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QUALITY ASSURANCE REPORT

Atlanta Central Laboratory

Denver Central Laboratory

By

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QUALITY ASSURANCE REPORT

INTRODUCTION

Standard reference materials taken from the U.S. Geological Survey Standard Reference Water Sample (SRWS) Program (Schroder and others, 1980; Skougstad and Fishman, 1975), EPA ampuls, and other non-Central Laboratory sources are prepared in the Ocala Water Quality Service Unit(QWSU), Ocala, Florida, disguised as routine samples, and distributed to Water Resources Division (WRD) offices. The reference materials are then submitted to the Central Laboratories by the WRD offices on a specified schedule for the determination of major constituents, nutrients, and trace metals. The analytical schedules are chosen to reflect the frequency of analyses for the various constituents. The program is designed so that at least one reference sample is sent to each laboratory each day for constituents that are determined daily. All constituents in reference materials used to date have been in the dissolved phase; data designated as "total" or "total recoverable" are from samples which have undergone a digestion process, rather than from unfiltered or "whole-water" samples.

Once the analysis has passed through the laboratories' quality control and quality assurance routines, the data are permanently stored in WATSTORE. These data reflect the typical quality of results produced by each laboratory and received by each district.

For the period of this report, analyses were limited to major constituents including limited nutrient analyses, specific conductance, and trace elements. A full complement of nutrient analyses was begun in January 1982. Submission of organic constituents including pesticides and priority pollutants began in October 1981 on a limited basis. This will be increased in the near future to a frequency of approximately one sample per week, dependent upon the latest production figures. Other types including splits, spikes, and sediment samples will be added to the program beginning in fiscal year 1983.

The purpose of this program is not to supply quality control data to the subject laboratories; that is, it is in no way intended to replace the internal quality assurance programs administered by the laboratory chiefs, but rather to document the quality of data that is generated by the laboratories.

Future plans include the addition of a computer routine whereby the laboratory chiefs may retrieve the most recently generated data on a weekly basis. This will then supplement their existing programs and aid in detecting problems at an earlier time.

Data are summarized in the appendices. All data were evaluated using programs developed from standard SAS (Helwig and Council, 1979) procedures.

Tables A1.1. and A1.2. summarize the satisfactory results for the Atlanta and Denver Central Laboratories, respectively. Expectation of a normal distribution implies that about 68 percent of the results would be within 1 standard deviation of the most probable value (MPV) and about 95 percent would be within 2 standard deviations, the acceptable level.

Tables A2.1. through A2.4. tabulate each individual value which exceeded the two most probable standard deviation (MPSD) criteria.

Table B1.1. tabulates data on four volatile organic samples that were split between the Atlanta and Denver Laboratories.

Table B1.2. tabulates data for chlorophyll a analyses of samples that were split between the Atlanta and Denver Laboratories and the Potomac Estuary project in Reston, Va.

Figures A1.1.1. through A1.2.45. are scatterplots of each constituent with time and give a pictorial view of the accuracy, bias, and possible trends of the data for each laboratory.

Evaluation and statistical criteria

Many of the reference samples were prepared by mixing together two or more SRWSs. The most probable values (MPV) were calculated averaging the known MPVs. Although a theoretical specific conductance which is calculated by simply averaging the individual specific conductance values may not always be accurate, this approach was considered acceptable for these samples, because the MPVs were all less than 2,000 μmhos . There should be no significant difference between the calculated and actual values in this range (Erdmann, personal communication).

In conformance with WRD Memorandum 81.79, an individual value was considered acceptable if it was less than or equal to 2 standard deviations from the most probable value. This is a liberal criterion in most cases because the SRWS mean is based on interlaboratory, multimethod data. As soon as the data become available, we will use instead, the means and standard deviations for the specific methods in use. The MPSD for each constituent was calculated using a least squares regression analysis of the means and standard deviations obtained from the interlaboratory analyses of SRWS #24 through SRWS #76. For nitrite-nitrogen, the above equation produced MPSDs in strong disagreement with the standard deviations stated on the individual SRWS reports. A new regression analysis was done using only samples being used in this quality assurance program (#62 through #76) with greatly improved results.

Many of the trace metal analyses can be requested at more than one precision level depending on the analytical method used. For the period of this report, chromium and molybdenum were requested such that they were reported only to the nearest 10 µg/L. Since the computed MPSDs were based on SRWS reports which contained analyses which were reported to the nearest µg/L, it was impossible for many chromium and molybdenum analyses to fall within the acceptable criteria; therefore, a minimum MPSD was set at 7.5 µg/L. This allowed the analyses to be reported to ± 10 µg/L from the MPV and still be within the acceptable criteria.

In certain other situations, only one or two values were considered acceptable by the general statistical criteria employed (e.g. table A2.1., sodium, items 3, 5, 6). This left little room for analytical error and should be kept in mind when evaluating these data.

As more fully described in WRD Memorandum 81.79, a binomial distribution was used to evaluate the overall analytical precision for each constituent. The criteria used give less than a 1 percent chance that a determination will be considered "unacceptable" solely due to random errors.

Similarly, bias was determined by first examining the number of values which were greater than and less than the MPVs. A binomial probability distribution (at the 50 percent level) was then used such that there was less than a 1 percent chance that a determination would be considered biased solely due to random errors.

ANALYTICAL PRECISION

Determination of the following constituents showed statistically significant lack of precision:

Atlanta Central Laboratory - aluminum;¹ antimony; cadmium; chloride; cobalt; mercury;¹ ~~nitrite-nitrogen~~; silver; silver, total recoverable; sodium; zinc; zinc, total recoverable.

Denver Central Laboratory - chromium; cobalt, total recoverable; mercury;¹ phosphorus; silver; silver, total recoverable; specific conductance; zinc; zinc, total recoverable.

ANALYTICAL BIAS

Determination of the following constituents showed statistically significant bias:

Atlanta Central Laboratory

Positive bias: arsenic; chromium; dissolved solids; manganese; mercury; nickel.

Negative bias: barium; boron;¹ nitrate plus nitrite-nitrogen; sulfate.

¹See Discussion and Recommendations.

Denver Central Laboratory

Positive bias: arsenic; specific conductance; zinc.

Negative bias: aluminum; nickel; silver.

DISCUSSION AND RECOMMENDATIONS

During the period of this report, there appeared to have been some confusion in the participating districts as to the shipping schedules for these reference materials. As a result, many less samples were analyzed than anticipated. The Atlanta Central Laboratory analyzed 42 samples for major constituent and 27 samples for trace elements. Sixty samples of each type were expected to be analyzed. The Denver Central Laboratory analyzed 19 major constituents and 16 trace element samples; 72 samples of each type were expected to be analyzed. Since not every constituent was determined in every sample, a few were determined too infrequently to make definitive statements concerning them: Bias could not be determined for any "total recoverable" parameters at either laboratory as well as for nitrite-nitrogen (three determinations) at Atlanta; and boron, beryllium, lithium, strontium (five determinations each); nitrite-nitrogen (zero determinations); antimony and iron (six determinations each) at Denver. At these levels, it is also difficult to determine the precision of the laboratories' analyses since the blind samples do not constitute a statistically significant sample of the population. Thus, even though a constituent shows a significant lack of precision, e.g., nitrite-nitrogen at Atlanta, it may not be representative of the quality of the laboratories' work. The data, in general, appear to show better precision than during the previous reporting period, although this may also be a result of the smaller sample size.

New instructions were prepared and distributed to participating districts, beginning in January 1982. Hopefully, these will eliminate the confusion and the problem.

One specific conductance value was reported an order of magnitude too low by the Atlanta Laboratory (table A2.1, specific conductance, item 1). This value caused a computer-generated flag and should have been noticed in the laboratory quality-control review.

Rejected mercury values for both laboratories were generally high. However, as in the previous report, these values all came from samples containing some portion of SRWS #73 with only two exceptions. The exceptions appear to be random errors. Of all samples that were composed of a portion of SRWS #73, one-fourth were within acceptable limits, but these were all higher than the associated MPVs as well. An investigation into this problem is being undertaken by the SRWS project chief.

Silver continues to show a negative bias. The need for an investigation into proper preservation techniques continues for this element.

Zero values were reported for nitrate plus nitrite as nitrogen, and phosphorus in Denver. Atlanta reported chromium values as 10, while Denver reported zeros. Some action should be taken to assure that both laboratories are consistent and in compliance with the Quality of Water Branch policy of reporting "less than the lower limit of detection" rather than zeros.

The Atlanta Laboratory has reported consistent problems in achieving acceptable results for alkalinity on analysis of SRWS #68 in their own quality control efforts. The Denver Laboratory also has documented similar problems. Both laboratories consistently report values of approximately 210 mg/L. The MPV is 185 mg/L. All of the rejected alkalinity values reported in table A2.1. and A2.3. are from samples composed either entirely or in large part of SRWS #68. Four rejected values from the Atlanta Laboratory and one from the Denver Laboratory, cited in the previous report, were affected by this phenomenon. In neither reporting period did this problem affect whether or not the determination showed a significant lack of precision. The SRWS project is looking into this problem.

When specific analytical methods are grouped, the original data from the SRWS program for aluminum in SRWS #73 show a bimodal distribution with widely divergent mean values. All the rejected values for aluminum in Atlanta were from SRWS #73. These reported values were near the mean for the specific method used (Table A1.2).

All determinations for iron, total recoverable, were rejected. However, all reported values were approximately in the same range, all came from the same sample mixture and most showed excellent correlation with the determinations for dissolved iron made on the same samples. The Ocala QWSU has recently analyzed this mixture and reported much higher iron values than did the Central Laboratories. Other constituents from this mixture did not show similar discrepancies in the Central Laboratories or Ocala. Ocala reports that the coating on the automatic stirrers used to prepare this mixture had become chipped and the stirrers had begun to rust. Therefore, we can be certain in concluding that the excess iron shown in tables A2.2. and A.2.4. is from contamination and that the iron determinations in both laboratories would not show a significant lack of precision otherwise. The coating problem is being corrected.

In many cases where the analytical precision appears good but bias is statistically significant (for example, see dissolved solids for Atlanta, fig. A1.1.14.), the bias may have little practical significance. Such bias should serve as a warning to the laboratory that an analytical problem appears to have developed but may have only a minor effect, if any, on data interpretation.

Nine chlorophyll a samples were split between the two Central Laboratories and the Potomac Estuary project that collected the samples. One of these was split six ways to determine precision. All three laboratories showed excellent within-laboratory precision on this sample. Denver and Atlanta are using the same methodology; the project laboratory uses a different method. However, the Denver Laboratory's results were approximately one-third those of the other two laboratories. There was no significant difference in the results of the Atlanta Laboratory and those of the project laboratory (see table B1.2.).

The reasons for the low chlorophyll results from Denver are not completely understood at this time. Both Central Laboratories are using standards from the same source and with the same lot number. The two laboratories are exchanging standards at this time in hopes that this may lead to some understanding. Other reasons may include a very small sample size (30 mL submitted versus 1 L requested), loss during extraction, and sample degradation. If further information becomes available, it will be presented in future reports.

Four samples for volatile organic analyses were split between the Atlanta and Denver Central Laboratories by project personnel in the Connecticut District. Denver was unable to analyze the samples because of instrumentation and personnel problems, so they sent their samples to the Atlanta Laboratory. This, of course, negated the purpose for which the samples were split. Following analysis in Atlanta, the data for the Denver sample set were sent to Denver for reporting. For the samples sent directly to Atlanta, no volatile organic substances were detected. The samples sent to Atlanta through Denver had positive values for benzene, methylene chloride, and trichloroethylene (table B1.1.) . Benzene and methylene chloride are commonly used in the laboratory. The positive values for these compounds may have been caused by contamination; most are not significantly different than zero. One trichloroethylene value was considerably higher than the detection limit and was considered "real" by project personnel since the sample was taken in a highly industrialized area, and the compound is common there. The two laboratories did not report non-detectable quantities in the same manner: Atlanta reported all such values as "ND," Denver reported all such values as "<1." As more fully defined in the Quality of Water Branch Technical Memorandum No. 81.22, there are specific differences in the meaning of these two designations. Among them are whether or not the detection level of the analytical technique is known. The two laboratories should take action to assure that consistency exists within the Central Laboratories System in this area.

REFERENCES

- Helwig, J. T., and Council, K. A., eds., 1979, SAS user's guide: Cary, North Carolina, SAS Institute, 494 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, AWWA Water Quality Technology Conference, December, 1974, American Water Works Association, p. XIX-1 - XIX-6.

APPENDIX A

Table A1.1.--Summary of satisfactory results for major constituents and specific conductance

[All constituents were in the dissolved phase]

Determination	Atlanta			Denver		
	No. of samples	Percent ≤ 1 standard deviation	Percent ≤ 2 standard deviations	No. of samples	Percent ≤ 1 standard deviation	Percent ≤ 2 standard deviations
Alkalinity	42	57.1	92.9	19	52.6	94.7
6 Boron	8	100	100	5	100	100
Calcium	35	88.6	97.1	16	100	100
Chloride	42	73.8	85.7	19	52.6	84.2
Dissolved solids	35	68.6	88.6	16	87.5	100
Fluoride	42	92.9	97.6	19	84.2	89.5
Magnesium	35	77.1	91.4	16	93.8	100
Nitrate plus nitrite-nitrogen	38	89.5	94.7	19	57.9	84.2
Nitrite-nitrogen	3	66.7	66.7	0	-	-
Phosphorus	33	81.8	90.9	16	75.0	81.3

Table A1.1.--Summary of satisfactory results for major constituents and specific conductance—Continued

Determination	Atlanta			Denver		
	No. of samples	Percent ≤ 1 standard deviation	Percent ≤ 2 standard deviations	No. of samples	Percent ≤ 1 standard deviation	Percent ≤ 2 standard deviations
Potassium	35	65.7	88.6	16	93.8	100
Silica	42	85.7	97.6	19	89.5	89.5
Sodium	35	51.4	74.3	15	68.8	100
Specific conductance	42	69.0	95.2	19	31.6	57.9
Sulfate	42	57.1	90.5	19	68.4	94.7

Table A1.2.--Summary of satisfactory results for trace metals

[All constituents were in the dissolved phase; data designated as "total recoverable" are from samples which have undergone a preliminary digestion]

Determination	Atlanta			Denver		
	No. of samples	Percent ≤ 1 standard deviation	Percent ≤ 2 standard deviations	No. of samples	Percent ≤ 1 standard deviation	Percent ≤ 2 standard deviations
Aluminum	21	61.9	81.0	12	58.3	83.3
Antimony	11	36.4	36.4	6	50.0	100
Arsenic	33	72.7	90.9	22	95.5	100
Barium	17	70.6	100	10	70	100
Barium, total recoverable	6	66.7	100	5	60	100
Beryllium	11	81.8	100	5	100	100
Cadmium	27	55.6	66.7	16	75	93.8
Cadmium, total recoverable	6	66.7	83.3	5	60	100
Chromium	27	81.5	100	17	82.4	82.4
Chromium, total recoverable	6	16.7	100	5	60	100

Table A1.2.--Summary of satisfactory results for trace metals—Continued

Determination	Atlanta			Denver		
	No. of samples	Percent ≤ 1 standard deviation	Percent ≤ 2 standard deviations	No. of samples	Percent ≤ 1 standard deviation	Percent ≤ 2 standard deviations
Cobalt	17	76.4	82.4	10	60	90
Cobalt, total recoverable	6	50	83.3	5	0	60
Copper	27	74.1	96.3	16	93.8	100
Copper, total recoverable	6	100	100	5	80	100
Iron	20	70	80	7	57.1	57.1
Iron, total recoverable	4	0	0	2	0	0
Lead	27	63.0	96.3	16	87.5	100
Lead, total recoverable	6	83.3	100	5	60	100
Lithium	11	27.3	81.8	5	60.0	80.0
Manganese	27	77.8	96.3	16	93.8	100

Table A1.2.--Summary of satisfactory results for trace metals--Continued

Determination	Atlanta			Denver		
	No. of samples	Percent ≤ 1 standard deviation	Percent ≤ 2 standard deviations	No. of samples	Percent ≤ 1 standard deviation	Percent ≤ 2 standard deviations
Manganese, total recoverable	6	83.3	100	5	100	100
Mercury	33	48.5	72.7	22	9.1	59.1
Molybdenum	21	90.5	100	11	100	100
Nickel	26	57.7	100	17	64.7	100
Nickel, total recoverable	6	66.7	100	5	60	100
Selenium	23	87.0	95.7	11	100	100
Silver	17	29.4	64.7	11	36.4	72.7
Silver, total recoverable	6	33.3	66.7	5	60	60
Strontium	11	100	100	5	100	100
Zinc	27	63	81.5	16	37.5	62.5
Zinc, total recoverable	6	0	33.3	5	40	40

Table A2.1.--Tabulation of data over 2 standard deviations from the most probable value for the Atlanta Laboratory: major constituents and specific conductance

[All constituents were in the dissolved phase]

Determination/ Percent >2 standard deviations/ Total analyses	Concentration range of reference samples (mg/L)	Reported value (mg/L)	Most probable value (mg/L)	Most probable standard deviation (mg/L)	Number of standard deviations
Alkalinity/ 7.1/ 42	18.2 - 262	1.0 210 210	185 185 185	9.17 9.17 9.17	-20.03 2.77 2.77
Calcium/ 2.9/ 35	7.48 - 156	42	49.9	3.80	- 2.08
Chloride/ 14.3/ 42	1.4 - 138	140 36 17 17 28 150	124 31.2 14.7 14.7 138 138	4.84 1.69 1.13 1.13 5.32 5.32	3.30 2.84 2.04 2.04 -20.68 2.26
Dissolved/ solids/ 11.4/ 35	70.6 - 1,433	1,580 163 907 1,200	1,433 336 847 1,121	45.9 15.6 29.7 37.3	3.20 -11.08 2.02 2.12
Fluoride/ 2.4/ 42	0.36 - 1.22	0.2	1.12	0.11	- 8.47
Magnesium/ 8.6/ 35	1.95 - 93.4	5.2 9.0 54	6.6 10.7 59.5	0.55 0.70 2.51	- 2.51 - 2.42 - 2.19
Nitrate plus nitrite- nitrogen/ 5.3/ 38	1.14 - 4.55	0.35 0.13	2.16 2.16	0.36 0.36	- 5.07 - 5.69
Nitrite- nitrogen/ 33.3/ 3	.008 - .024	0.05	0.024	0.01	3.39

Table A2.1.--Tabulation of data over 2 standard deviations from the most probable value for the Atlanta Laboratory: major constituents and specific conductance—Continued

Determination/ Percent >2 standard deviations/ Total analyses	Concentration range of reference samples (mg/L)	Reported value (mg/L)	Most probable value (mg/L)	Most probable standard deviation (mg/L)	Number of standard deviations
Phosphorus/ 9.1/ 33	.265 - 2.17	0.12 2.10 3.40	0.505 1.47 1.47	0.05 0.12 0.12	- 7.52 5.38 16.48
Potassium/ 11.4/ 35	3.2 - 9.35	4.4 2.2 2.3 4.8	3.5 3.2 3.2 6.0	0.34 0.30 0.30 0.60	2.72 - 3.28 - 2.95 - 2.04
Silica/ 2.4/ 42	5.12 - 12.7	10	12.7	1.00	- 2.69
Sodium/ 25.7/ 35	2.77 - 133	48 39 5.6 140 7.7 7.3 120 120 110	43.4 43.4 4.3 129 9.1 9.1 133 97.8 97.8	1.76 1.76 0.42 4.69 0.58 0.58 4.82 3.62 3.62	2.62 - 2.50 3.14 2.35 - 2.39 - 3.08 - 2.70 6.14 3.37
Specific conductance ¹ / 4.8/ 42	103.4 - 1,735	116 606	1,167 569	39.0 18.3	-26.97 2.02
Sulfate/ 9.5/ 42	14.3 - 724.5	230 570 36 33	279 725 42.4 42.4	15.2 38.2 3.00 3.00	- 3.22 - 4.04 - 2.13 - 3.13

¹Units are $\mu\text{mhos}/\text{cm}^2$ at 25°C.

Table A2.2.--Tabulation of data over 2 standard deviations from the most probable value for the Atlanta Laboratory: trace metals

[All constituents were in the dissolved phase; data designated as "total recoverable" are from samples which have undergone a preliminary digestion]

Determination/ Percent >2 standard deviations/ Total analyses	Concentration range of reference samples (µg/L)	Reported value (µg/L)	Most probable value (µg/L)	Most probable standard deviation (µg/L)	Number of standard deviations
Aluminum ¹ / 19/ 21	18 - 633	100 90 110 110	235 235 235 235	58.4 58.4 58.4 58.4	- 2.31 - 2.48 - 2.14 - 2.14
Antimony/ 63.6/ 11	2.0 - 10	6 4 5 5 6 7 8	8.0 8.0 8.0 8.0 8.0 2.0 10.0	0.8 0.8 0.8 0.8 0.8 0.9 0.7	- 2.57 - 5.15 - 3.86 - 3.86 - 2.57 5.63 - 2.70
Arsenic/ 9.09/ 33	2.5 - 34.2	42 56 6	26.3 34.2 34.2	6.4 7.4 7.4	2.46 2.95 - 3.82
Cadmium/ 33.3/ 27	0.8 - 15.9	1 2 2 3 1 1 6 14 13	5.5 0.8 0.8 0.8 15.9 15.9 3.8 5.2 5.2	1.4 0.5 0.5 0.5 3.3 3.3 1.1 1.3 1.3	- 3.21 2.31 2.31 4.23 - 4.45 - 4.45 2.03 6.55 5.80
Cadmium, total recoverable/ 16.7/ 6	5.5 - 12.9	1	5.5	1.4	- 3.21
Cobalt/ 17.6/ 17	3.4 - 14.3	3 4 9	13.8 14.3 14.3	2.5 2.6 2.6	- 4.25 - 3.96 - 2.04

Table A2.2.--Tabulation of data over 2 standard deviations from the most probable value for the Atlanta Laboratory:
trace metals—Continued

Determination/ Percent > 2 standard deviations/ Total analyses	Concentration range of reference samples (µg/L)	Reported value (µg/L)	Most probable value (µg/L)	Most probable standard deviation (µg/L)	Number of standard deviations
Cobalt, total recoverable/ 16.7/ 6	13.8 - 14.3	3	13.8	2.5	- 4.25
Copper/ 3.7/ 27	18.8 - 482	3	51.7	6.9	- 7.03
Iron ¹ / 20/ 20	134 - 760	310 320 340 290	188 188 188 188	19.9 19.9 19.9 19.9	6.13 6.63 7.64 5.12
Iron, total recoverable ¹ / 100/ 4	188	380 390 740 490	188 188 188 188	19.9 19.9 19.9 19.9	9.65 10.15 27.73 15.17
Lead/ 3.7/ 27	5.1 - 38.4	37	10.7	6.3	4.19
Lithium/ 18.2/ 11	55 - 627	540 42	627 55	41.5 4.8	- 2.10 - 2.73
Manganese/ 3.7/ 27	35 - 571	380	341	19.5	2.00
Mercury ¹ / 27.3/ 33	0.34 - 5.4	5.4 5.8 1.1 2.9 5.2 4.8 7.0 5.8 5.8	2.67 2.67 2.01 2.01 3.45 3.45 3.45 2.67 2.67	0.52 0.52 0.41 0.41 0.65 0.65 0.65 0.52 0.52	5.23 6.00 - 2.20 2.15 2.69 2.08 5.46 6.00 6.00

Table A2.2.--Tabulation of data over 2 standard deviations from the most probable value for the Atlanta Laboratory:
trace metals—Continued

Determination/ Percent >2 standard deviations/ Total analyses	Concentration range of reference samples (µg/L)	Reported value (µg/L)	Most probable value (µg/L)	Most probable standard deviation (µg/L)	Number of standard deviations
Selenium/ 4.4/ 23	4.6 - 17.2	8	4.6	1.4	2.43
Silver/ 35.3/ 17	2.7 - 13.3	4	10.4	3.0	- 2.15
		1	10.4	3.0	- 3.16
		1	10.4	3.0	- 3.16
		0	11.0	3.1	- 3.52
		1	11.0	3.1	- 3.20
		3	13.3	3.7	- 2.76
Silver, total recoverable/ 33.3/ 6	2.7 - 10.4	1	10.4	3.0	- 3.16
		1	10.4	3.0	- 3.16
Zinc/ 18.5/ 27	17 - 489	240	195	16.0	2.81
		230	195	16.0	2.18
		49	28.0	5.4	3.86
		34	22.5	5.1	2.26
		50	22.5	5.1	5.40
Zinc, total recoverable/ 66.7/ 6	89 - 195	230	195	16	2.18
		250	195	16	3.43
		120	89	9.3	3.33
		110	89	9.3	2.26

¹See Discussion and Recommendations.

Table A2.3.--Tabulation of data over 2 standard deviations from the most probable value for the Denver Laboratory: major constituents and specific conductance

[All constituents were in the dissolved phase]

Determination/ Percent >2 standard deviations/ Total analyses	Concentration range of reference samples (mg/L)	Reported value (mg/L)	Most probable value (mg/L)	Most probable standard deviation (mg/L)	Number of standard deviations
Alkalinity/ 5.3/ 19	18.2 - 262	170	146	8.22	2.87
Chloride/ 15.8/ 19	1.4 - 63.3	36 12 8.7	27.9 14.7 31.2	1.57 1.13 1.69	5.14 - 2.40 -13.34
Fluoride/ 10.5/ 19	0.36 - 1.22	0.5 0.2	0.36 0.79	0.05 0.08	2.88 - 7.15
Nitrate plus nitrite/ 15.8/ 19	1.14 - 4.55	0.45 0.00 0.00	1.14 1.14 1.14	0.23 0.23 0.23	- 2.99 - 4.94 - 4.94
Phosphorus/ 25/ 16	.298 - 2.17	0.73 0.00 0.00 1.80	0.30 0.40 0.40 2.17	0.04 0.04 0.04 0.16	11.66 - 9.07 - 9.07 - 2.24
Silica/ 10.5/ 19	5.12 - 10.8	4.6 16	6.6 5.9	0.85 0.83	- 2.38 12.26
Specific conductance ¹ / 42.1/ 19	103.4 - 1,735	109 668 688 126 124 945 1,060 1,890	103.4 569 569 118.5 118.5 878 878 1,735	2.17 18.3 18.3 2.69 2.69 29.0 29.0 58.6	2.58 5.42 6.51 2.78 2.04 2.31 6.28 2.64
Sulfate/ 5.3/ 19	14.3 - 724.5	5	14.3	1.55	- 5.99

¹Units are $\mu\text{mhos}/\text{cm}^2$ at 25°C.

