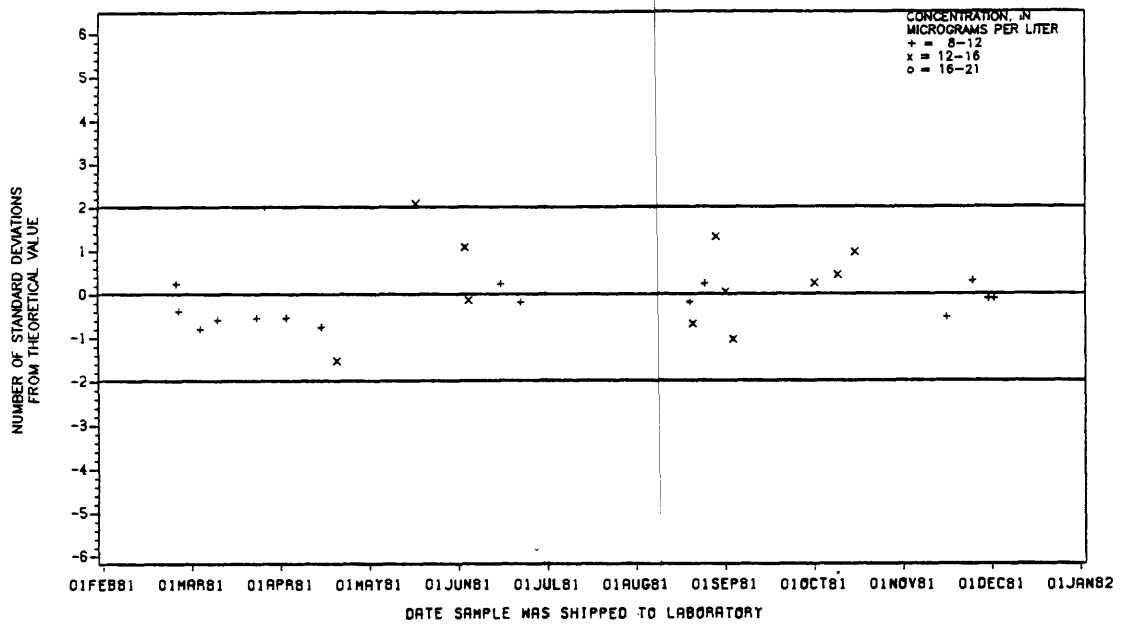


Figure 63.--Nickel, total recoverable, data from the Atlanta laboratory.

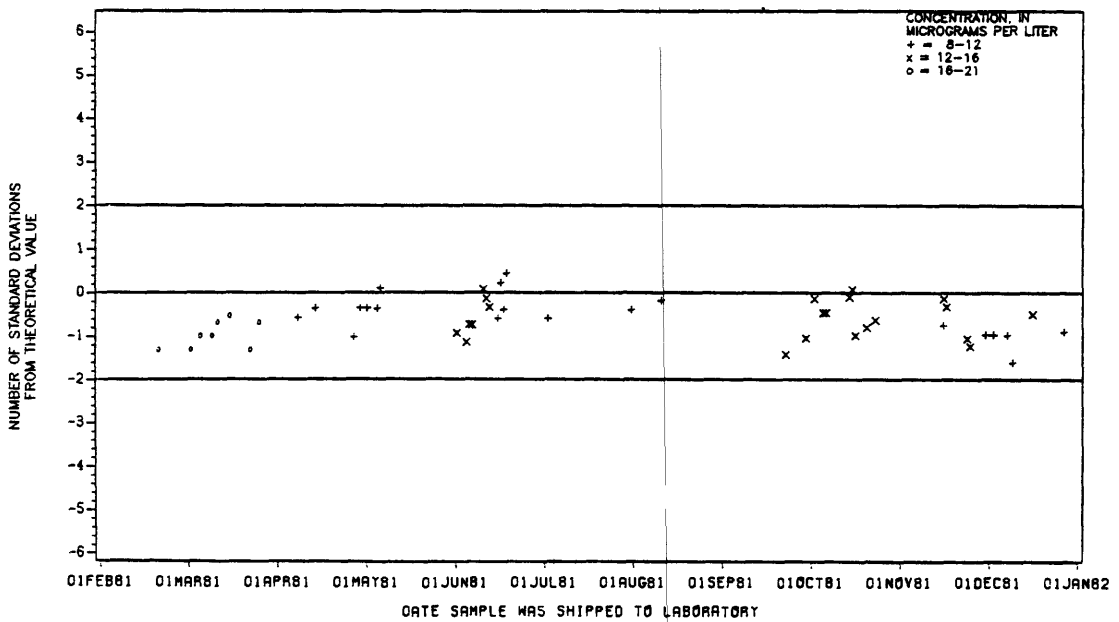


Figure 64.--Nickel, total recoverable, data from the Denver laboratory.

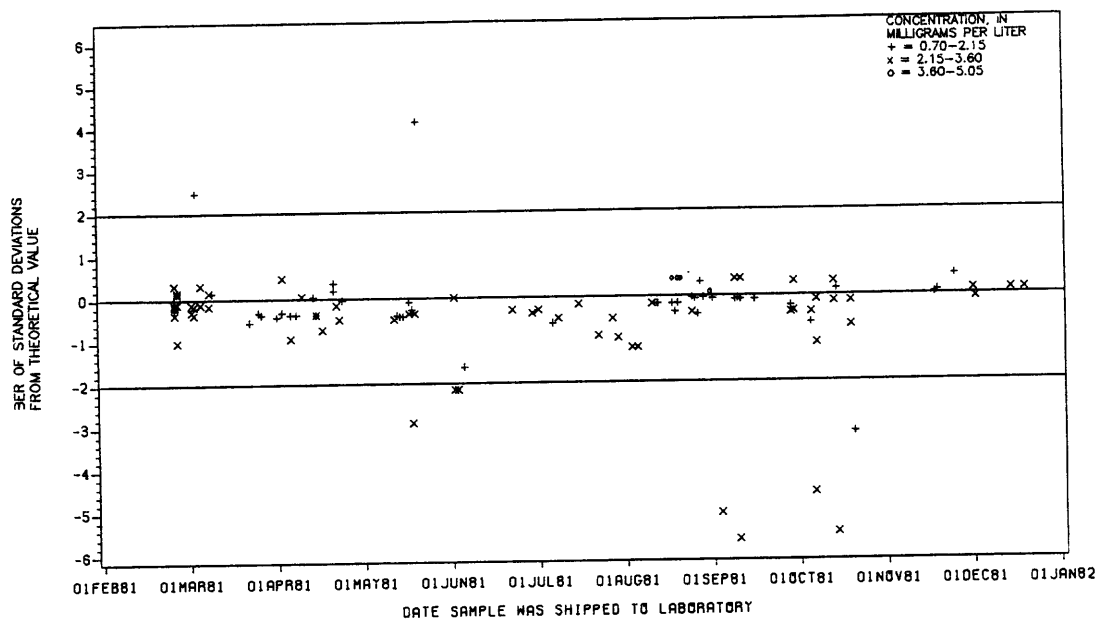


Figure 65.--Nitrate plus nitrite- nitrogen, dissolved, data from the Atlanta laboratory.

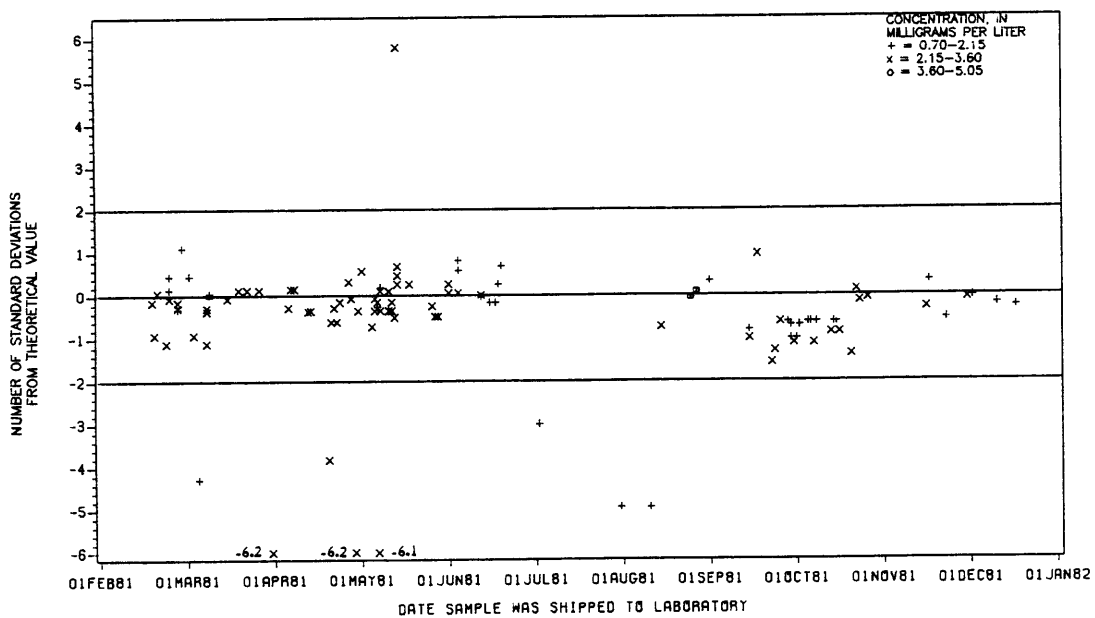


Figure 66.--Nitrate plus nitrite- nitrogen, dissolved, data from the Denver laboratory.

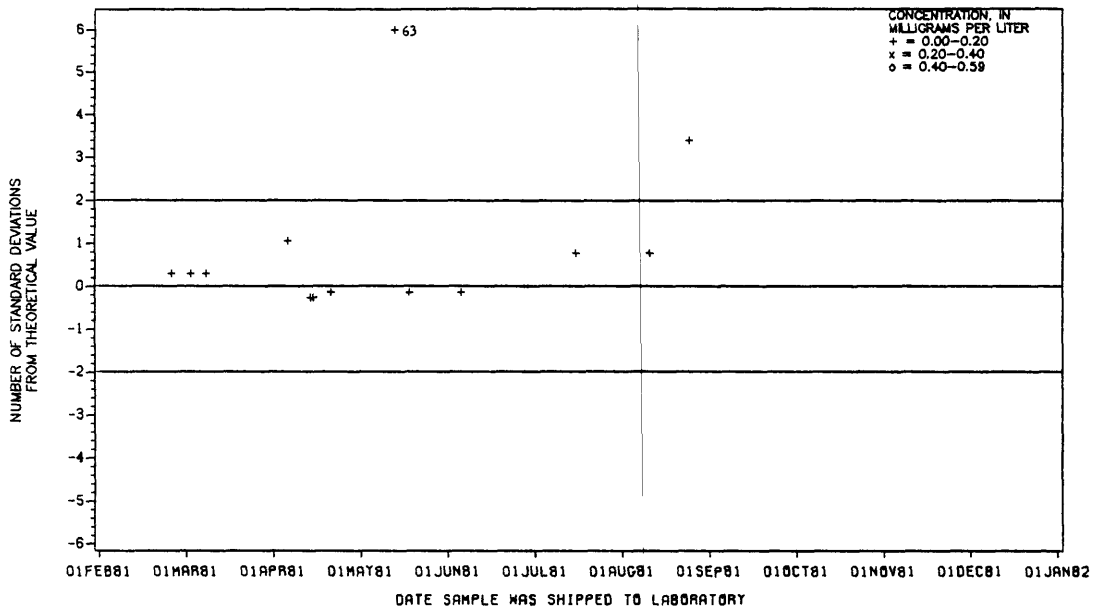


Figure 67.--Nitrite-nitrogen, data from the Atlanta laboratory.

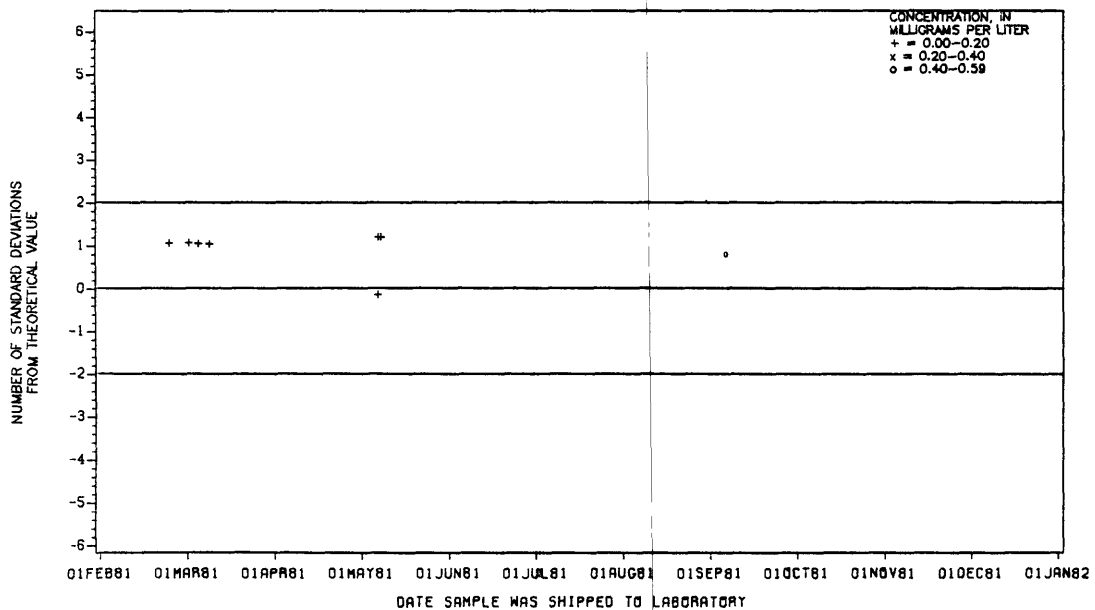


Figure 68.--Nitrite-nitrogen, data from the Denver laboratory.

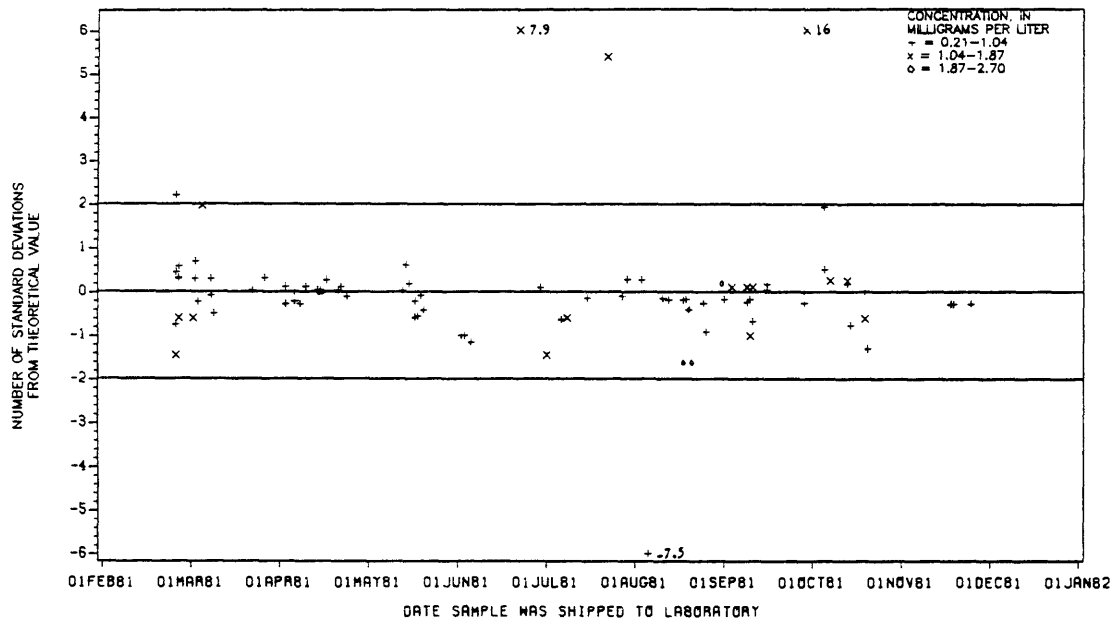


Figure 69.--Phosphorus, dissolved, data from the Atlanta laboratory.

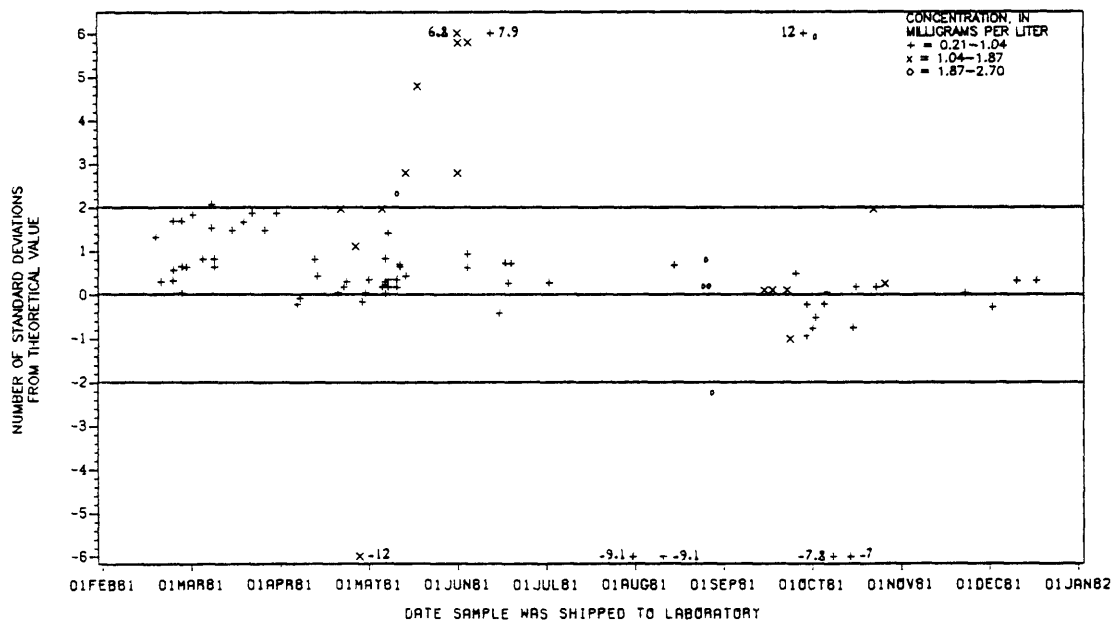


Figure 70.--Phosphorus, dissolved, data from the Denver laboratory.

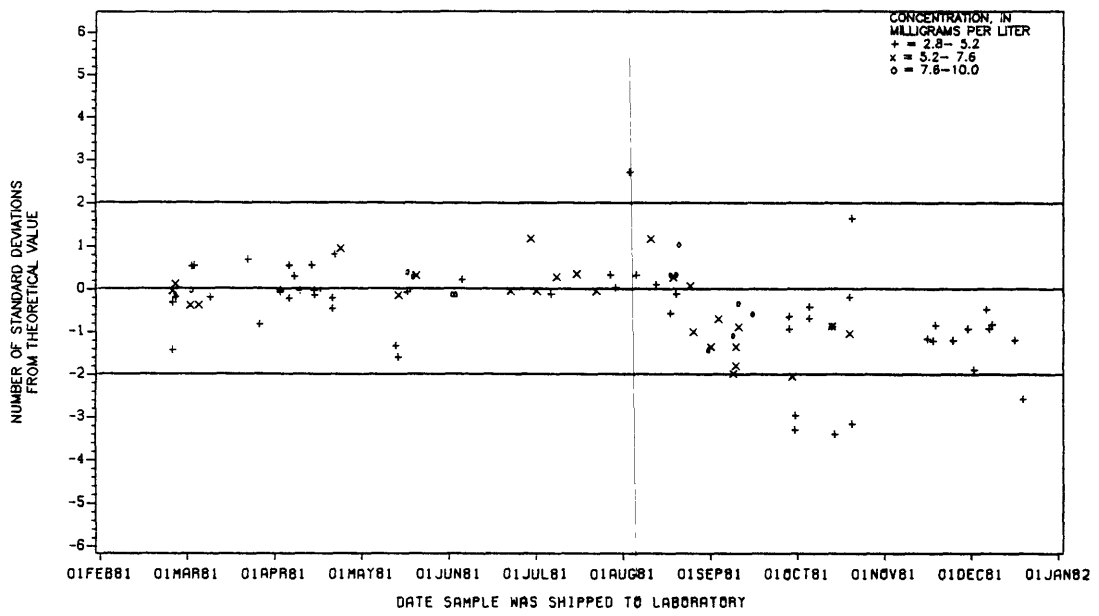


Figure 71.--Potassium, dissolved, data from the Atlanta laboratory.

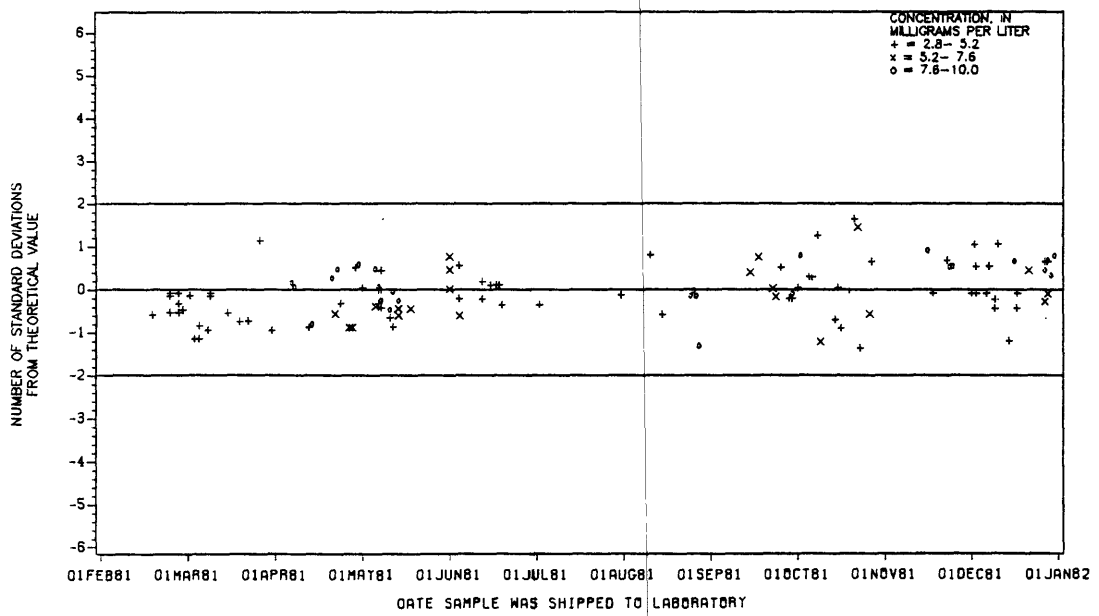


Figure 72.--Potassium, dissolved, data from the Denver laboratory.

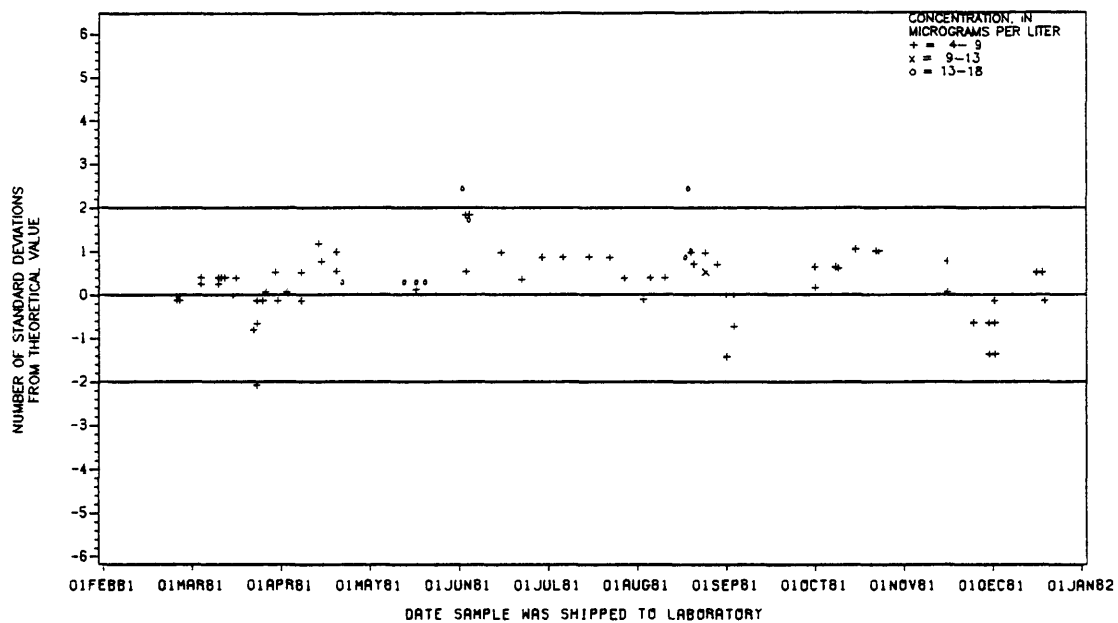


Figure 73.--Selenium, dissolved, data from the Atlanta laboratory.

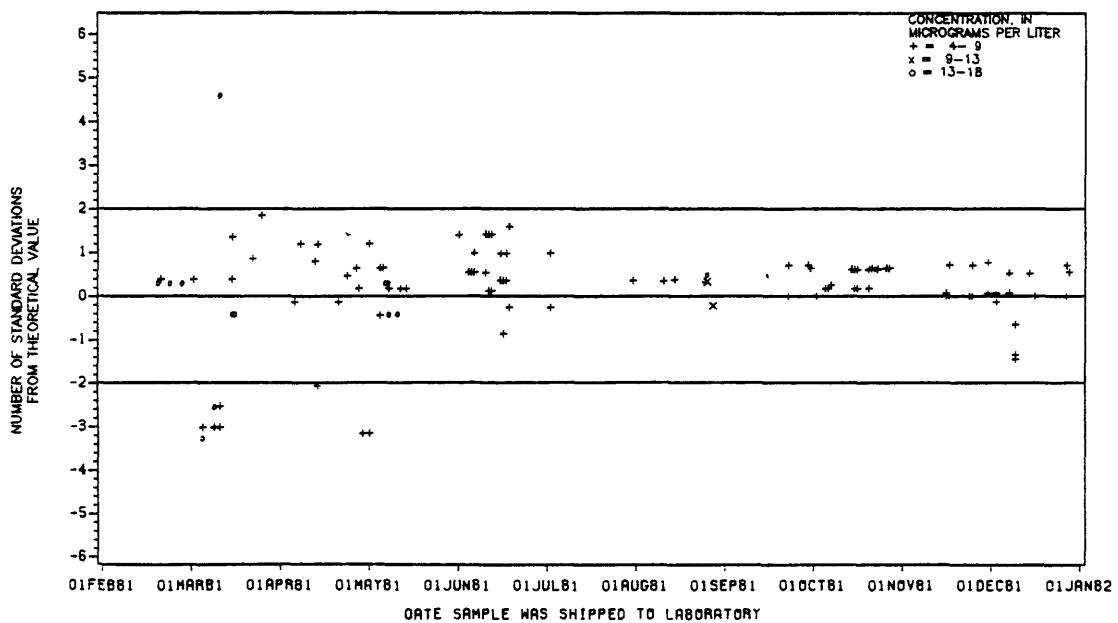


Figure 74.--Selenium, dissolved, data from the Denver laboratory.

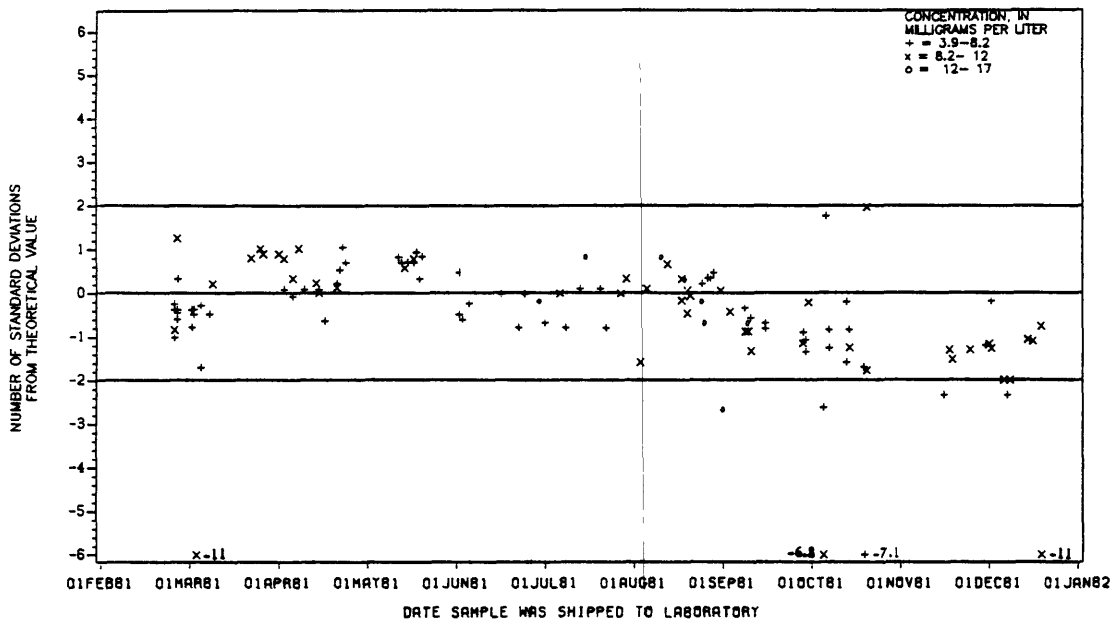


Figure 75.--Silica, dissolved, data from the Atlanta laboratory.