Table A2.4.--Tabulation of data over 2 standard deviations from the most probable value for the Denver Laboratory: trace metals

[All constituents were in the dissolved phase; data designated as "total recoverable" are from samples which have undergone a preliminary digestion]

Determination/ Percent > 2 standard deviations/ Total analyses	Concentration range of reference samples (µg/L)	Reported value (µg/L)	Most probable value (µg/L)	Most probable standard deviation (µg/L)	Number of standard deviations
Aluminum ¹ / 16.7/ 12	18 - 633	230 230	405 405	75.5 75.5	- 2.32 - 2.32
Cadmium/ 6.2/ 16	0.8 - 12.9	2	6.7	1.6	- 2.89
Chromium/ 17.6/ 17	5.0 - 27.7	0 0 0	19.2 19.2 19.2	7.5 7.5 7.5	- 2.56 - 2.56 - 2.56
Cobalt/ 10/ 10	3.4 - 14.3	9	14.3	2.6	- 2.04
Cobalt, total recoverable/ 40/ 5	13.8 - 14.3	7 9	14.3 14.3	2.6 2.6	- 2.81 - 2.04
Iron ¹ / 42.9/ 7	158 - 760	290 310 300	158 188 188	17.6 19.9 19.9	7.48 6.13 5.63
Iron, total recoverable ¹ / 100/ 2	188	260 450	188 188	19.9 19.9	3.62 13.16
Lithium/ 20/ 5	105 - 627	3	105	8.0	-12.8

Table A2.4.--Tabulation of data over 2 standard deviations from the most probable value for the Denver Laboratory: trace metals--Continued

Determination/ Percent >2 standard deviations/ Total analyses	Concentration range of reference samples (µg/L)	Reported value (µg/L)	Most probable value (µg/L)	Most probable standard deviation (µg/L)	Number of standard deviations
Mercury ¹ / 40.9/ 22	0.6 - 5.4	1.5 4.0 5.0 4.4 3.4 4.0 4.6 5.2 0.3	0.68 2.67 2.67 2.67 5.40 2.67 2.67 2.67 2.01	0.19 0.52 0.52 0.52 0.97 0.52 0.52 0.52 0.41	4.21 2.55 4.46 3.31 - 2.06 2.55 3.70 4.85 4.14
Silver/ 27.3/ 11	2.7 - 13.3	3 1 4	13.3 13.3 10.4	3.7 3.7 3.0	- 2.76 - 3.30 - 2.15
Silver, total recoverable/ 40/ 5	2.7 - 10.4	4 4	10.4 10.4	3.0 3.0	- 2.15 - 2.15
Zinc/ 37.5/ 16	17 - 489	56 240 240 250 33 32	28 195 195 195 19.8 19.8	5.4 16 16 16 4.9 4.9	5.15 2.81 2.81 3.43 2.68 2.48
Zinc, total recoverable/ 60/ 5	89 - 195	240 230 230	195 195 195	16.0 16.0 16.0	2.81 2.18 2.18

¹See Discussion and Recommendations.

LAB=ATLANTA

23

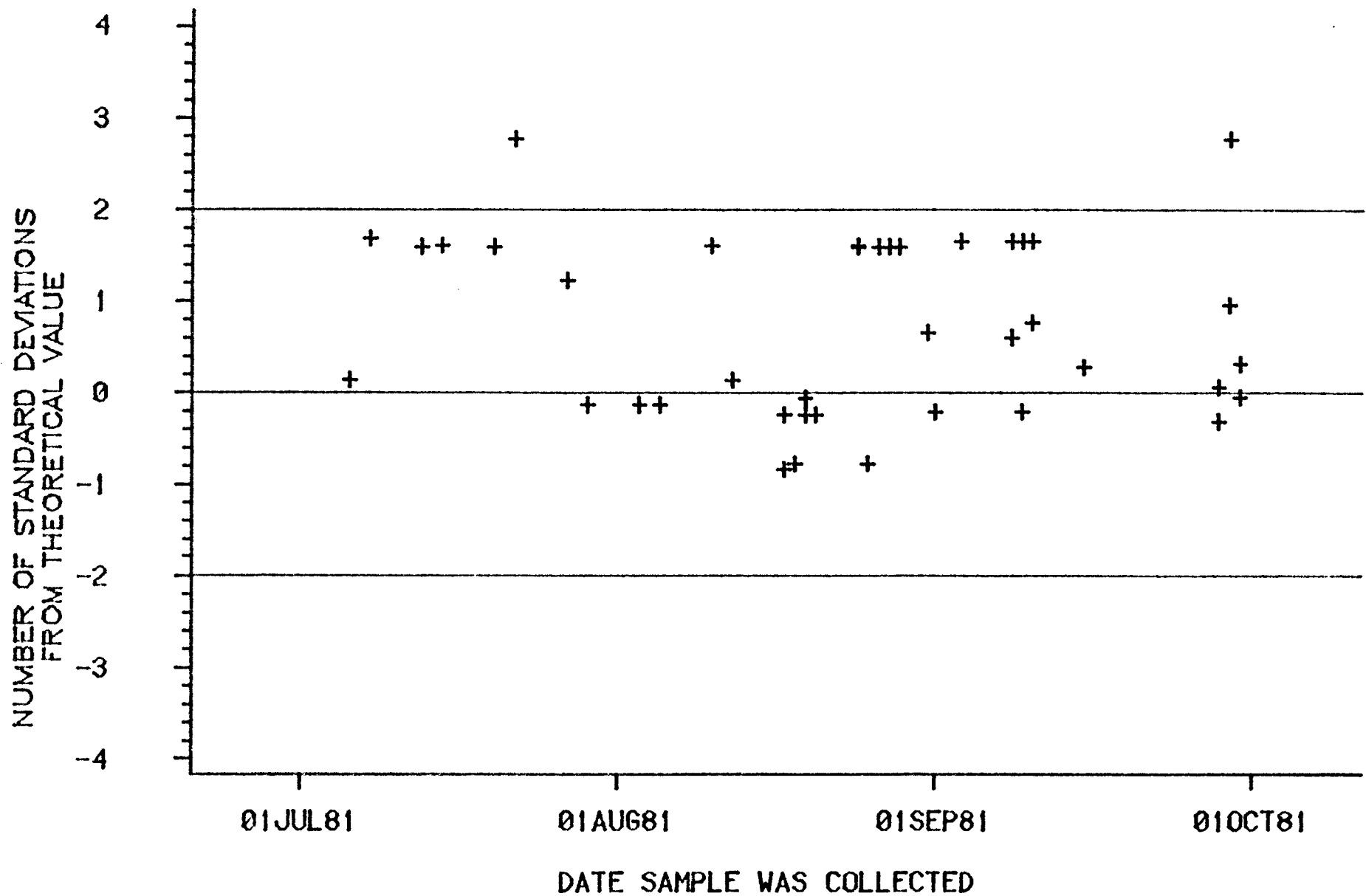


Figure A1.1.1.--Alkalinity data for the Atlanta Laboratory.
(One observation was out of range.)

LAB=ATLANTA

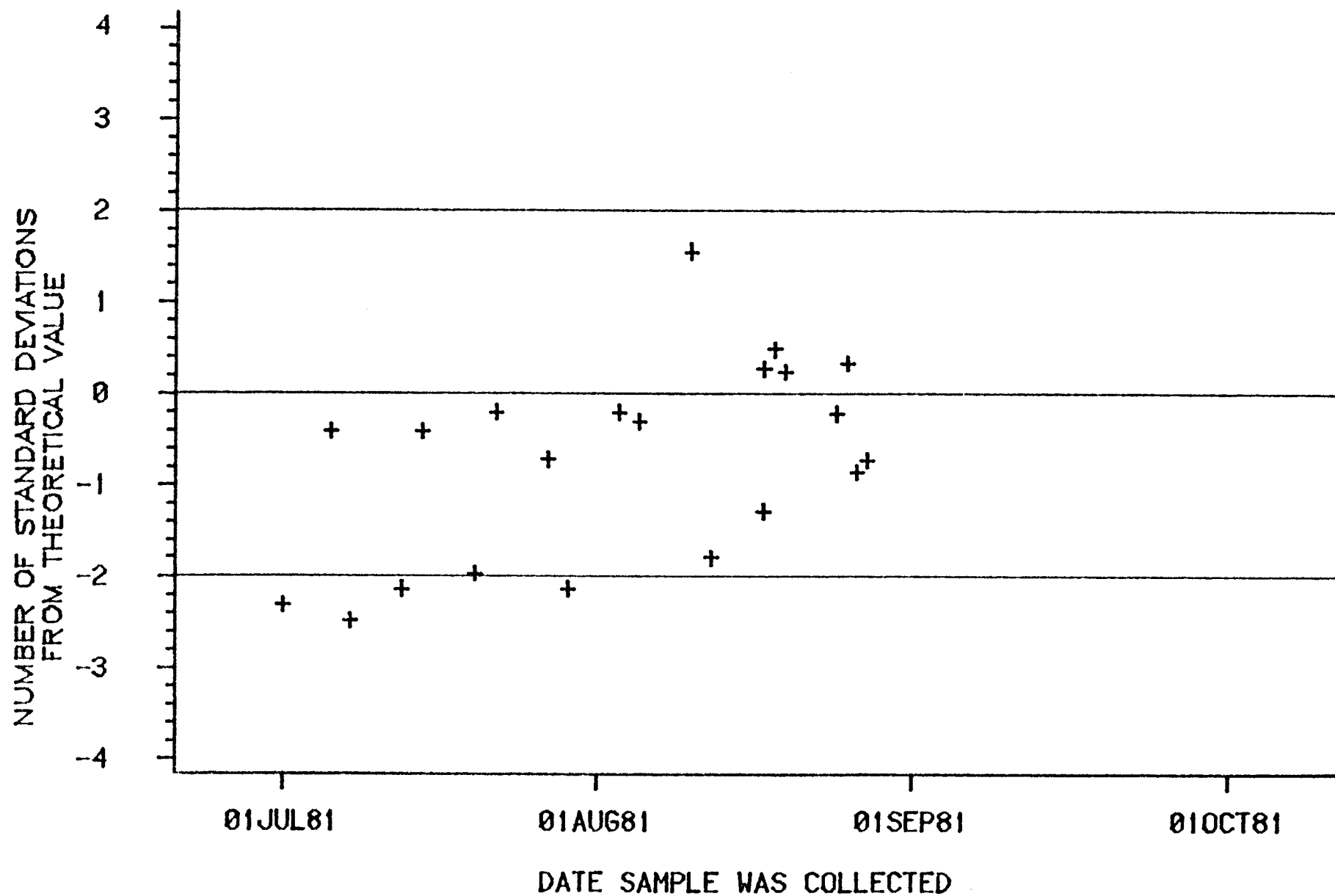


Figure A1.1.2.--Aluminum data for the Atlanta Laboratory.

LAB=ATLANTA

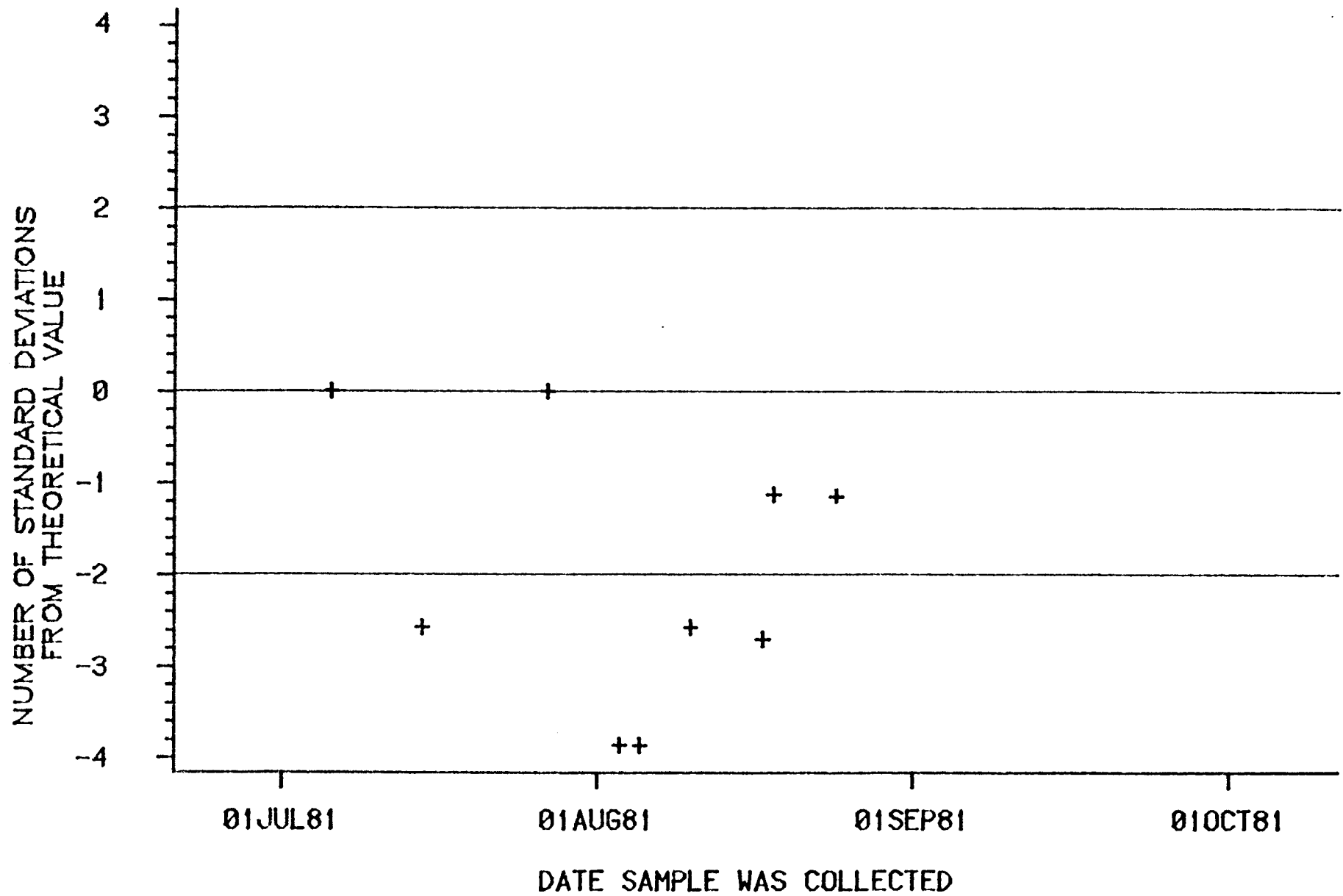


Figure A1.1.3.--Antimony data for the Atlanta Laboratory.
(Two observations were out of range.)

LAB=ATLANTA

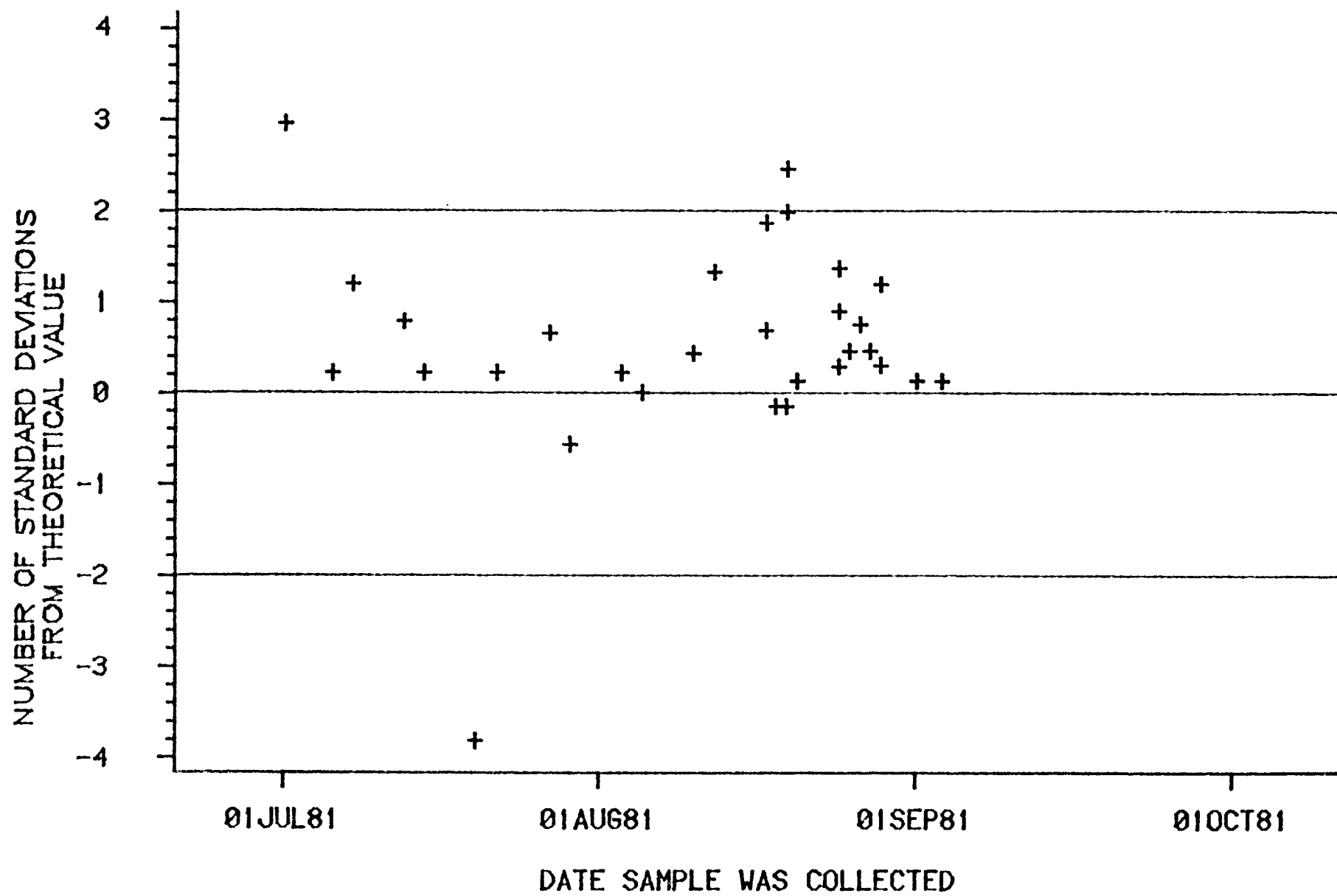


Figure A1.1.4.--Arsenic data for the Atlanta Laboratory.

LAB=ATLANTA

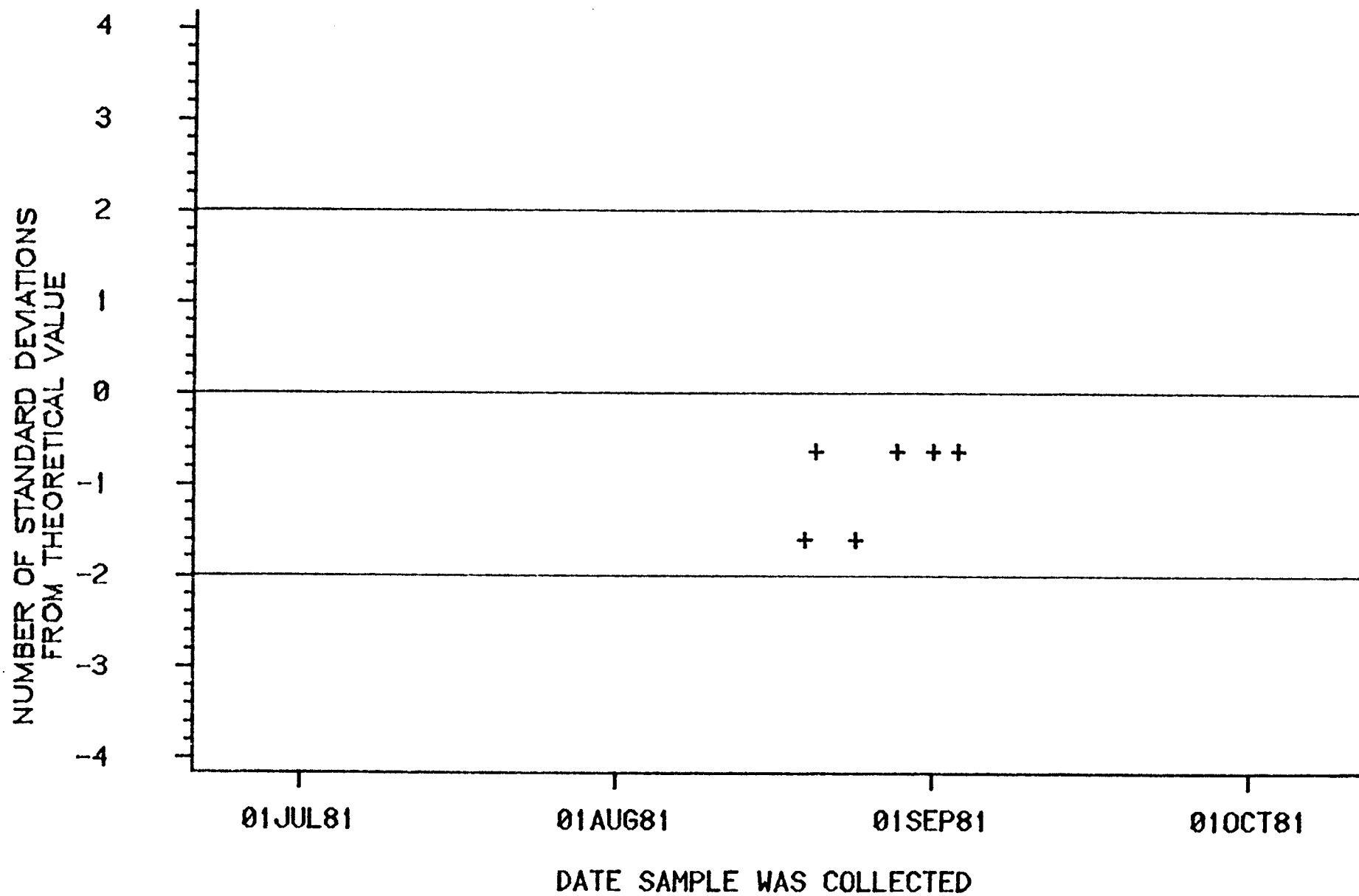


Figure A1.1.6.--Barium, total recoverable data for the Atlanta Laboratory.

29

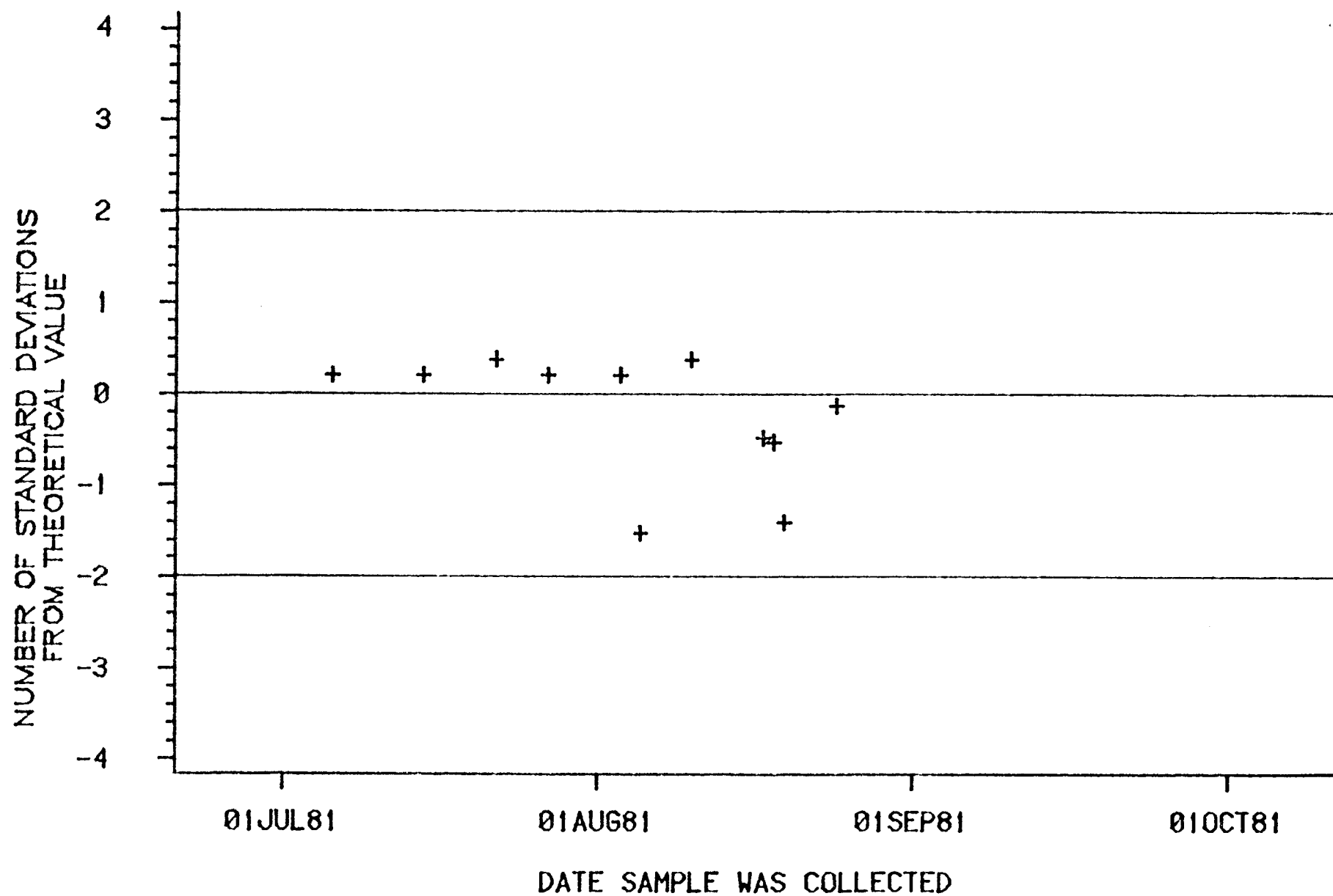


Figure A1.1.7.--Beryllium data for the Atlanta Laboratory.

LAB=ATLANTA

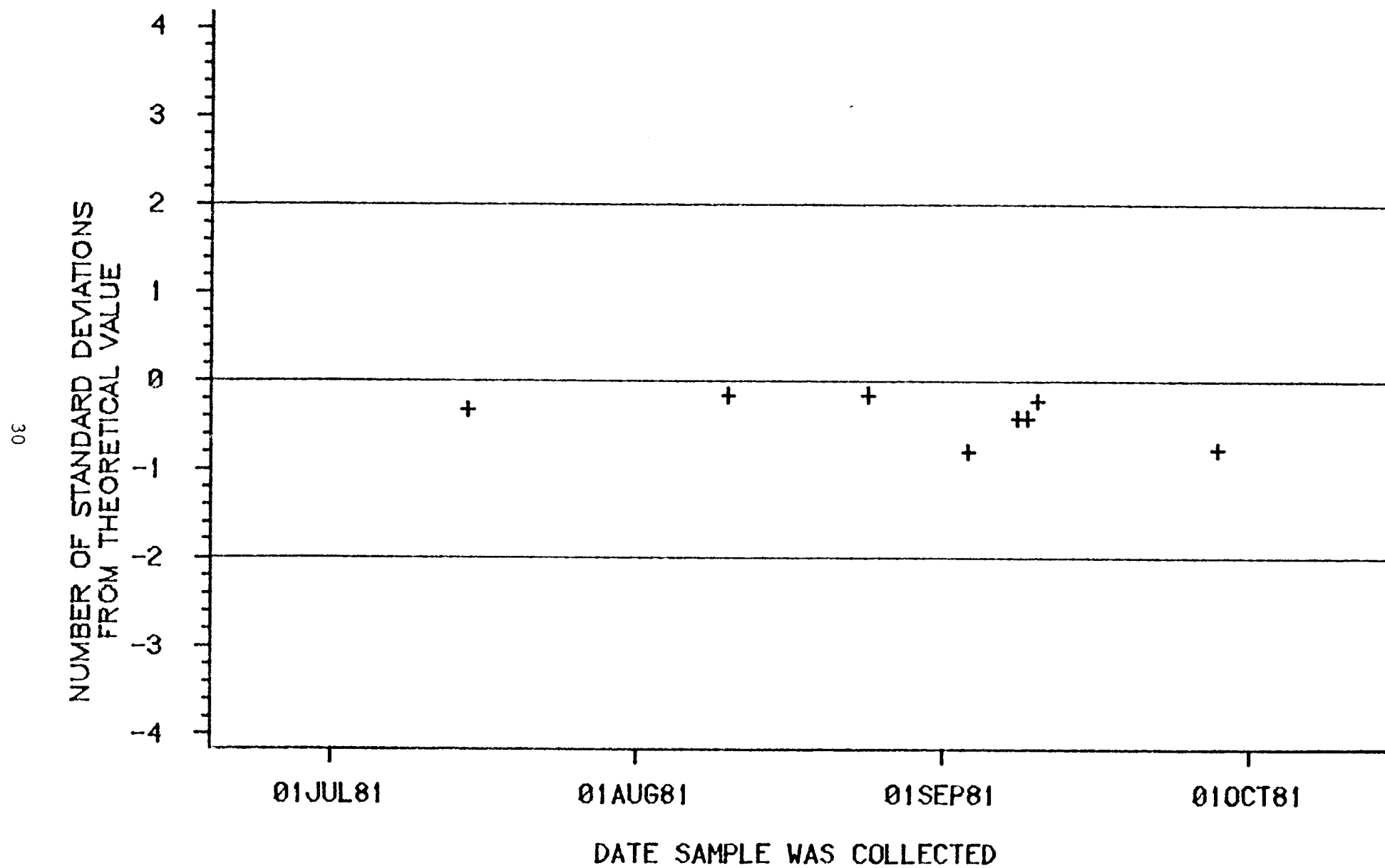


Figure A1.1.8.--Boron data for the Atlanta Laboratory.