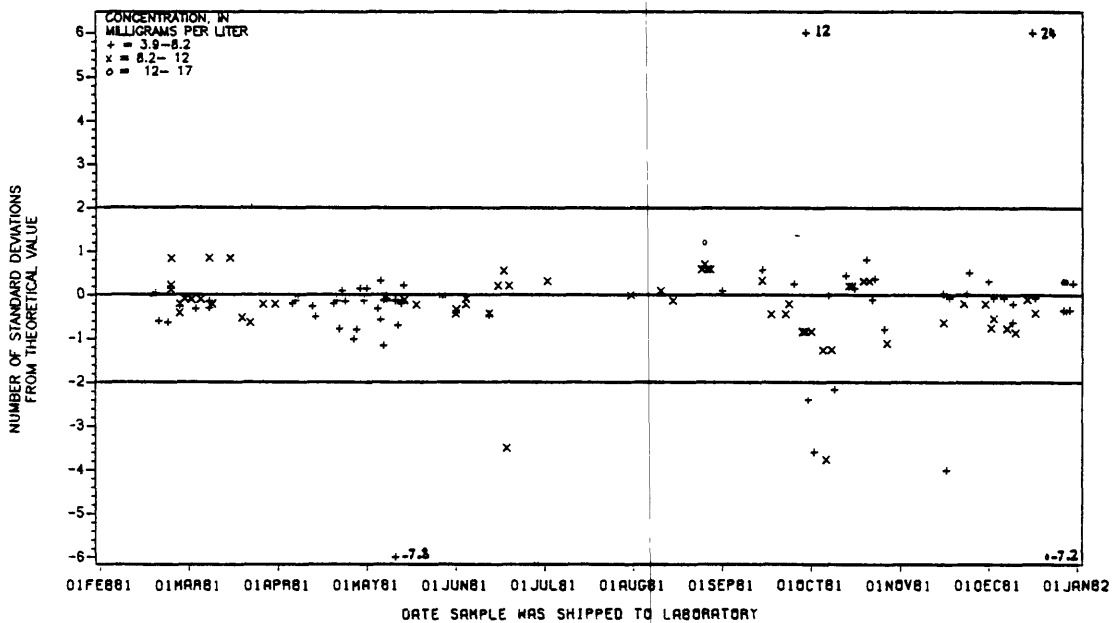


Figure 76.--Silica, dissolved, data from the Denver laboratory.

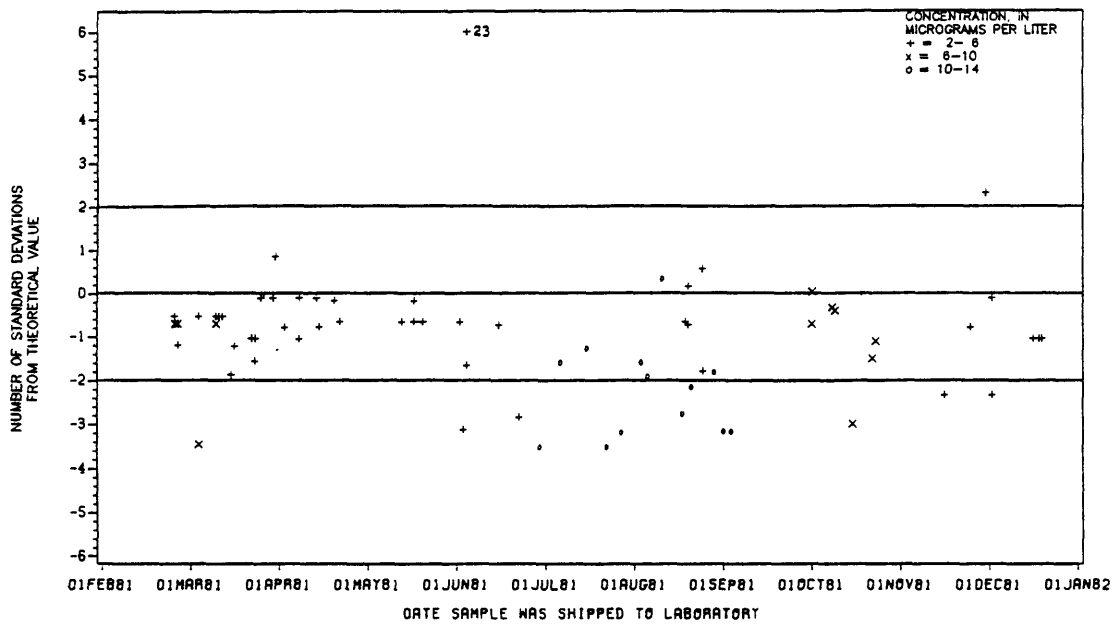


Figure 77.--Silver, dissolved, data from the Atlanta laboratory.

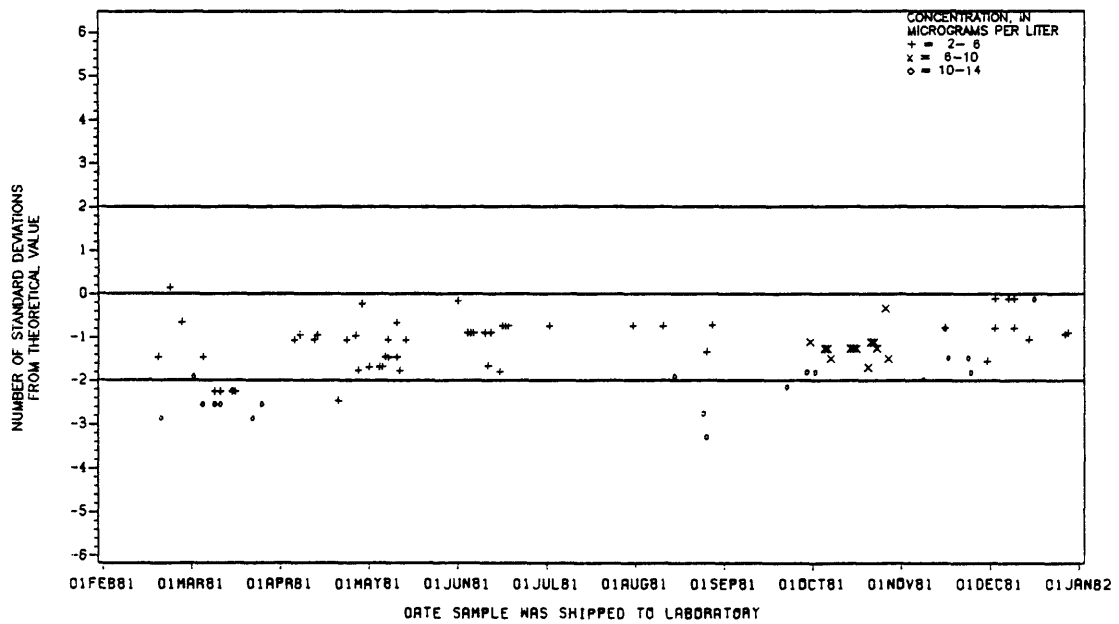


Figure 78.--Silver, dissolved, data from the Denver laboratory.

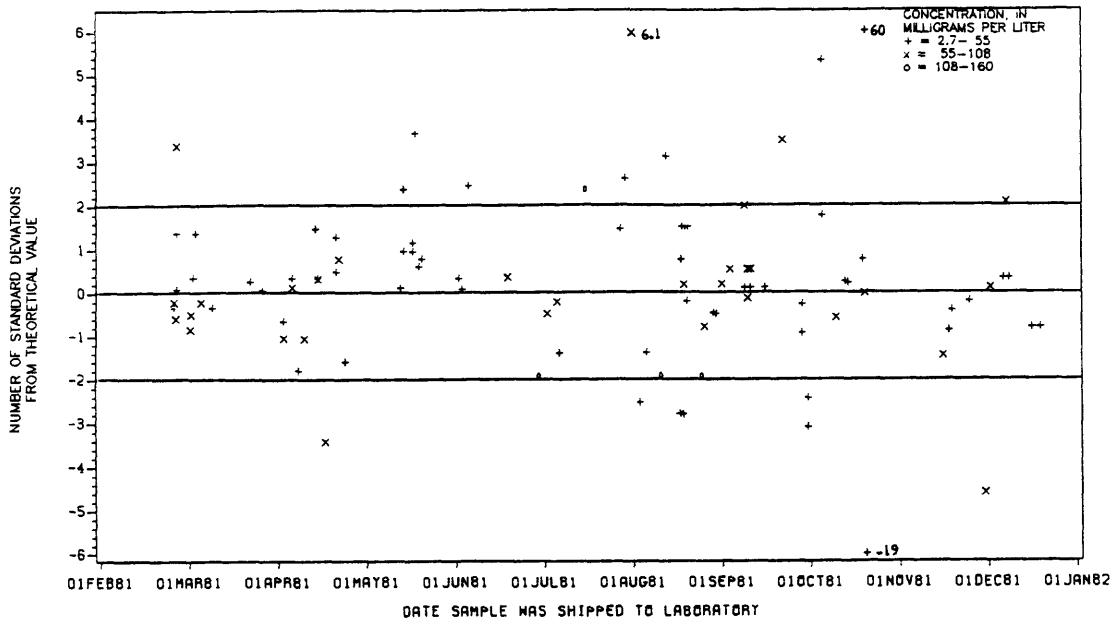


Figure 81.--Sodium, dissolved, data from the Atlanta laboratory.

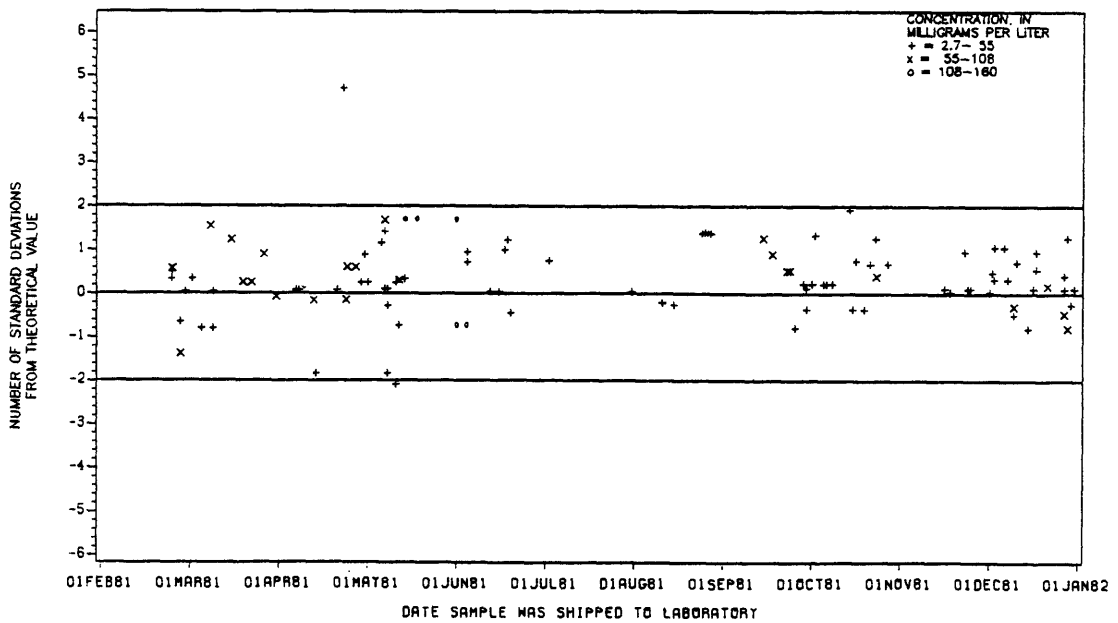


Figure 82.--Sodium, dissolved, data from the Denver laboratory.

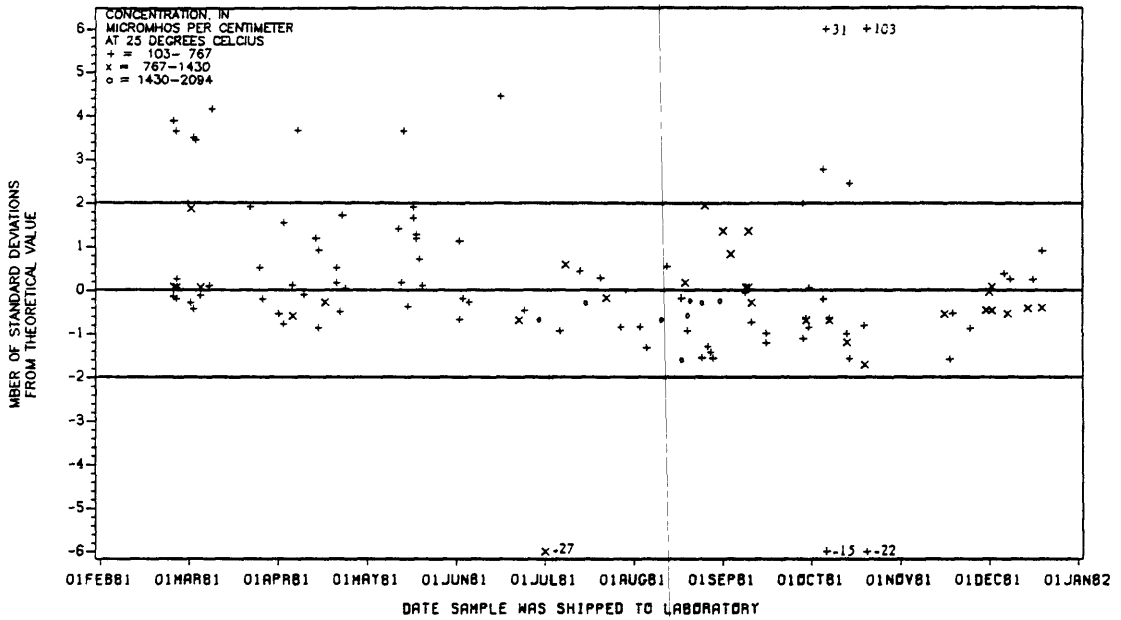


Figure 83.--Specific conductance, data from the Atlanta laboratory.

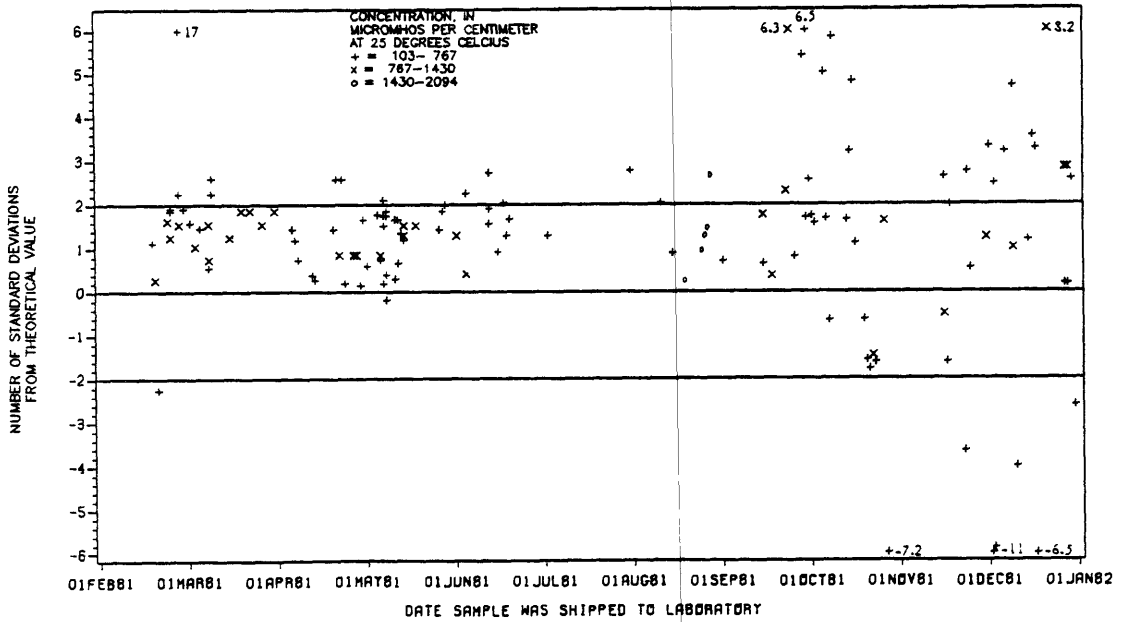


Figure 84.--Specific conductance, data from the Denver laboratory.

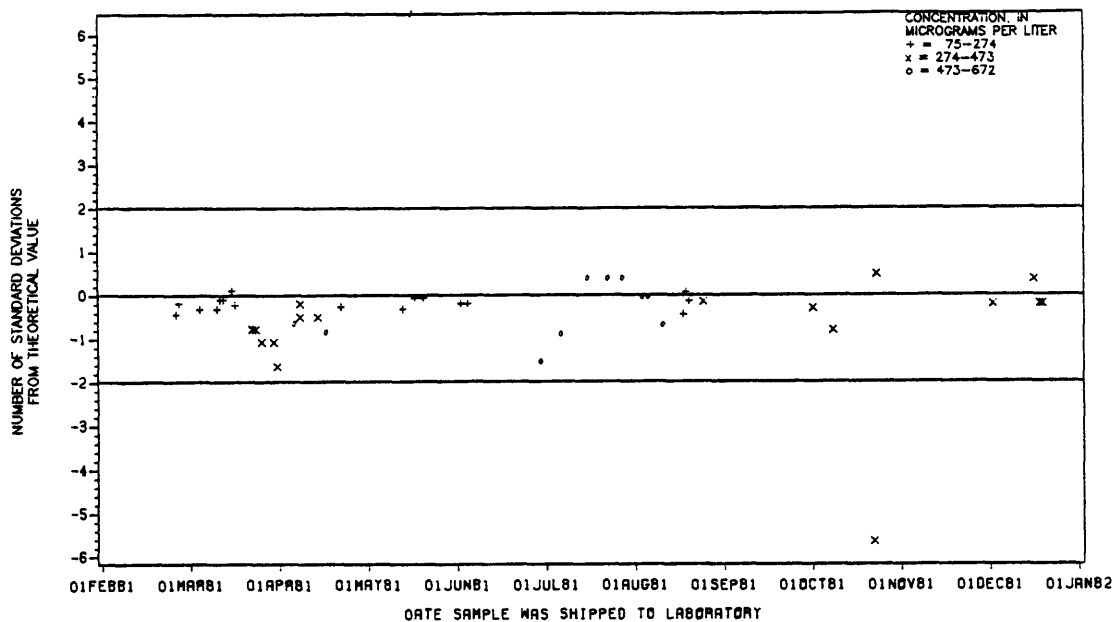


Figure 85.--Strontium, dissolved, data from the Atlanta laboratory.

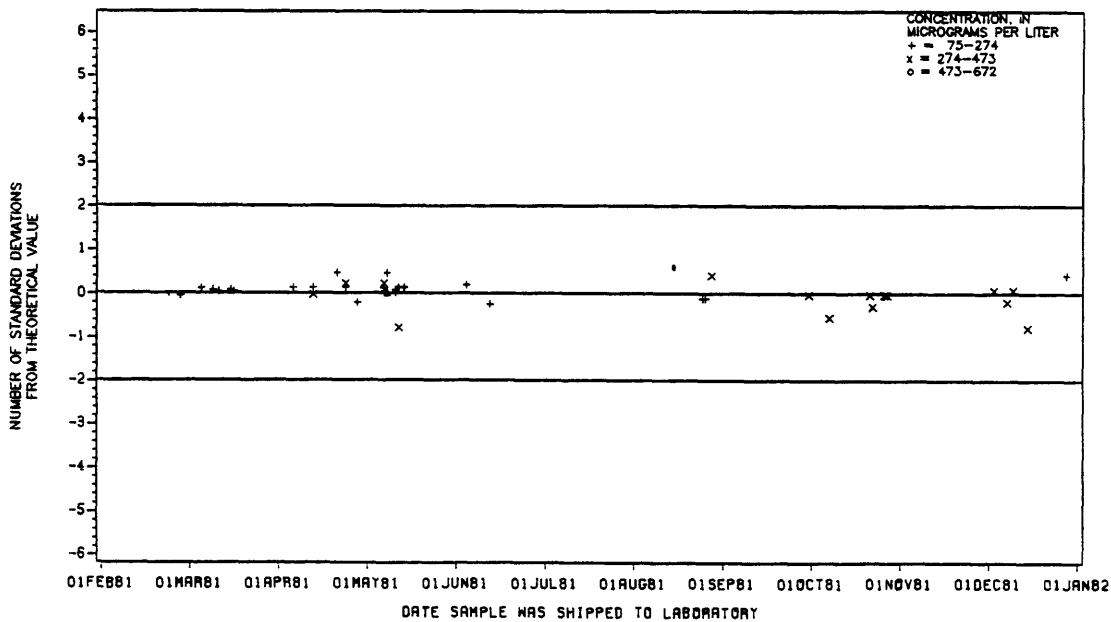


Figure 86.--Strontium, dissolved, data from the Denver laboratory.

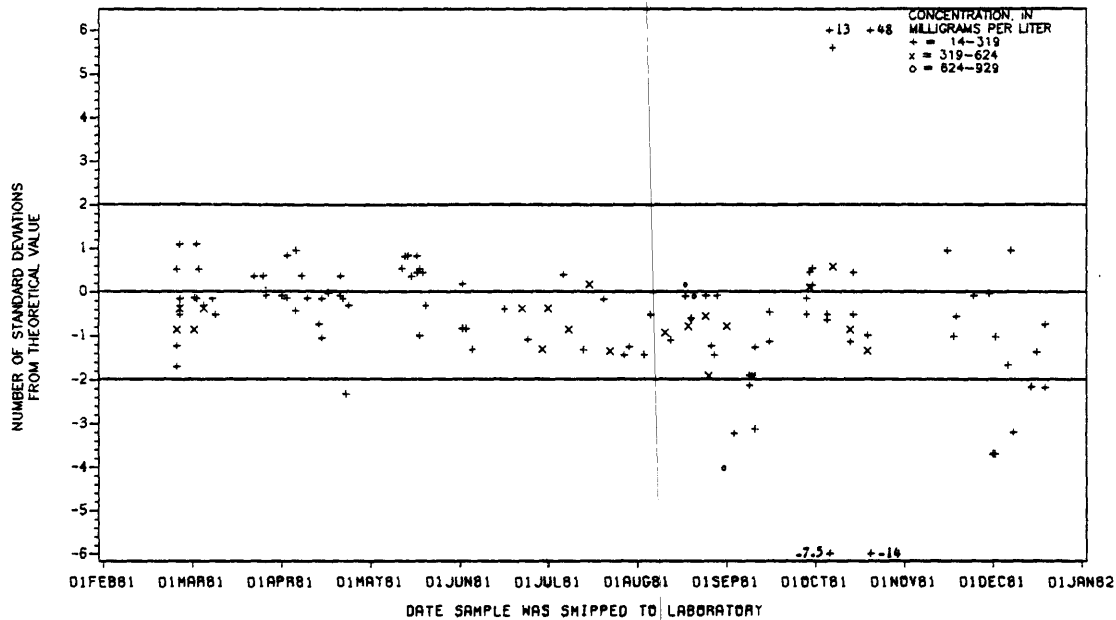


Figure 87.--Sulfate, dissolved, data from the Atlanta laboratory.

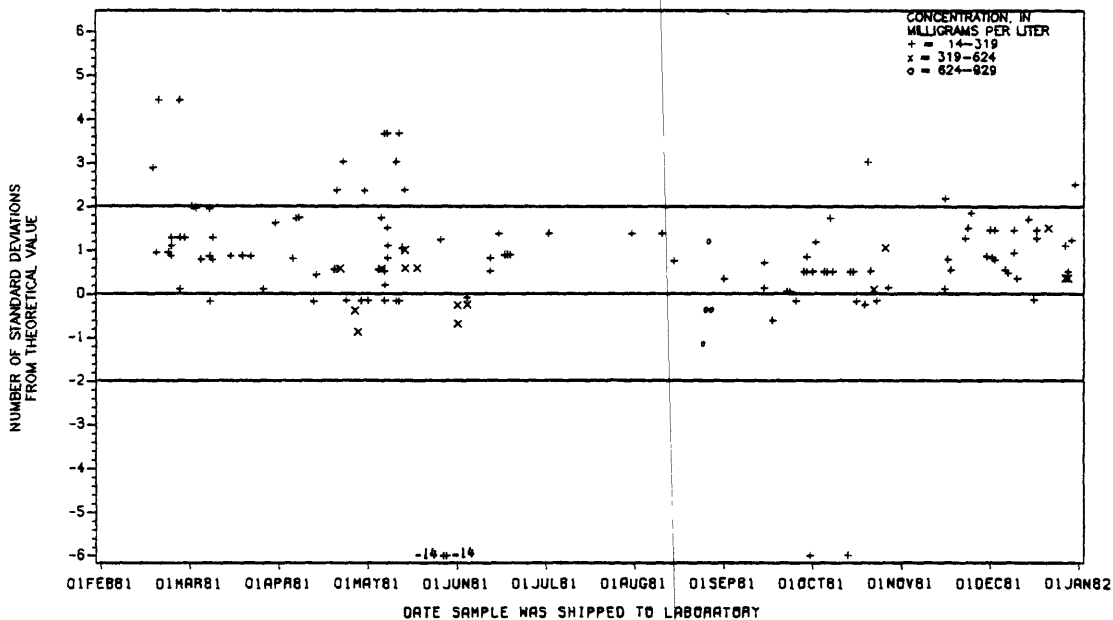


Figure 88.--Sulfate, dissolved, data from the Denver laboratory.

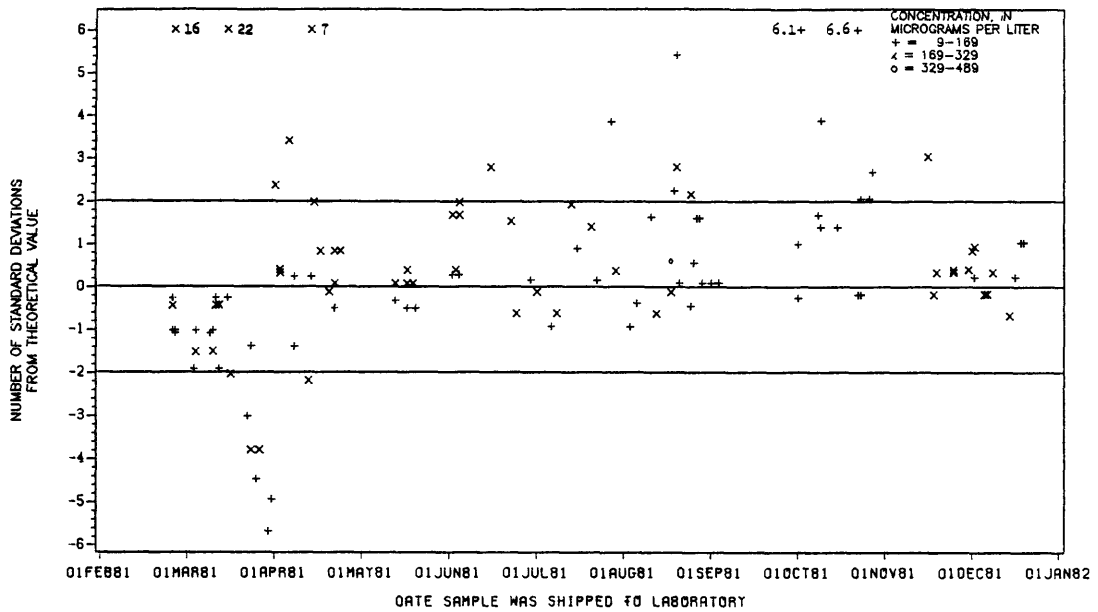


Figure 89.--Zinc, dissolved, data from the Atlanta laboratory.

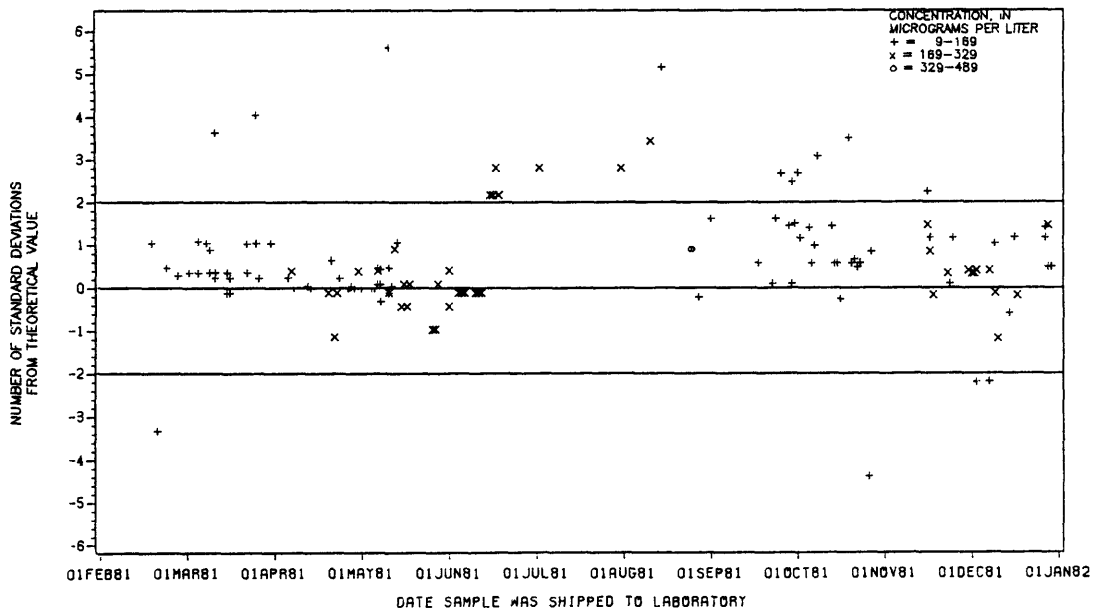


Figure 90.--Zinc, dissolved, data from the Denver laboratory.