LAB=ATLANTA

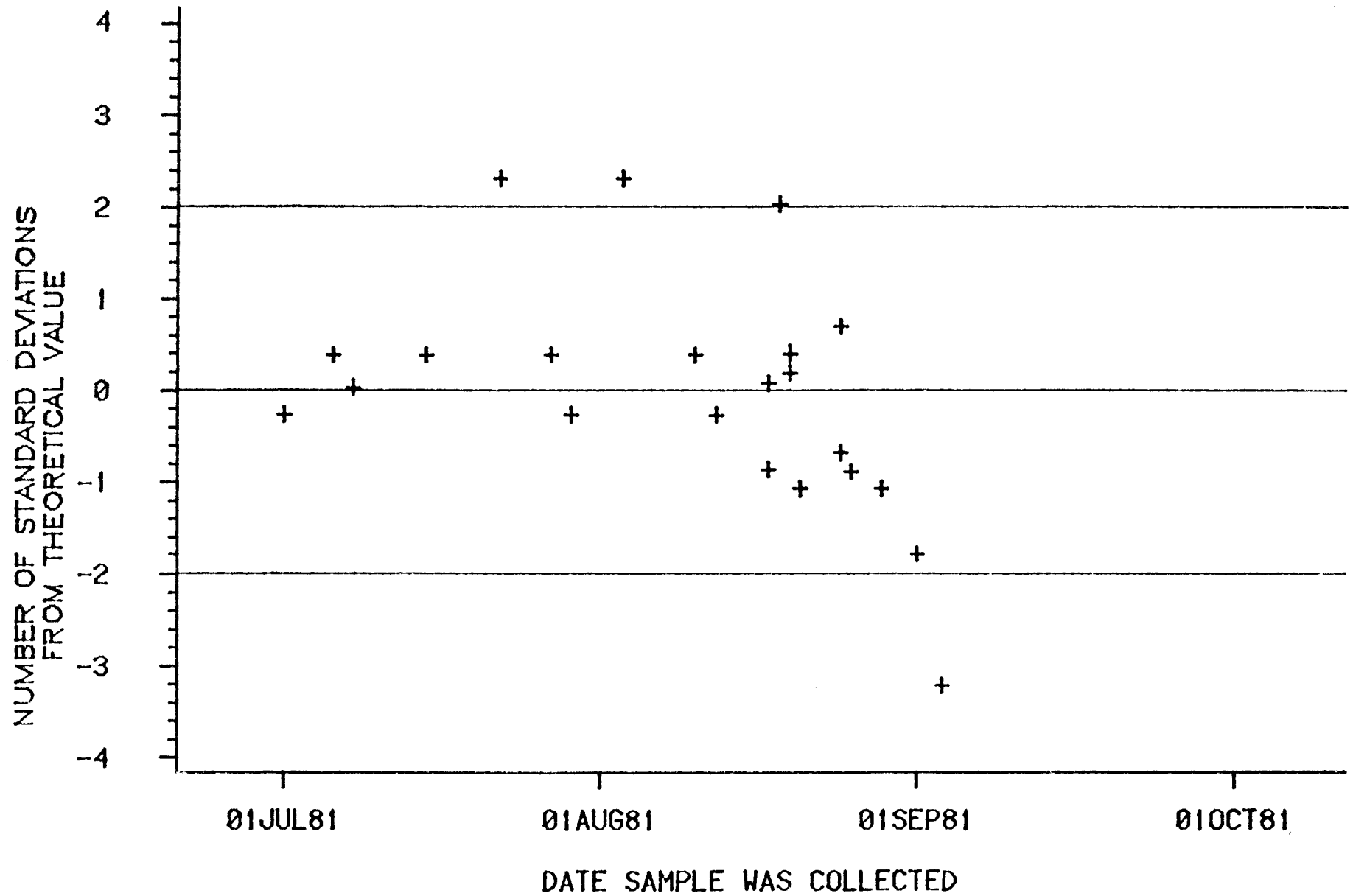


Figure A1.1.9---Cadmium data for the Atlanta Laboratory.
(Five observations were out of range.)

LAB=ATLANTA

32

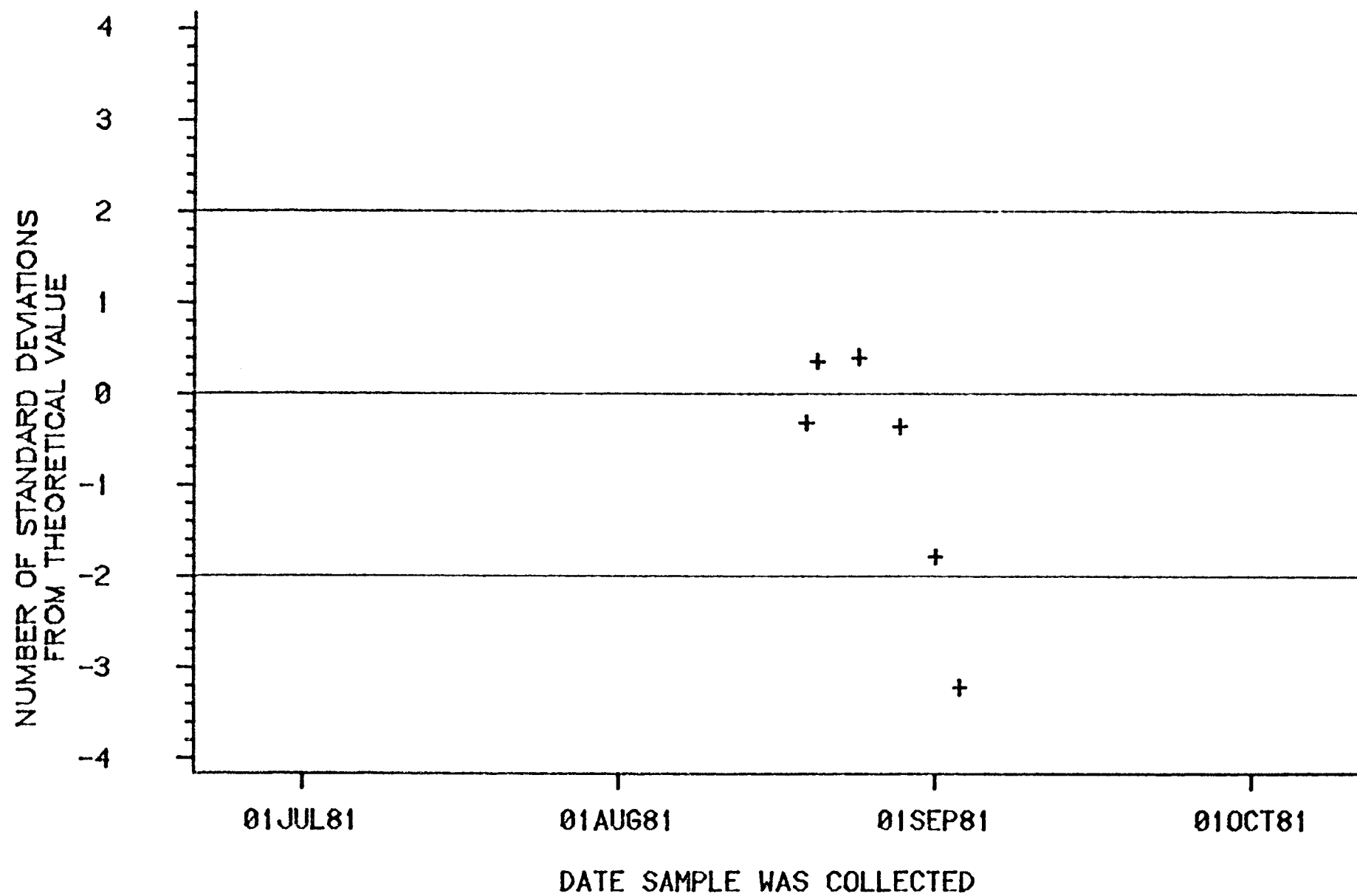


Figure A1.1.10.--Cadmium, total recoverable data for the Atlanta Laboratory.

LAB=ATLANTA

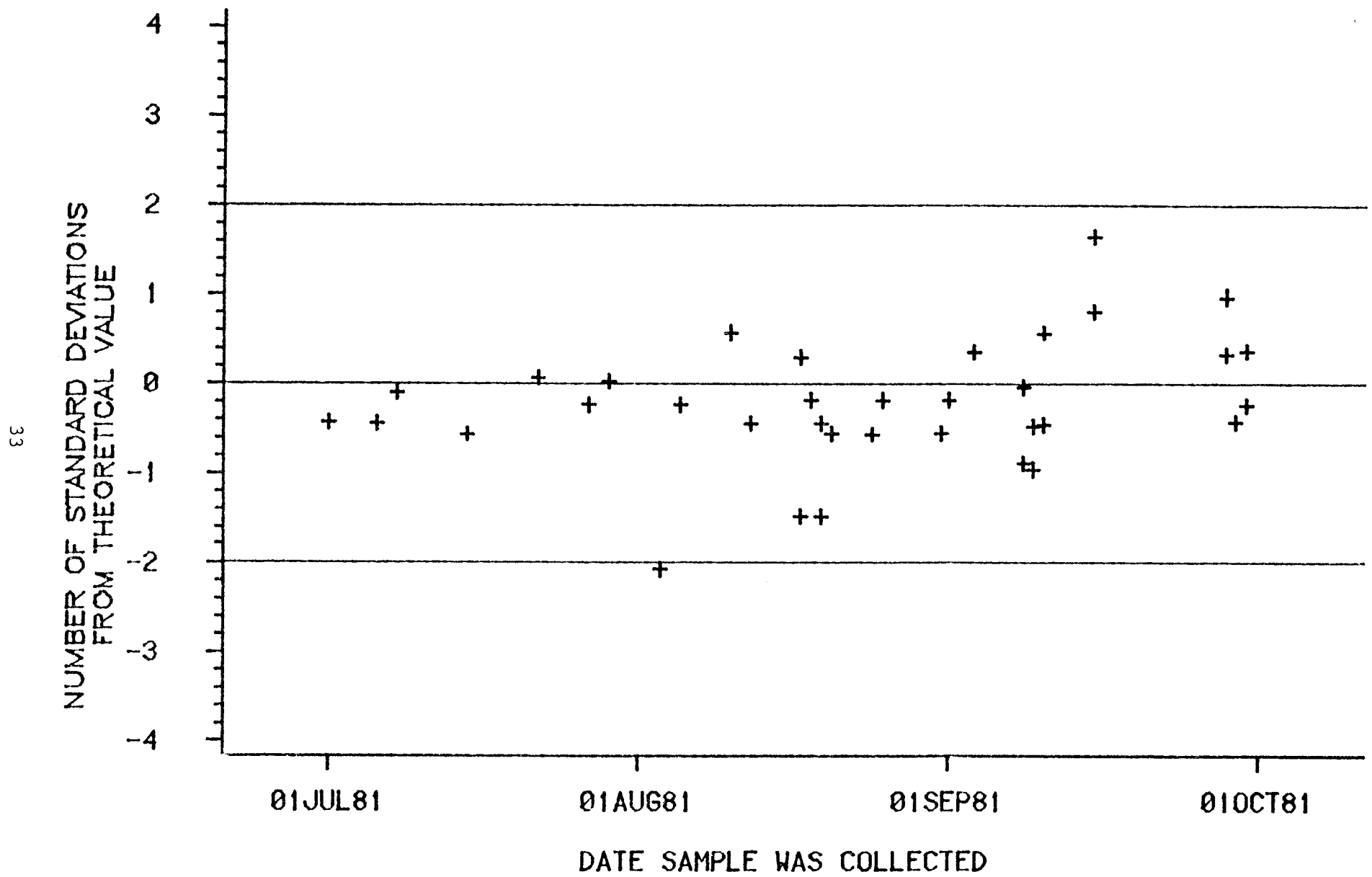


Figure A1.1.11.--Calcium data for the Atlanta Laboratory.

LAB=ATLANTA

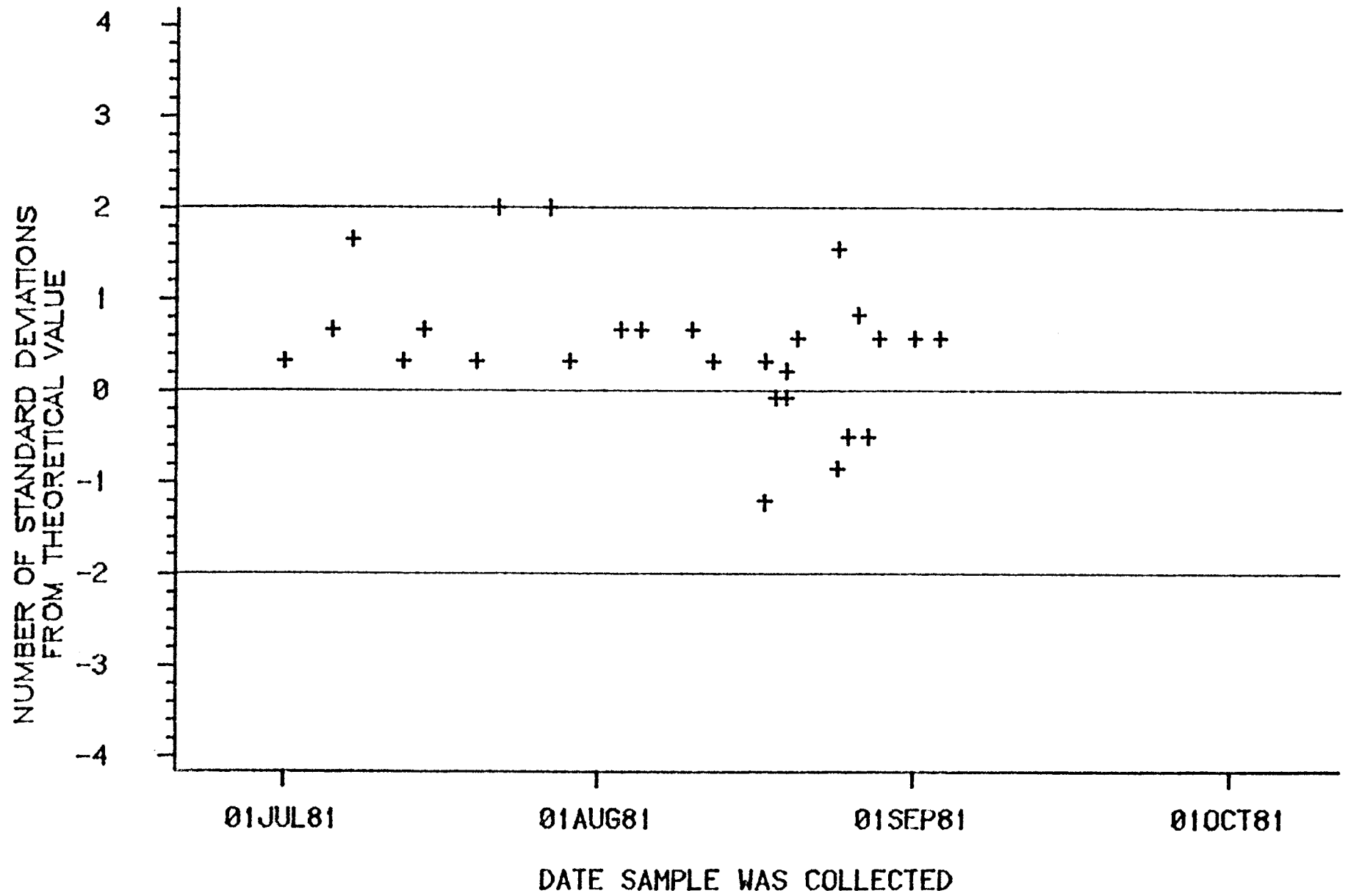


Figure A1.1.12.--Chromium data for the Atlanta Laboratory.

LAB=ATLANTA

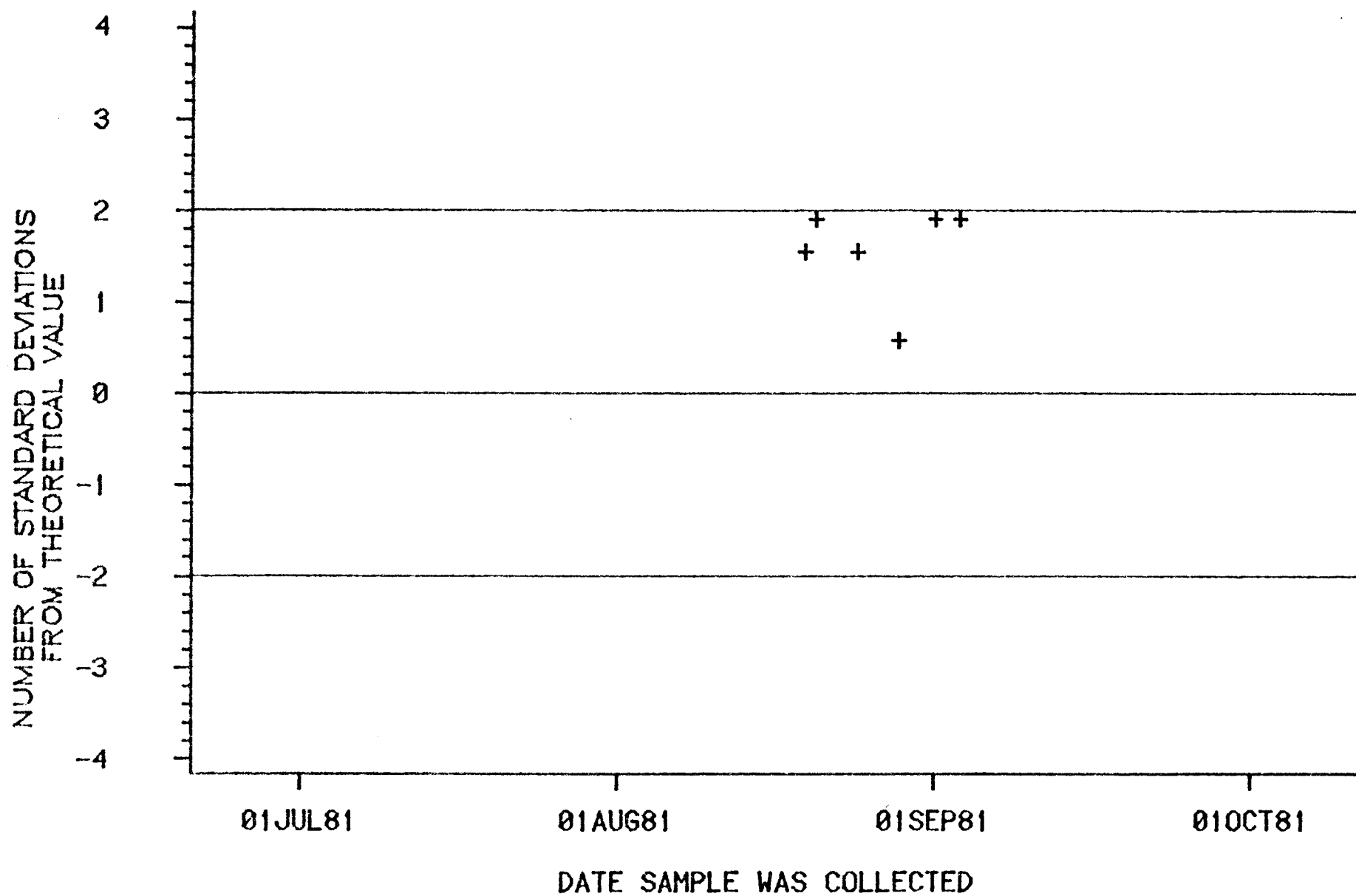


Figure A1.1.13.--Chromium, total recoverable data for the Atlanta Laboratory.
(One observation was out of range.)

LAB=ATLANTA

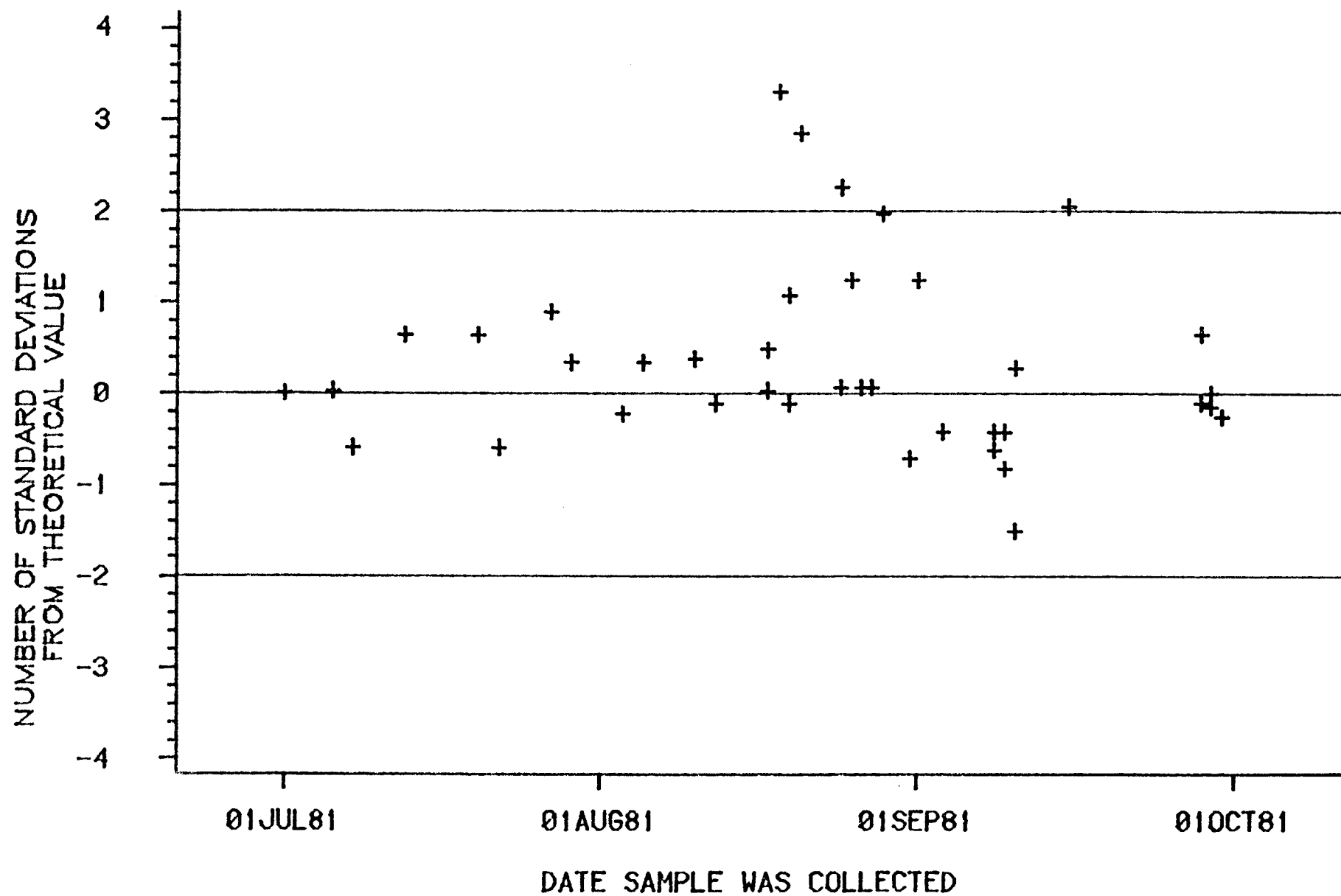


Figure A1.1.14.--Chloride data for the Atlanta Laboratory.
(One observation was out of range.)

LAB=ATLANTA

37

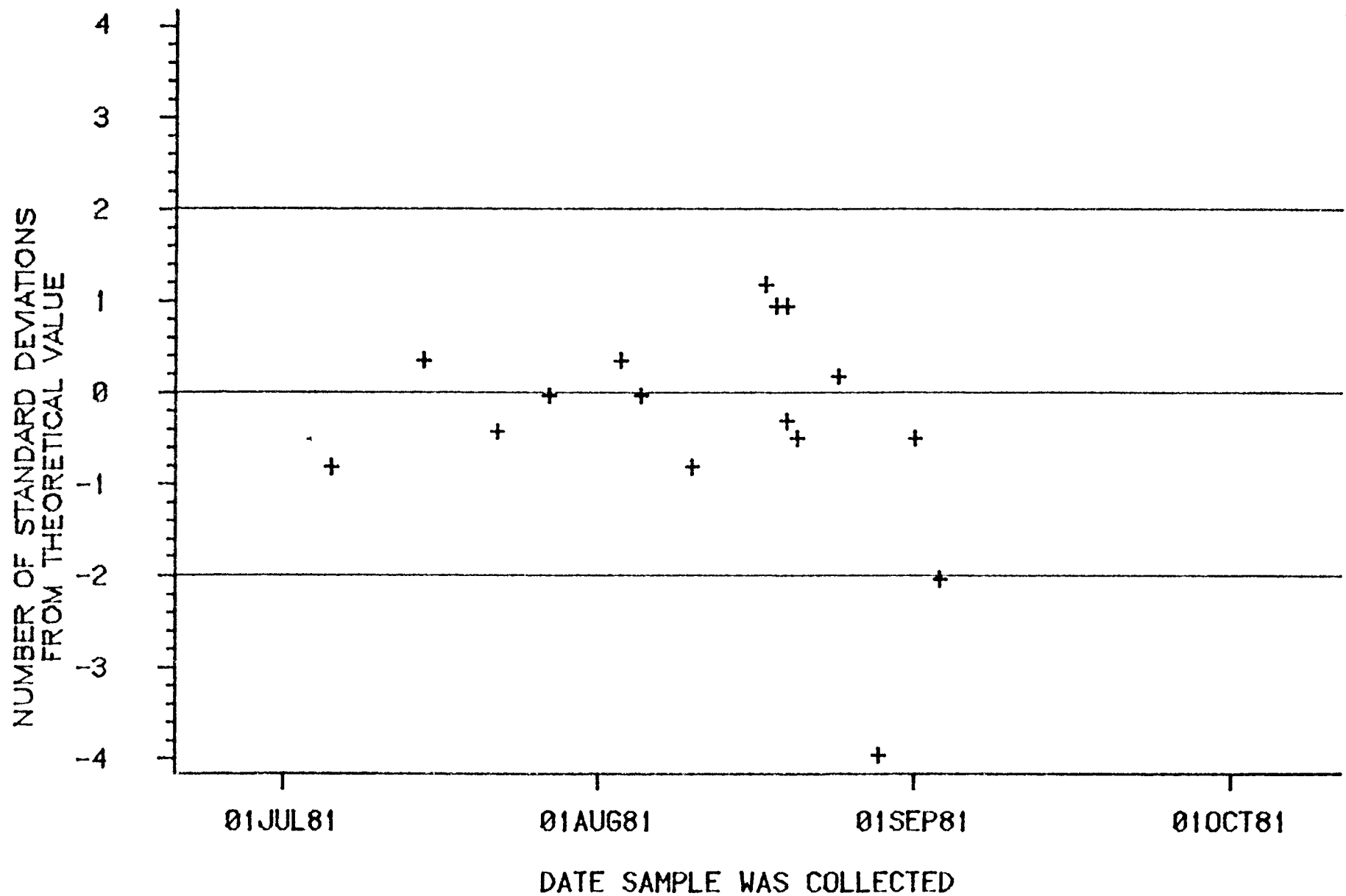


Figure A1.1.15.--Cobalt data for the Atlanta Laboratory.
(One observation was out of range.)

LAB=ATLANTA

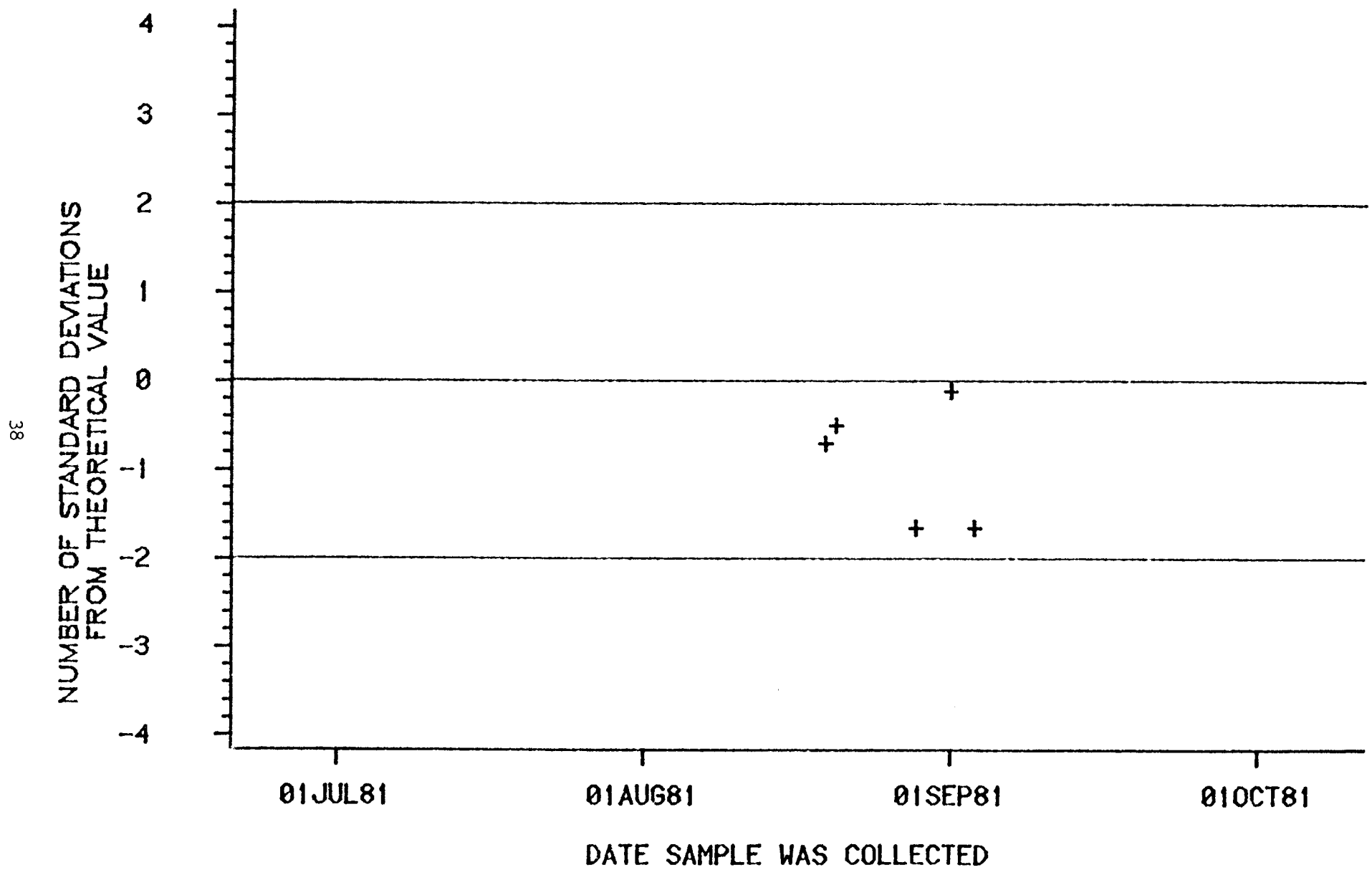


Figure A1.1.16.--Cobalt, total recoverable data for the Atlanta Laboratory.
(One observation was out of range.)

LAB=ATLANTA

63

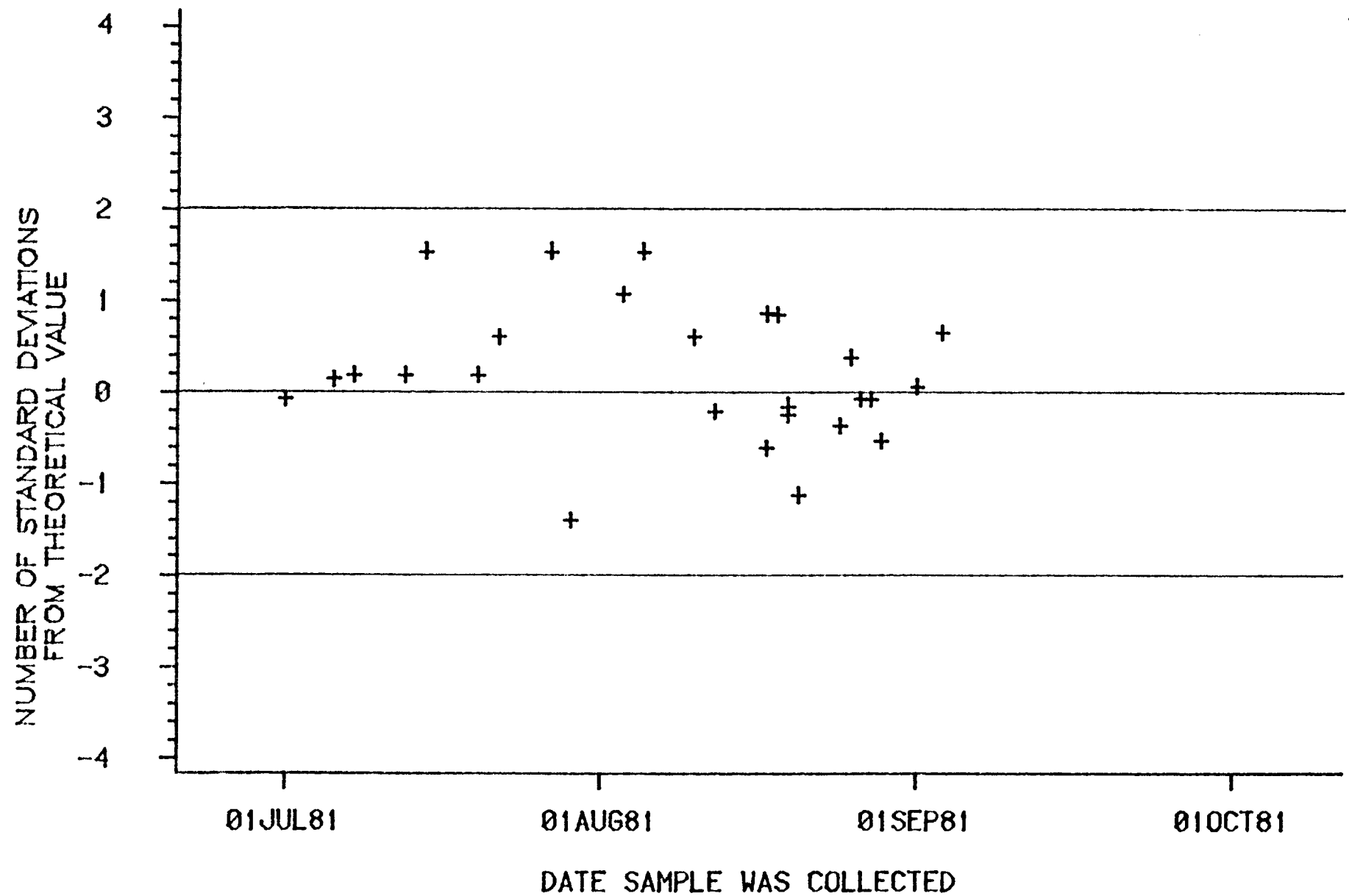


Figure A1.1.17.--Copper data for the Atlanta Laboratory.
(One observation was out of range.)

LAB=ATLANTA

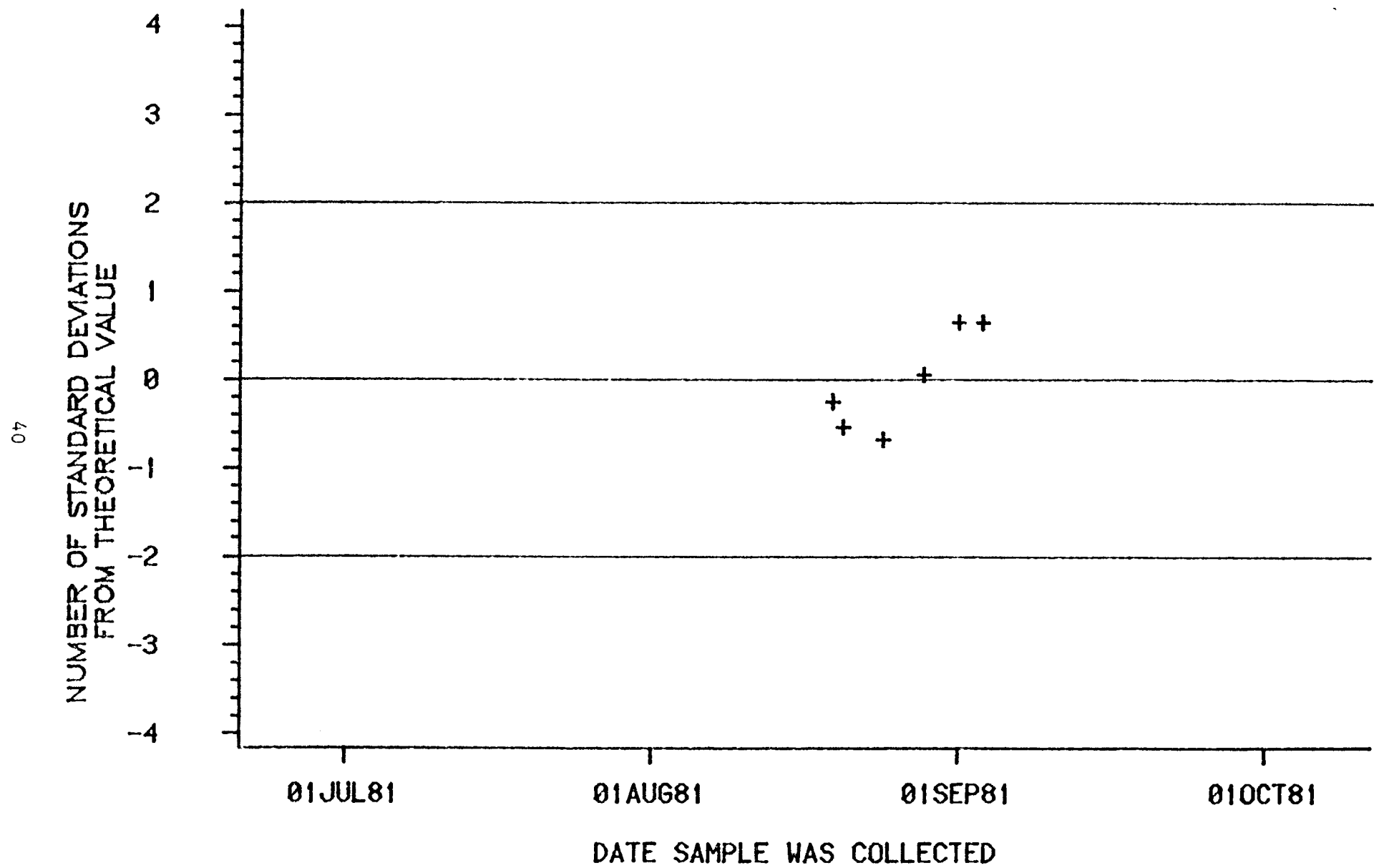


Figure A1.1.18.--Copper, total recoverable data for the Atlanta Laboratory.

LAB=ATLANTA

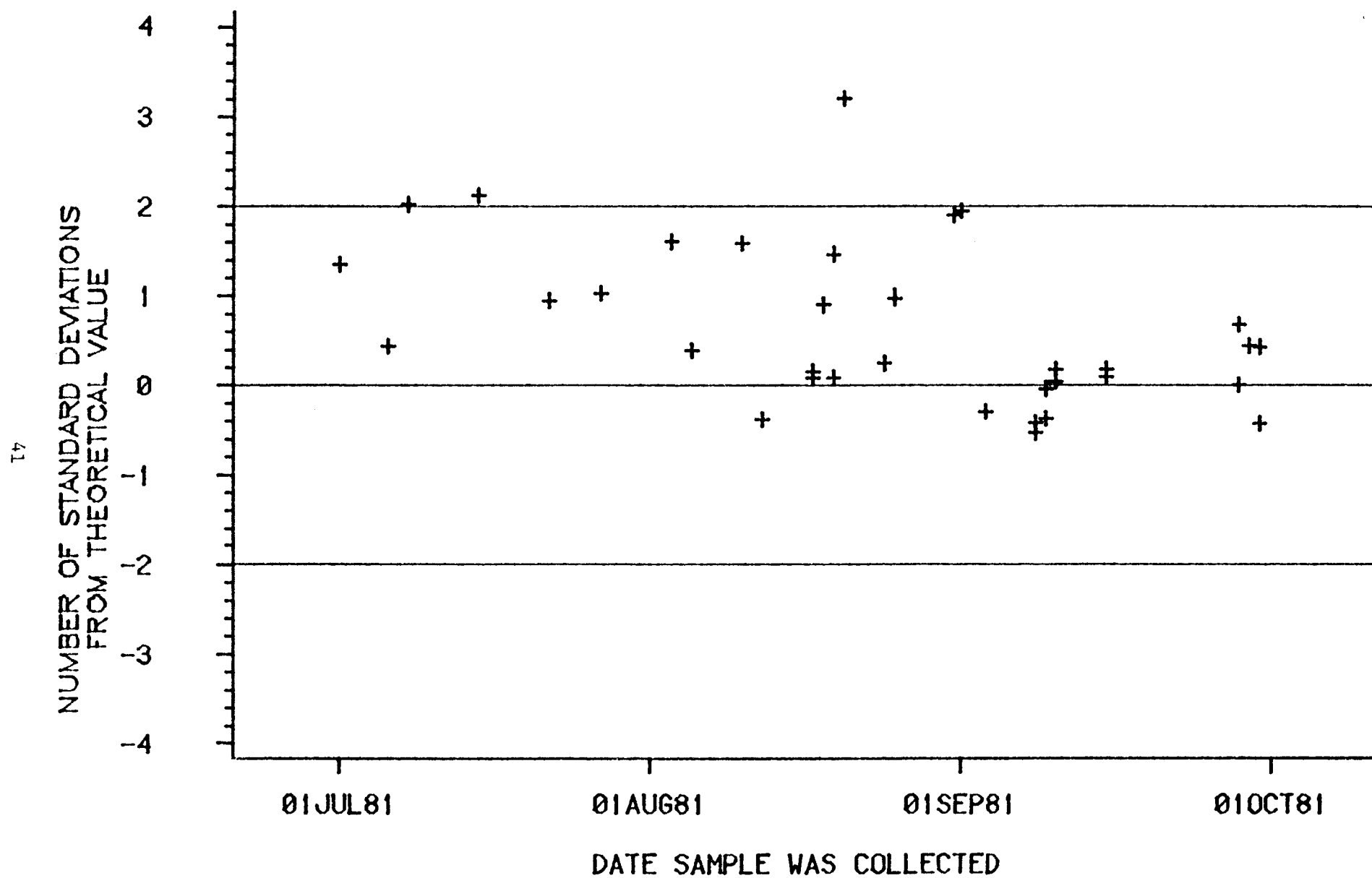


Figure A1.1.19.--Dissolved solids data for the Atlanta Laboratory.
(One observation was out of range.)

LAB=ATLANTA

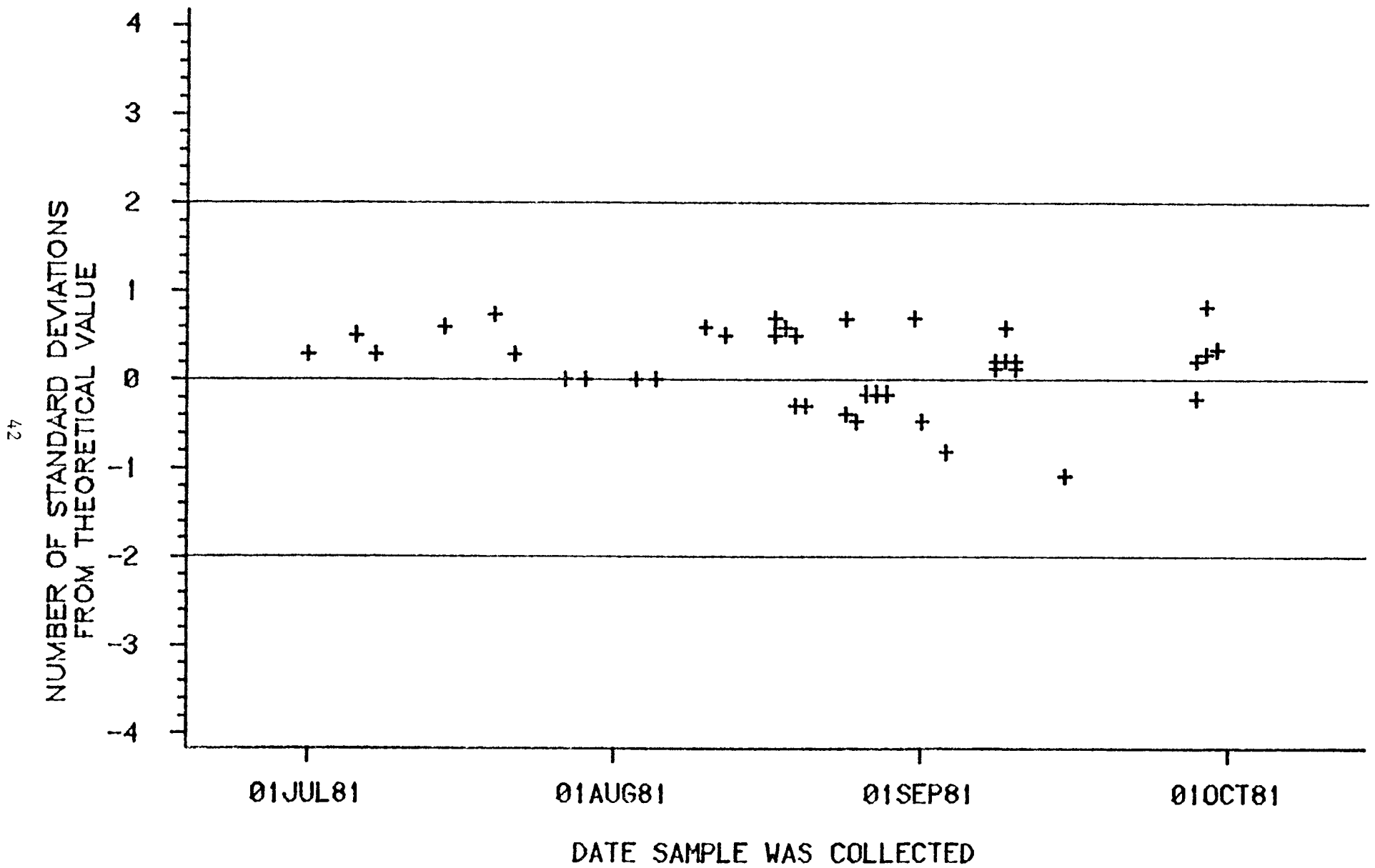


Figure A1.1.20.--Fluoride data for the Atlanta Laboratory.
(One observation was out of range.)

LAB=ATLANTA

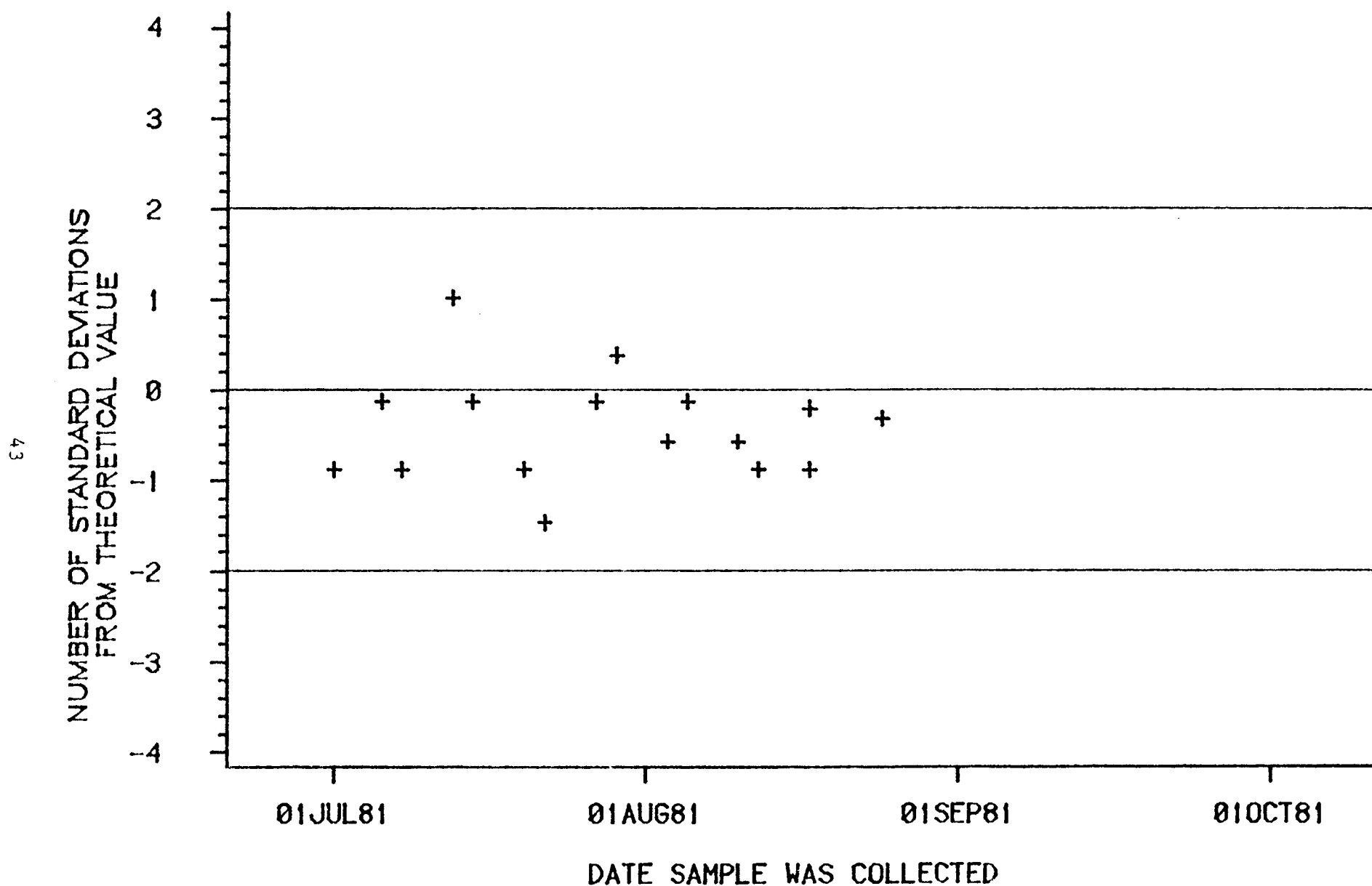


Figure A1.1.21.--Iron data for the Atlanta Laboratory.
(Four observations were out of range.)

LAB=ATLANTA

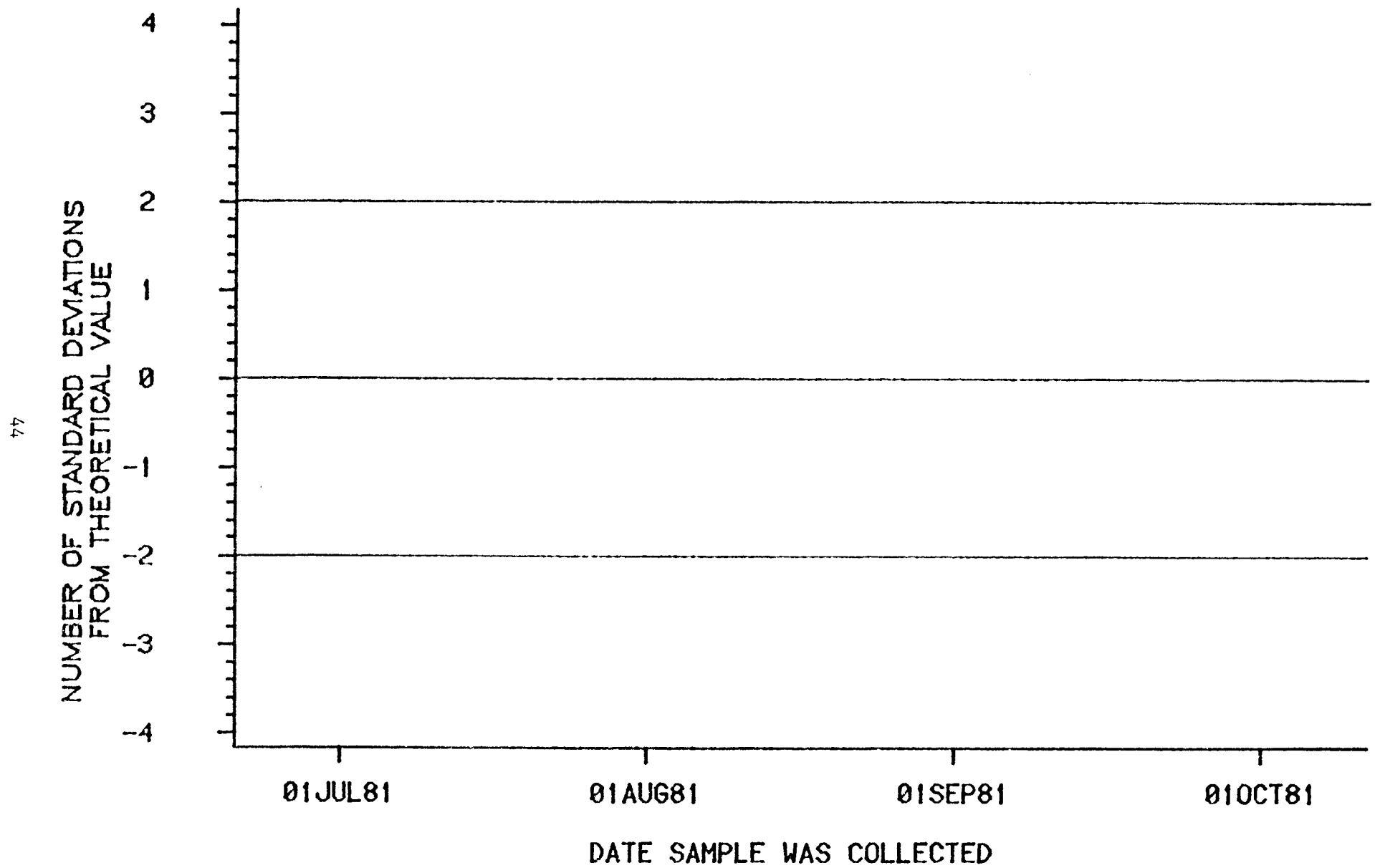


Figure A1.1.22.--Iron, total recoverable data for the Atlanta Laboratory.
(Four observations were out of range, see Discussion.)