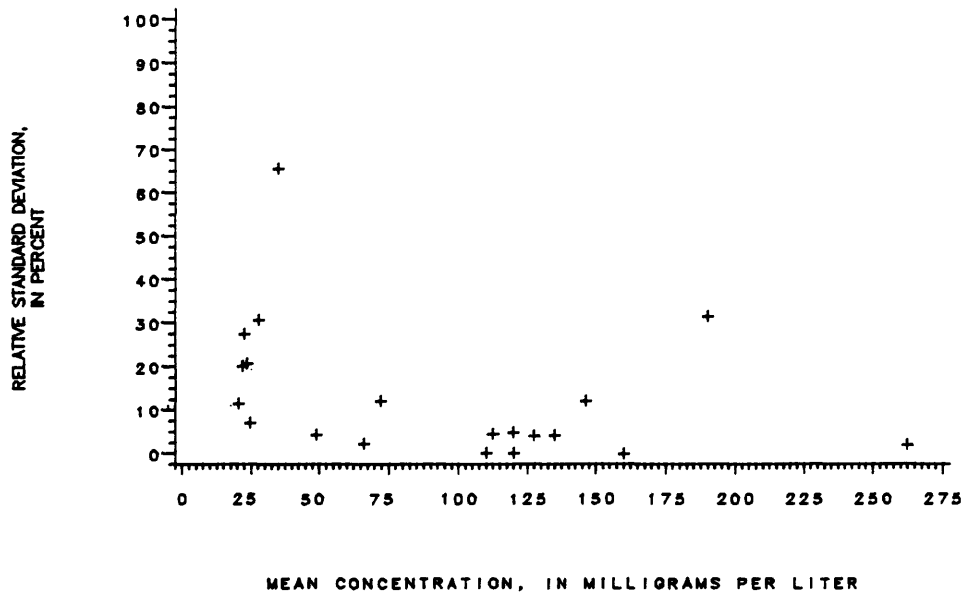


Figure 93.--Precision data for alkalinity at the Atlanta Laboratory.

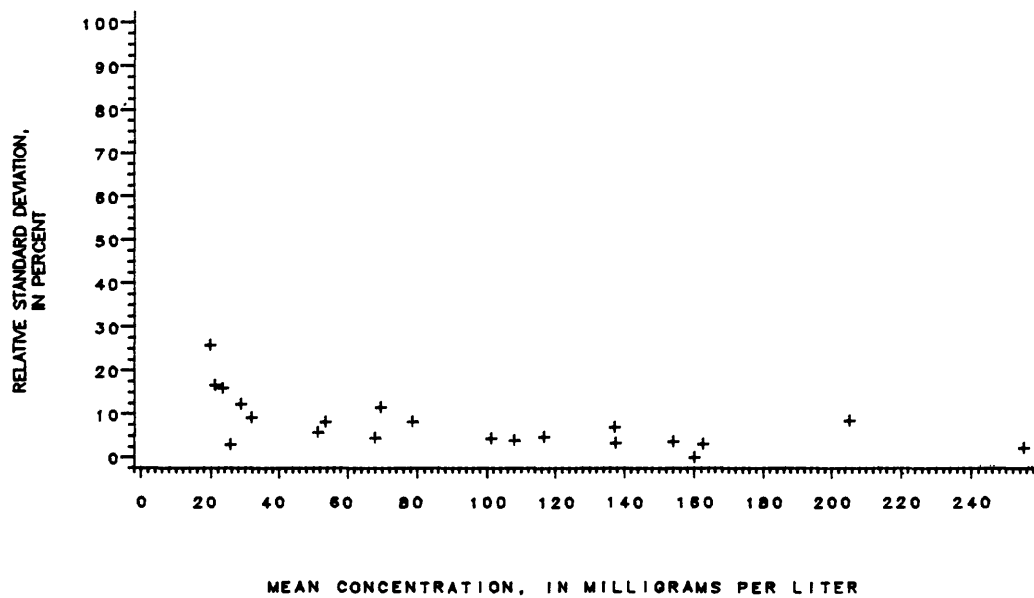


Figure 94.--Precision data for alkalinity at the Denver Laboratory.

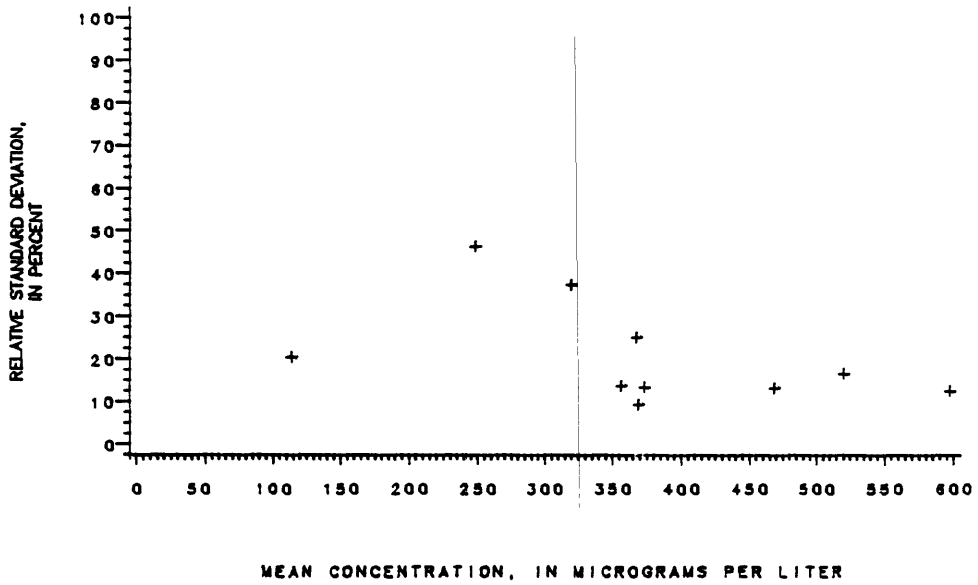


Figure 95.--Precision data for aluminum at the Atlanta Laboratory.

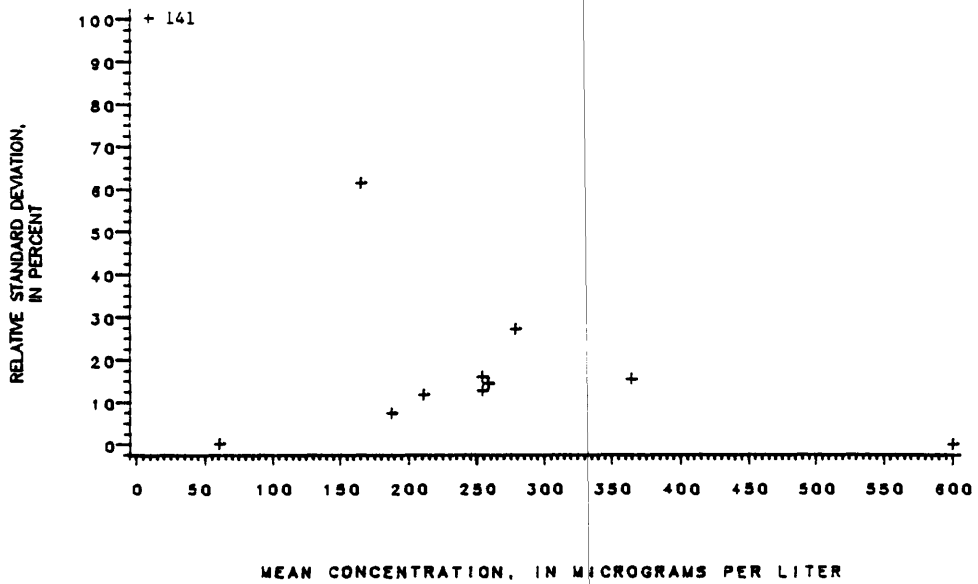


Figure 96.--Precision data for aluminum at the Denver Laboratory.

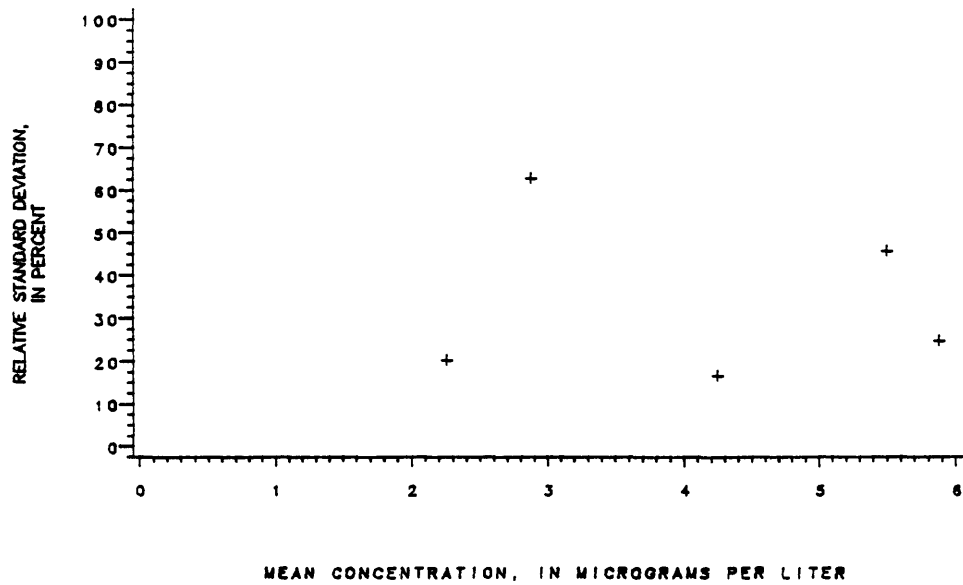


Figure 97.-- Precision data for antimony at the Atlanta Laboratory.

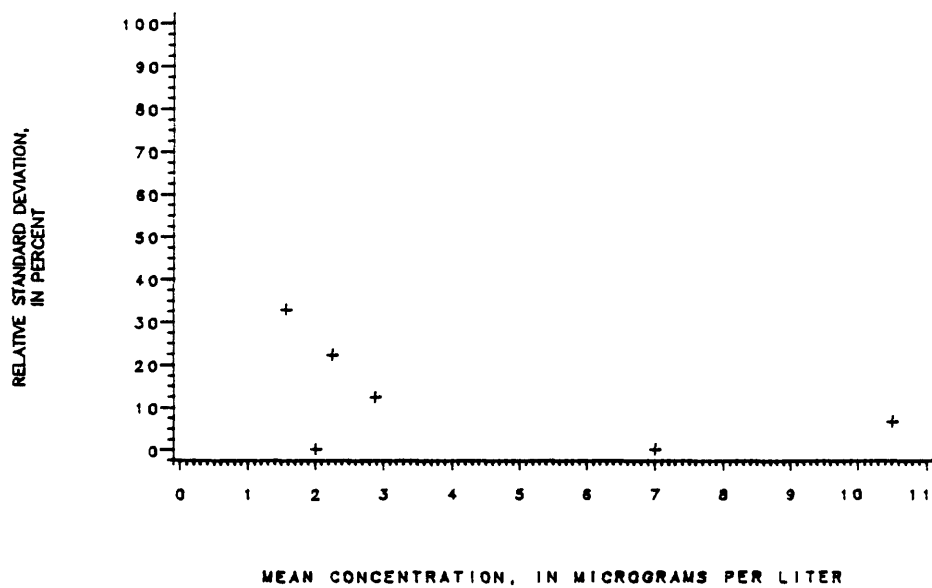


Figure 98.--Precision data for antimony at the Denver Laboratory.

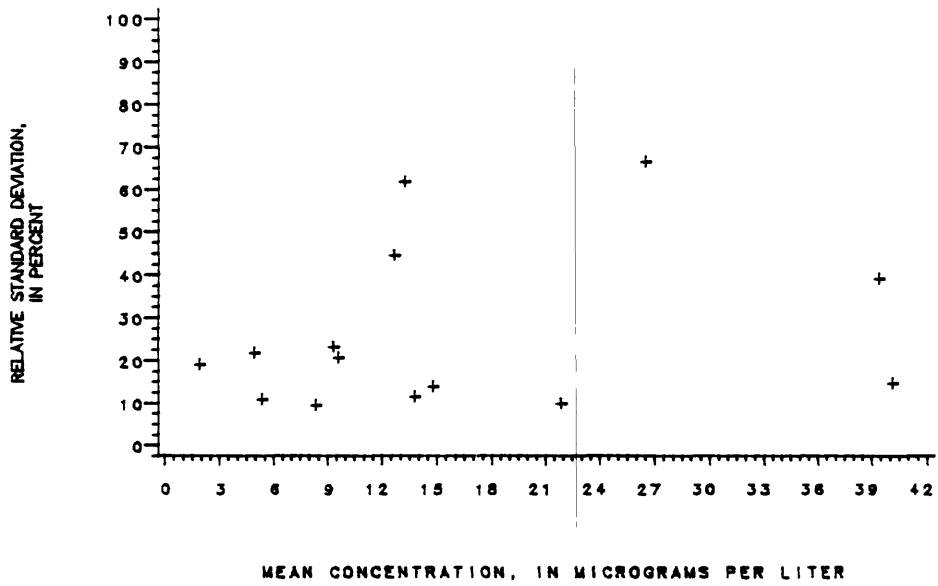


Figure 99.--Precision data for arsenic at the Atlanta Laboratory.

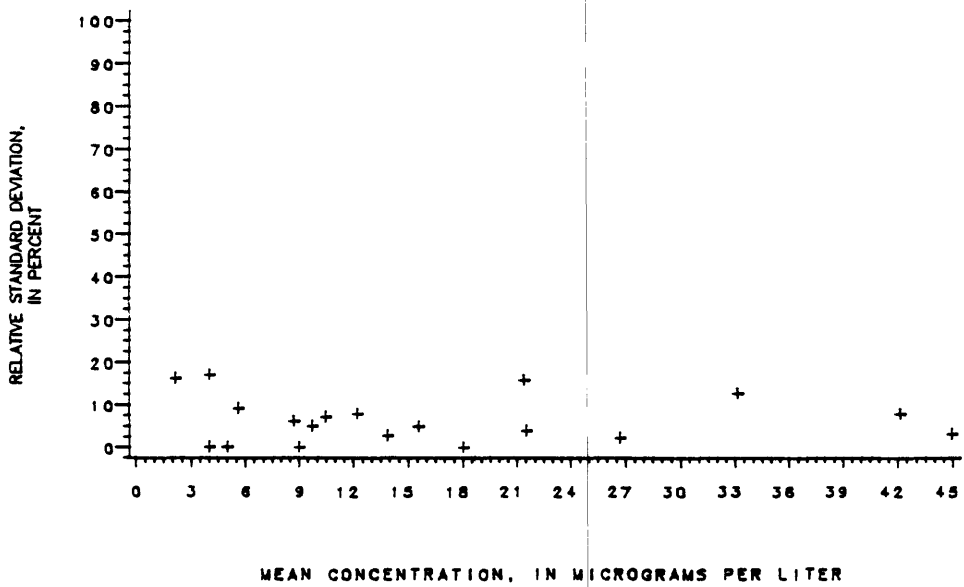


Figure 100.--Precision data for arsenic at the Denver Laboratory.

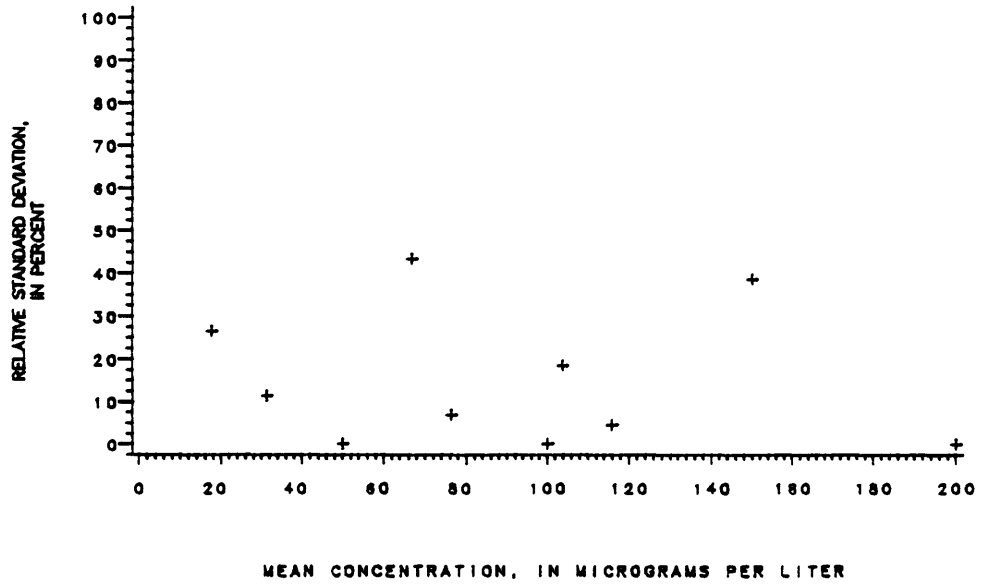


Figure 101.--Precision data for barium at the Atlanta Laboratory.

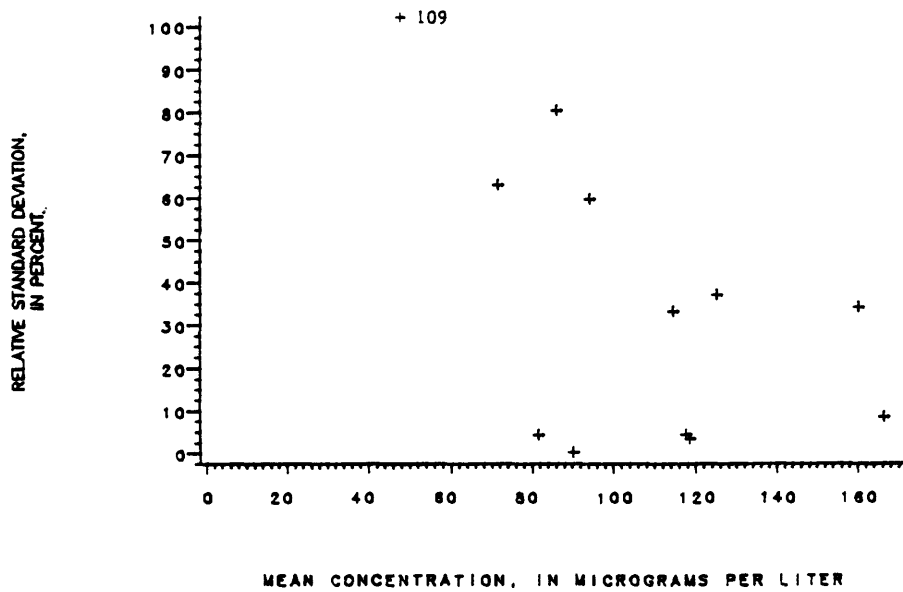


Figure 102.--Precision data for barium at the Denver Laboratory.

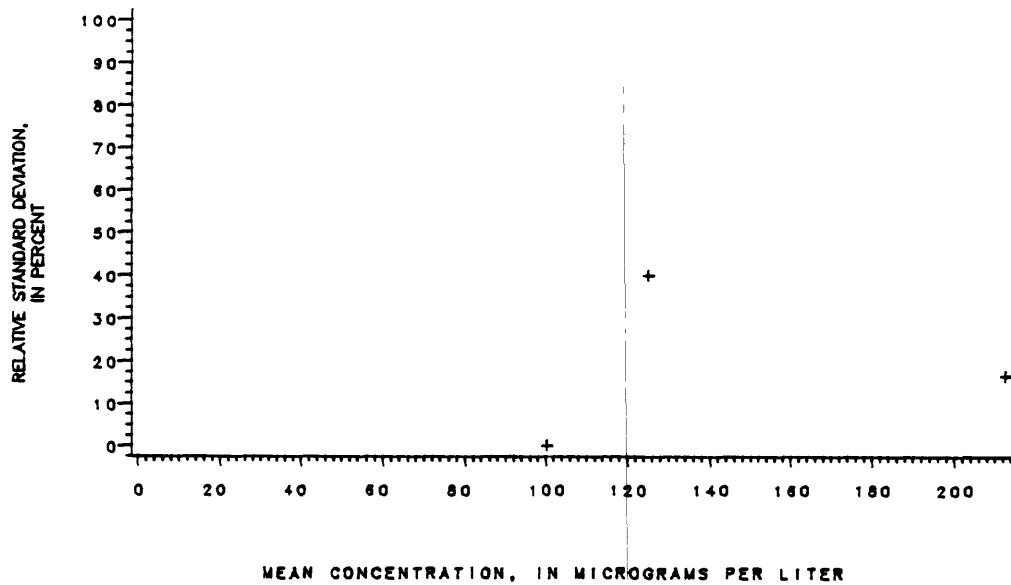


Figure 103.--Precision data for barium, total recoverable at the Atlanta Laboratory.

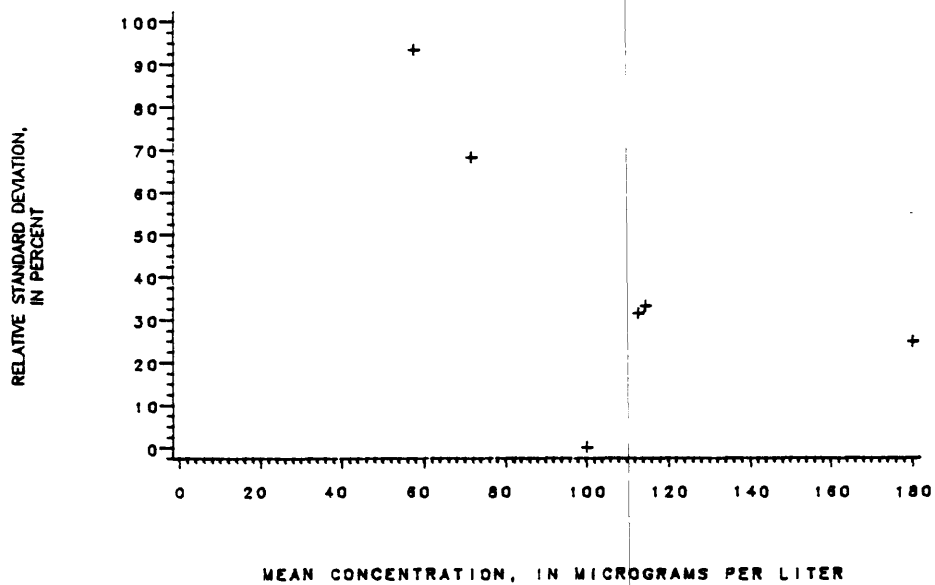


Figure 104.--Precision data for barium, total recoverable at the Denver Laboratory.

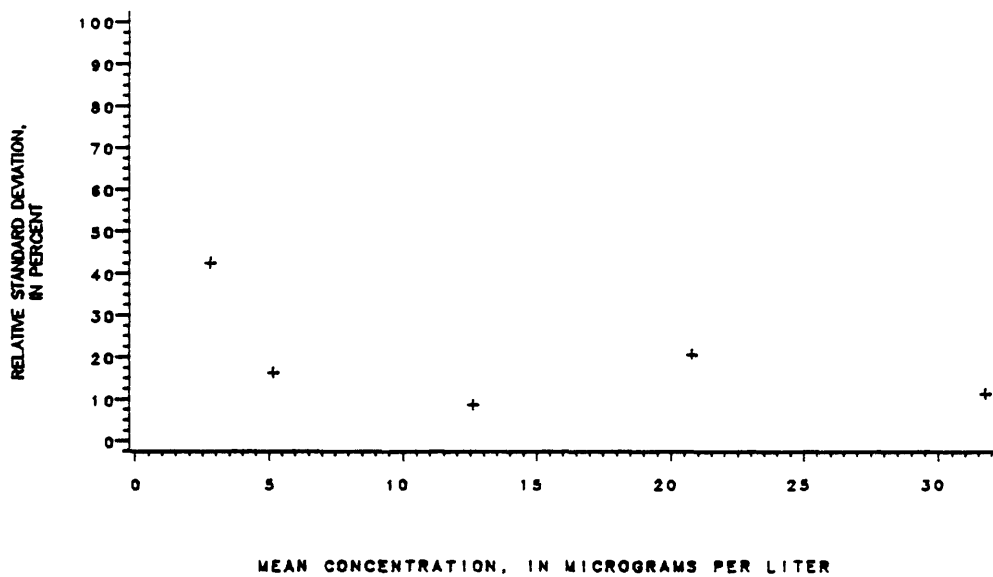


Figure 105.--Precision data for beryllium at the Atlanta Laboratory.

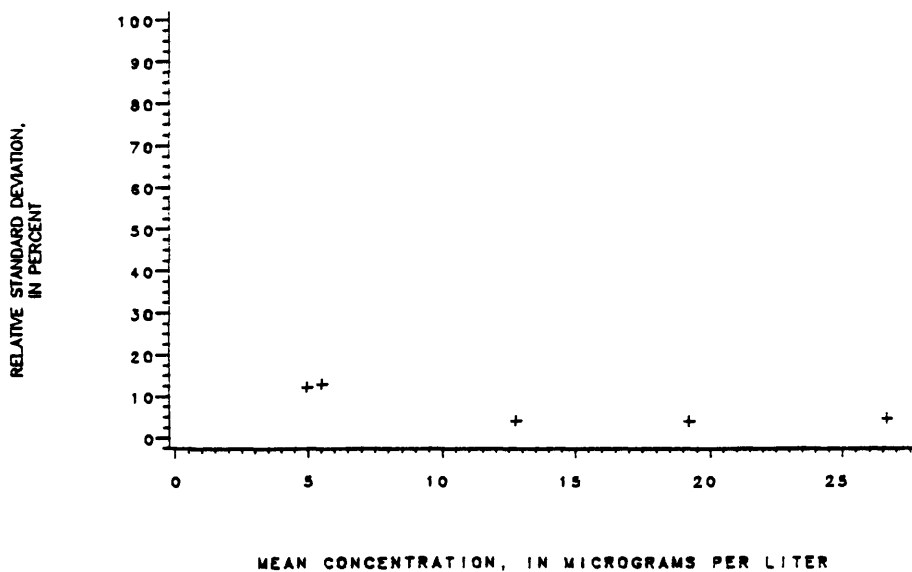


Figure 106.--Precision data for beryllium at the Denver Laboratory.

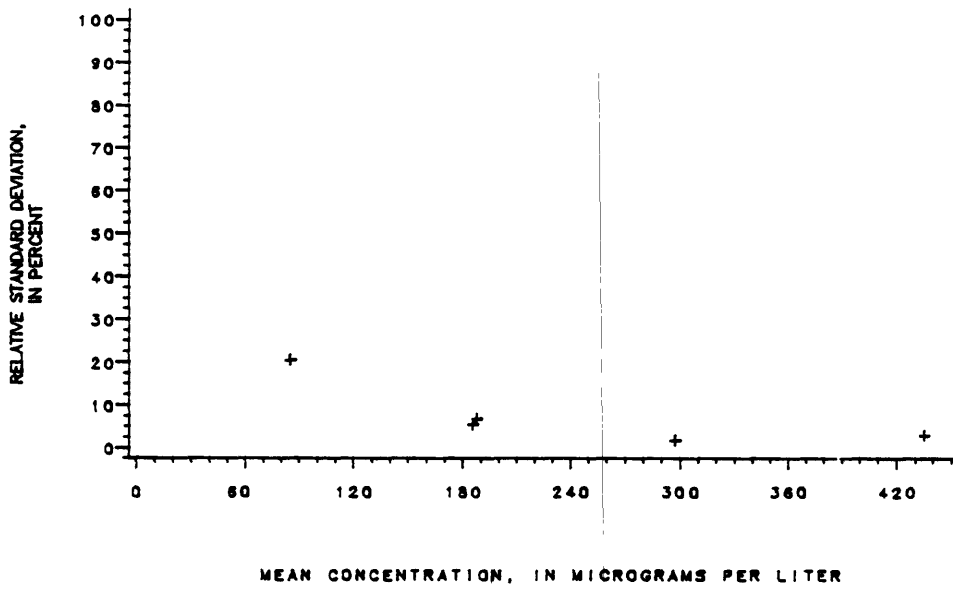


Figure 107.—Precision data for boron at the Atlanta Laboratory.

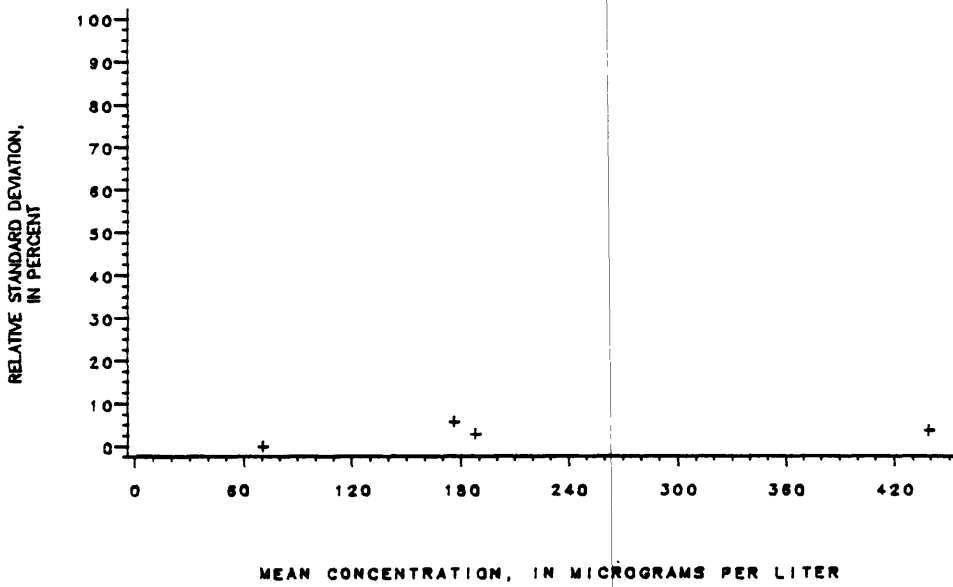


Figure 108.—Precision data for boron at the Denver Laboratory.

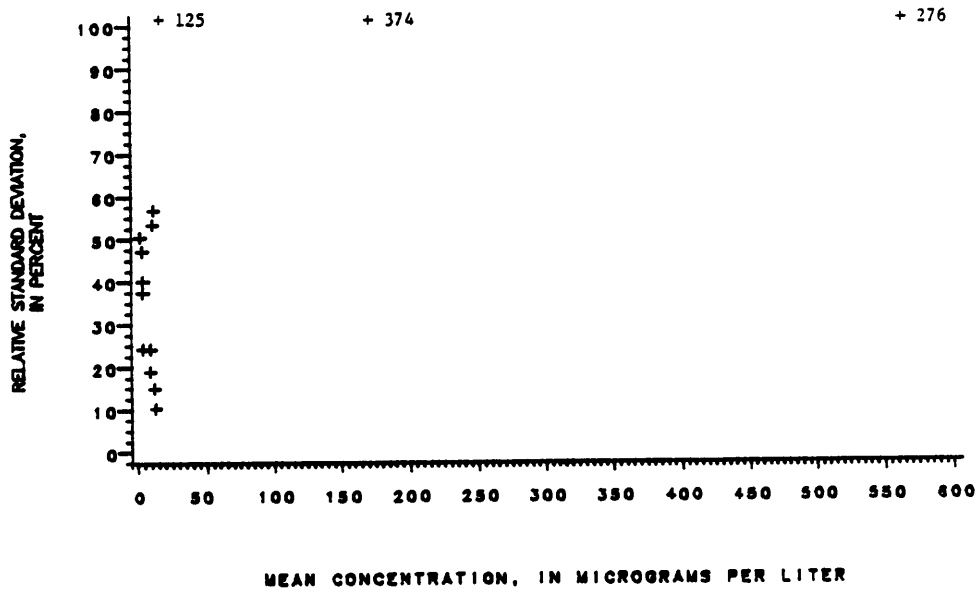


Figure 109.—Precision data for cadmium at the Atlanta Laboratory.

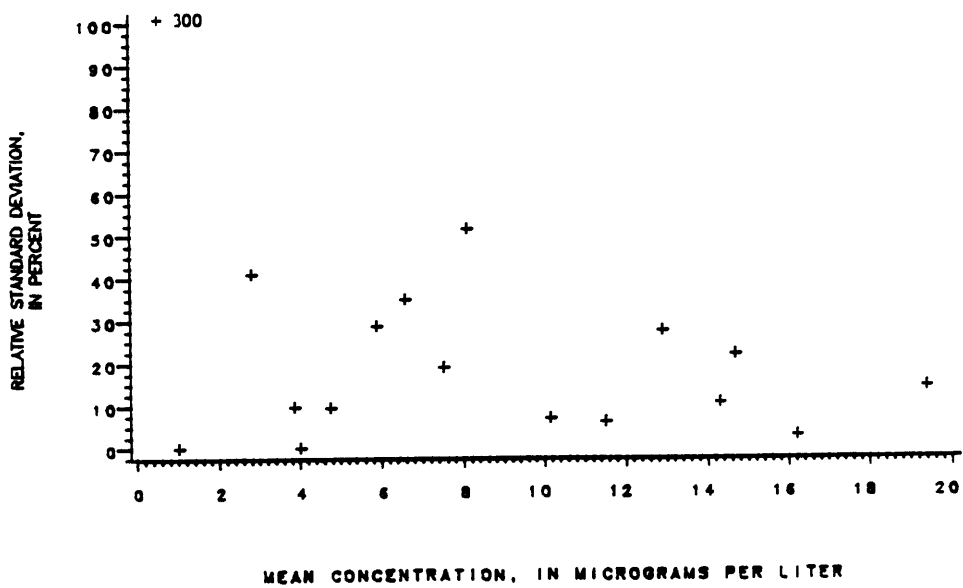


Figure 110.—Precision data for cadmium at the Denver Laboratory.

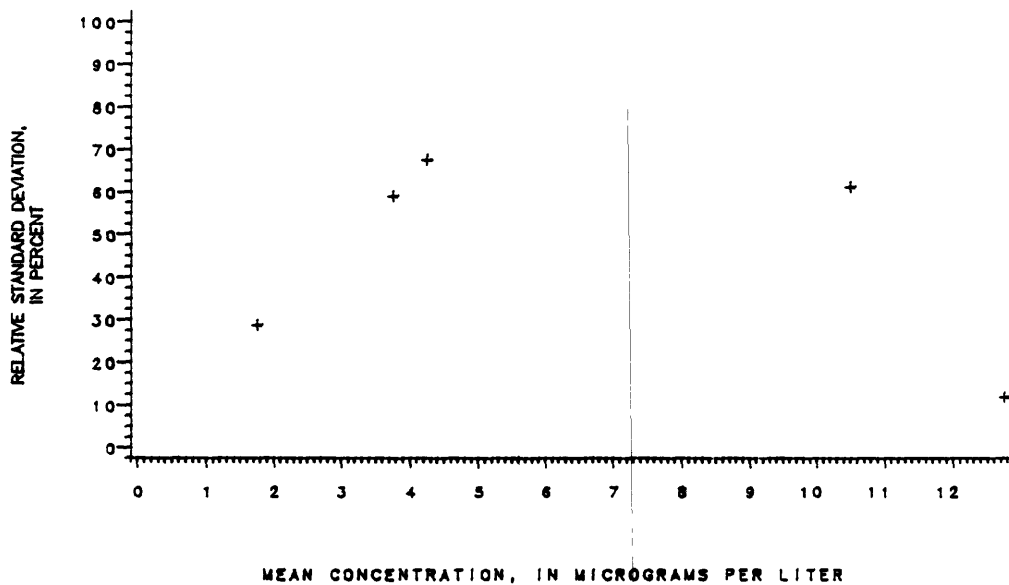


Figure 111.--Precision data for cadmium, total recoverable at the Atlanta Laboratory.

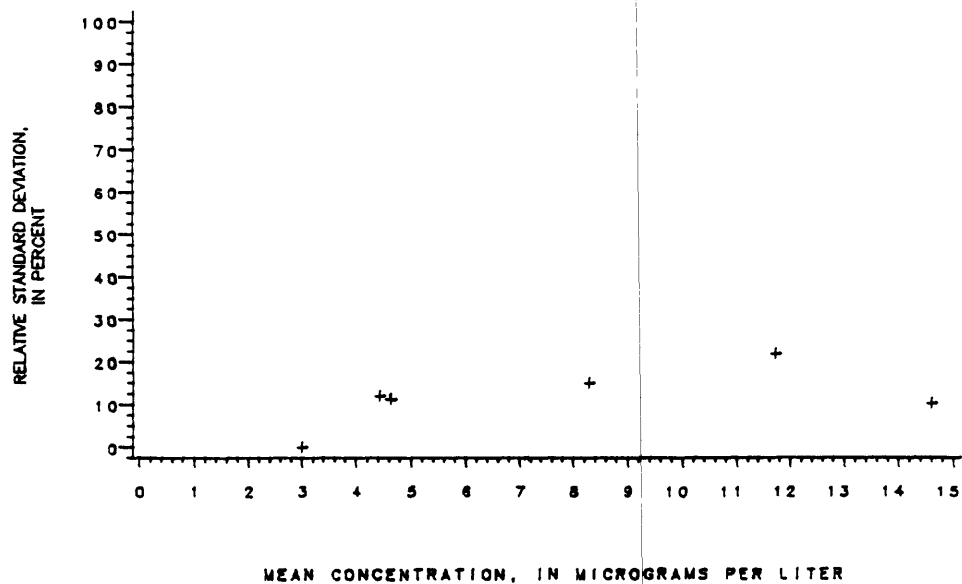


Figure 112.--Precision data for cadmium, total recoverable at the Denver Laboratory.

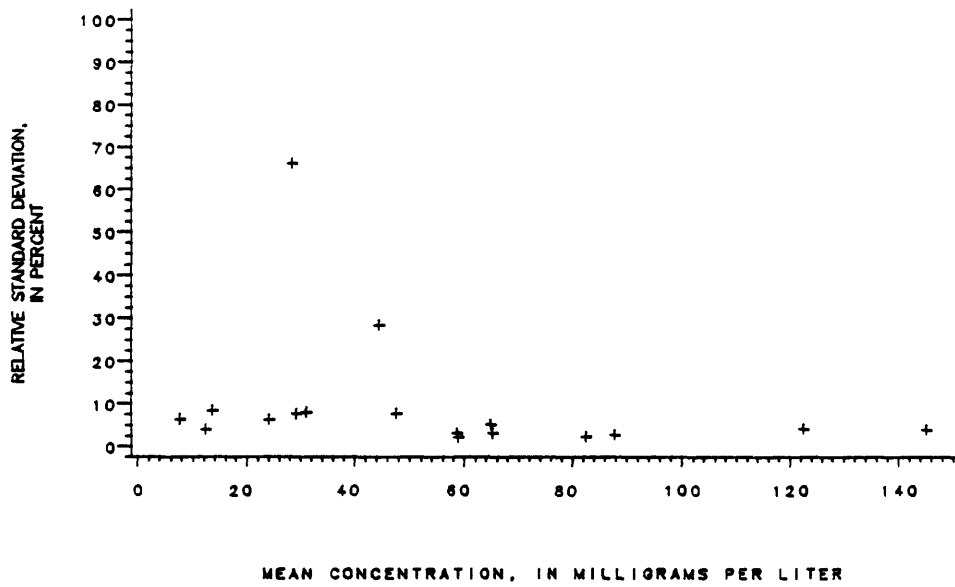


Figure 113.--Precision data for calcium at the Atlanta Laboratory.

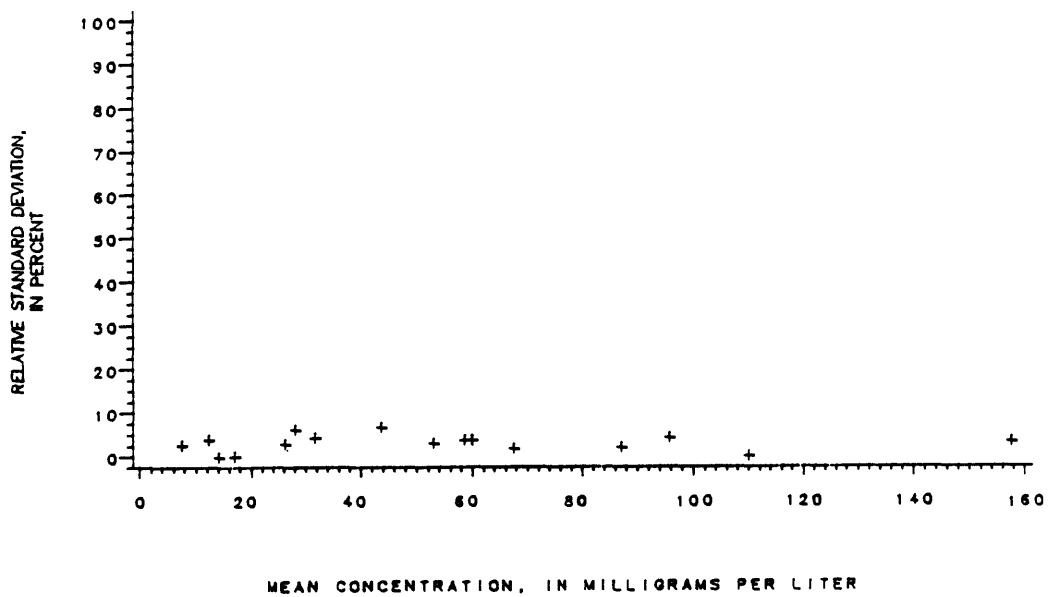


Figure 114.--Precision data for calcium at the Denver Laboratory.

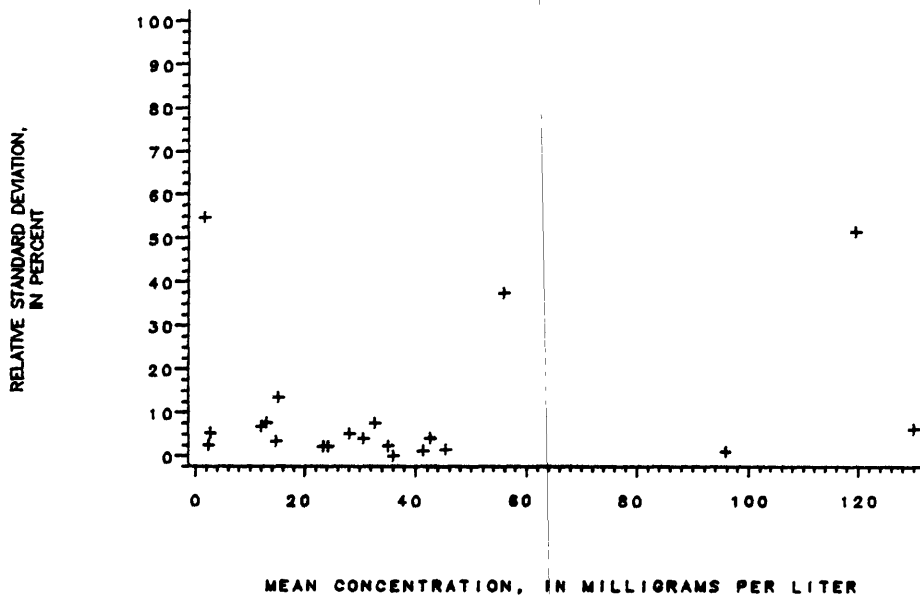


Figure 115.--Precision data for chloride at the Atlanta Laboratory.

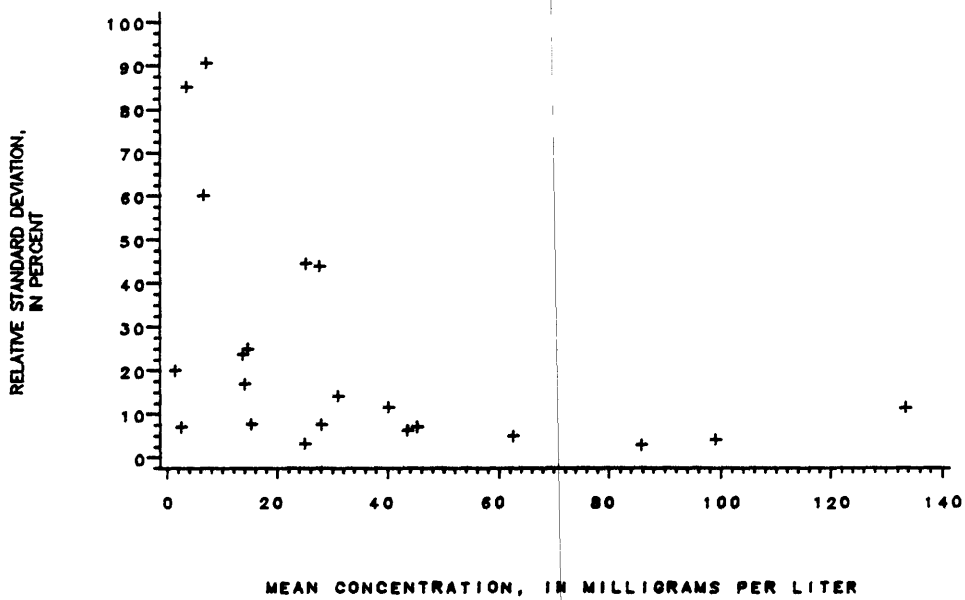


Figure 116.--Precision data for chloride at the Denver Laboratory.

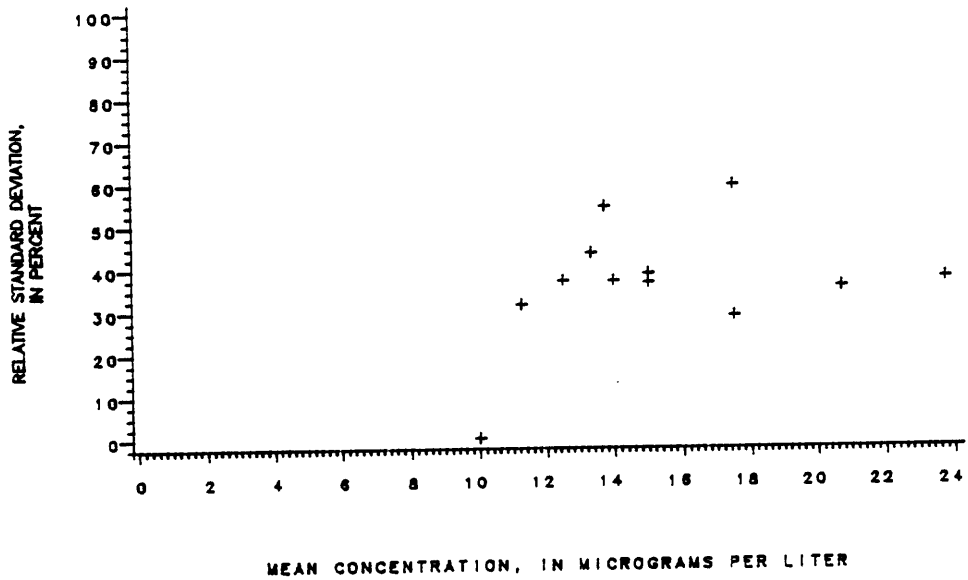


Figure 117.--Precision data for chromium at the Atlanta Laboratory.

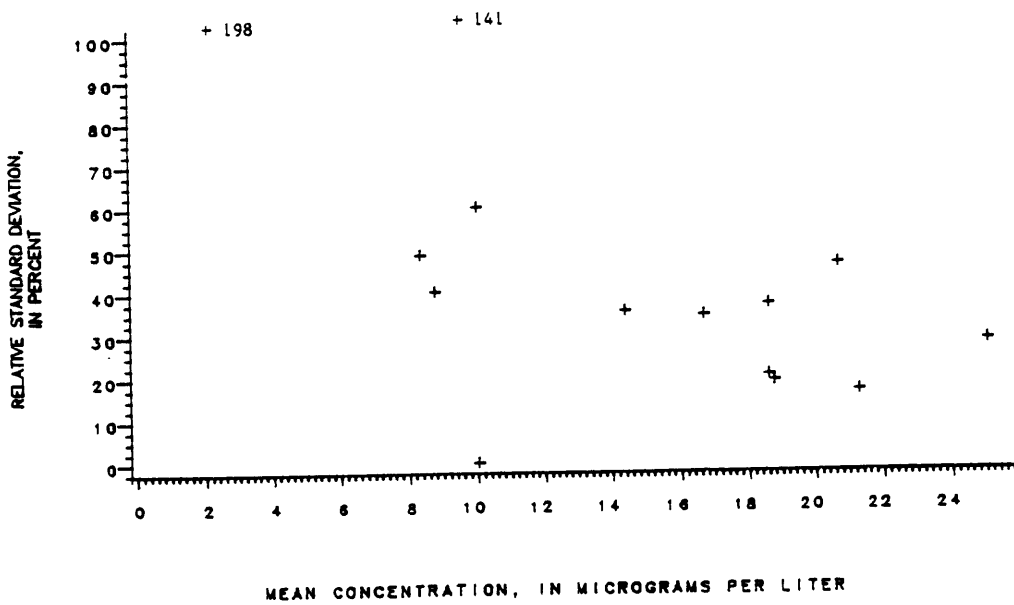


Figure 118.--Precision data for chromium at the Denver Laboratory.

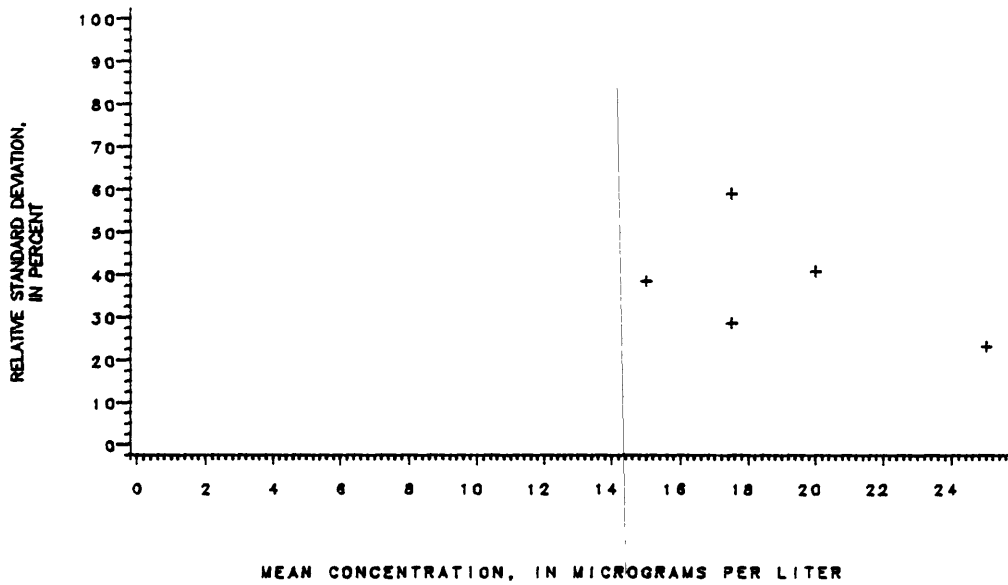


Figure 119.--Precision data for chromium, total recoverable at the Atlanta Laboratory.

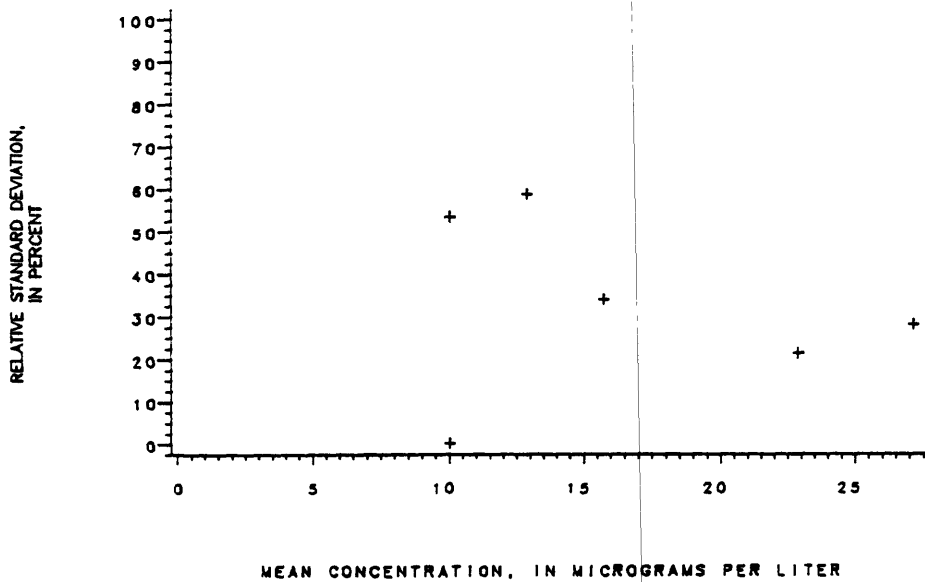


Figure 120.--Precision data for chromium, total recoverable at the Denver Laboratory.

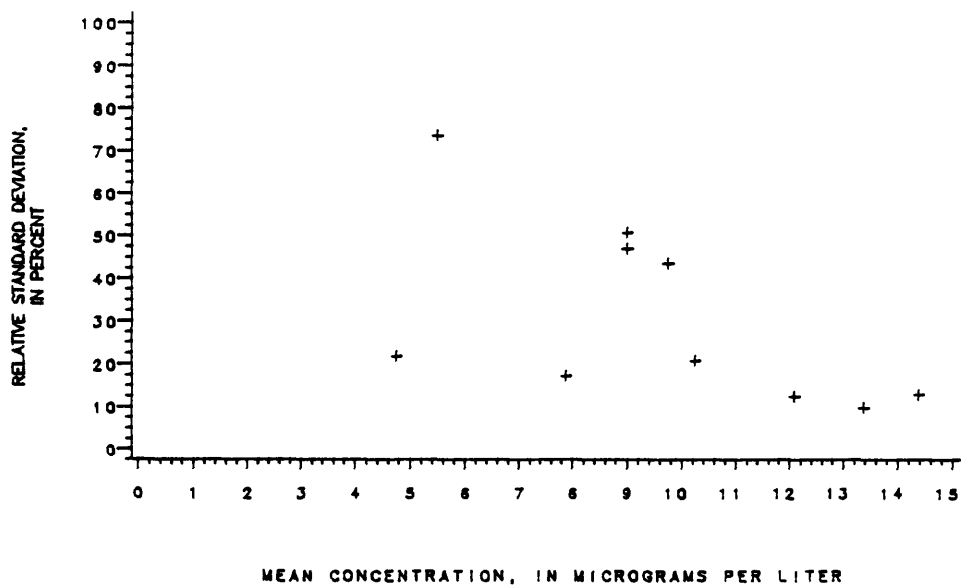


Figure 121.—Precision data for cobalt at the Atlanta Laboratory.

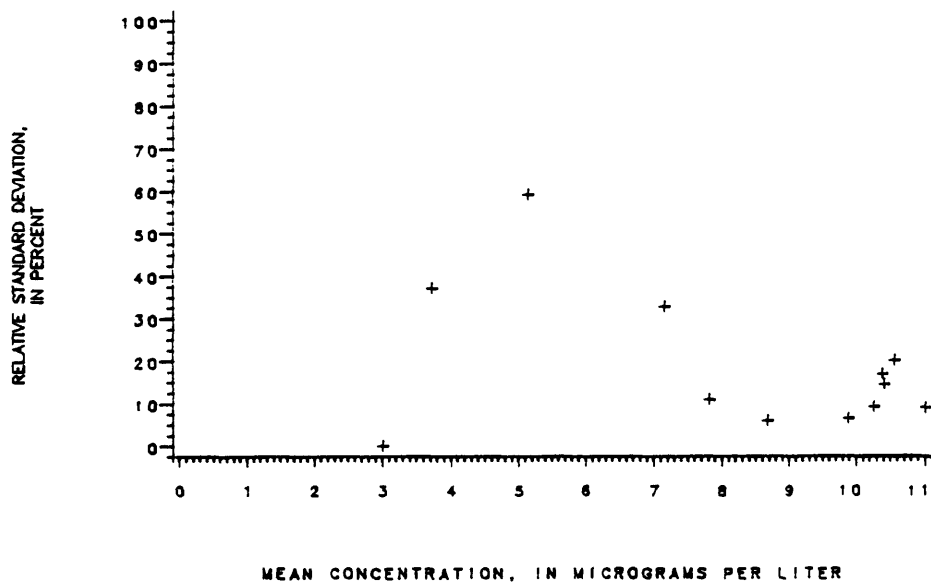


Figure 122.—Precision data for cobalt at the Denver Laboratory.

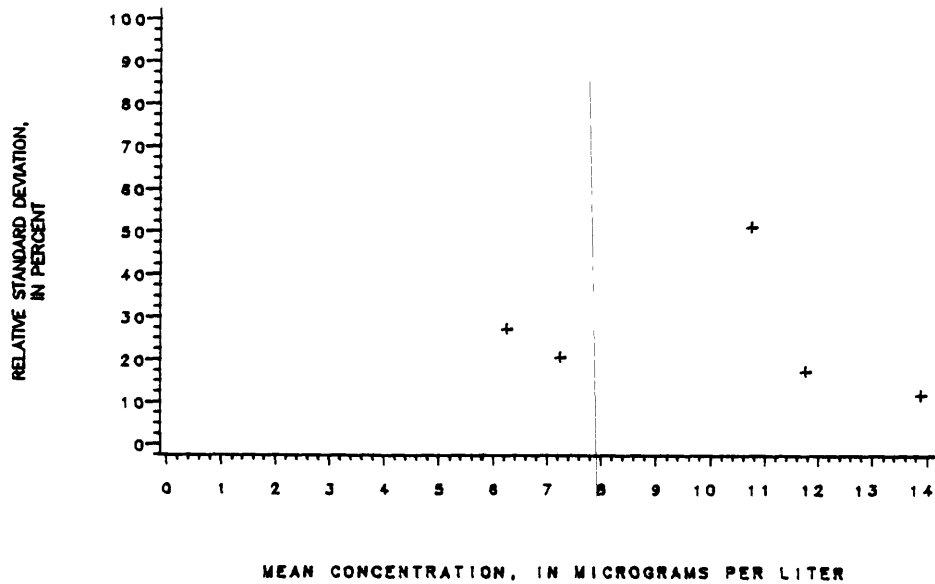


Figure 123.--Precision data for cobalt, total recoverable at the Atlanta Laboratory.