LAB=ATLANTA

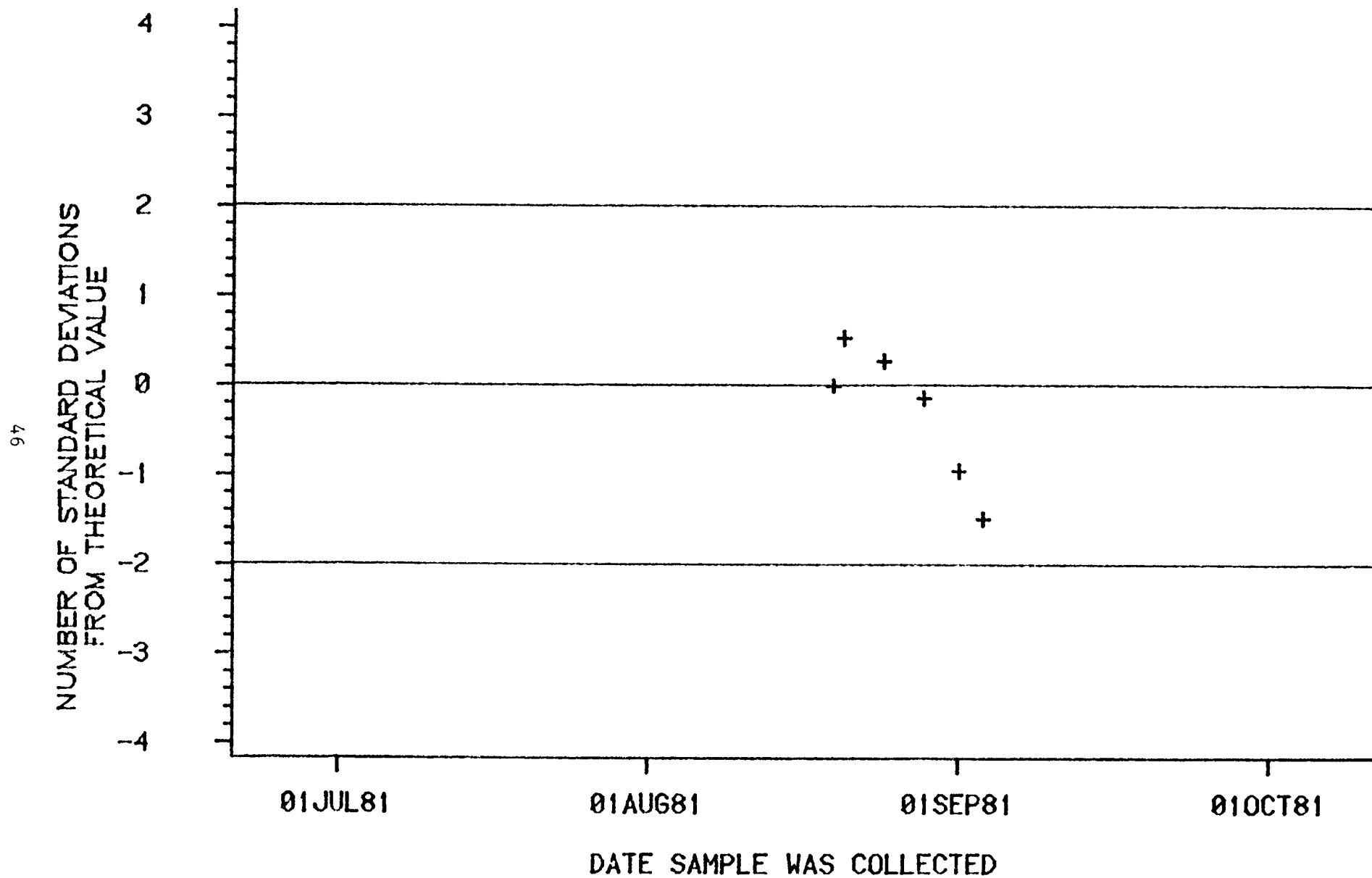


Figure A1.1.24.--Lead, total recoverable data for the Atlanta Laboratory.

LAB=ATLANTA

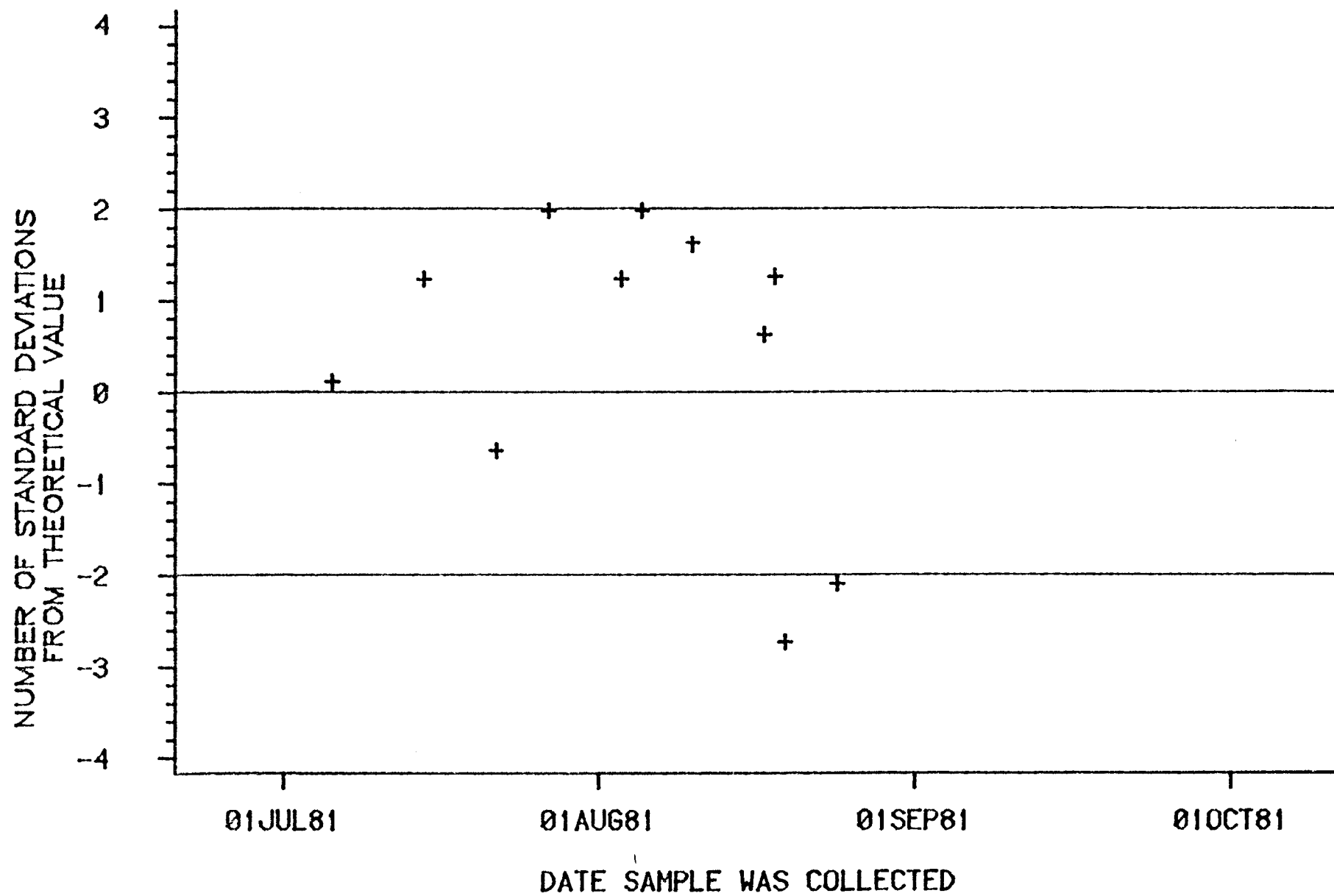


Figure A1.1.25.--Lithium data for the Atlanta Laboratory.

LAB=ATLANTA

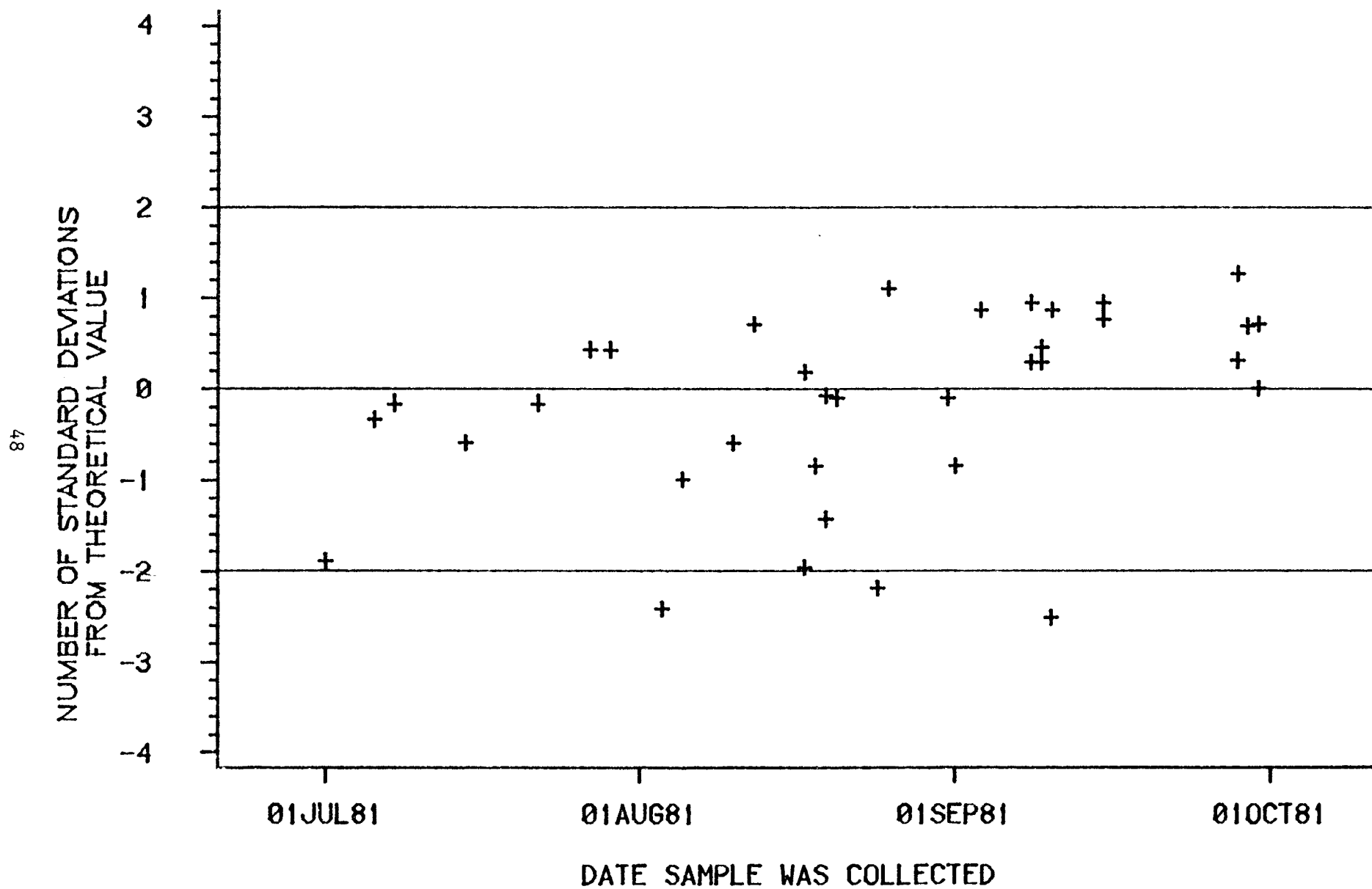


Figure A1.1.26.--Magnesium data for the Atlanta Laboratory.

LAB=ATLANTA

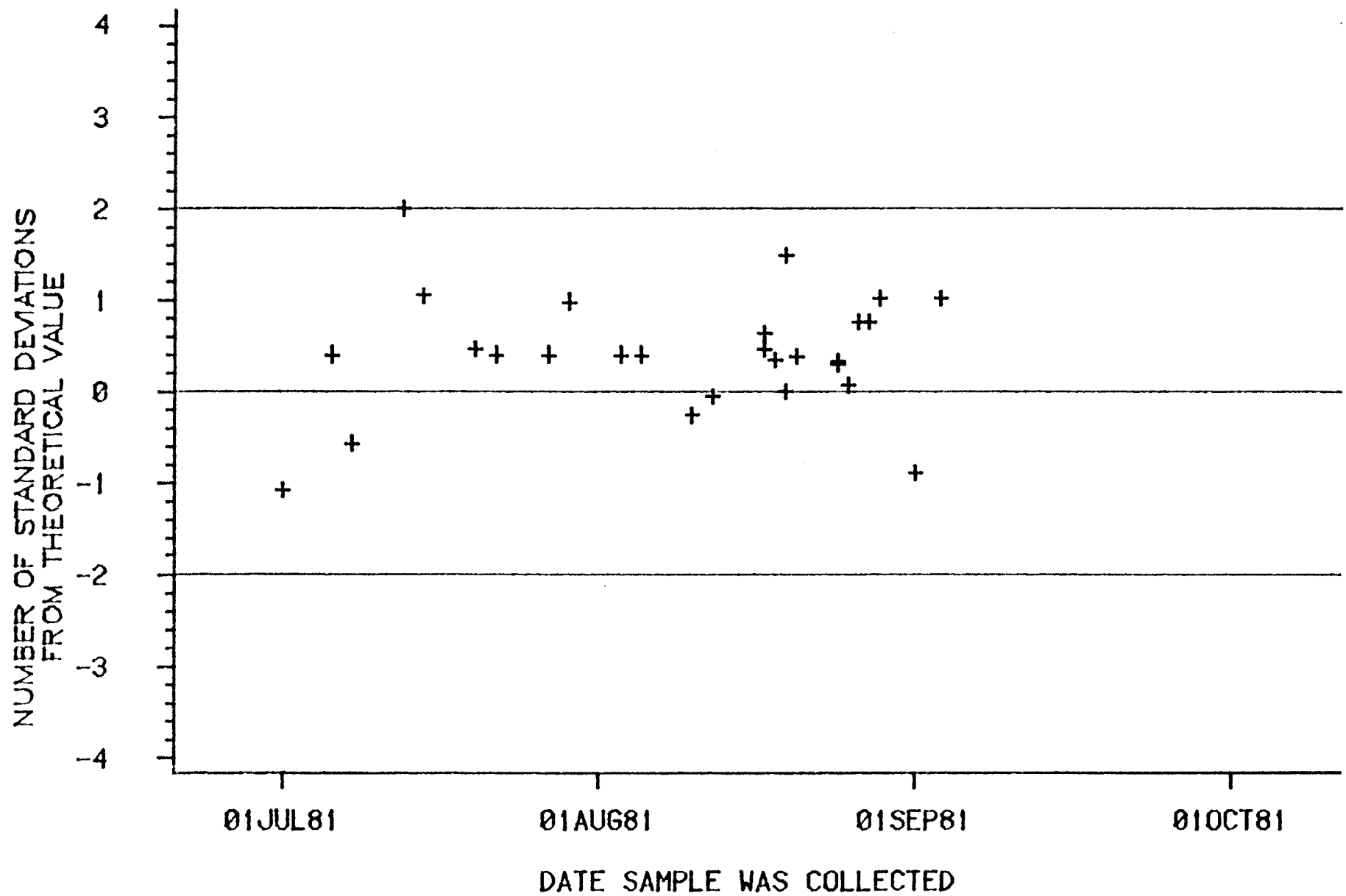


Figure A1.1.27.--Manganese data for the Atlanta Laboratory.

LAB=ATLANTA

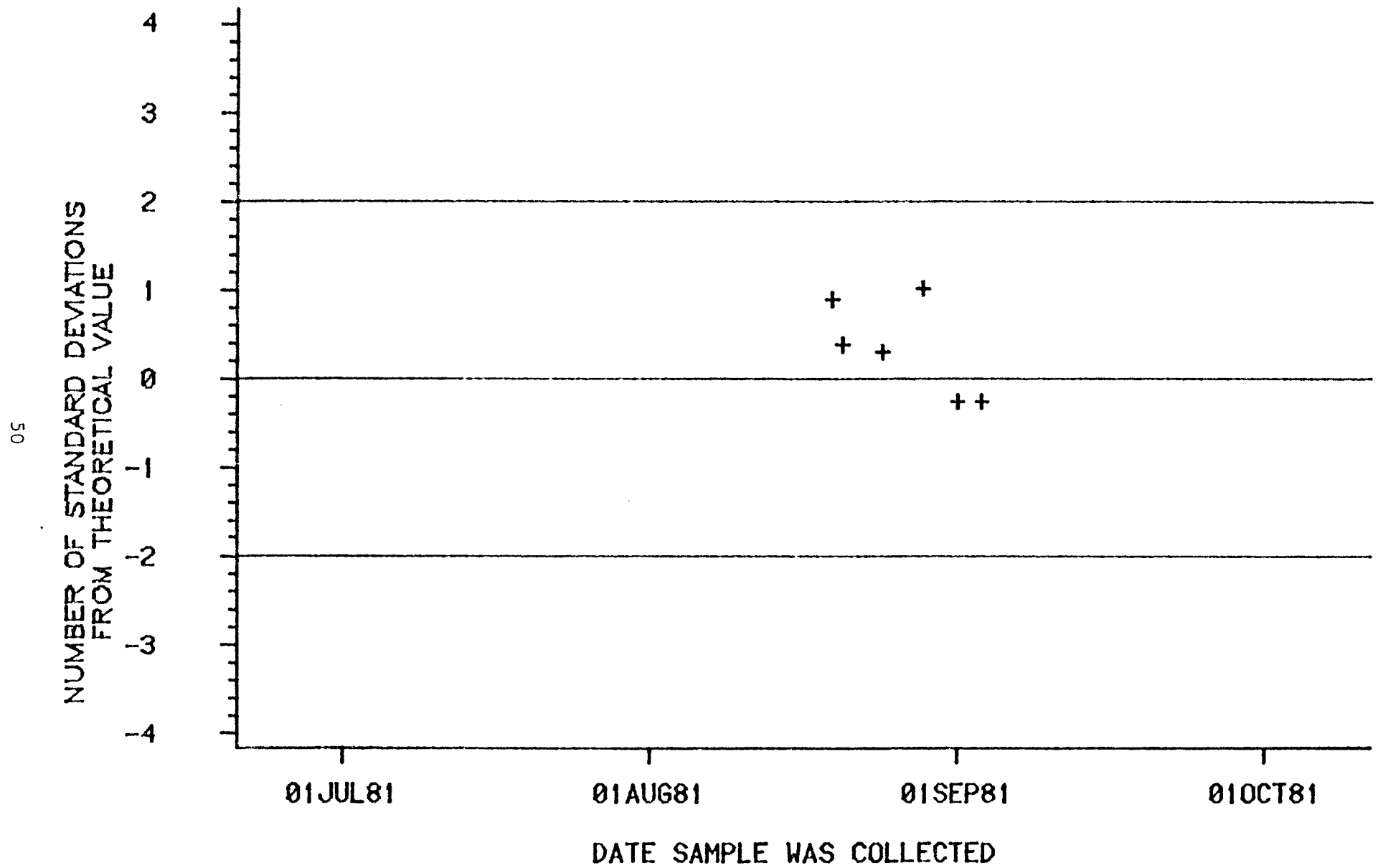


Figure A1.1.28.--Manganese, total recoverable data for the Atlanta Laboratory.

LAB=ATLANTA

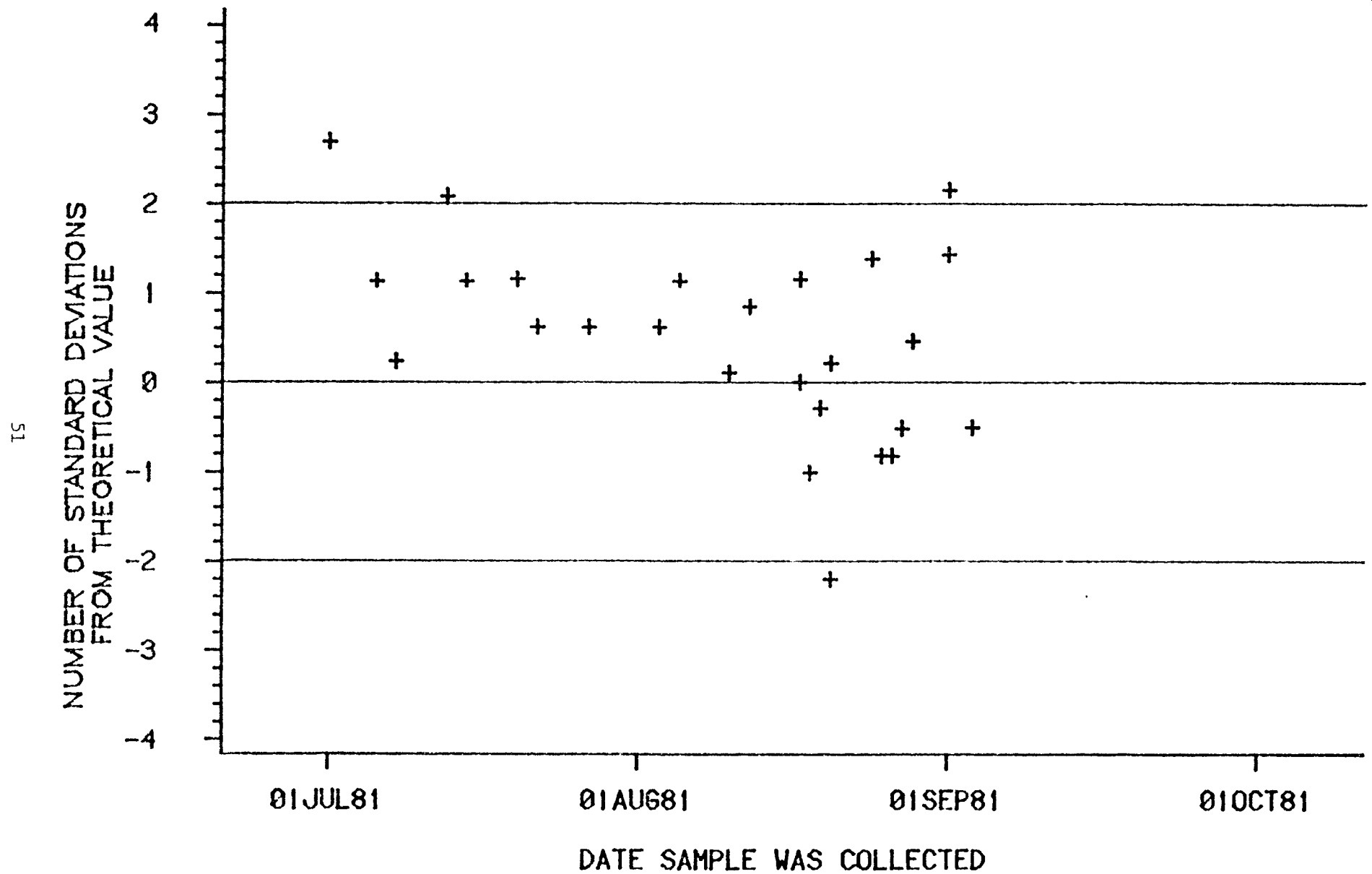


Figure A1.1.29.--Mercury data for the Atlanta Laboratory.
(Five observations were out of range.)

LAB=ATLANTA

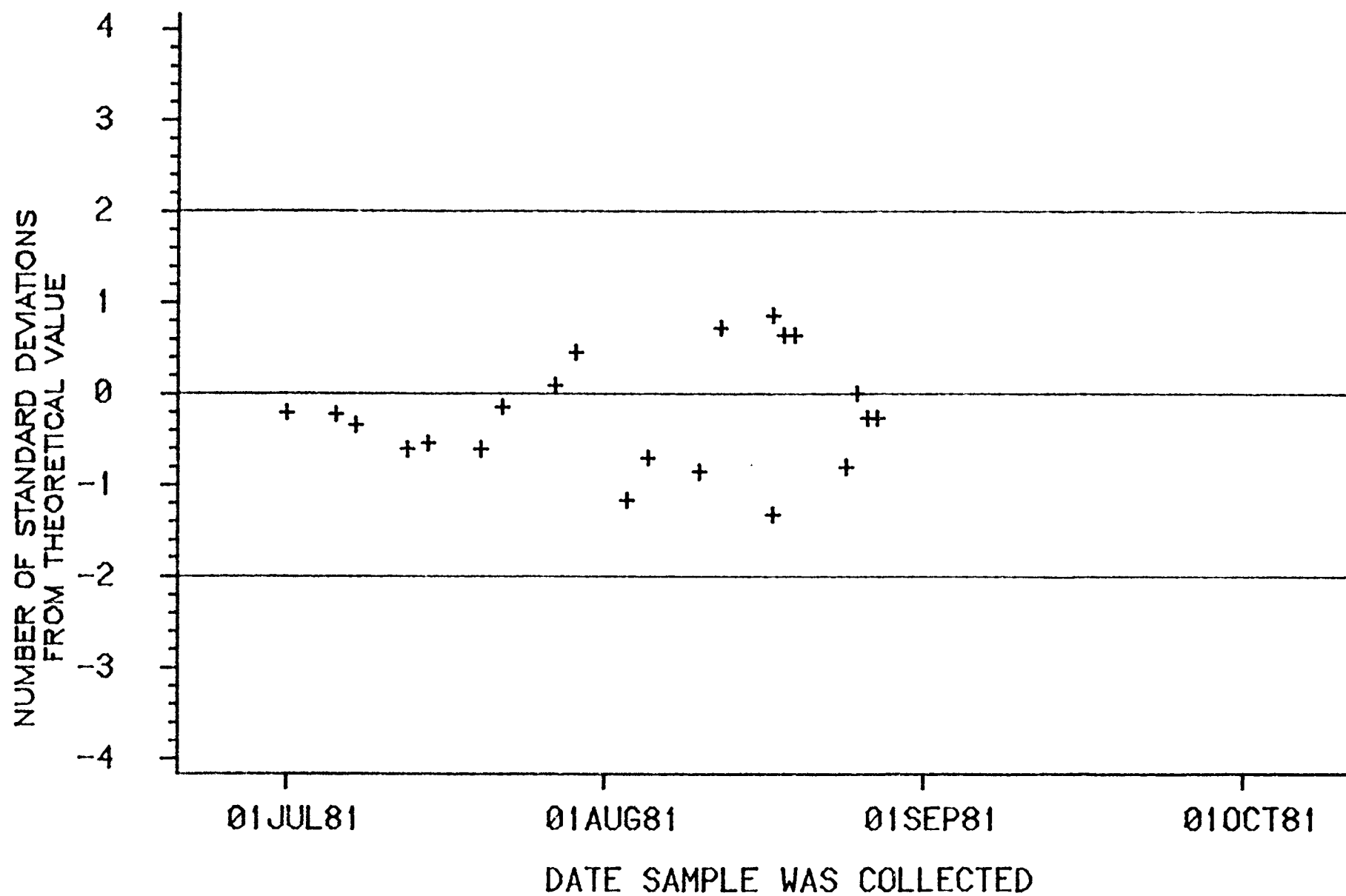


Figure A1.1.30.--Molybdenum data for the Atlanta Laboratory.