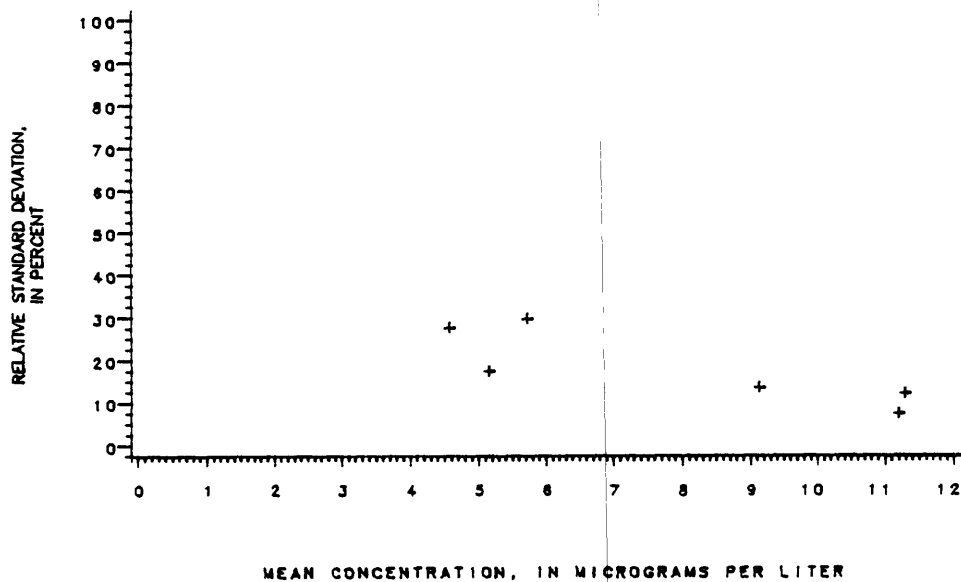


Figure 124.--Precision data for cobalt, total recoverable at the Denver Laboratory.

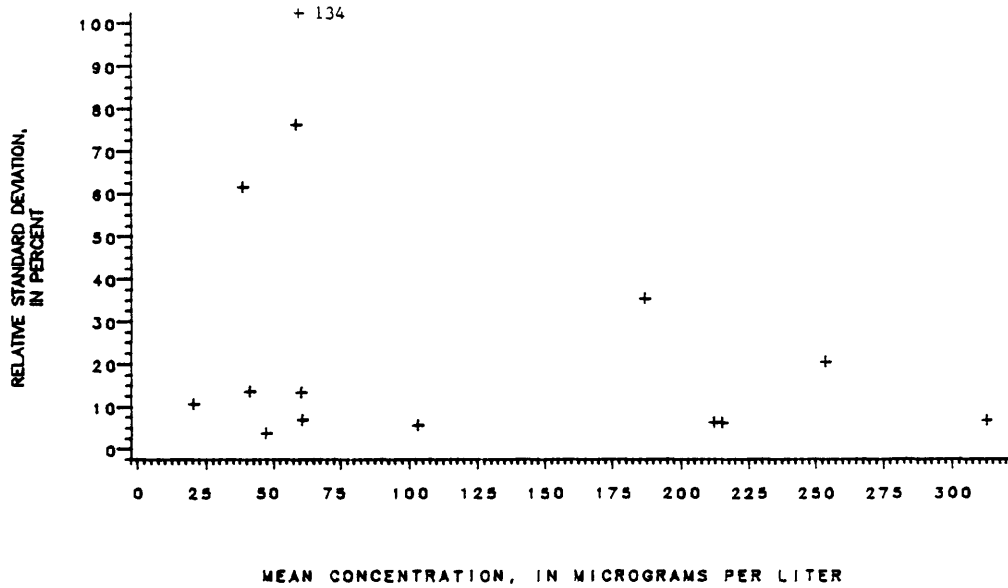


Figure 125.--Precision data for copper at the Atlanta Laboratory.

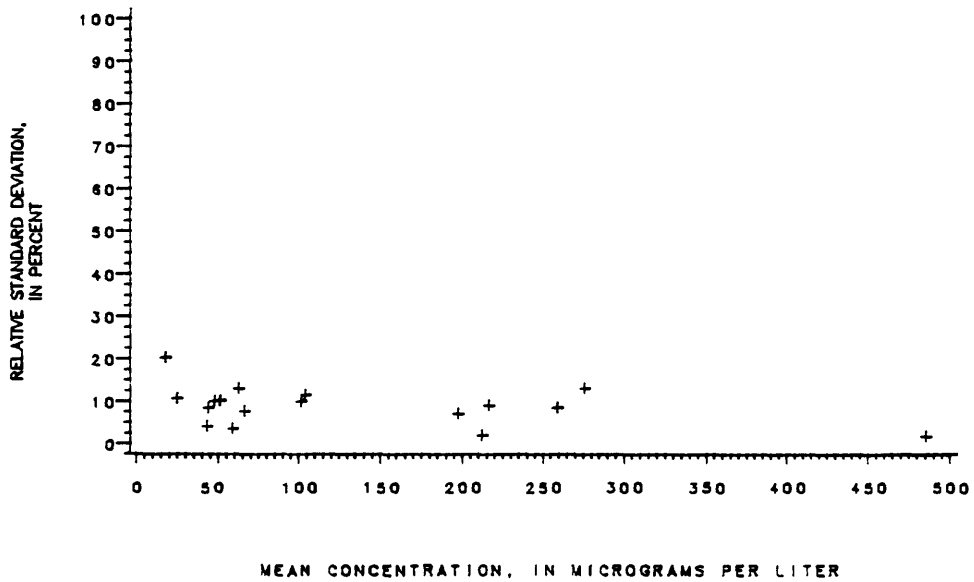


Figure 126.--Precision data for copper at the Denver Laboratory.

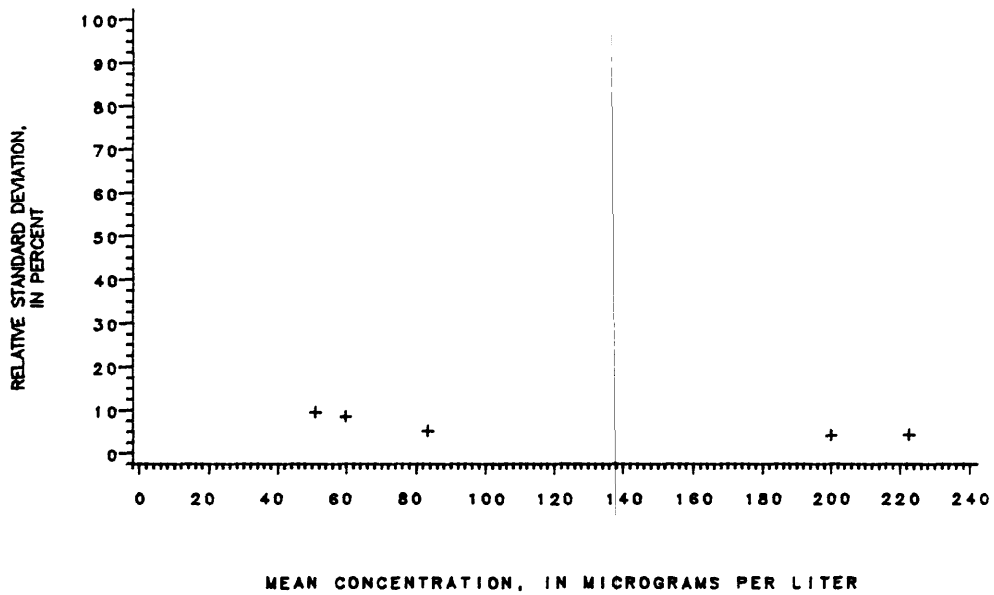


Figure 127.--Precision data for copper, total recoverable at the Atlanta Laboratory.

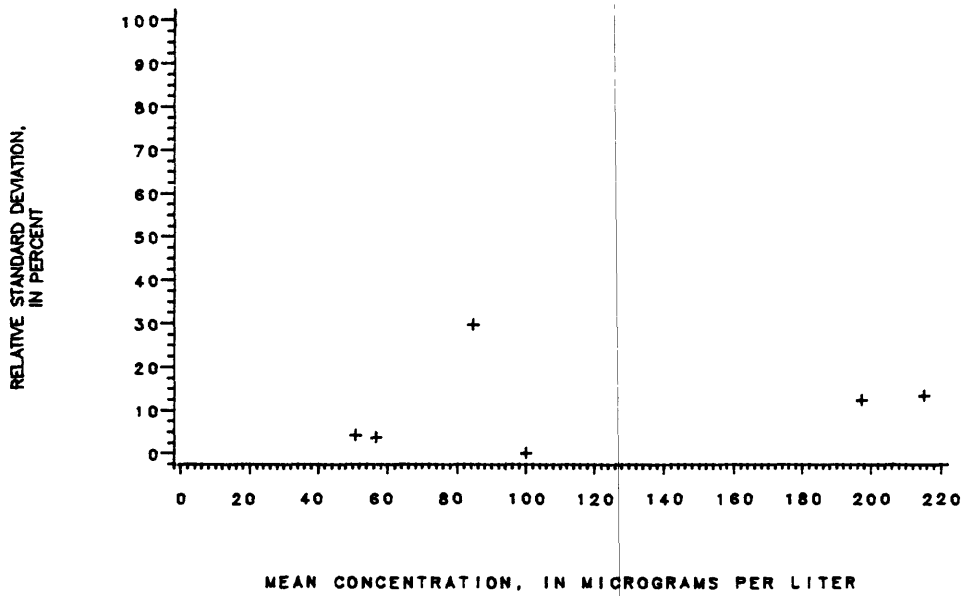


Figure 128.--Precision data for copper, total recoverable at the Denver Laboratory.

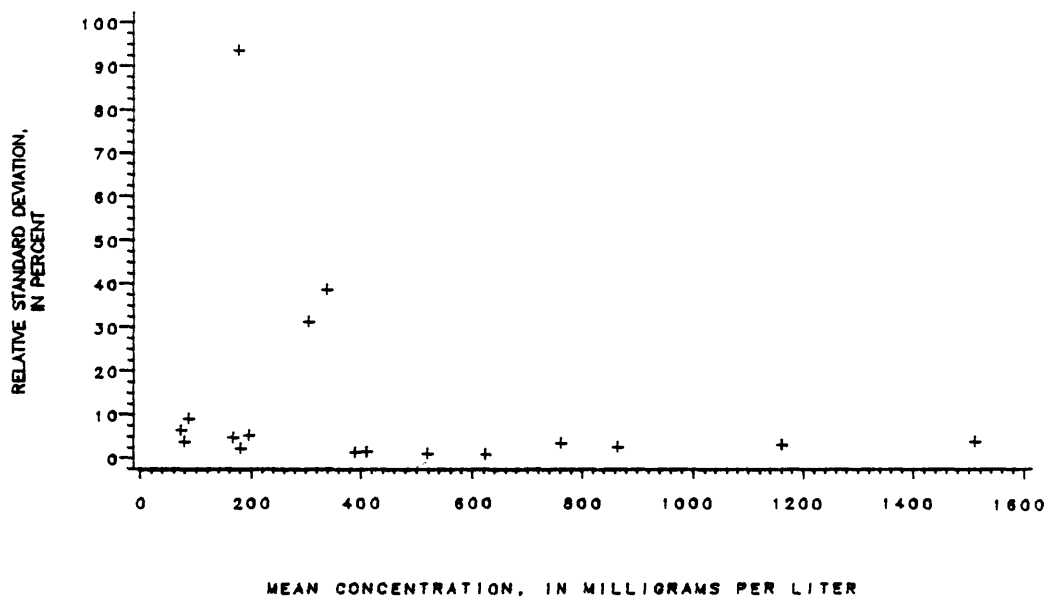


Figure 129.--Precision data for dissolved solids at the Atlanta Laboratory.

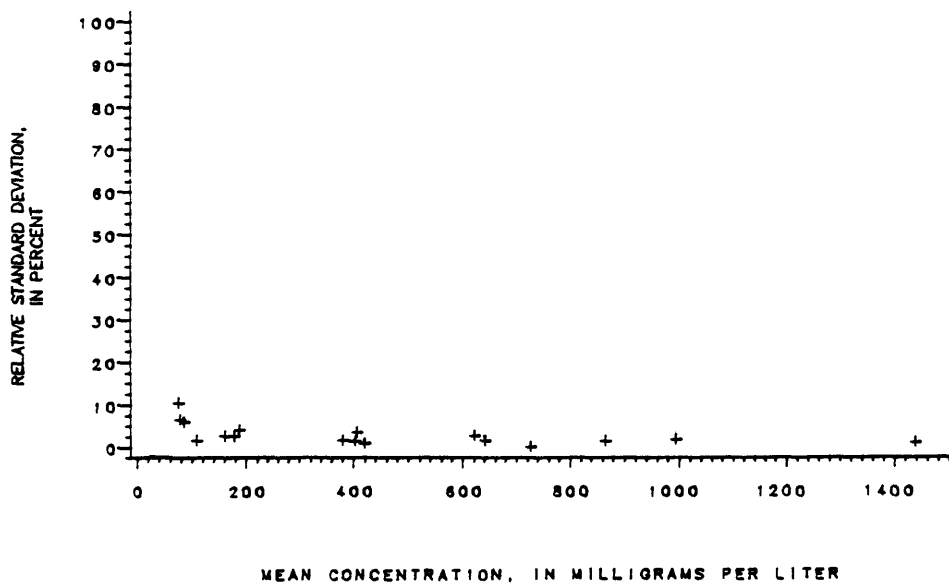


Figure 130.--Precision data for dissolved solids at the Denver Laboratory.

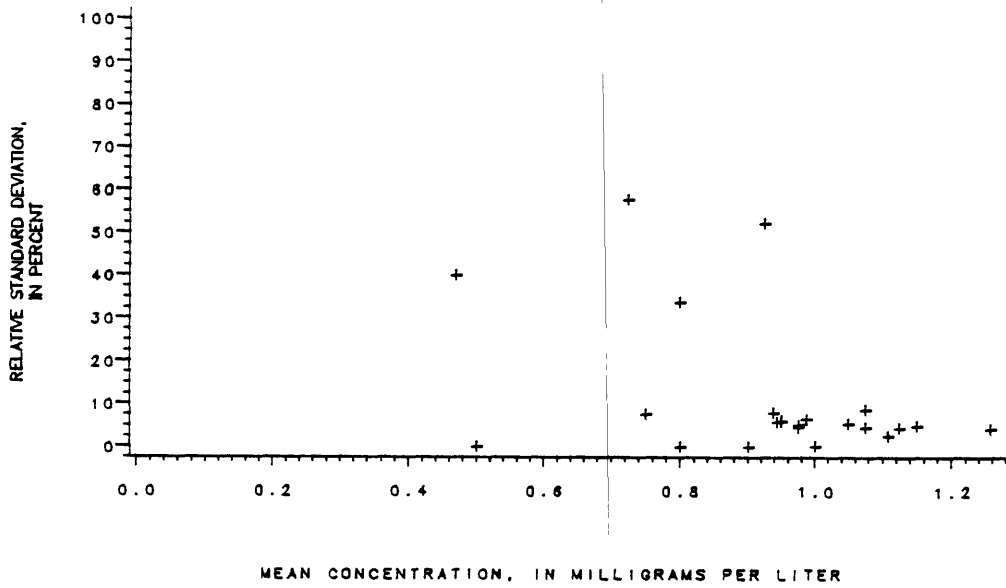


Figure 131.--Precision data for fluoride at the Atlanta Laboratory.

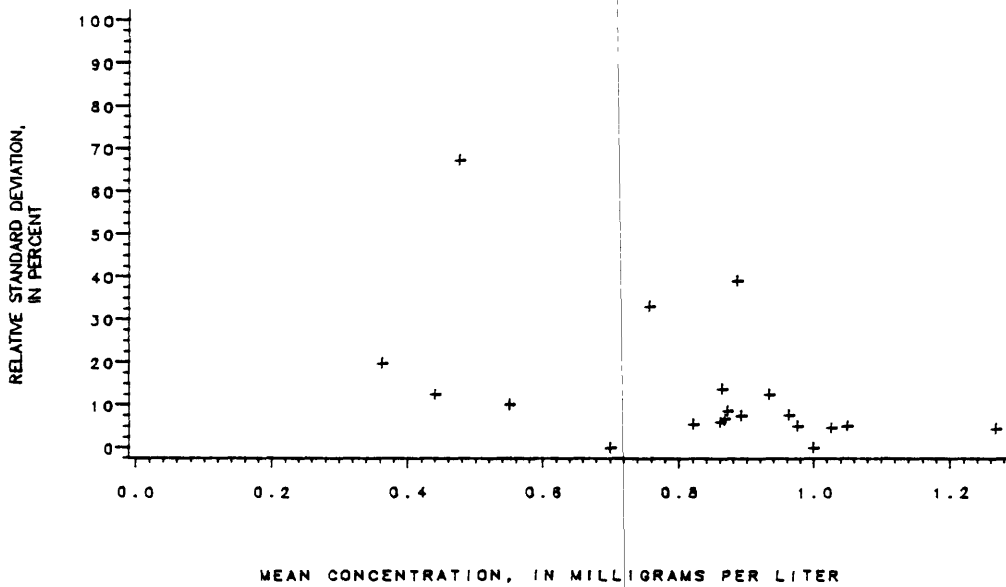


Figure 132.--Precision data for fluoride at the Denver Laboratory.

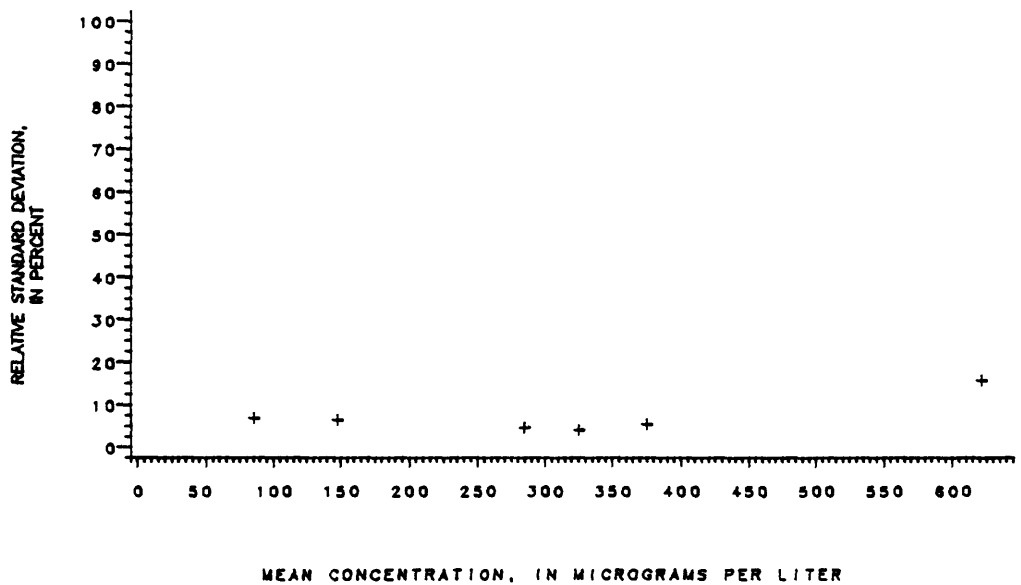


Figure 133.--Precision data for iron at the Atlanta Laboratory.

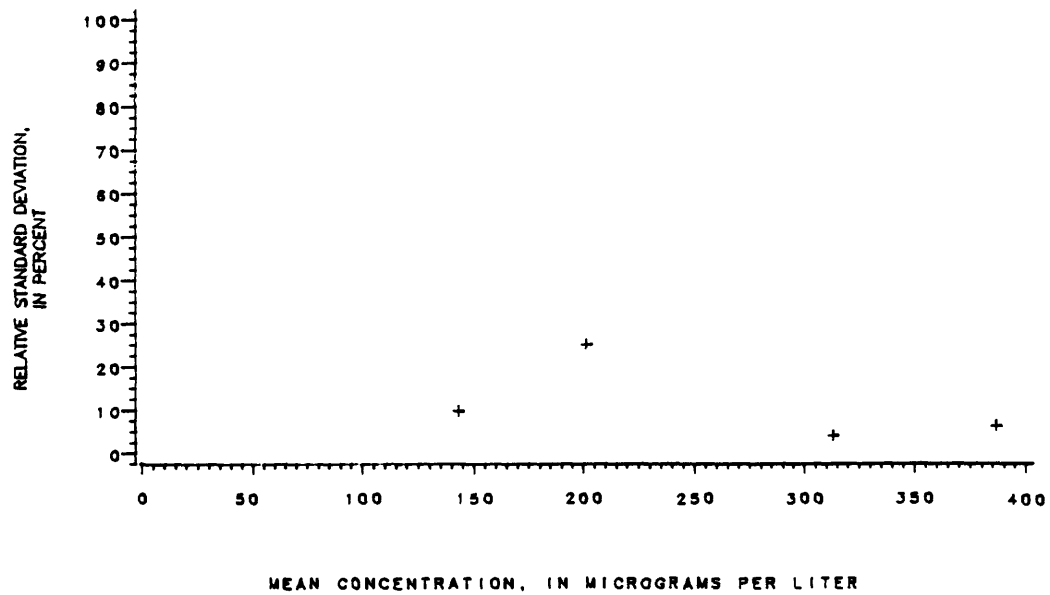


Figure 134.--Precision data for iron at the Denver Laboratory.

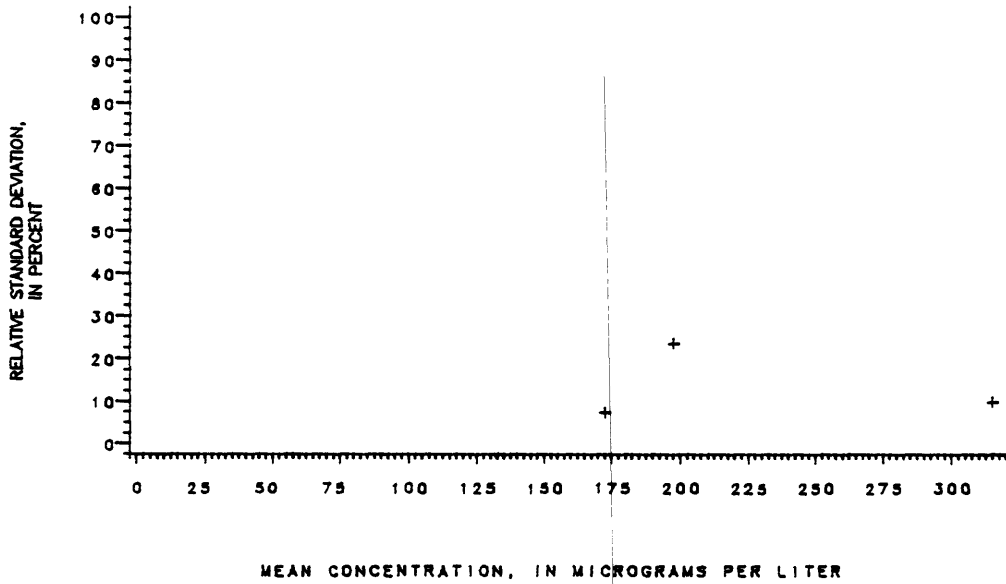


Figure 135.--Precision data for iron, total recoverable at the Atlanta Laboratory.

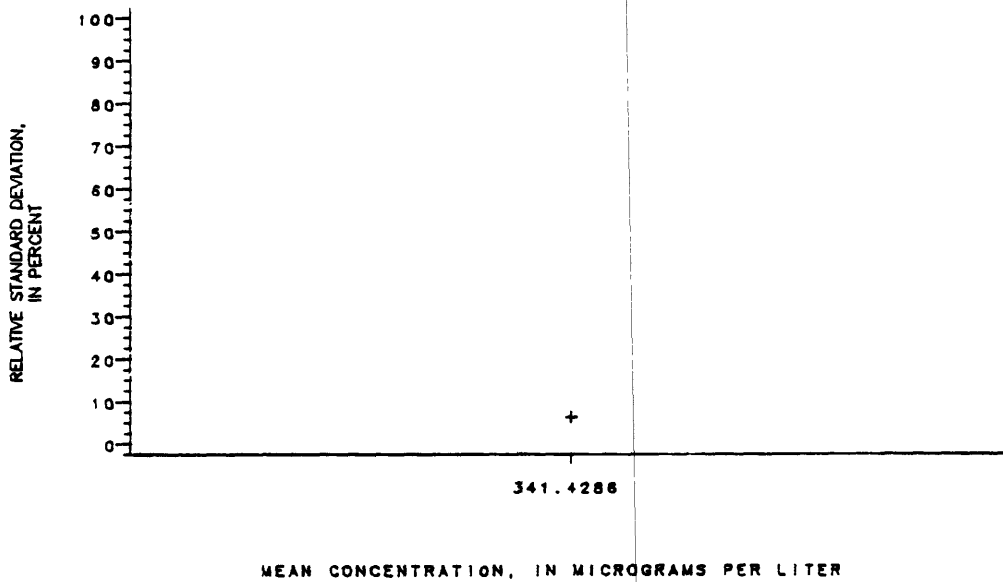


Figure 136.--Precision data for iron, total recoverable at the Denver Laboratory.

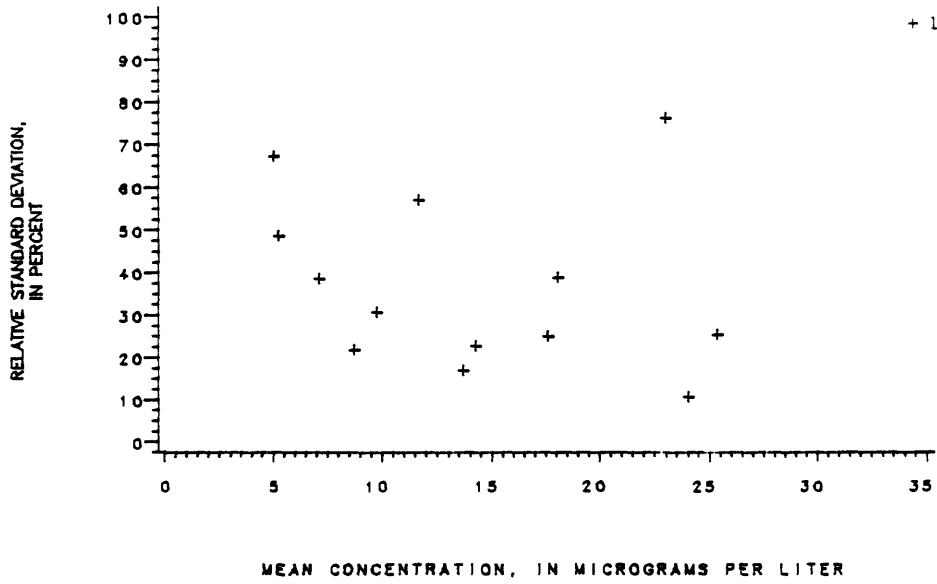


Figure 137.--Precision data for lead at the Atlanta Laboratory.

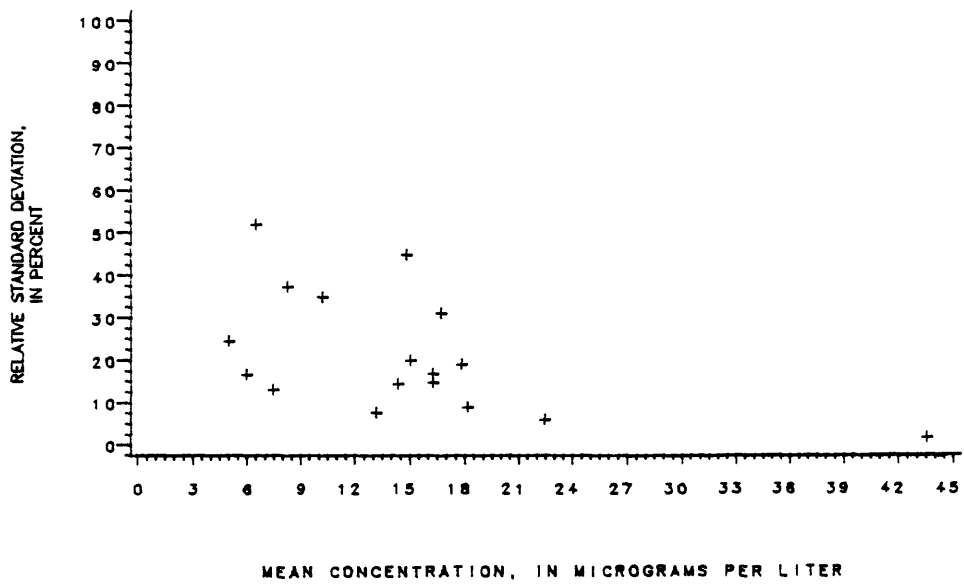


Figure 138.--Precision data for lead at the Denver Laboratory.

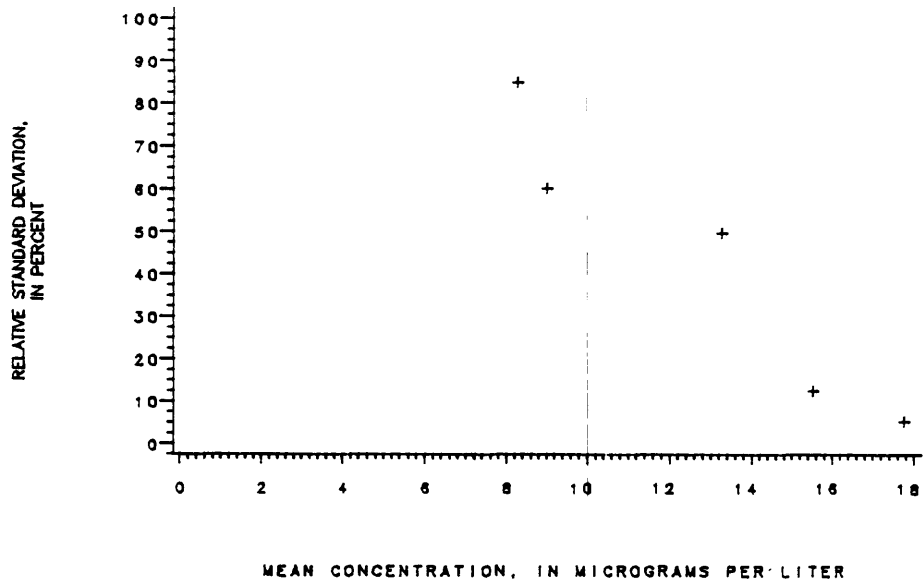


Figure 139.--Precision data for lead, total recoverable at the Atlanta Laboratory.

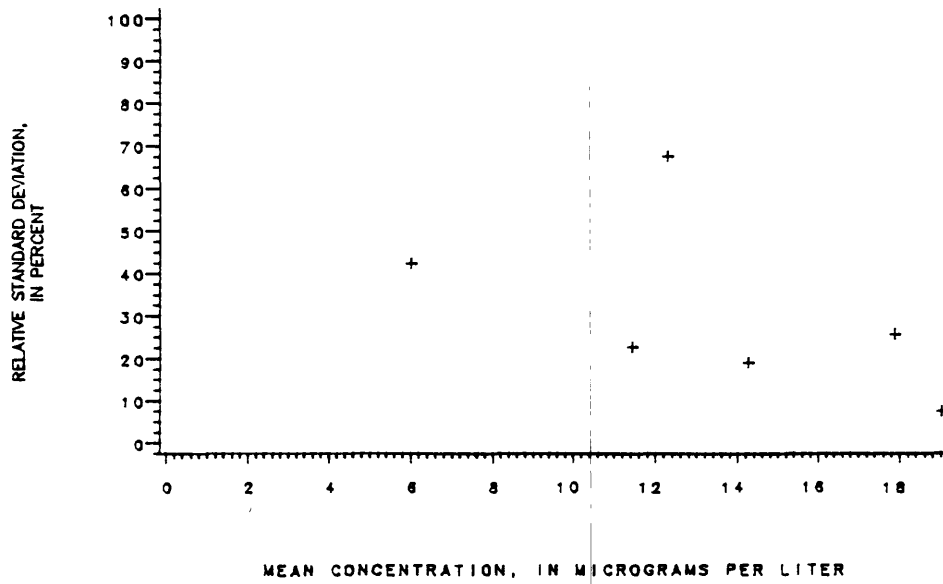


Figure 140.--Precision data for lead, total recoverable at the Denver Laboratory.

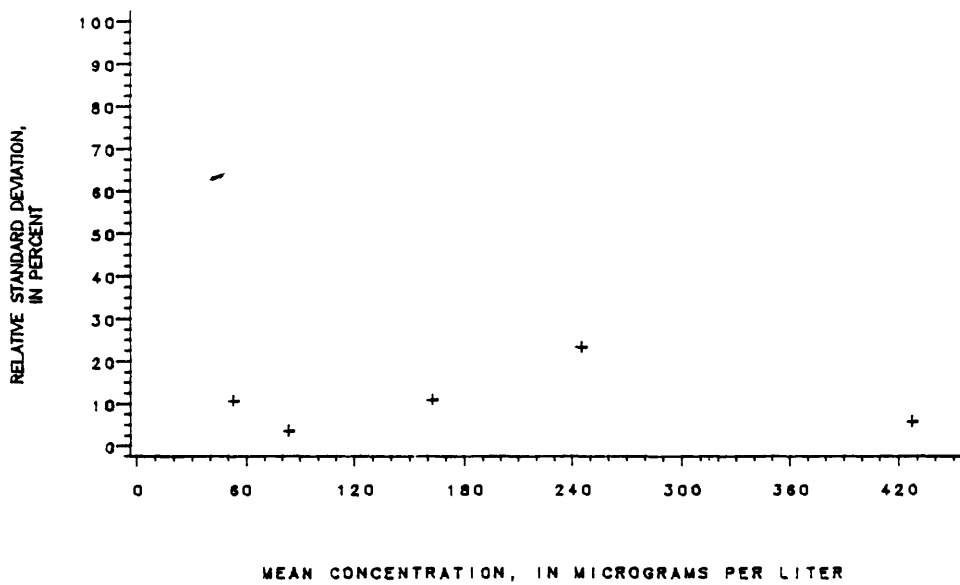


Figure 141.--Precision data for lithium at the Atlanta Laboratory.

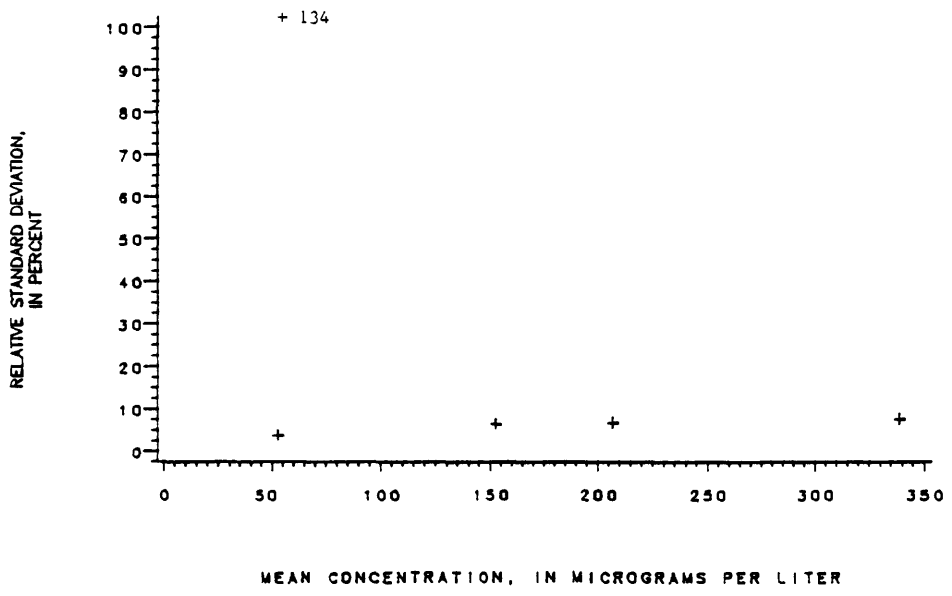


Figure 142.--Precision data for lithium at the Denver Laboratory.

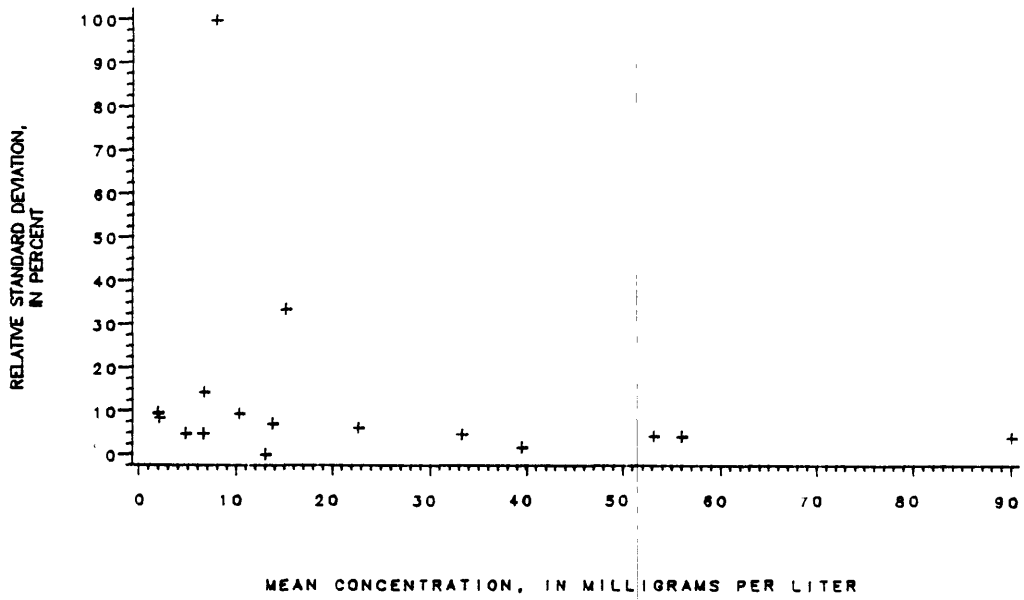


Figure 143.--Precision data for magnesium at the Atlanta Laboratory.

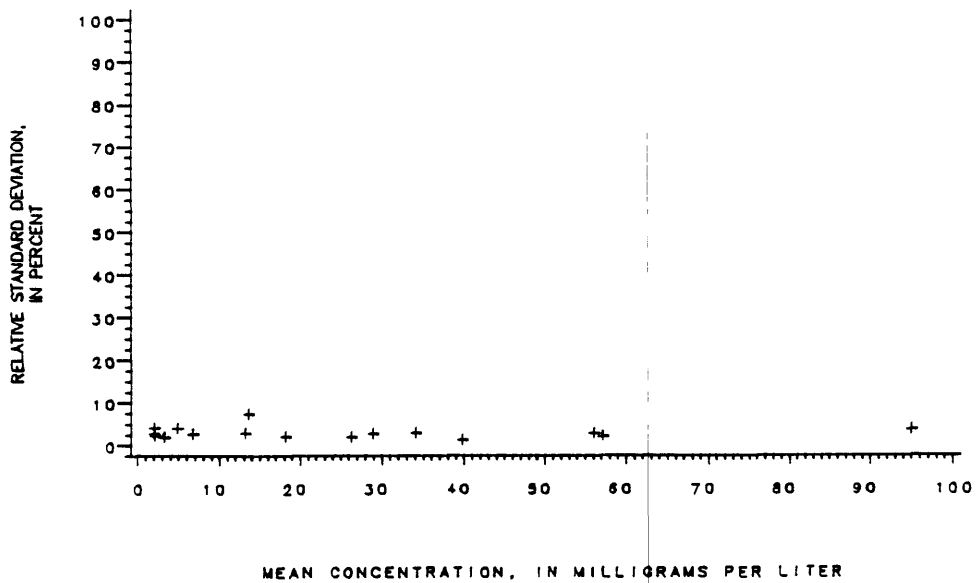


Figure 144.--Precision data for magnesium at the Denver Laboratory.

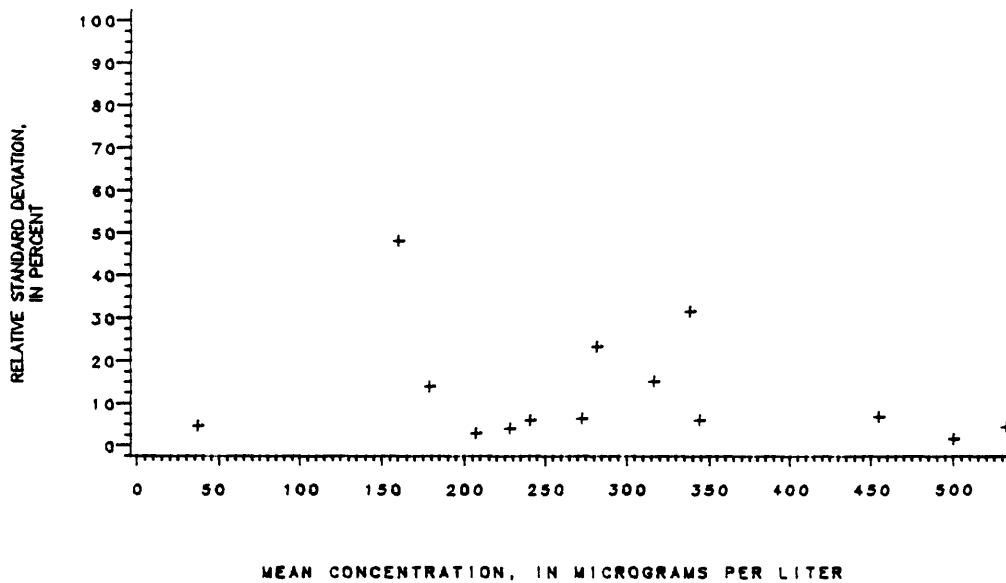


Figure 145.--Precision data for manganese at the Atlanta Laboratory.

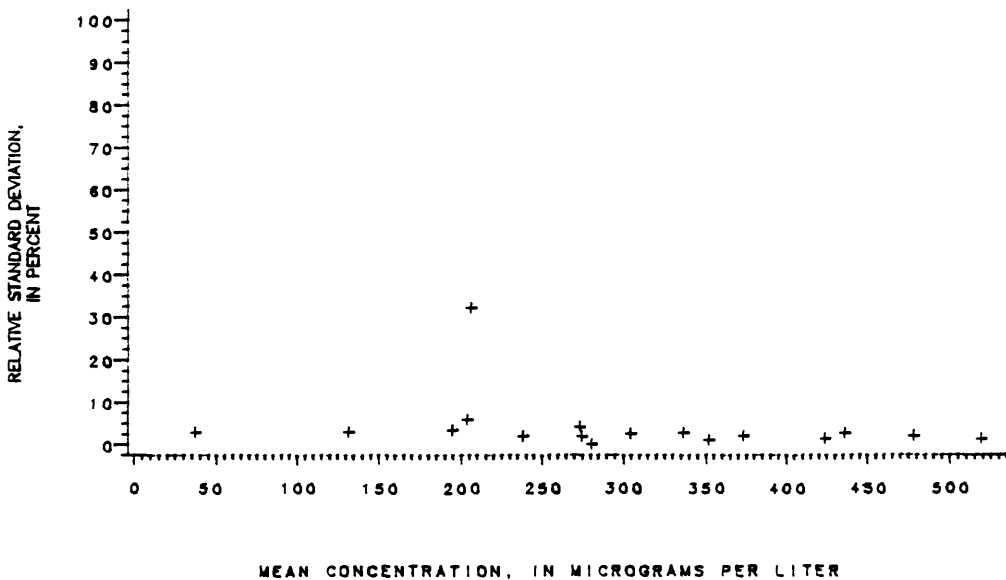


Figure 146.--Precision data for manganese at the Denver Laboratory.

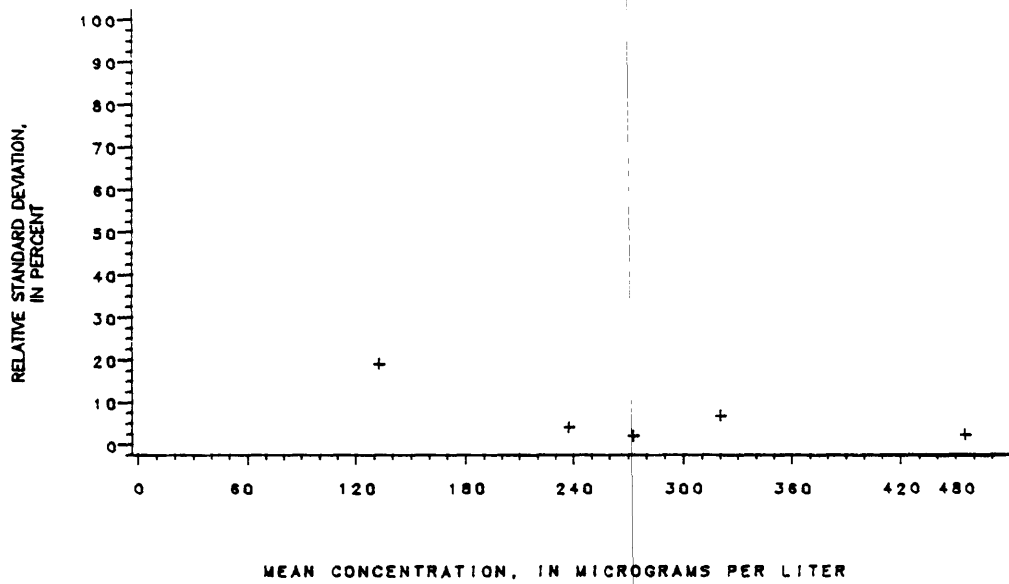


Figure 147.--Precision data for manganese, total recoverable at the Atlanta Laboratory.

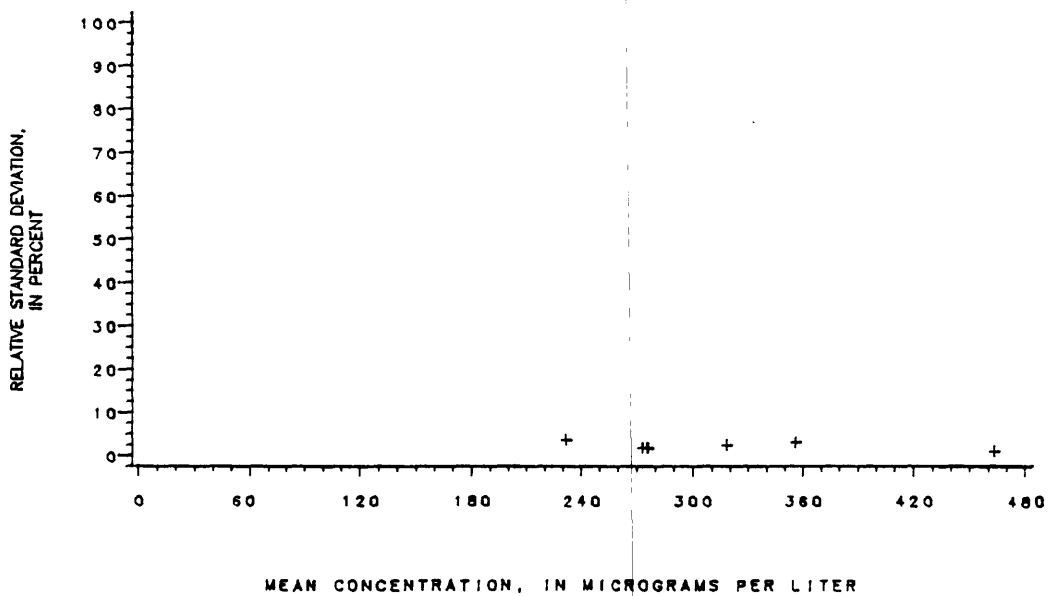


Figure 148.--Precision data for manganese, total recoverable at the Denver Laboratory.

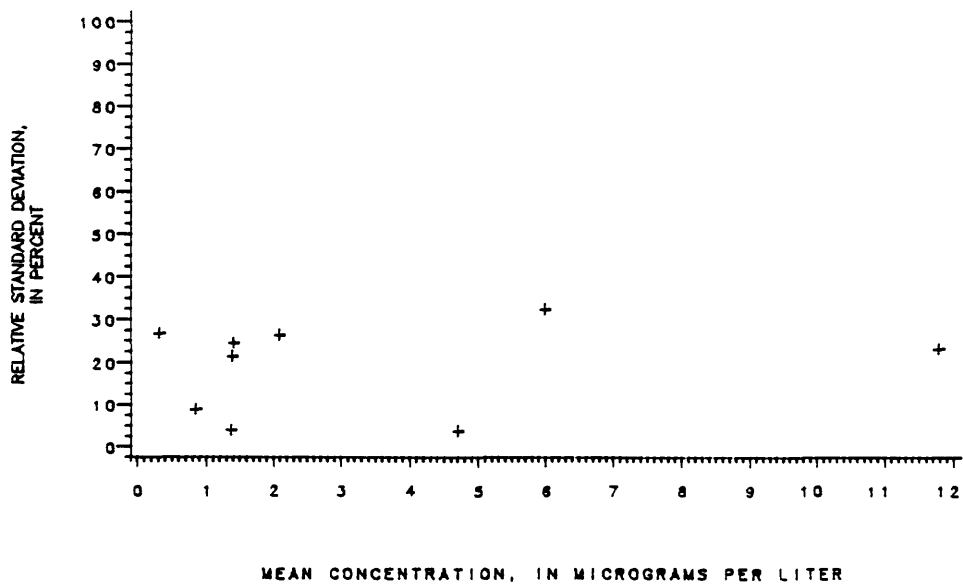


Figure 149.--Precision data for mercury at the Atlanta Laboratory.

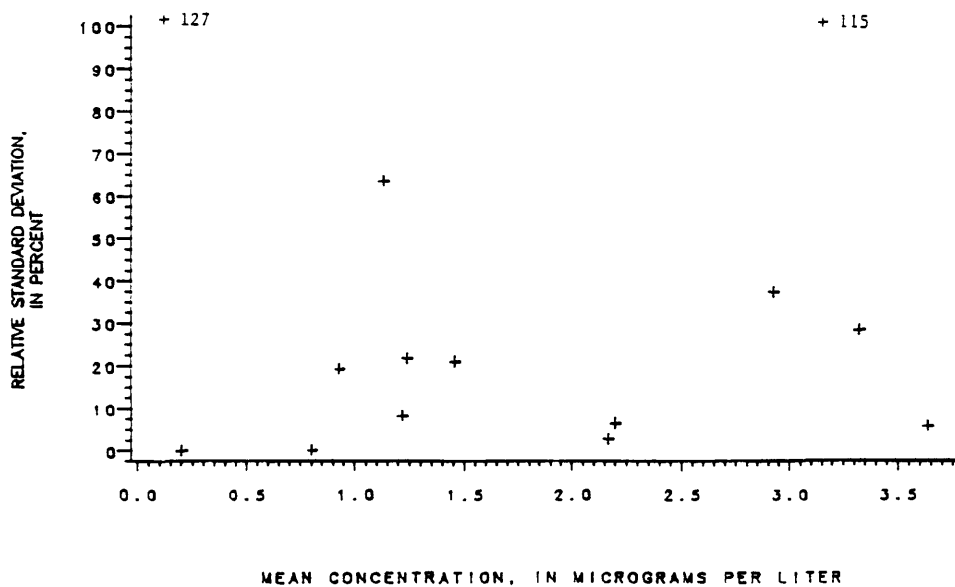


Figure 150.--Precision data for mercury at the Denver Laboratory.

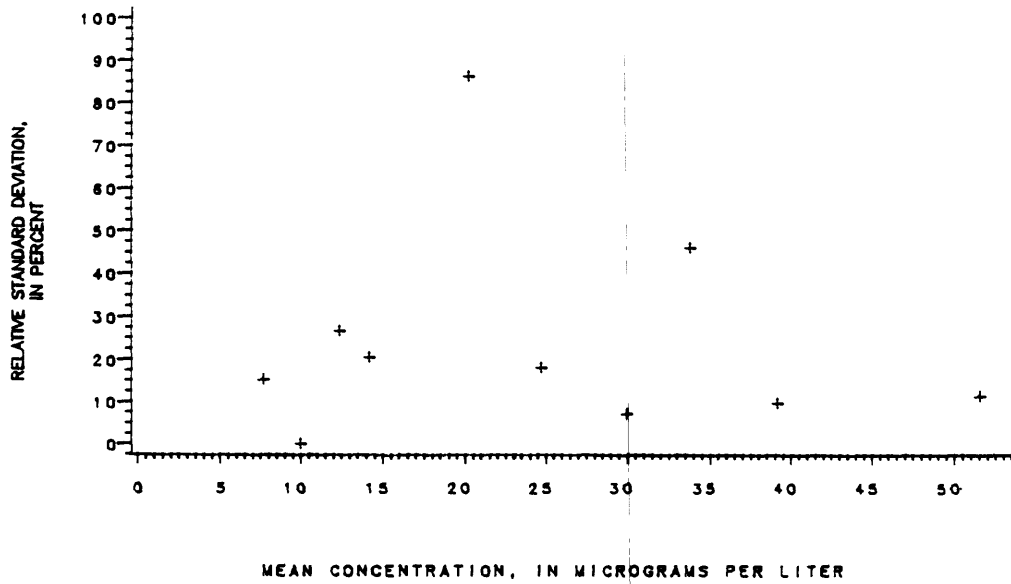


Figure 151.—Precision data for molybdenum at the Atlanta Laboratory.

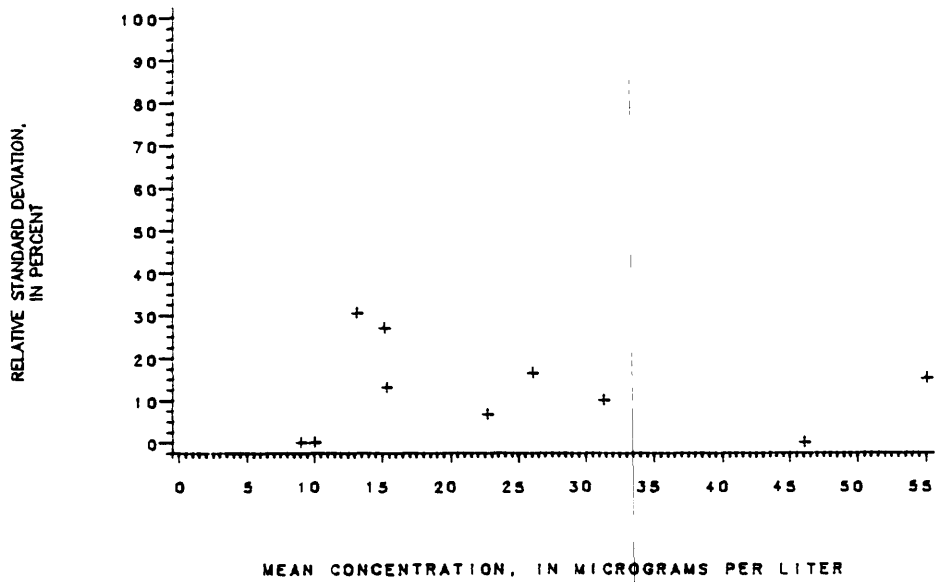


Figure 152.—Precision data for molybdenum at the Denver Laboratory.

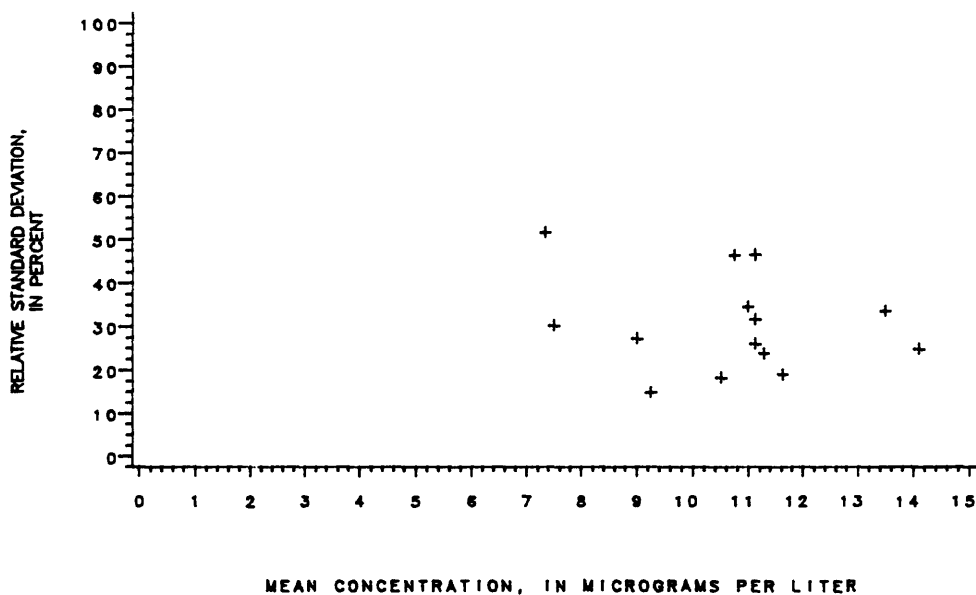


Figure 153.--Precision data for nickel at the Atlanta Laboratory.

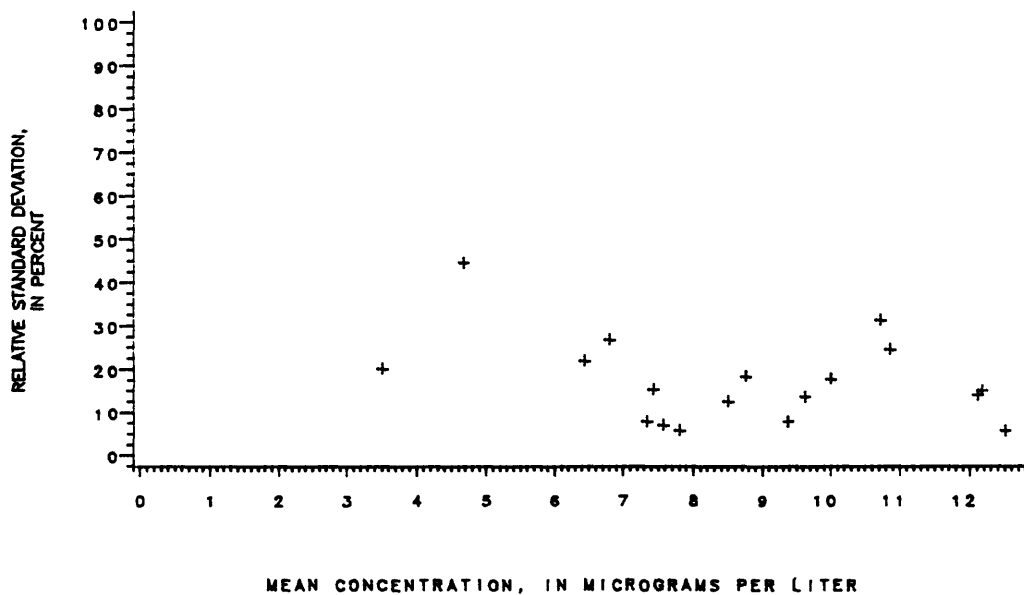


Figure 154.--Precision data for nickel at the Denver Laboratory.