53

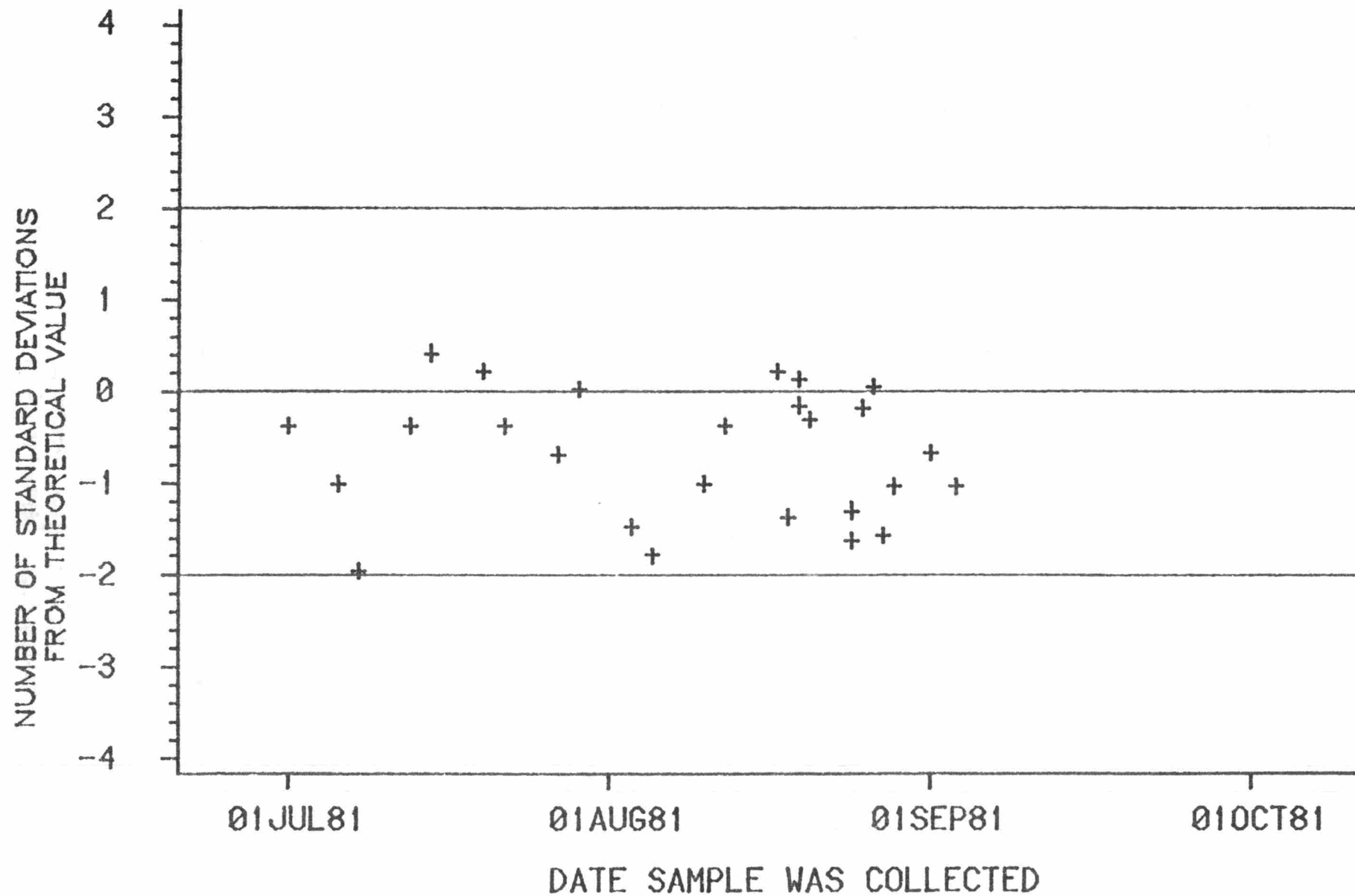


Figure A1.1.31.--Nickel data for the Atlanta Laboratory.

LAB=ATLANTA

54

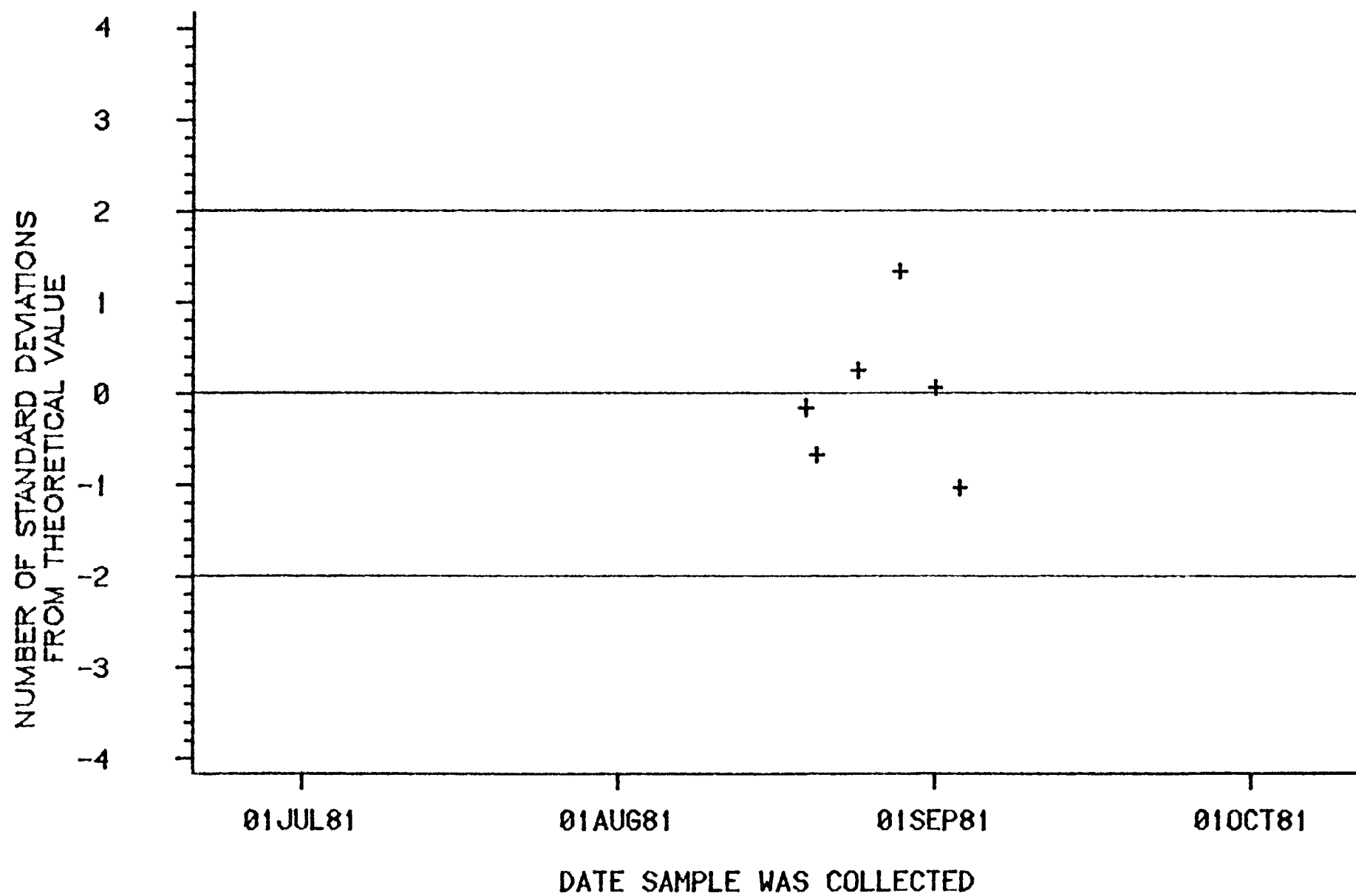


Figure A1.1.32.--Nickel, total recoverable data for the Atlanta Laboratory.

LAB=ATLANTA

55

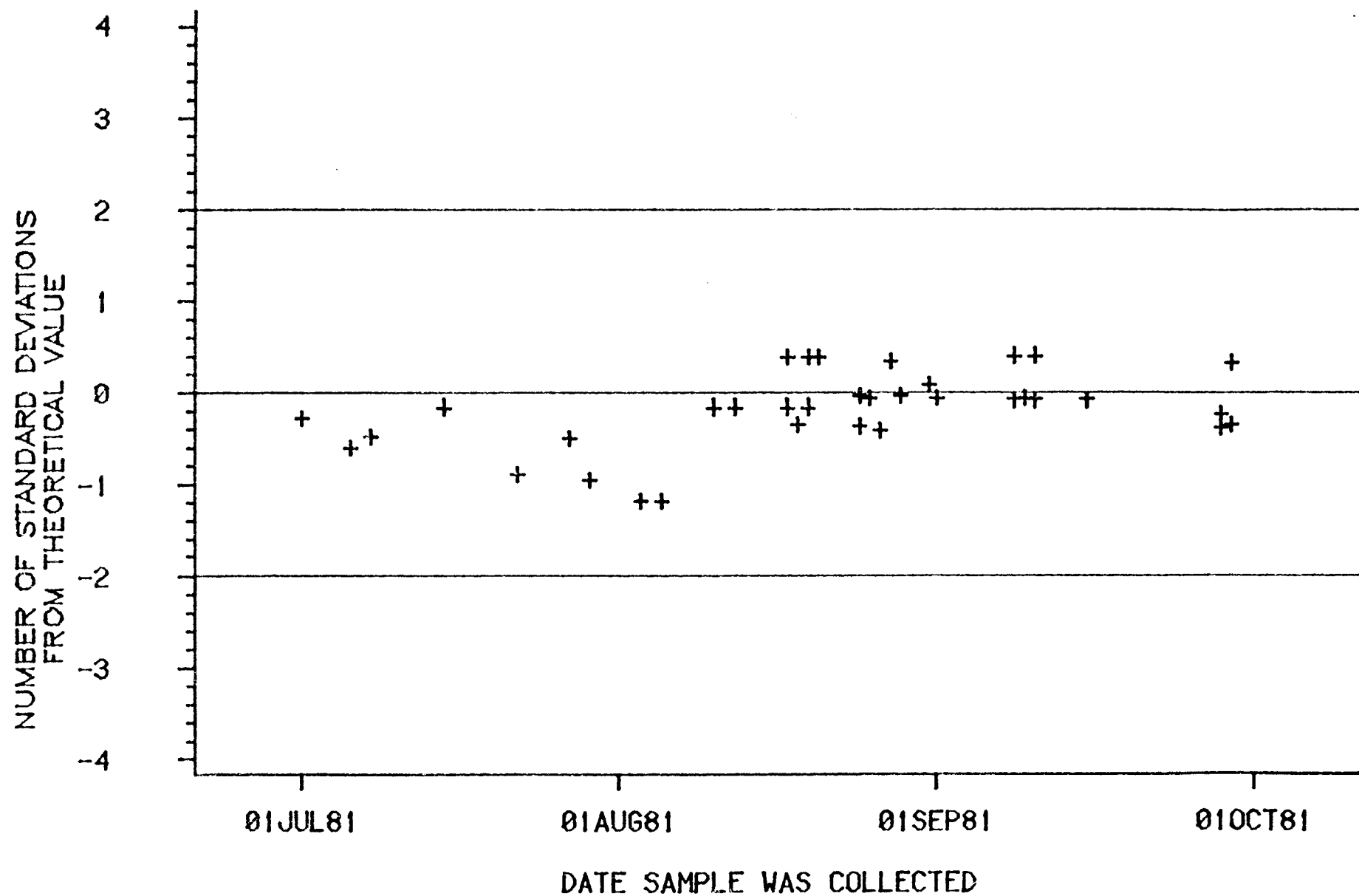


Figure A1.1.33.--Nitrate plus nitrite-nitrogen data for the Atlanta Laboratory.
(Two observations were out of range.)

LAB=ATLANTA

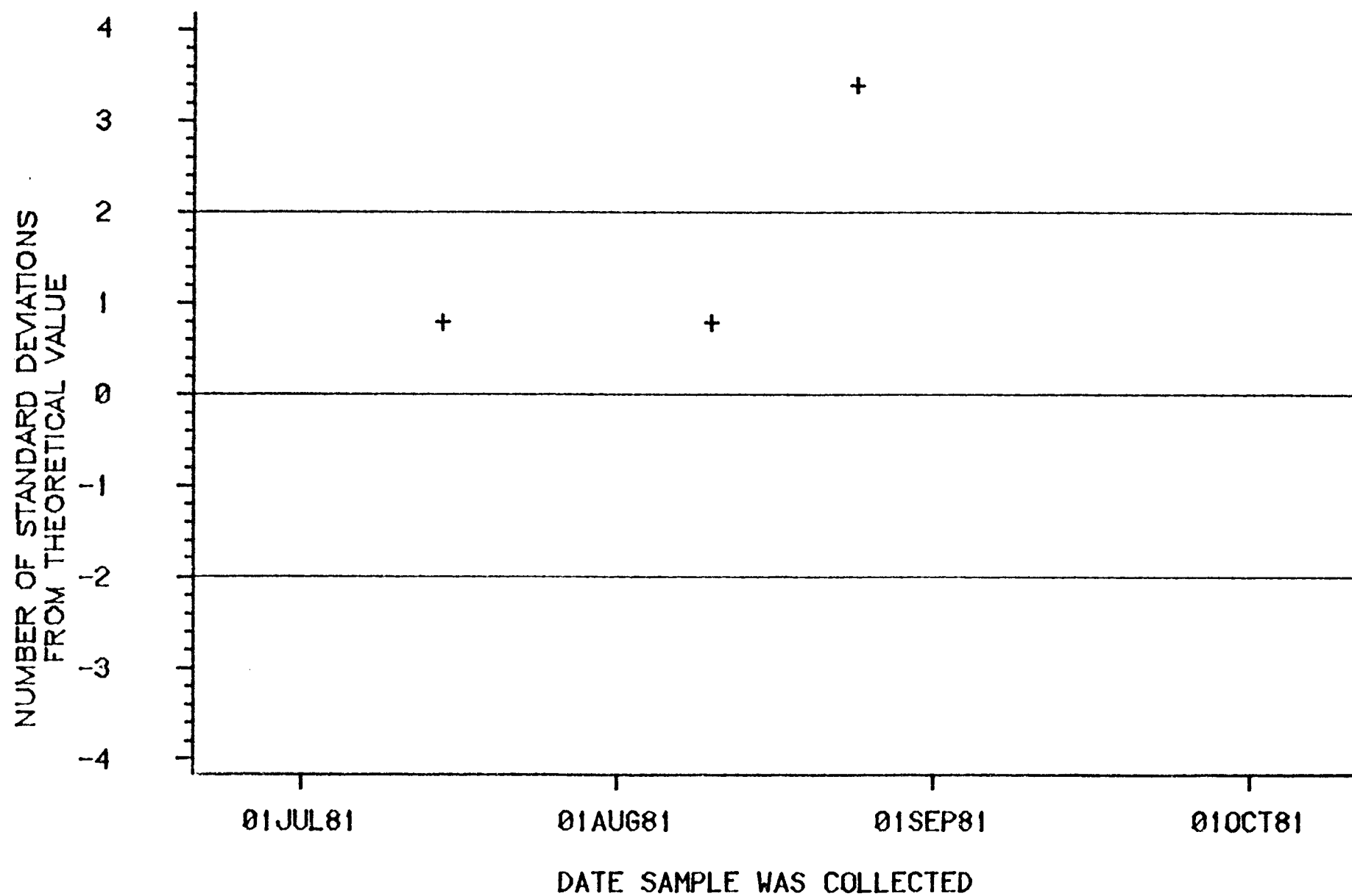


Figure A1.1.34.--Nitrite-nitrogen data for the Atlanta Laboratory.

LAB=ATLANTA

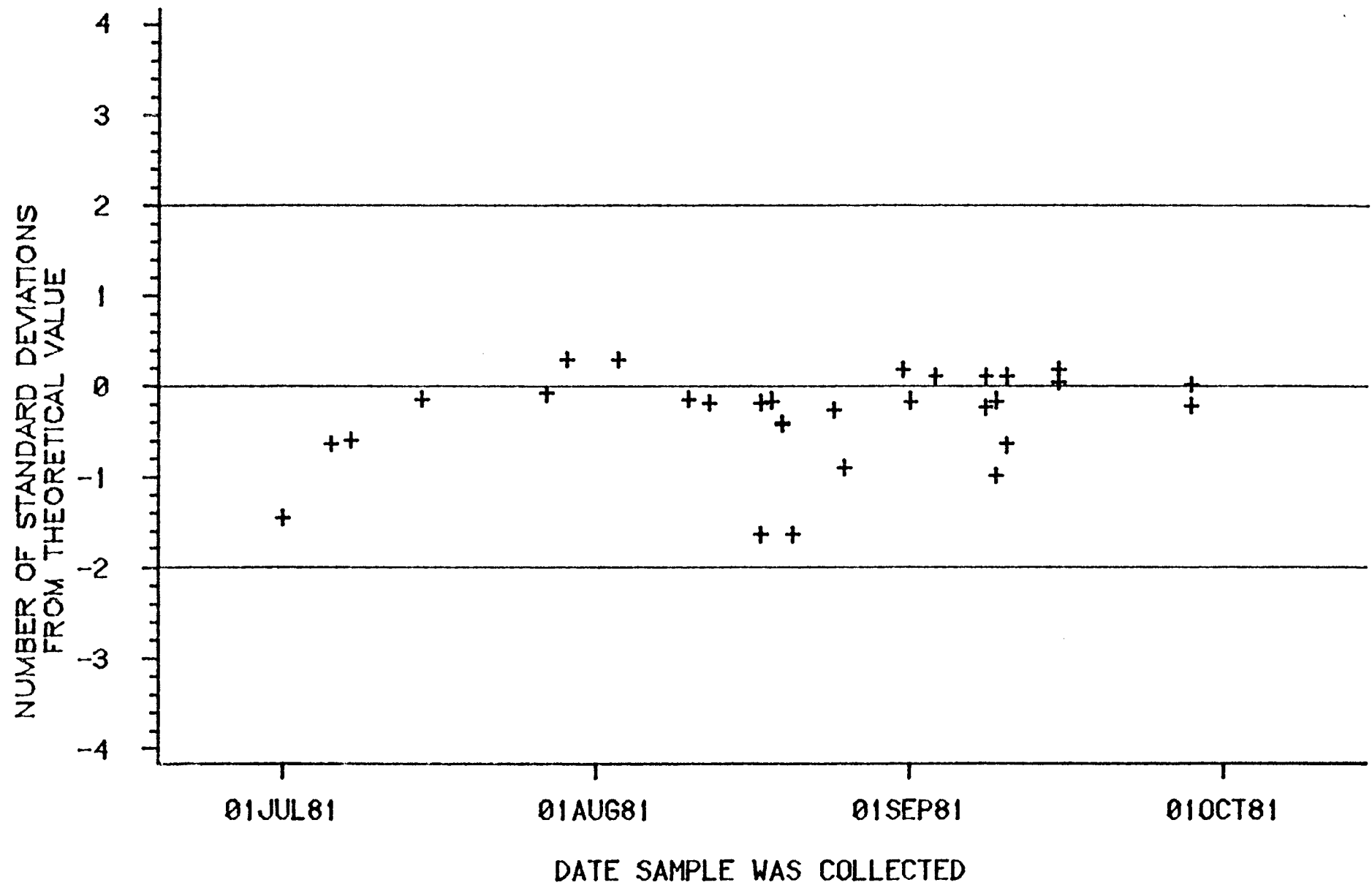


Figure A1.1.35.--Phosphorus data for the Atlanta Laboratory.
(Three observations were out of range.)

LAB=ATLANTA

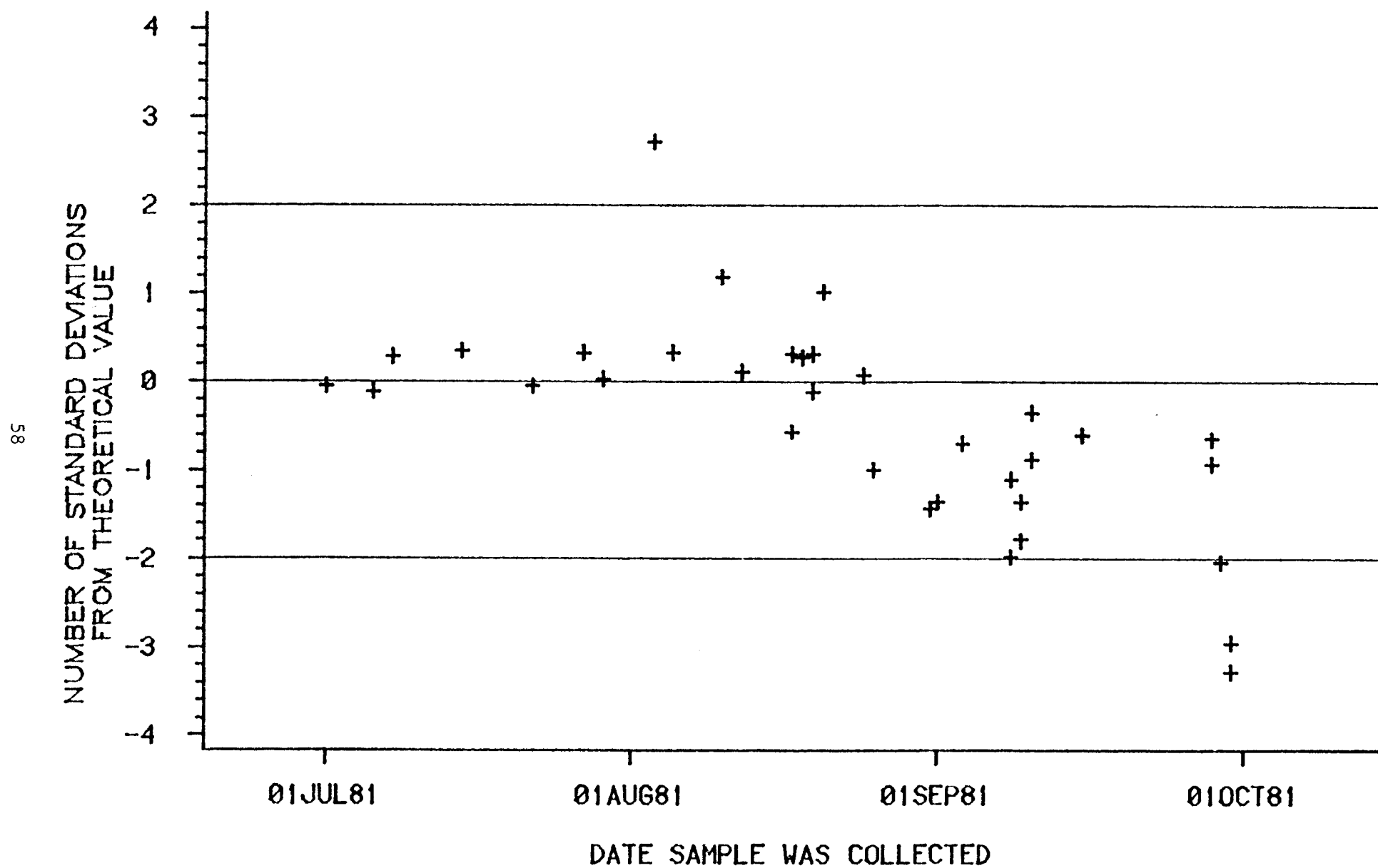


Figure A1.1.36.--Potassium data for the Atlanta Laboratory.

LAB=ATLANTA

65

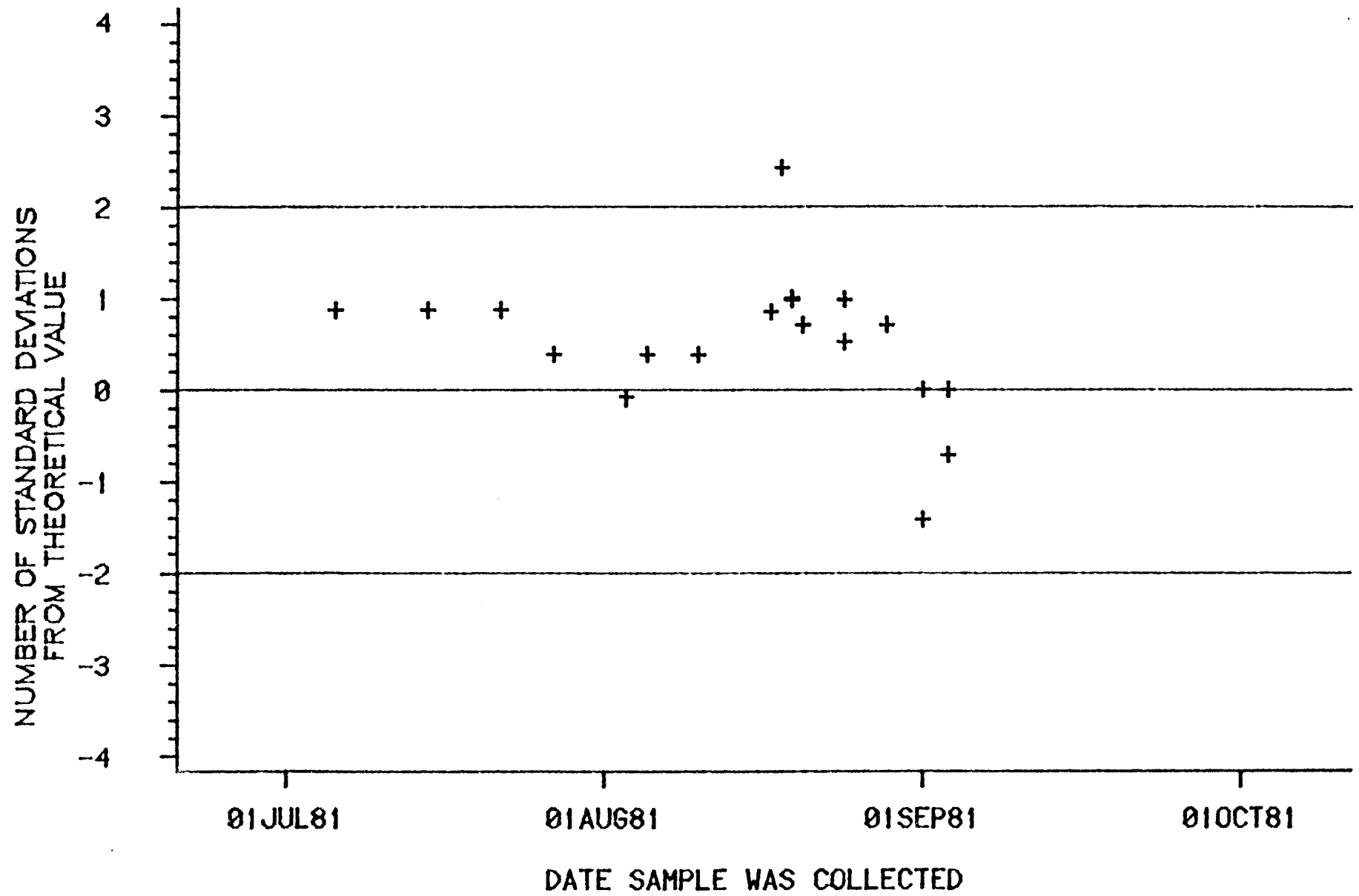


Figure A1.1.37.--Selenium data for the Atlanta Laboratory.

LAB=ATLANTA

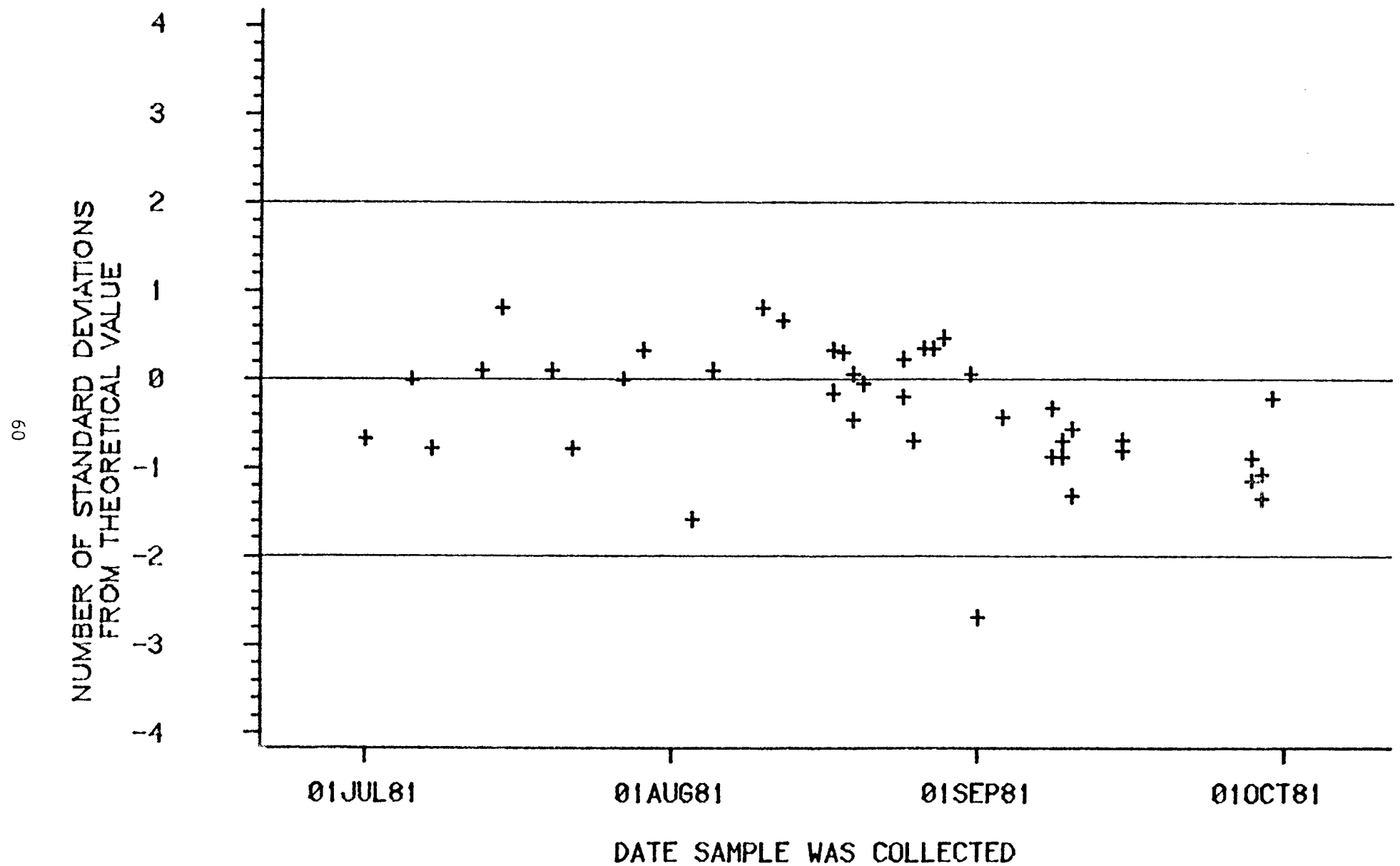


Figure A1.1.38.--Silica data for the Atlanta Laboratory.