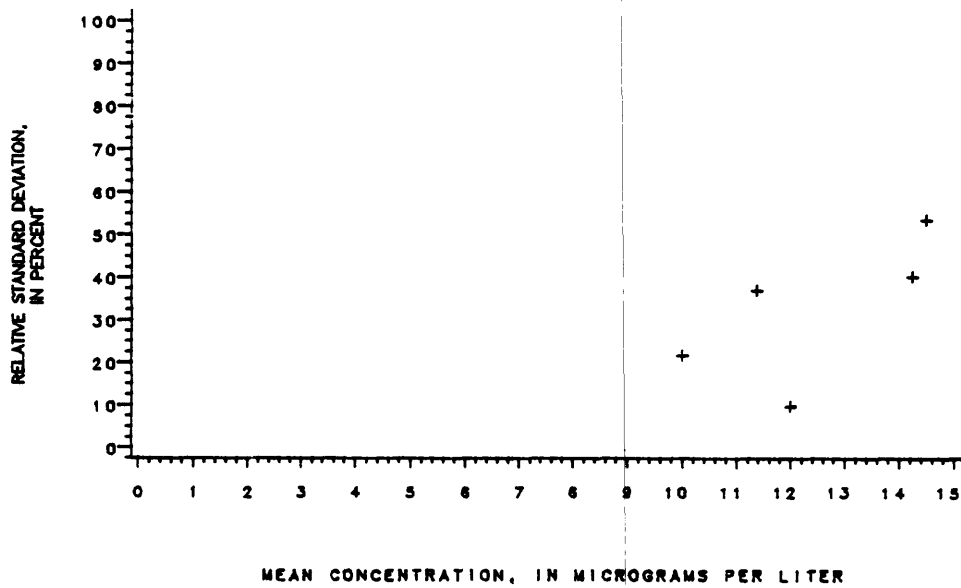


Figure 155.--Precision data for nickel, total recoverable at the Atlanta Laboratory.

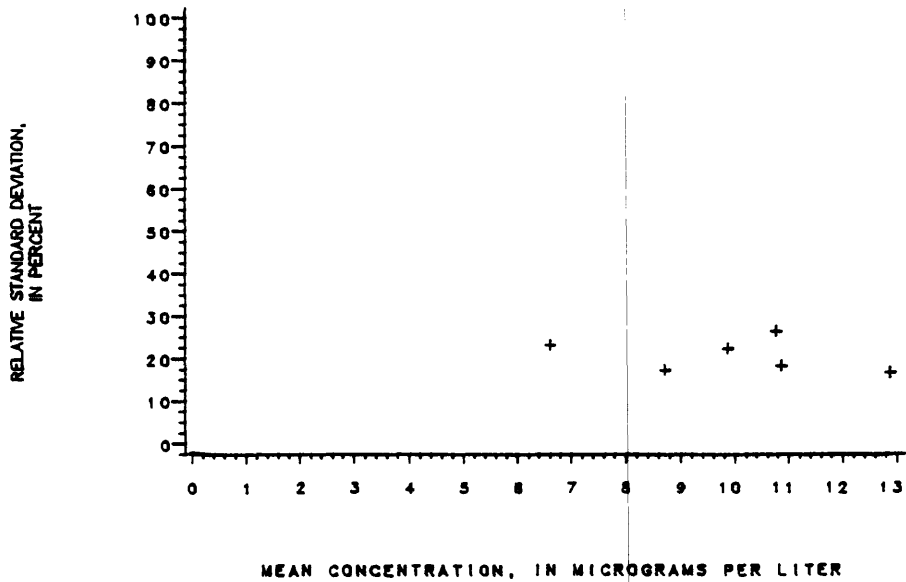


Figure 156.--Precision data for nickel, total recoverable at the Denver Laboratory.

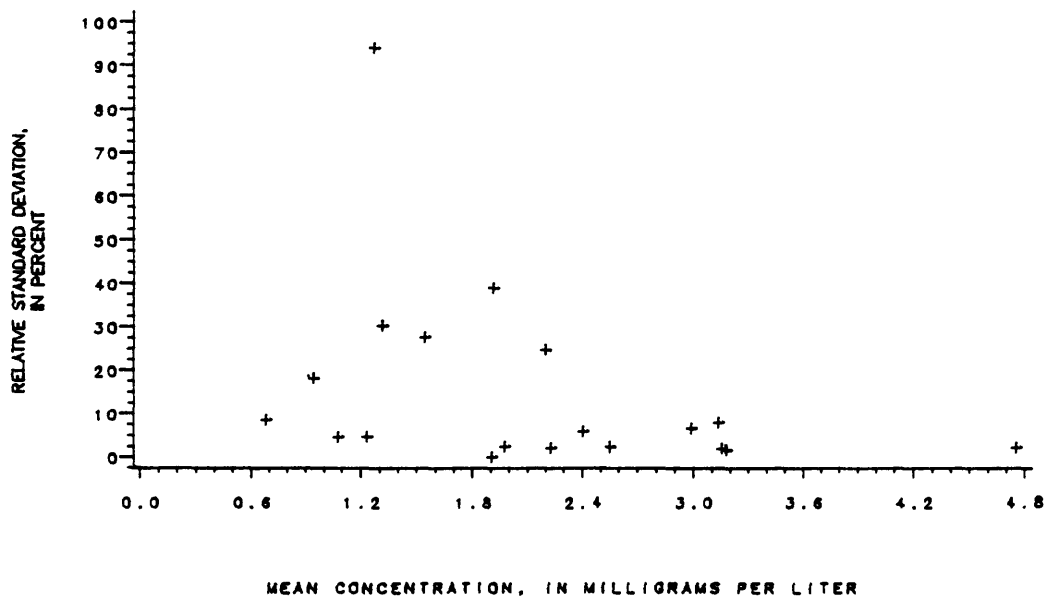


Figure 157.--Precision data for nitrate plus nitrite-nitrogen at the Atlanta Laboratory.

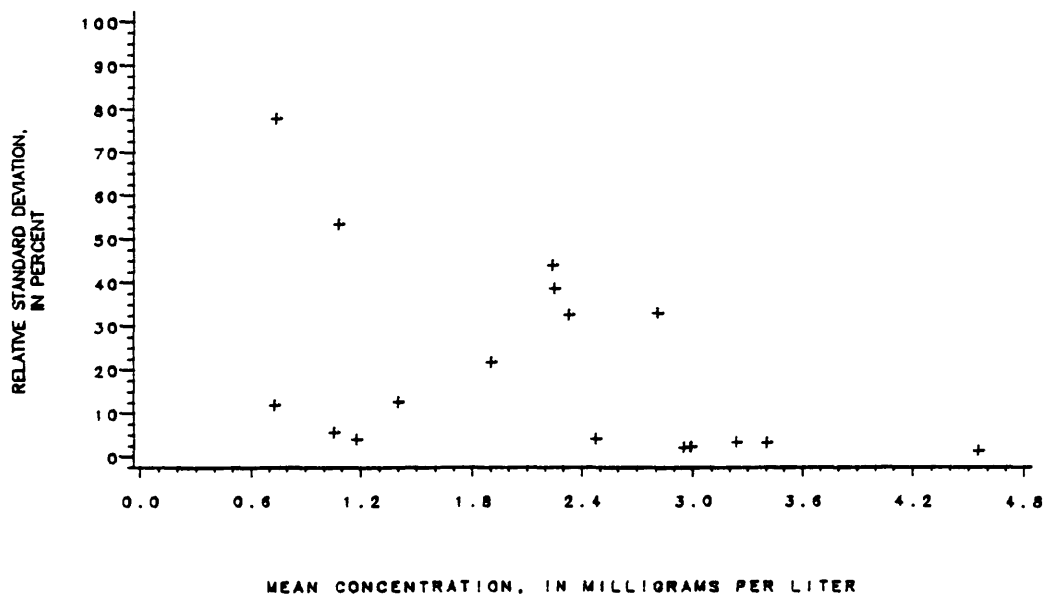


Figure 158.--Precision data for nitrate plus nitrite-nitrogen at the Denver Laboratory.

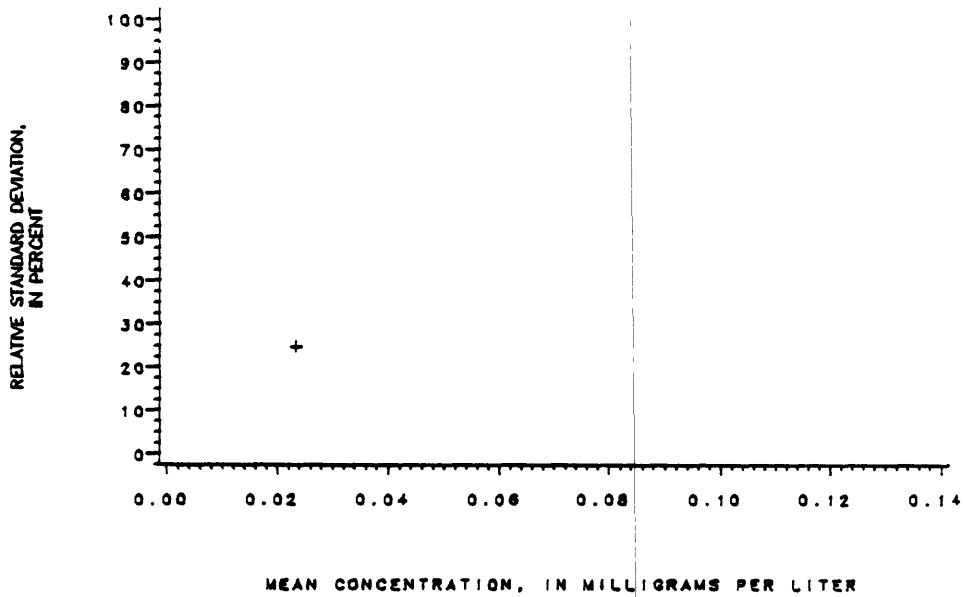


Figure 159.—Precision data for nitrite-nitrogen at the Atlanta Laboratory.

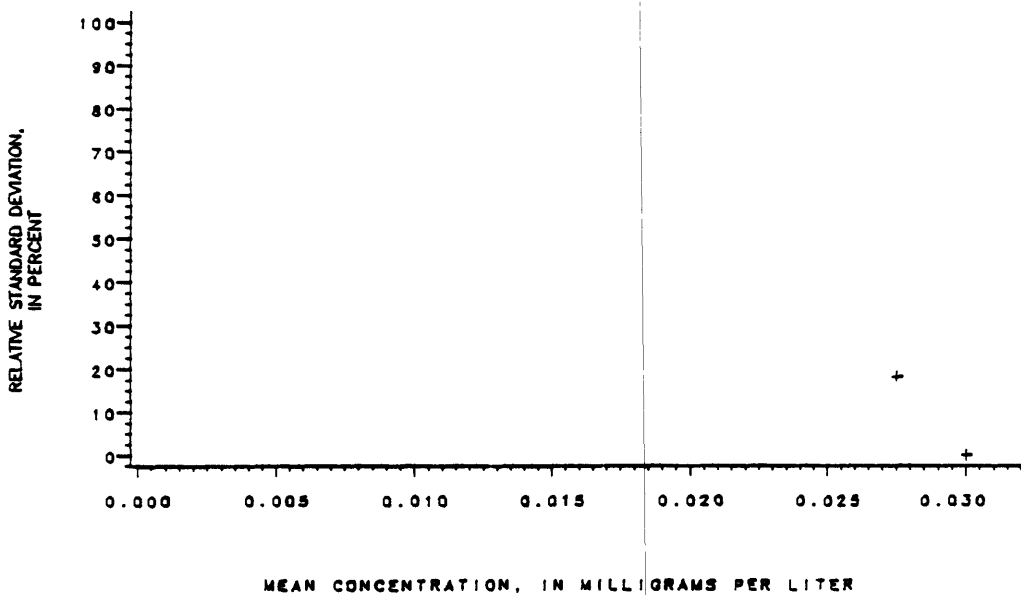


Figure 160.—Precision data for nitrite-nitrogen at the Denver Laboratory.

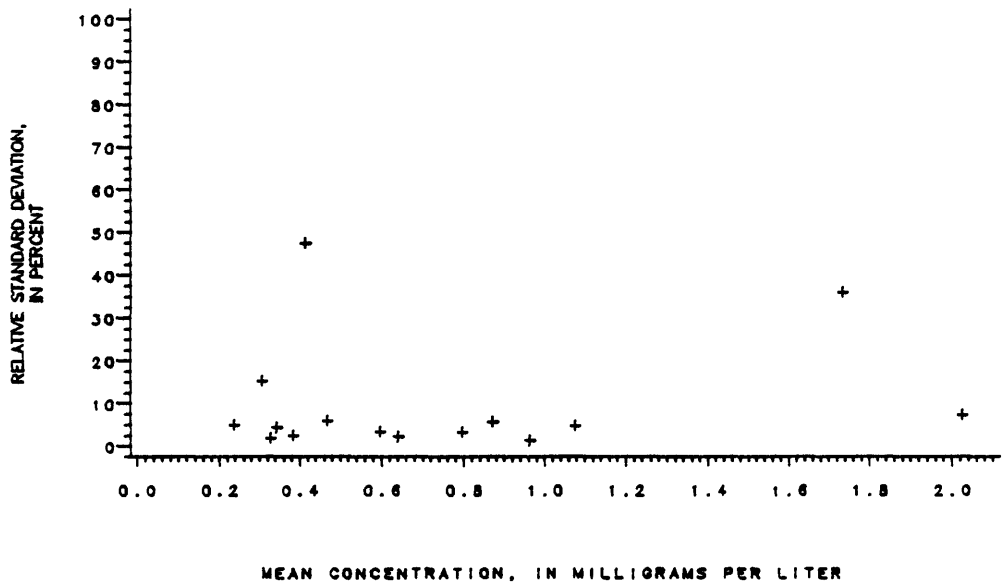


Figure 161.—Precision data for phosphorus at the Atlanta Laboratory.

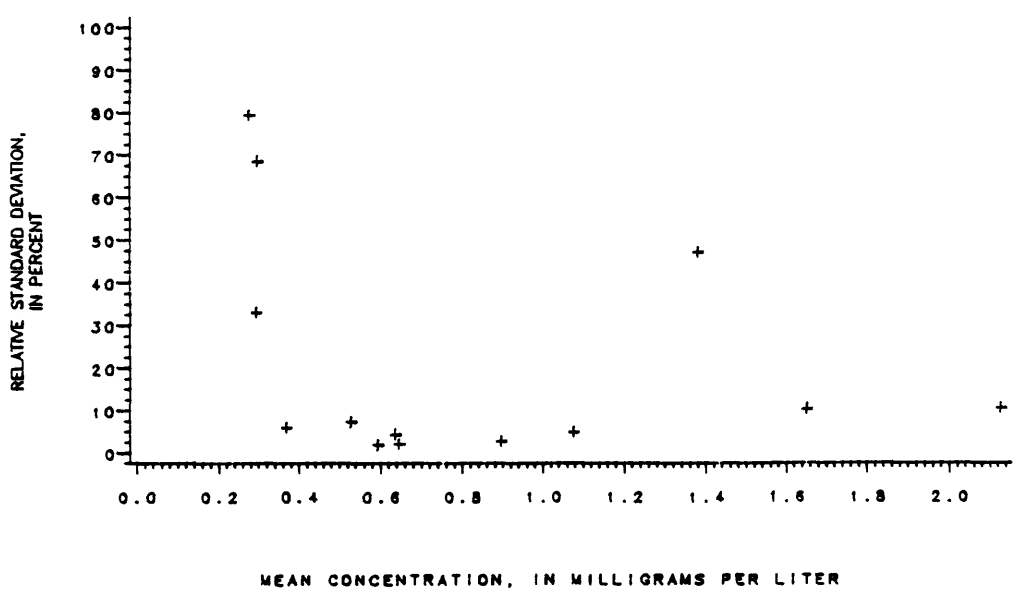


Figure 162.—Precision data for phosphorus at the Denver Laboratory.

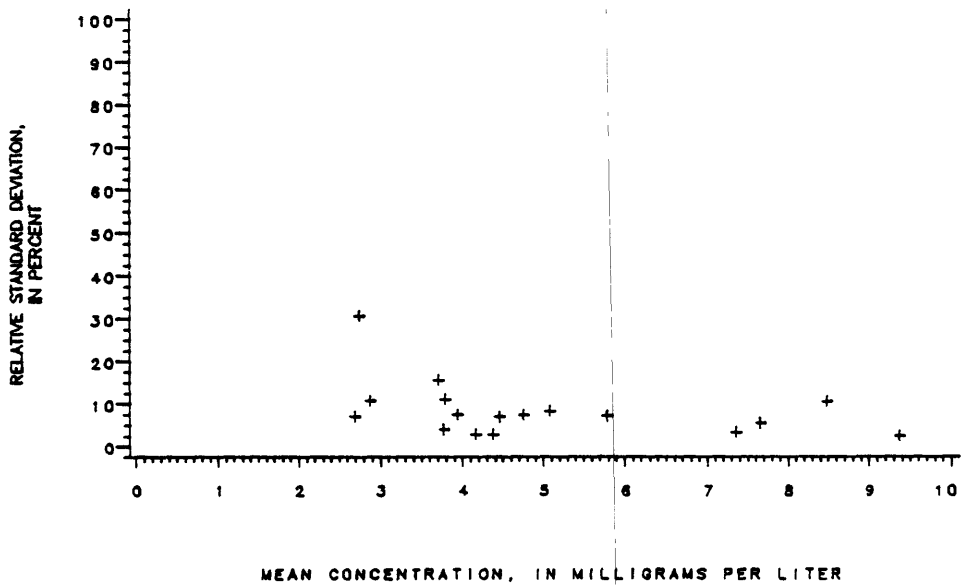


Figure 163.—Precision data for potassium at the Atlanta Laboratory.

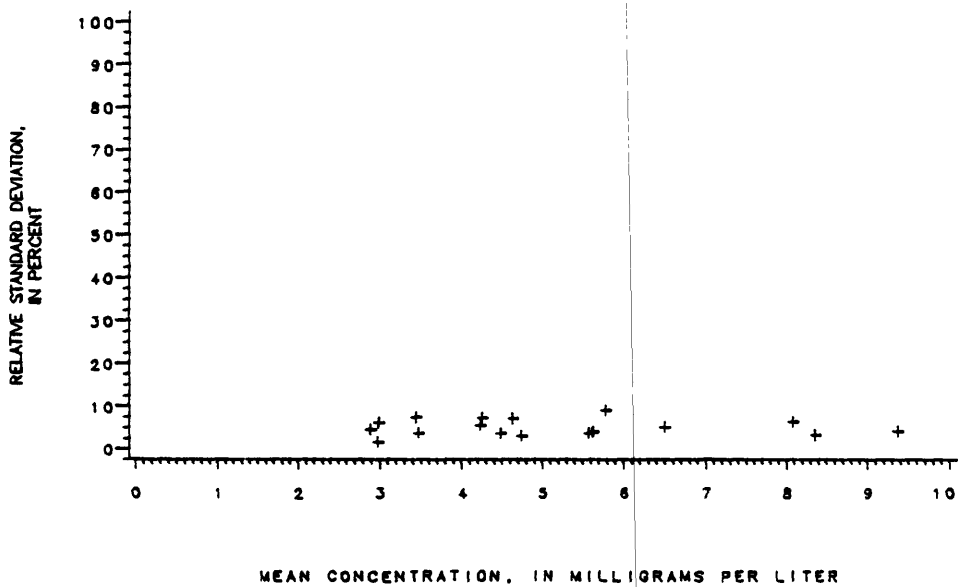


Figure 164.—Precision data for potassium at the Denver Laboratory.

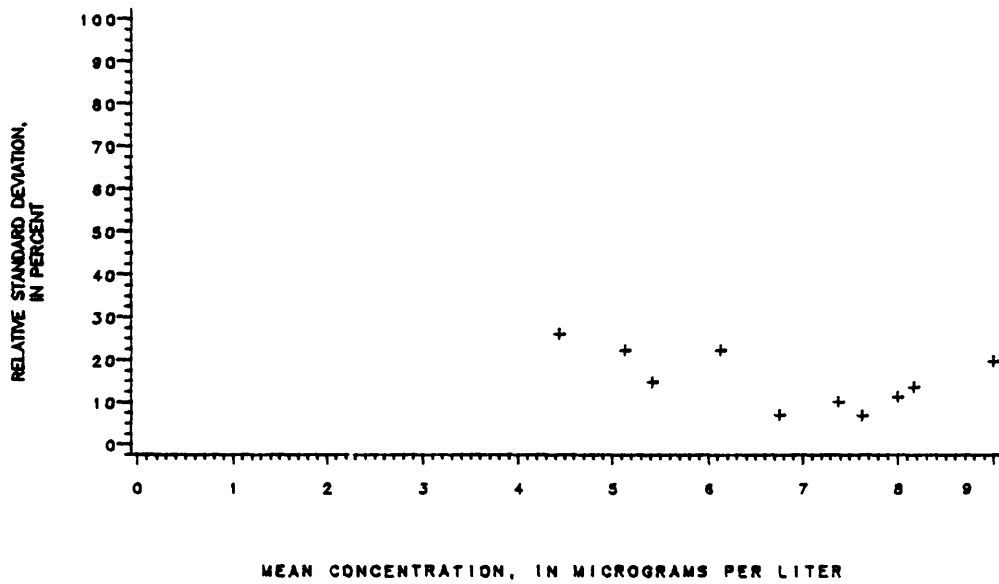


Figure 165.--Precision data for selenium at the Atlanta Laboratory.

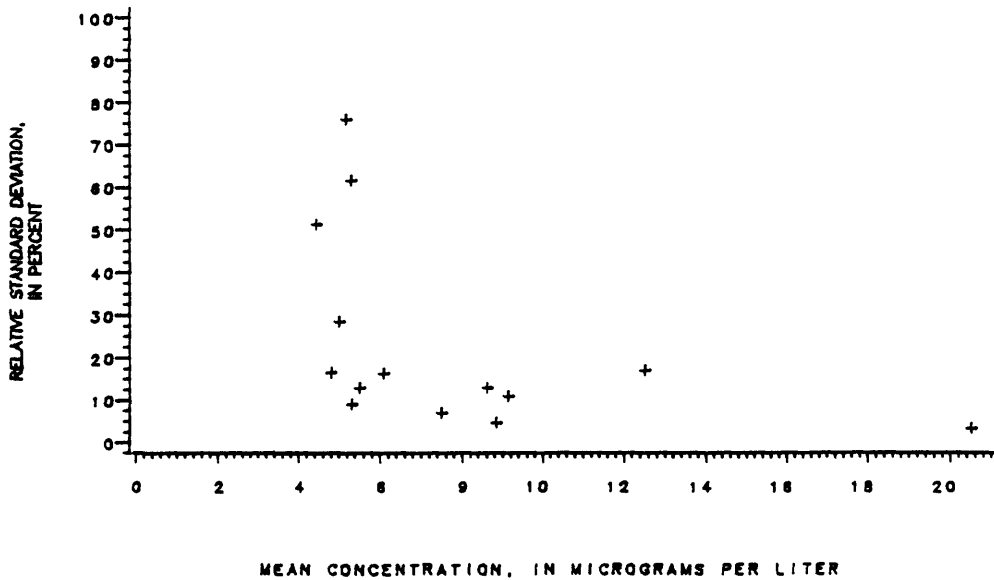


Figure 166.--Precision data for selenium at the Denver Laboratory.

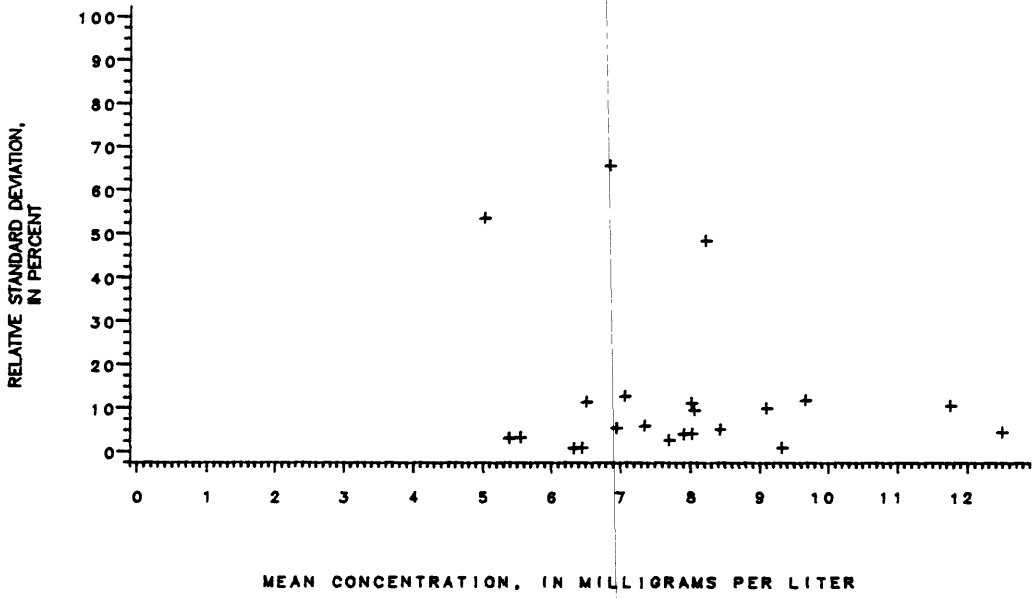


Figure 167.—Precision data for silica at the Atlanta Laboratory.

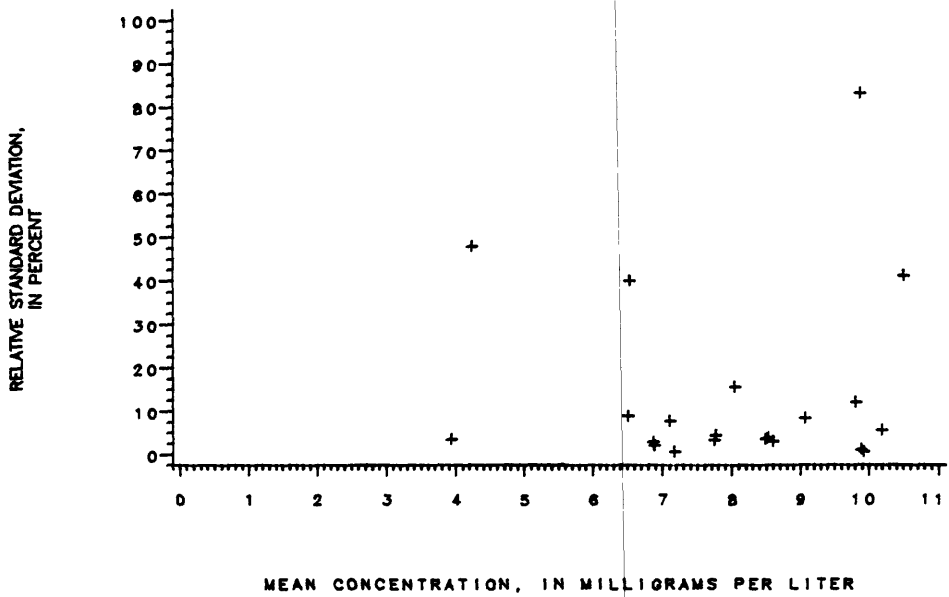


Figure 168.—Precision data for silica at the Denver Laboratory.

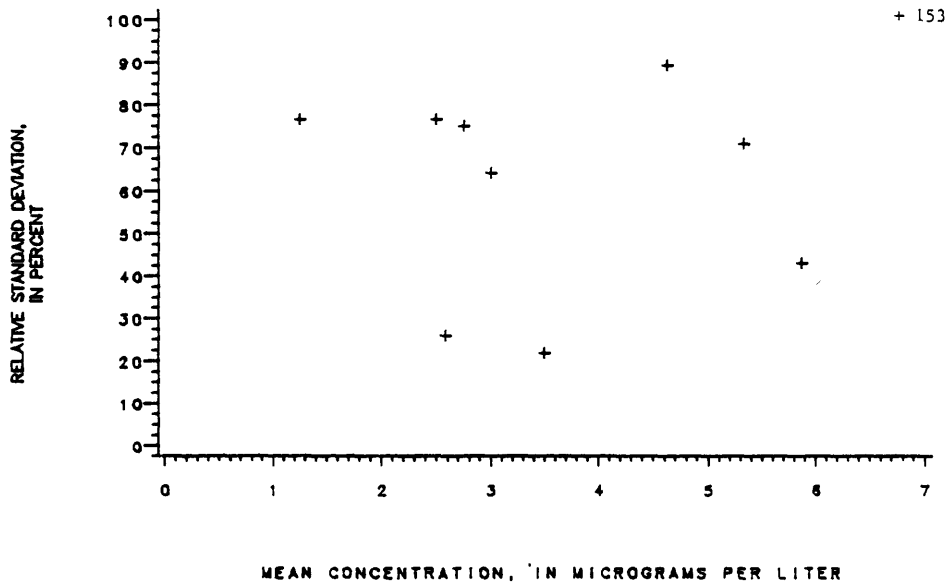


Figure 169.--Precision data for silver at the Atlanta Laboratory.

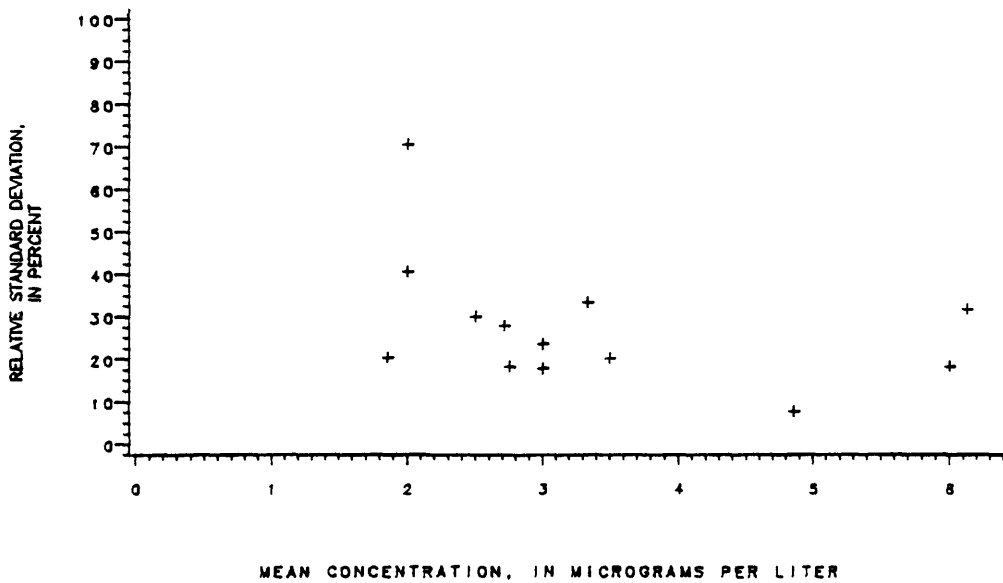


Figure 170.--Precision data for silver at the Denver Laboratory.

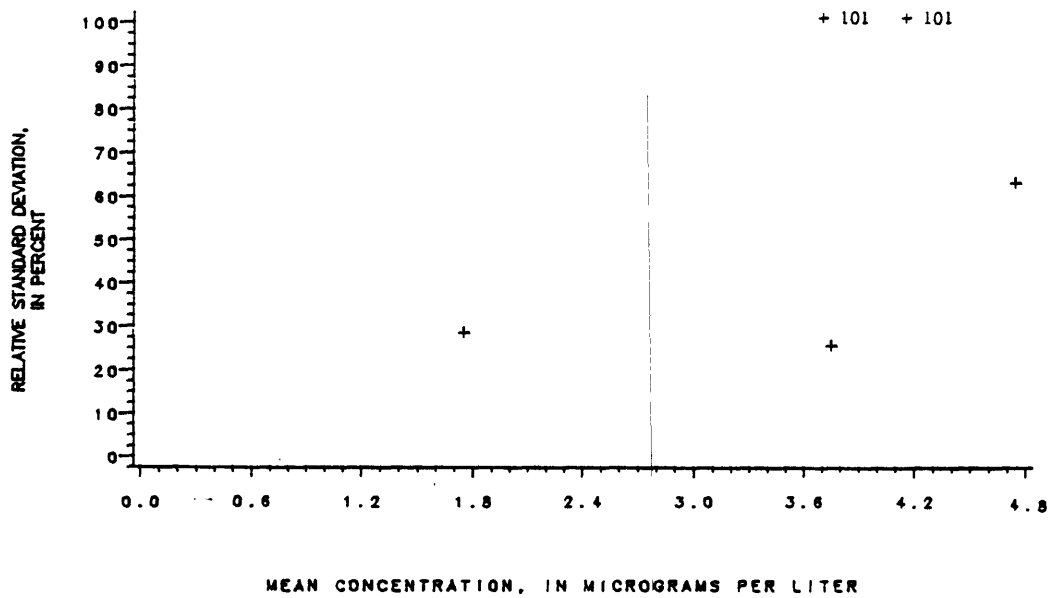


Figure 171.—Precision data for silver, total recoverable at the Atlanta Laboratory.

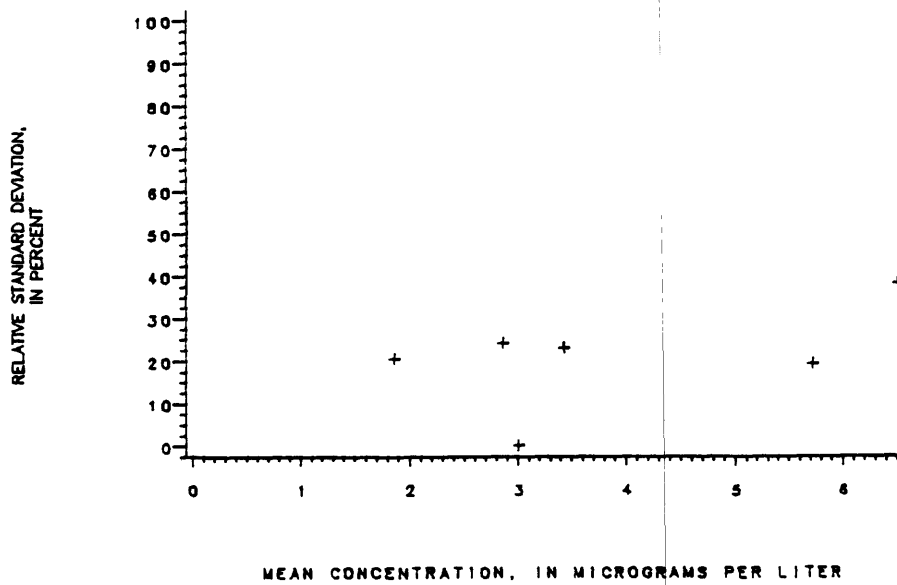


Figure 172.—Precision data for silver, total recoverable at the Denver Laboratory.

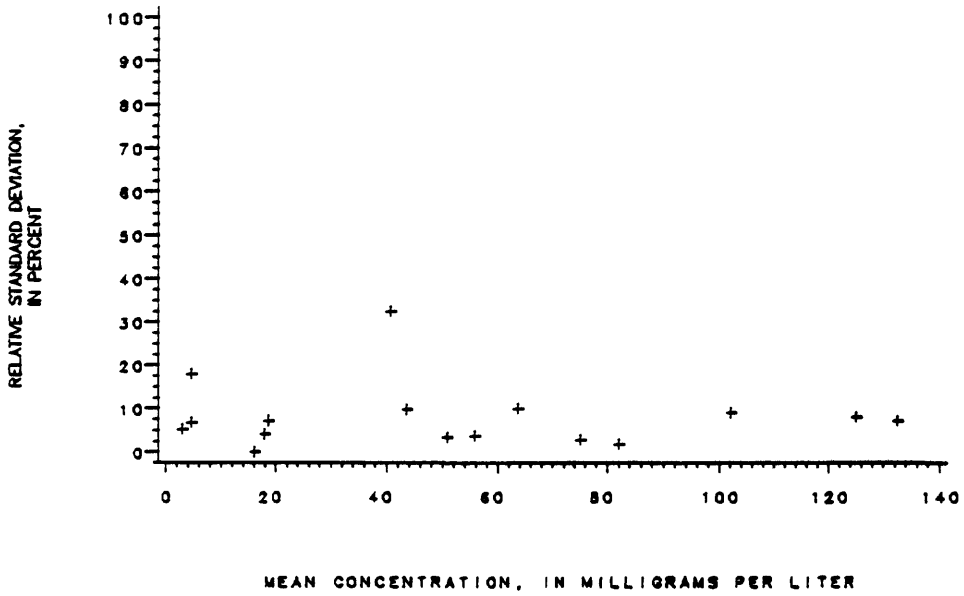


Figure 173.—Precision data for sodium at the Atlanta Laboratory.

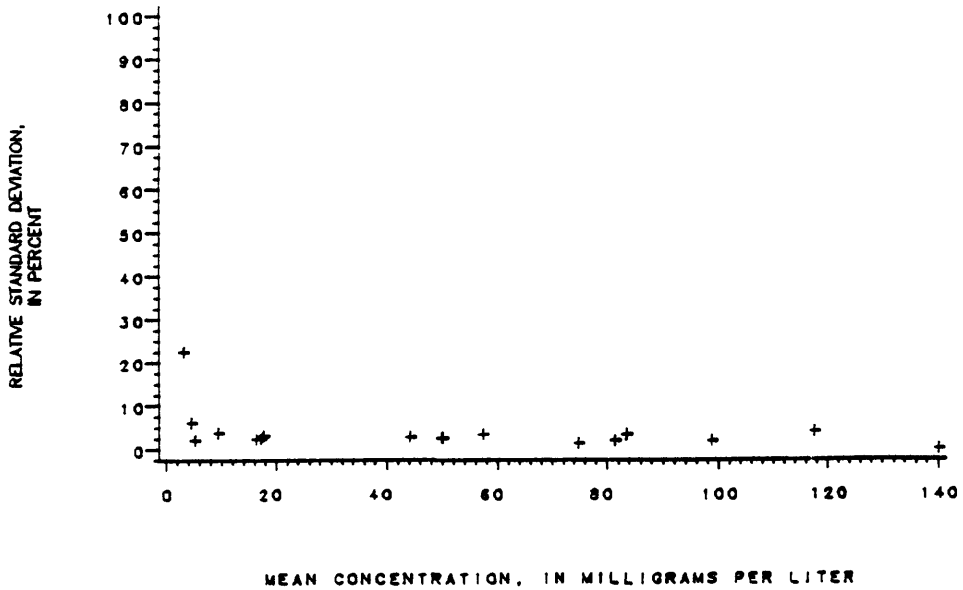


Figure 174.—Precision data for sodium at the Denver Laboratory.

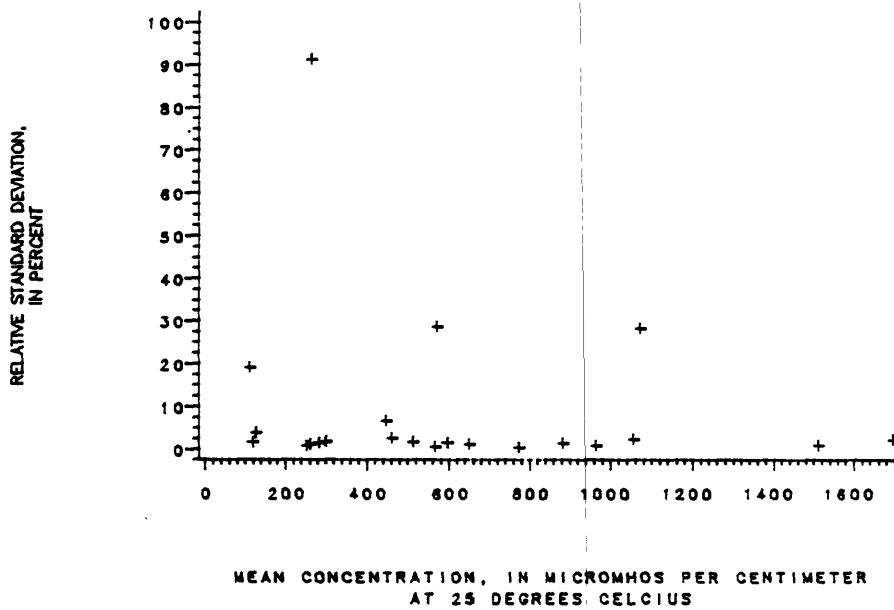


Figure 175.--Precision data for specific conductance at the Atlanta Laboratory.

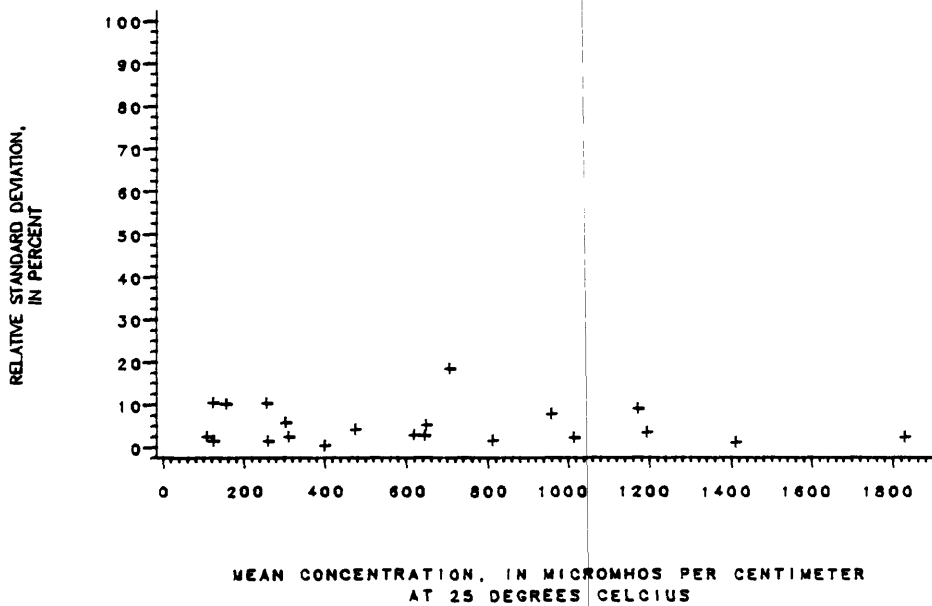


Figure 176.--Precision data for specific conductance at the Denver Laboratory.

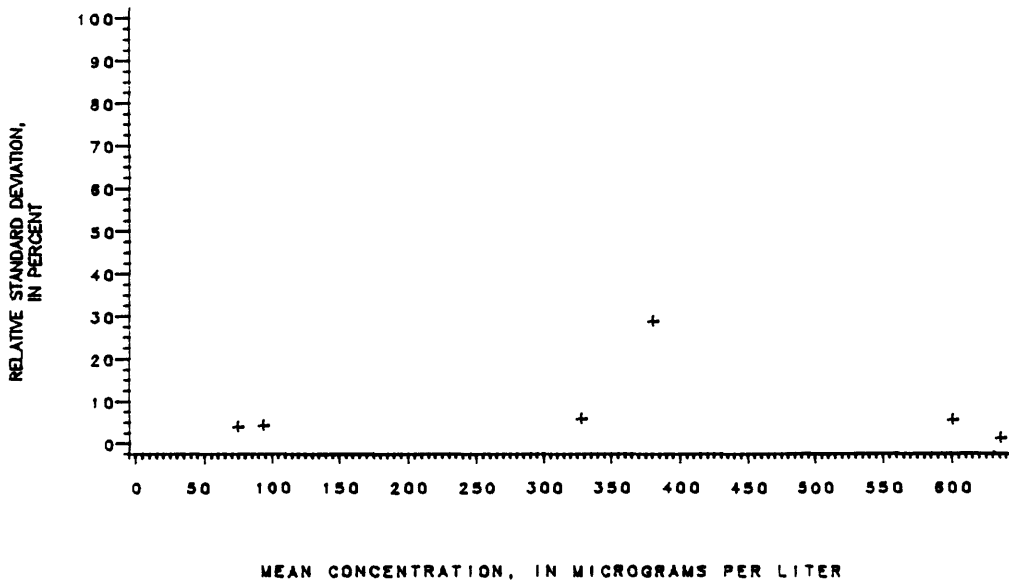


Figure 177.--Precision data for strontium at the Atlanta Laboratory.

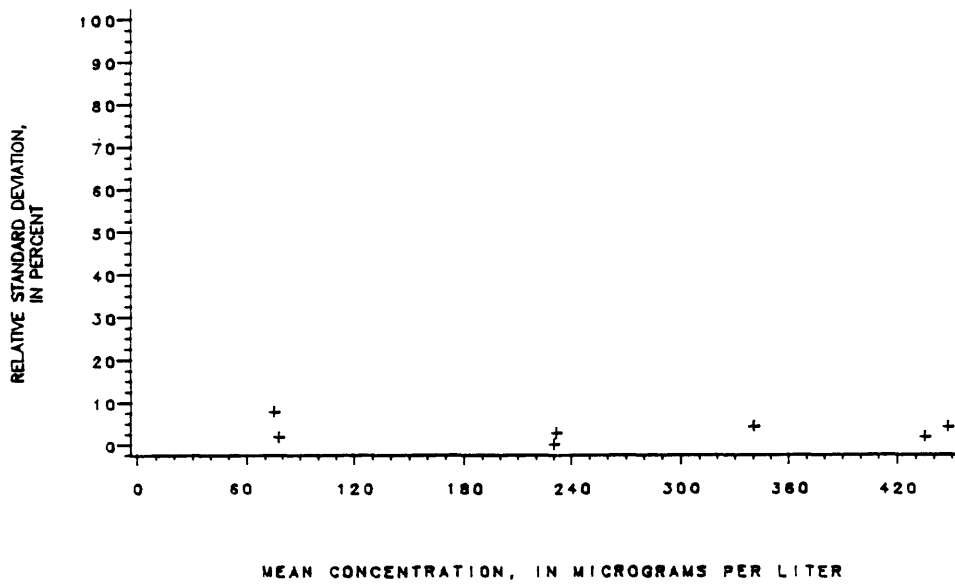


Figure 178.--Precision data for strontium at the Denver Laboratory.

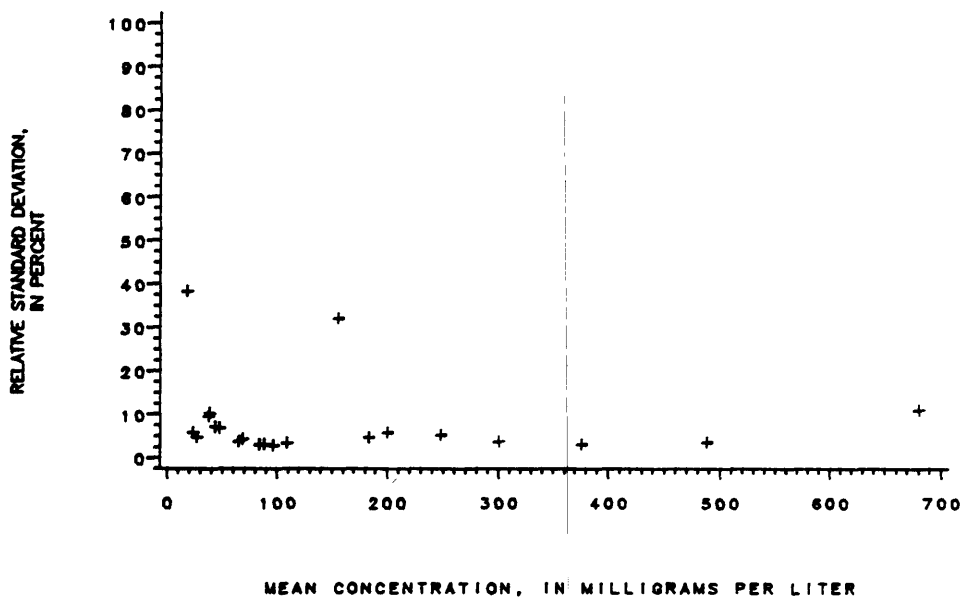


Figure 179.—Precision data for sulfate at the Atlanta Laboratory.

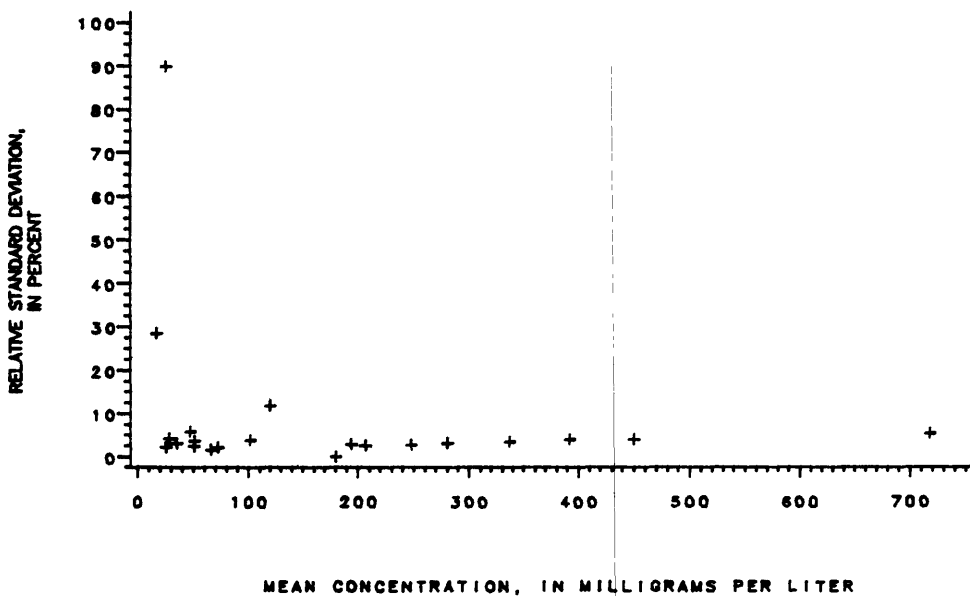


Figure 180.—Precision data for sulfate at the Denver Laboratory.

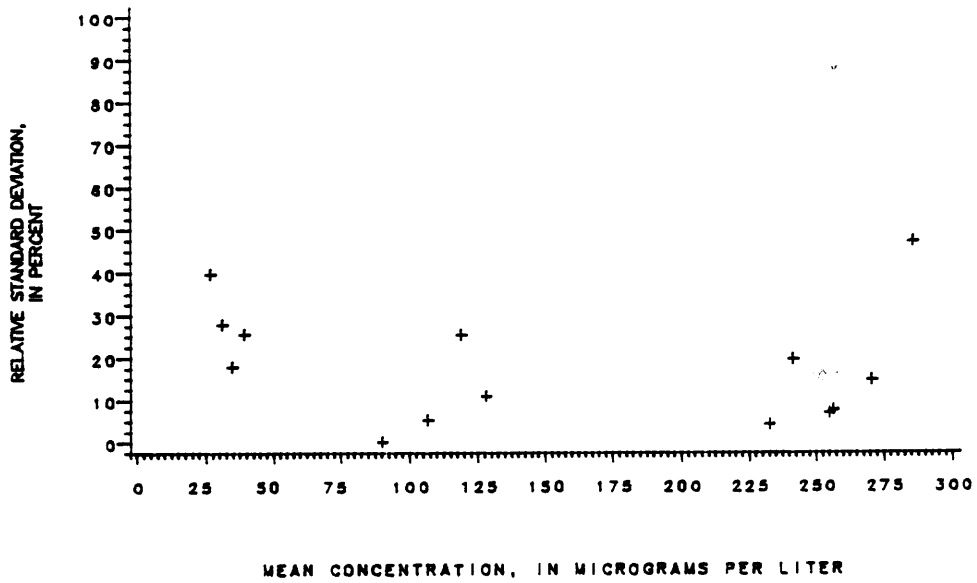


Figure 181.--Precision data for zinc at the Atlanta Laboratory.

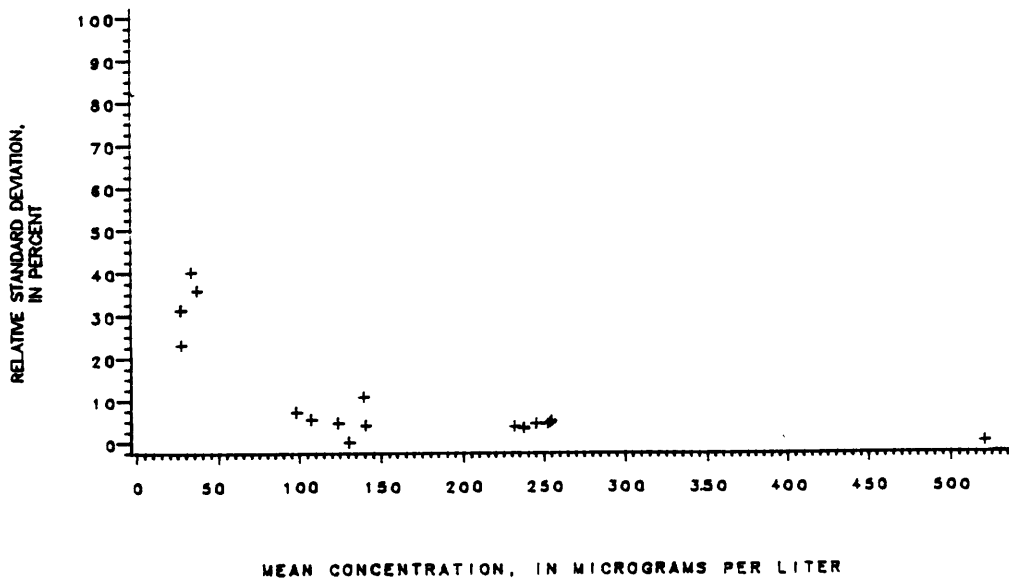


Figure 182.--Precision data for zinc at the Denver Laboratory.

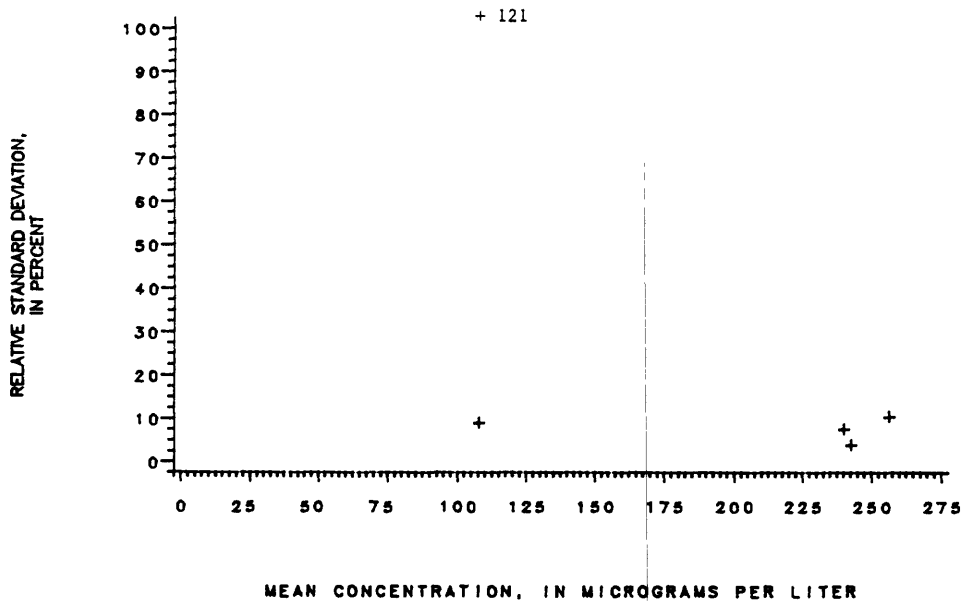


Figure 183.--Precision data for zinc, total recoverable at the Atlanta Laboratory.

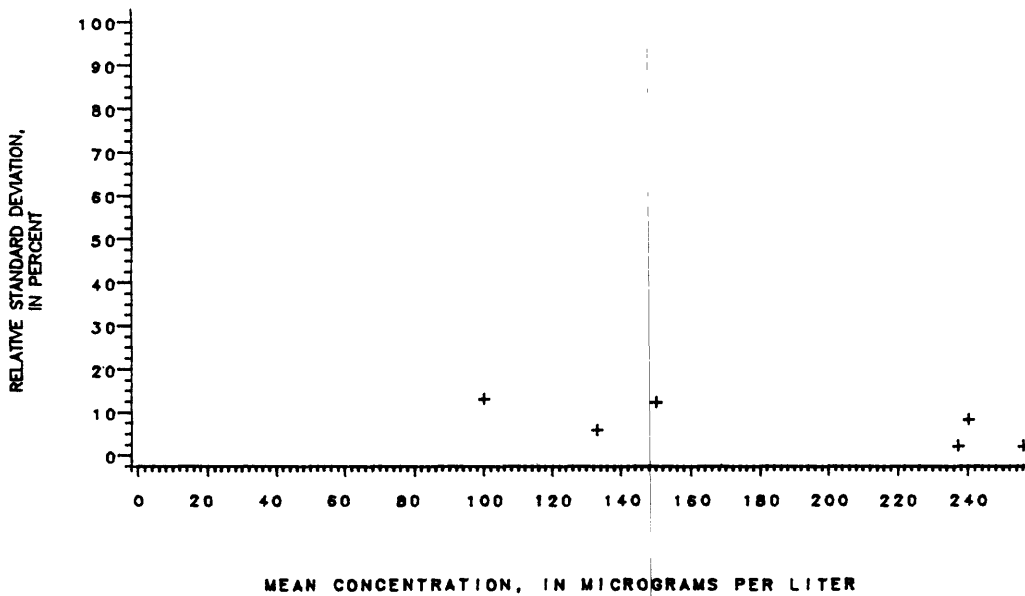


Figure 184.--Precision data for zinc, total recoverable at the Denver Laboratory.