LAB=ATLANTA

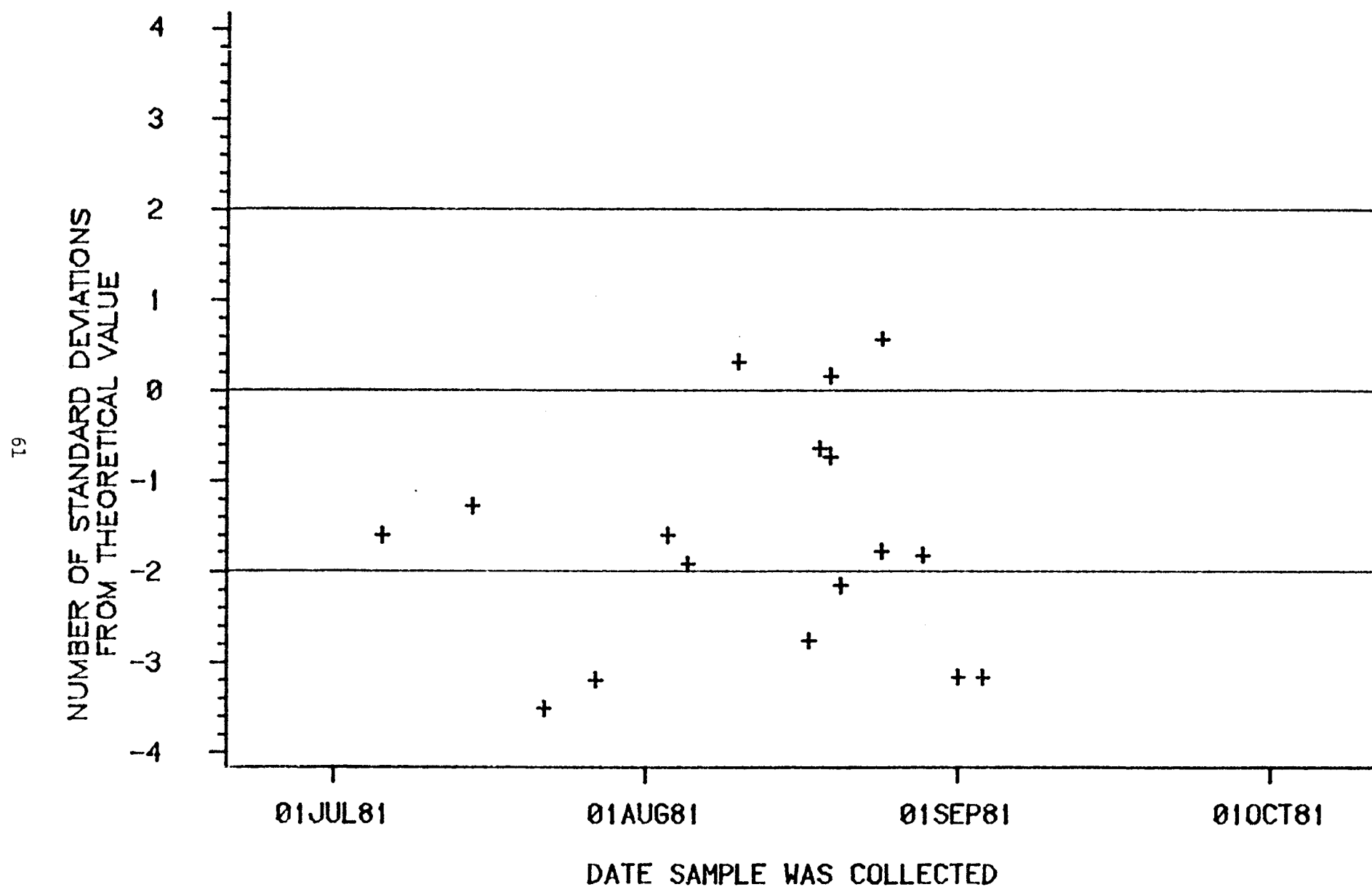


Figure A1.1.39.--Silver data for the Atlanta Laboratory.

LAB=ATLANTA

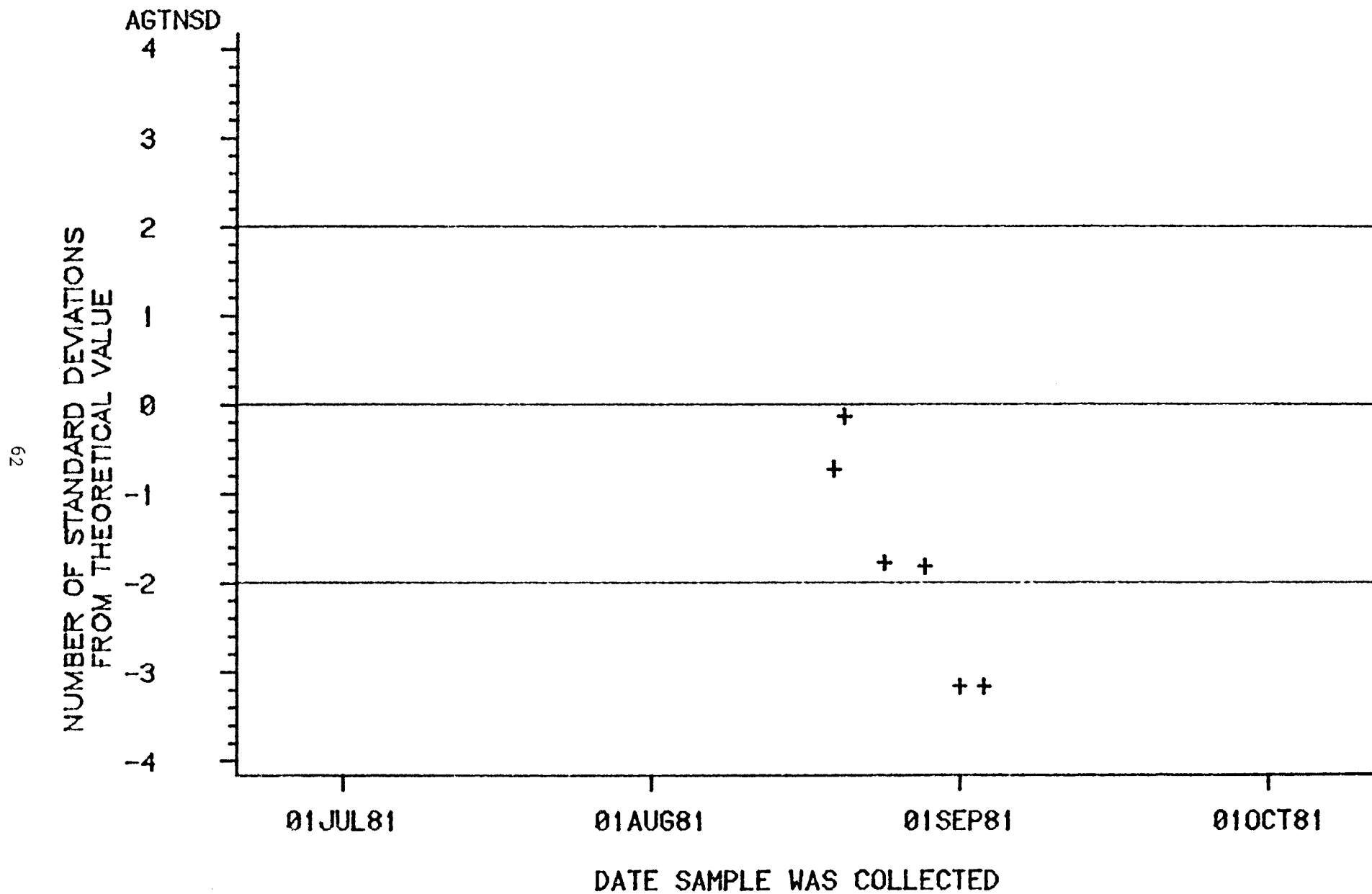


Figure A1.1.40.--Silver, total recoverable data for the Atlanta Laboratory.

LAB=ATLANTA

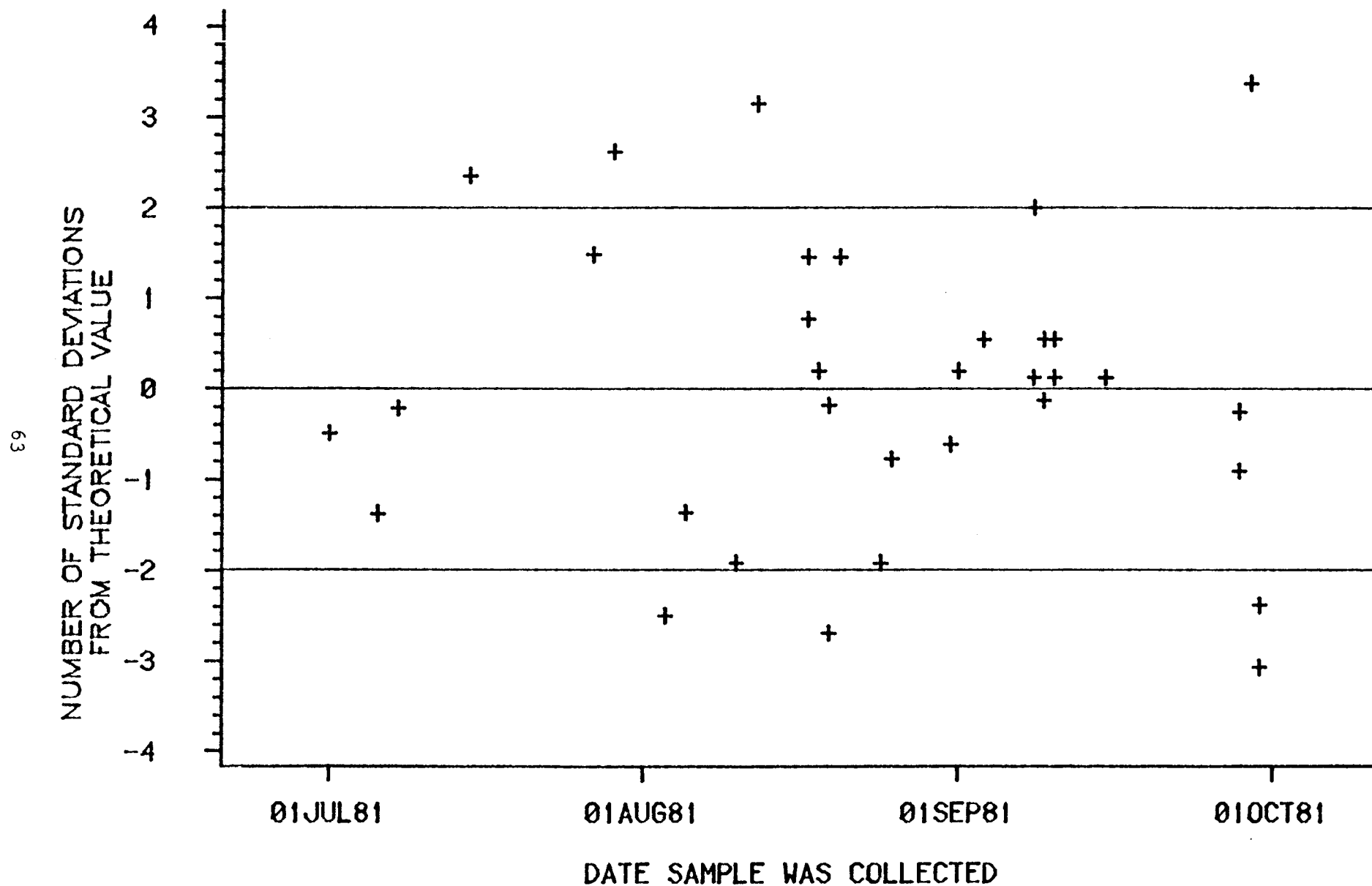


Figure A1.1.41.--Sodium data for the Atlanta Laboratory.
(One observation was out of range.)

LAB=ATLANTA

64

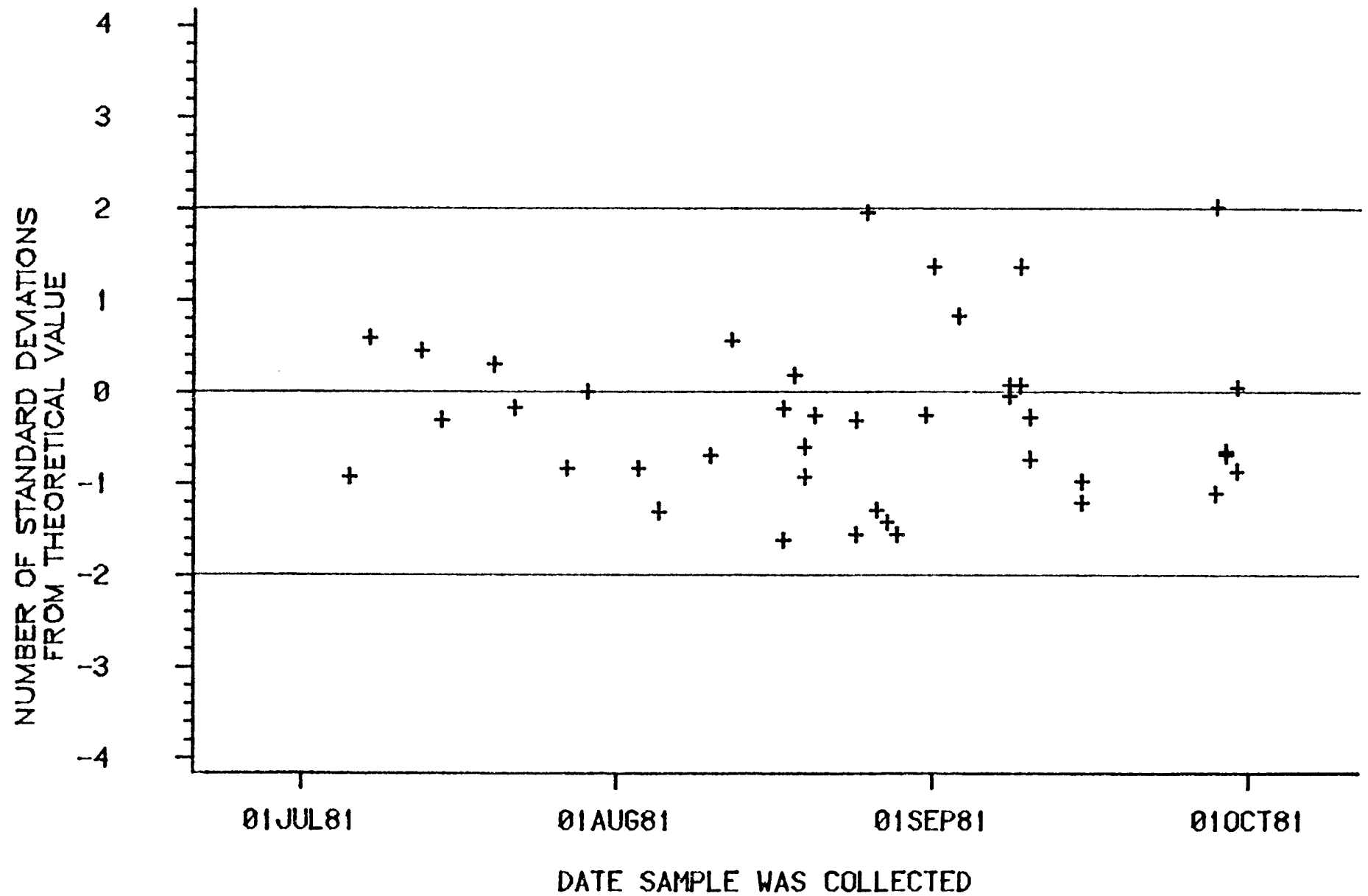


Figure A1.1.42.--Specific conductance data for the Atlanta Laboratory.
(One observation was out of range.)

LAB=ATLANTA

65

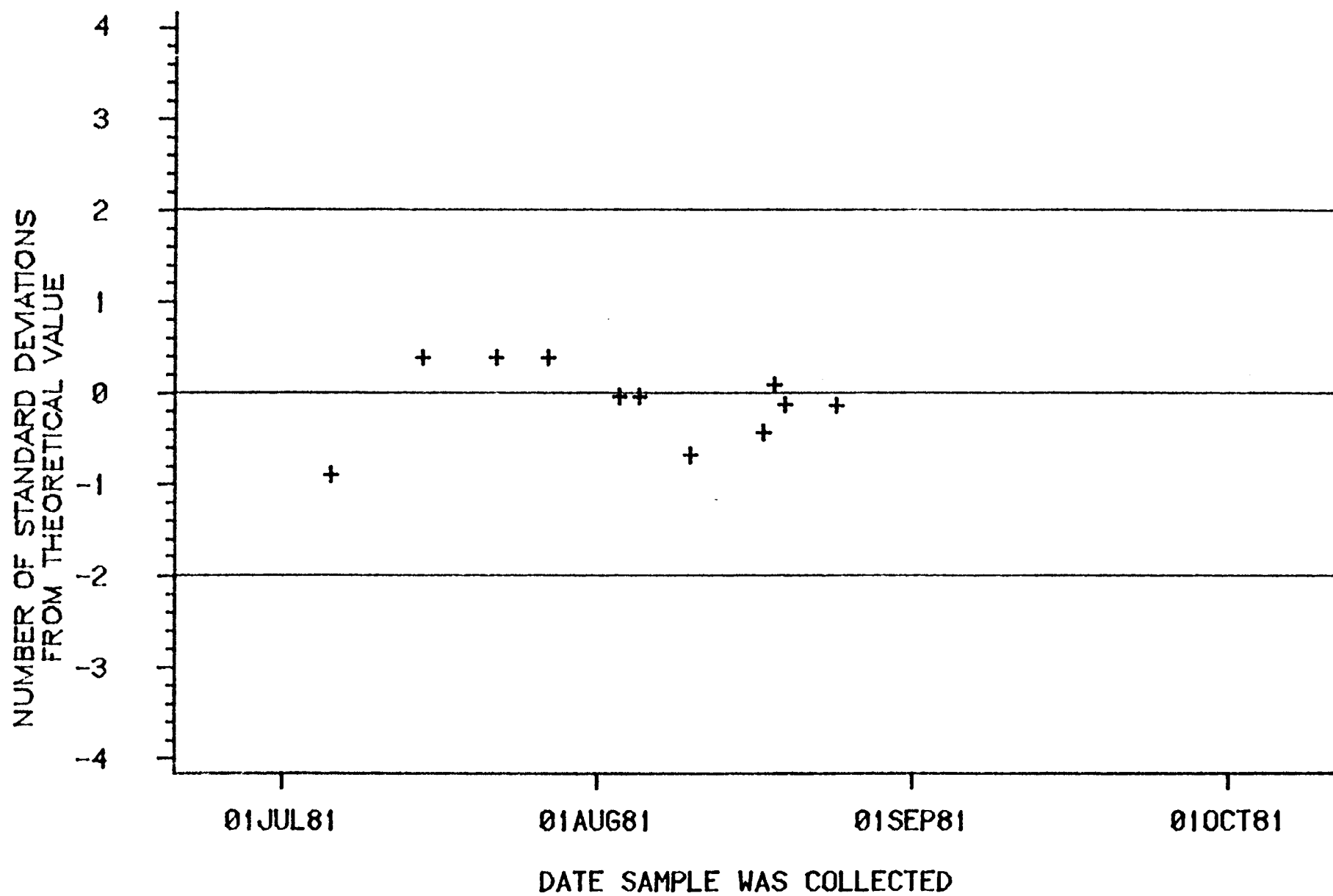


Figure A1.1.43.--Strontium data for the Atlanta Laboratory.

LAB=ATLANTA

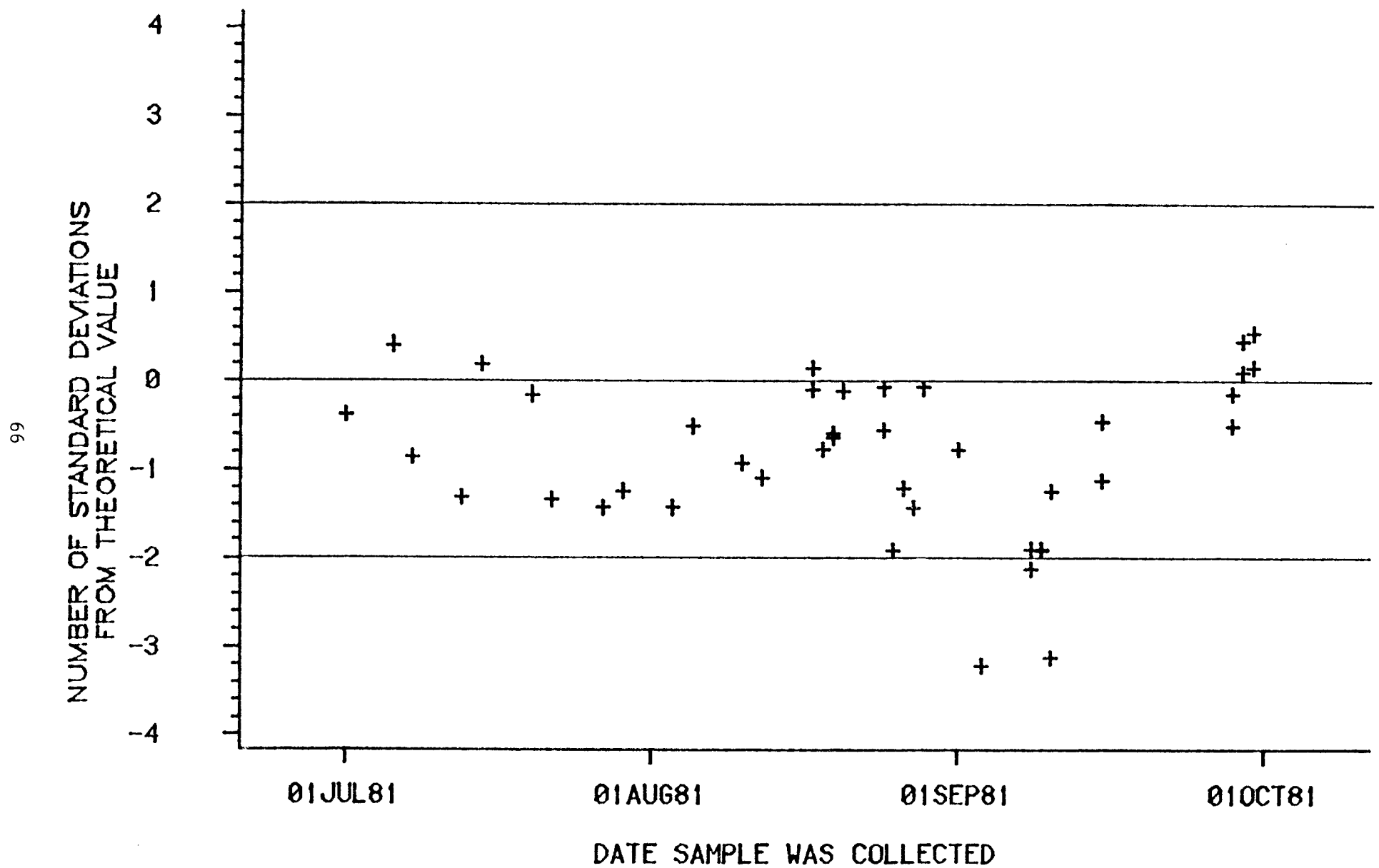


Figure A1.1.44.--Sulfate data for the Atlanta Laboratory.
(One observation was out of range.)

LAB=ATLANTA

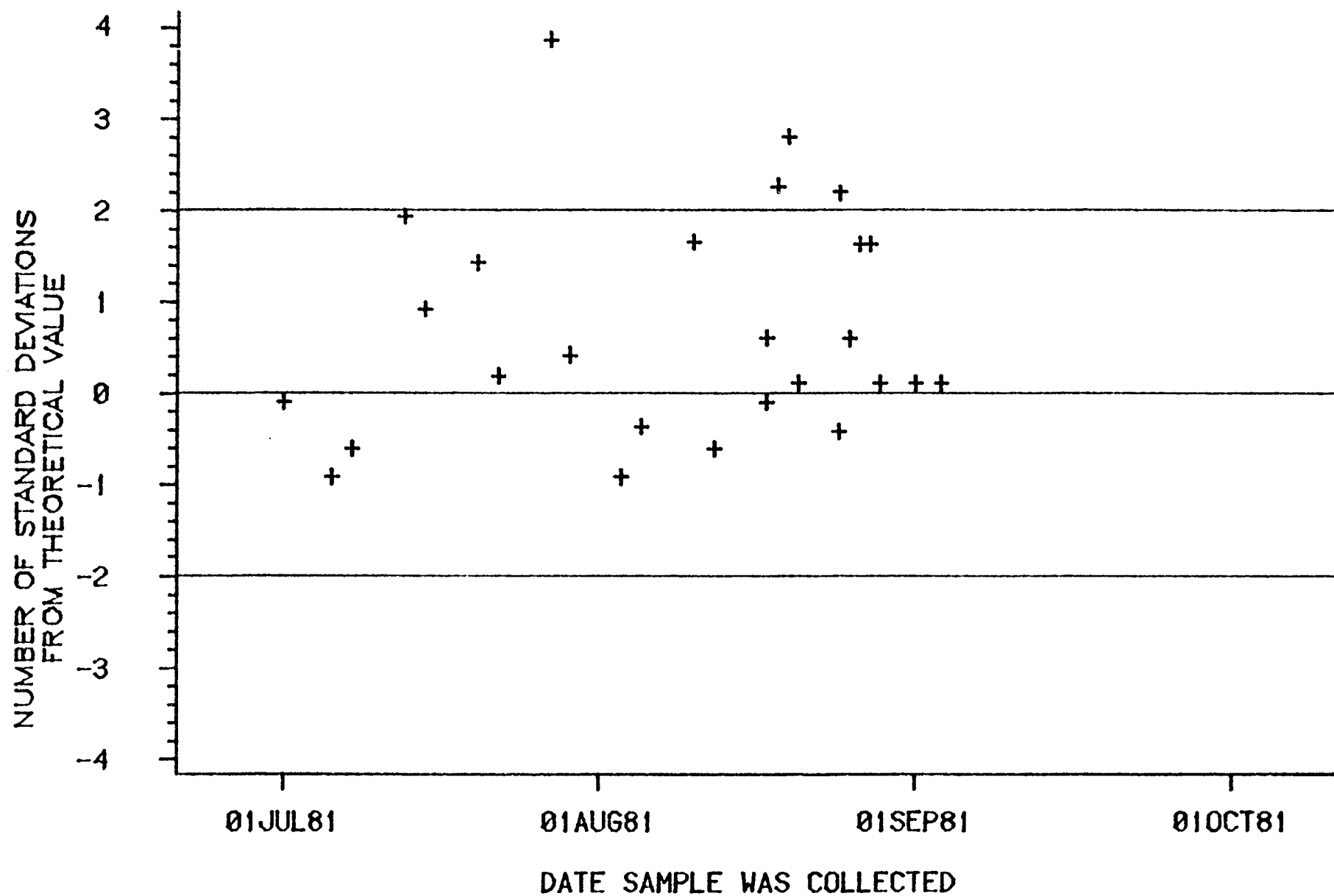


Figure A1.1.45.--Zinc data for the Atlanta Laboratory.
(One observation was out of range.)

LAB=ATLANTA

89

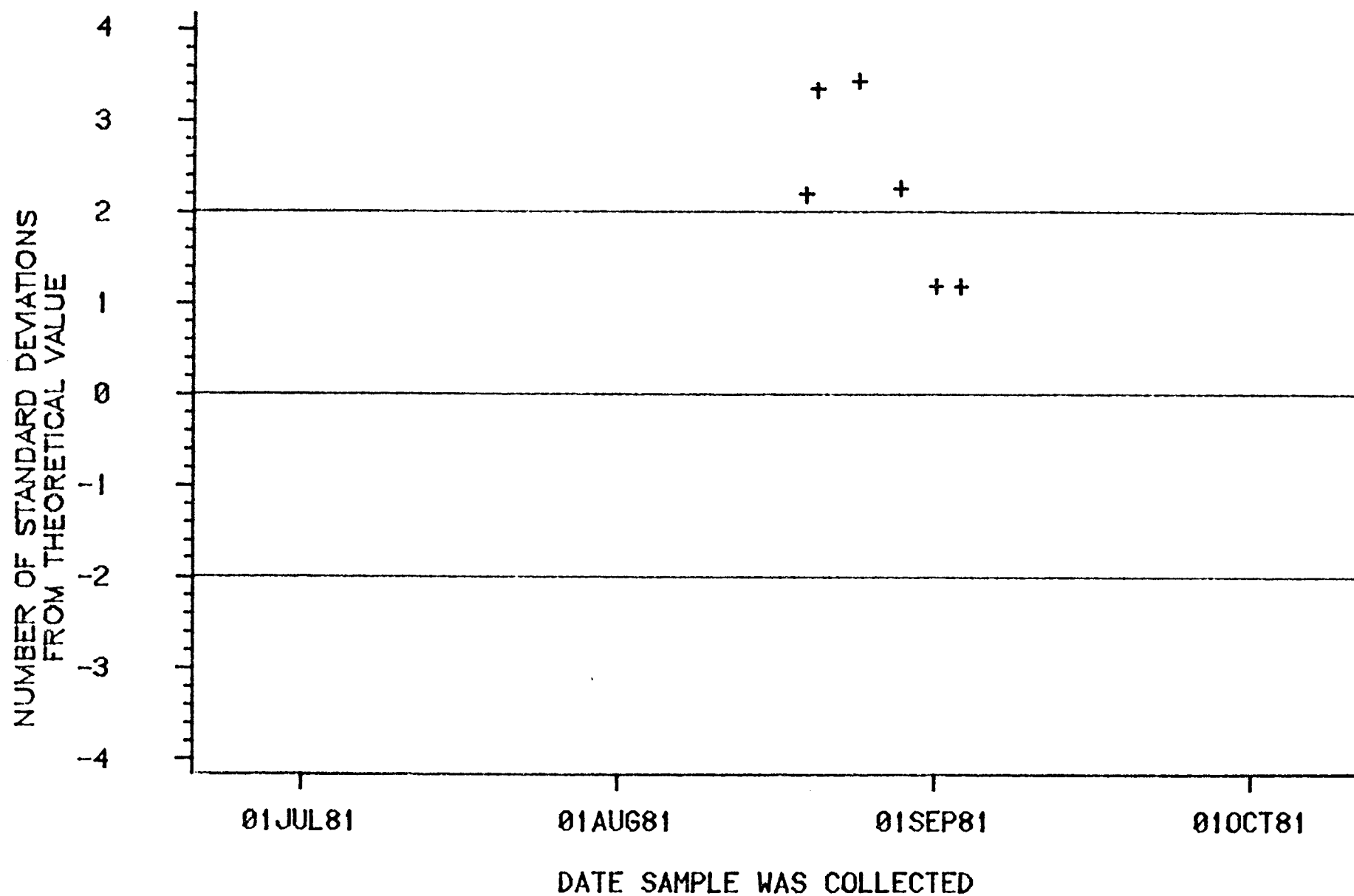


Figure A1.1.46.--Zinc, total recoverable data for the Atlanta Laboratory.

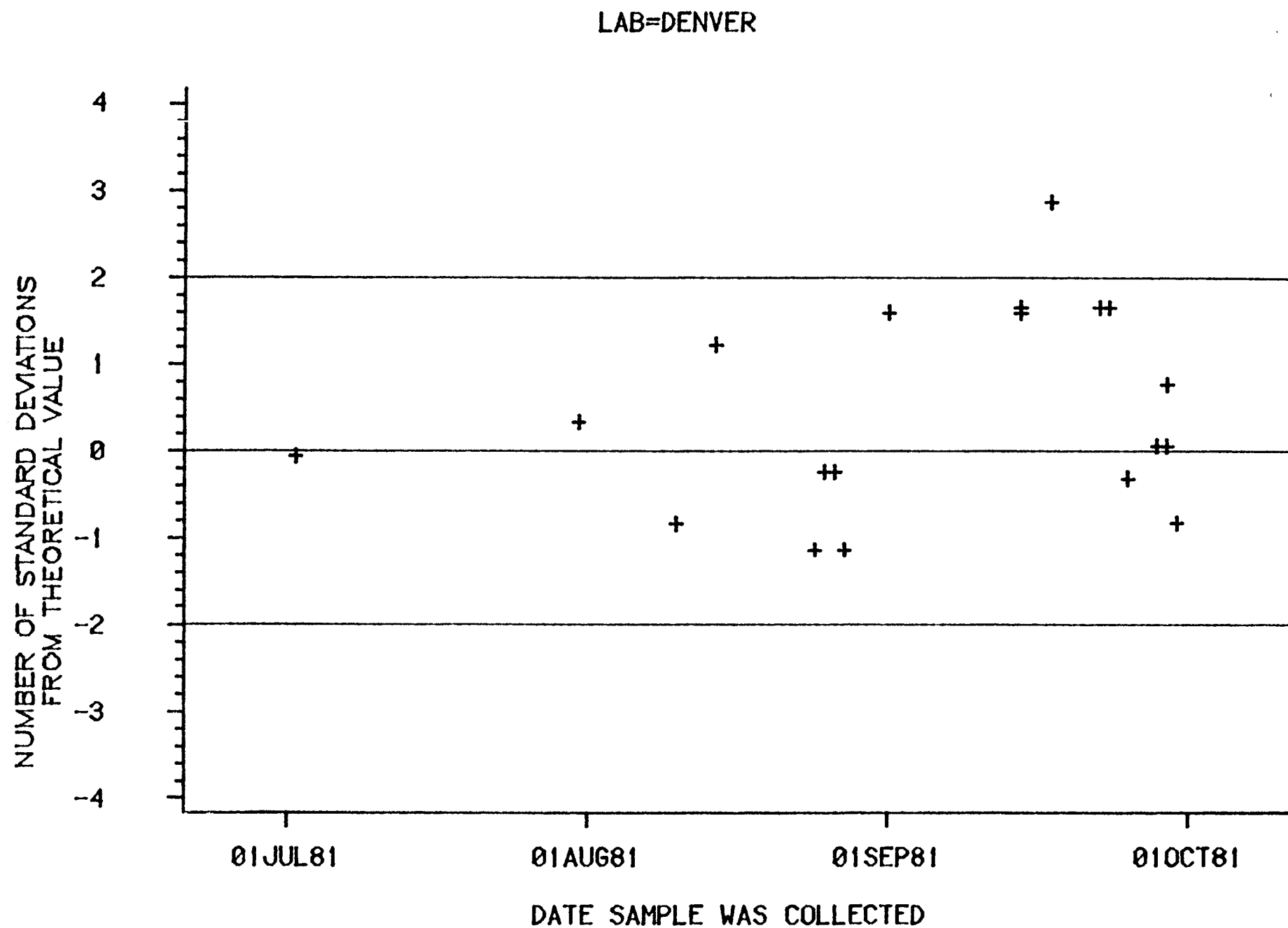


Figure A1.2.1.--Alkalinity data for the Denver Laboratory.

LAB=DENVER

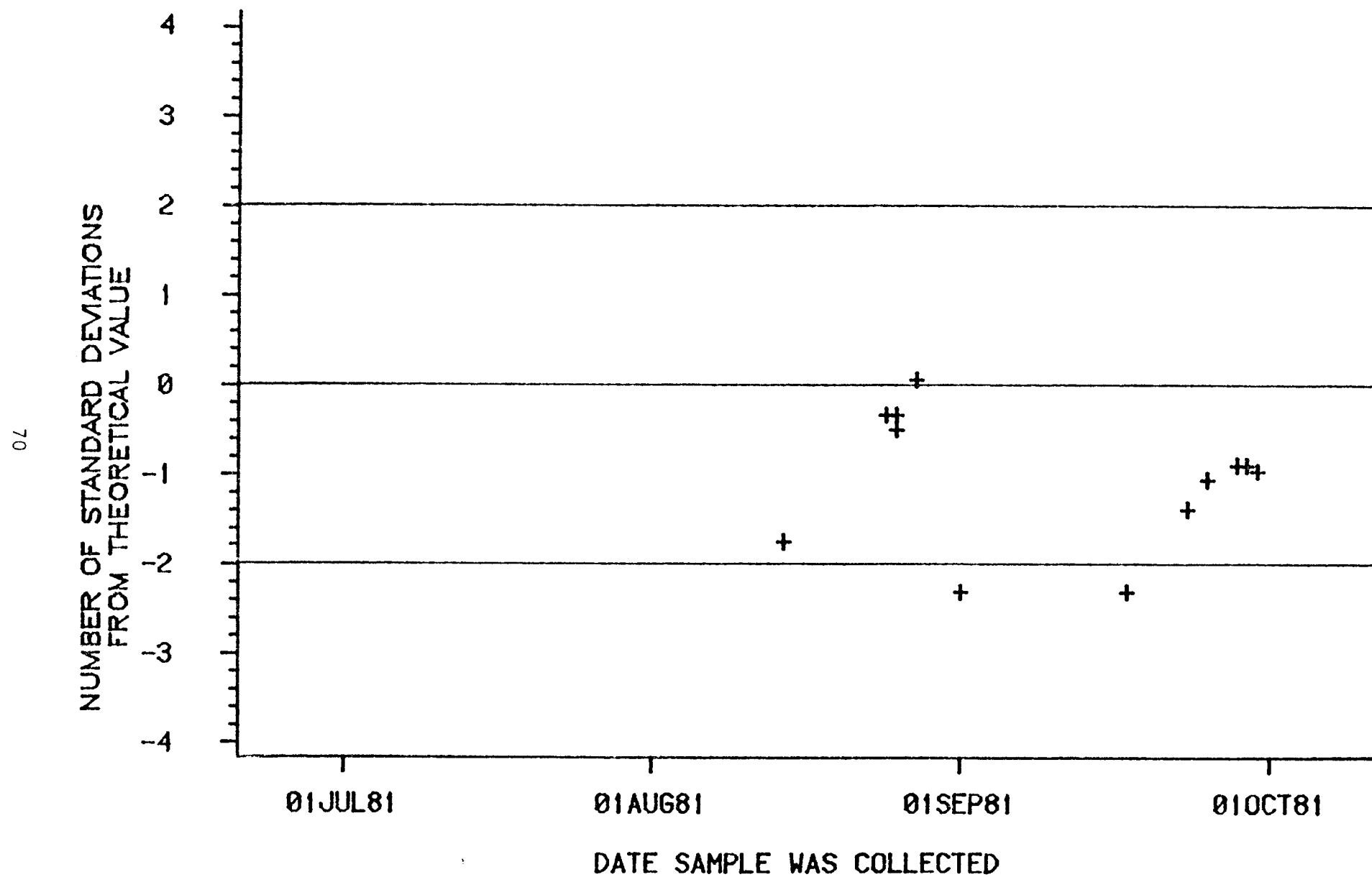


Figure A1.2.2.--Aluminum data for the Denver Laboratory.

LAB=DENVER

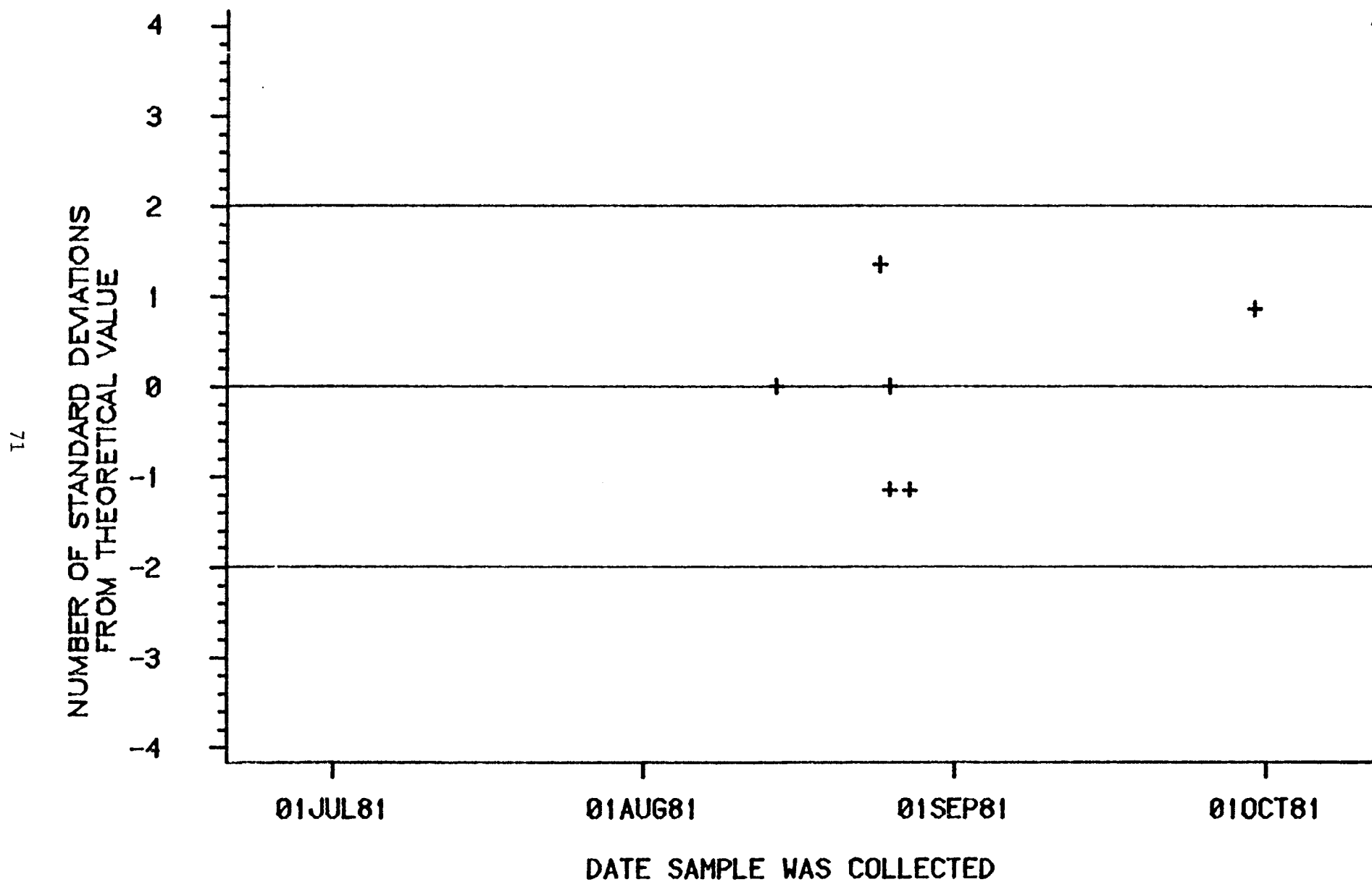


Figure A1.2.3.--Antimony data for the Denver Laboratory.

LAB=DENVER

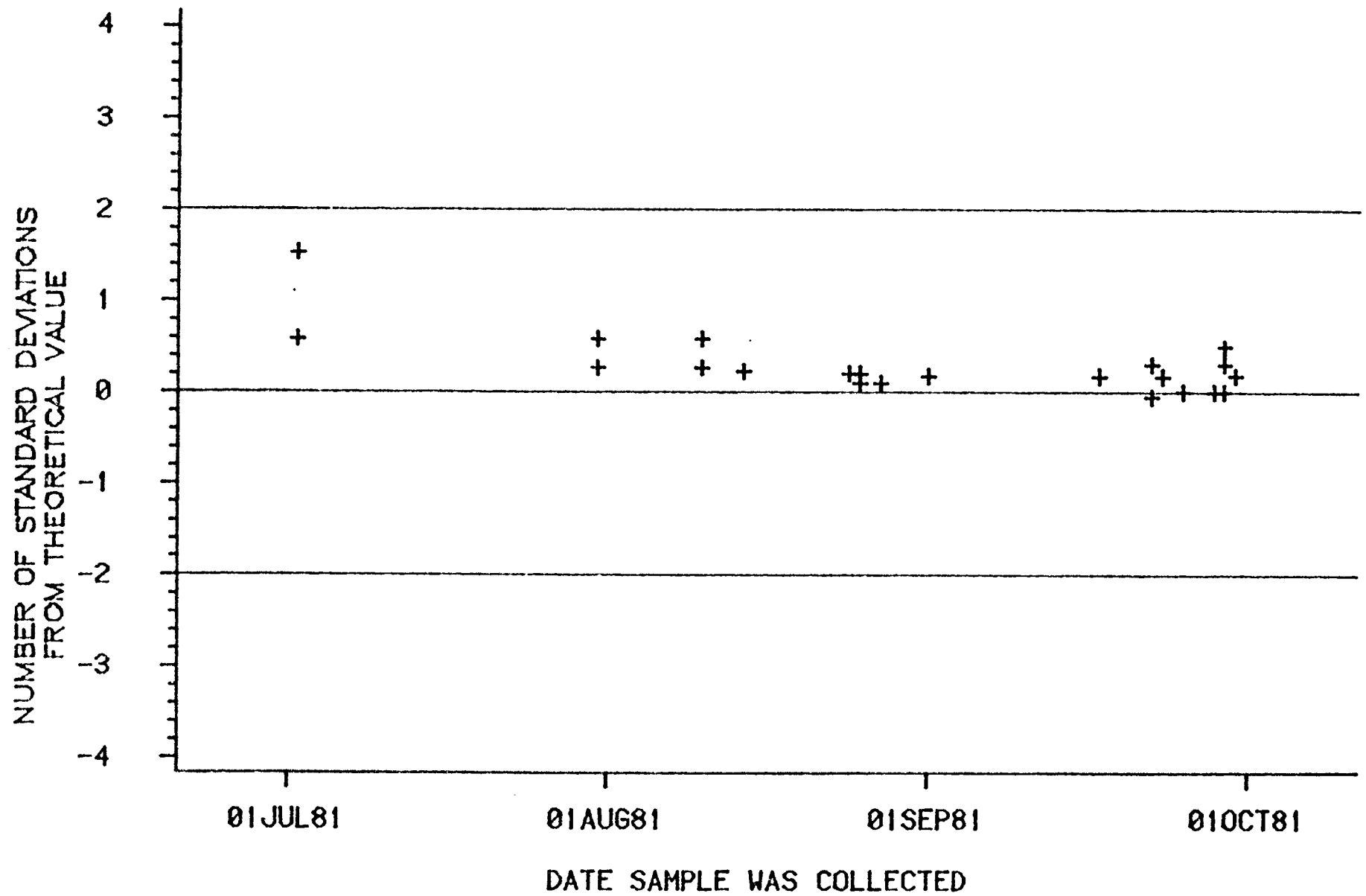


Figure A1.2.4.--Arsenic data for the Denver Laboratory.

LAB=DENVER

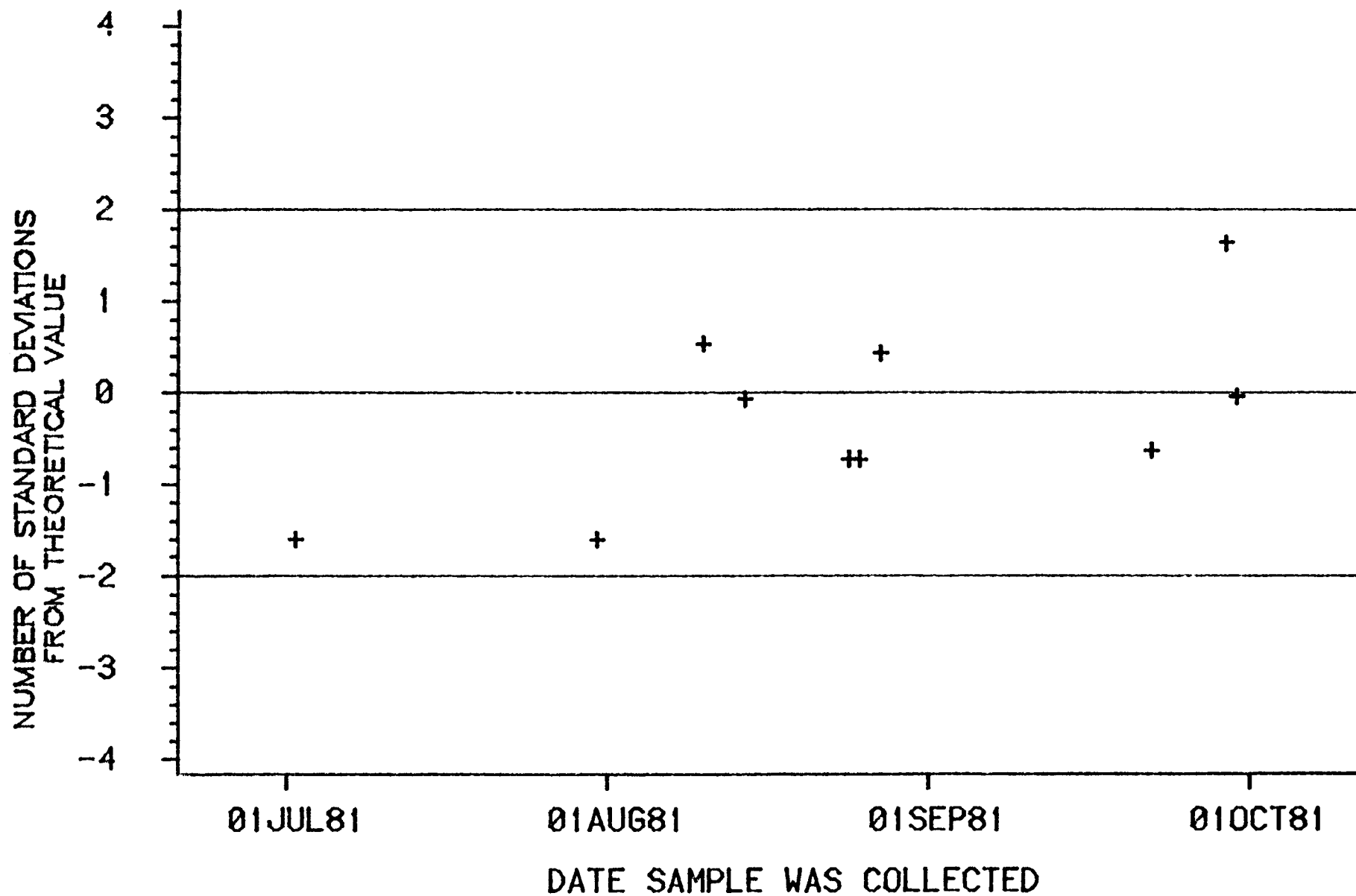


Figure A1.2.5-- Barium data for the Denver Laboratory.

LAB=DENVER

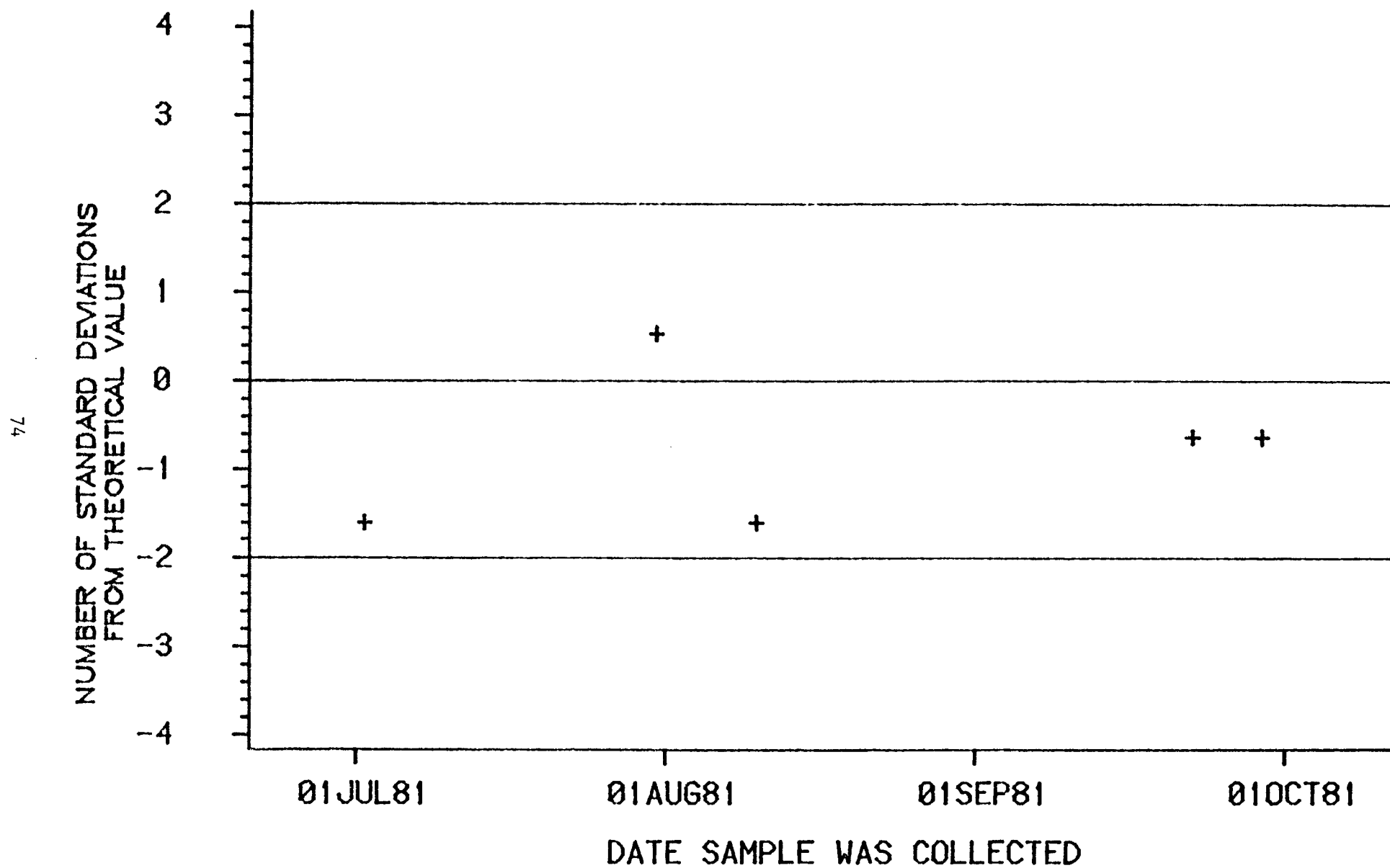


Figure A1.2.6.--Barium, total recoverable data for the Denver Laboratory.

LAB=DENVER

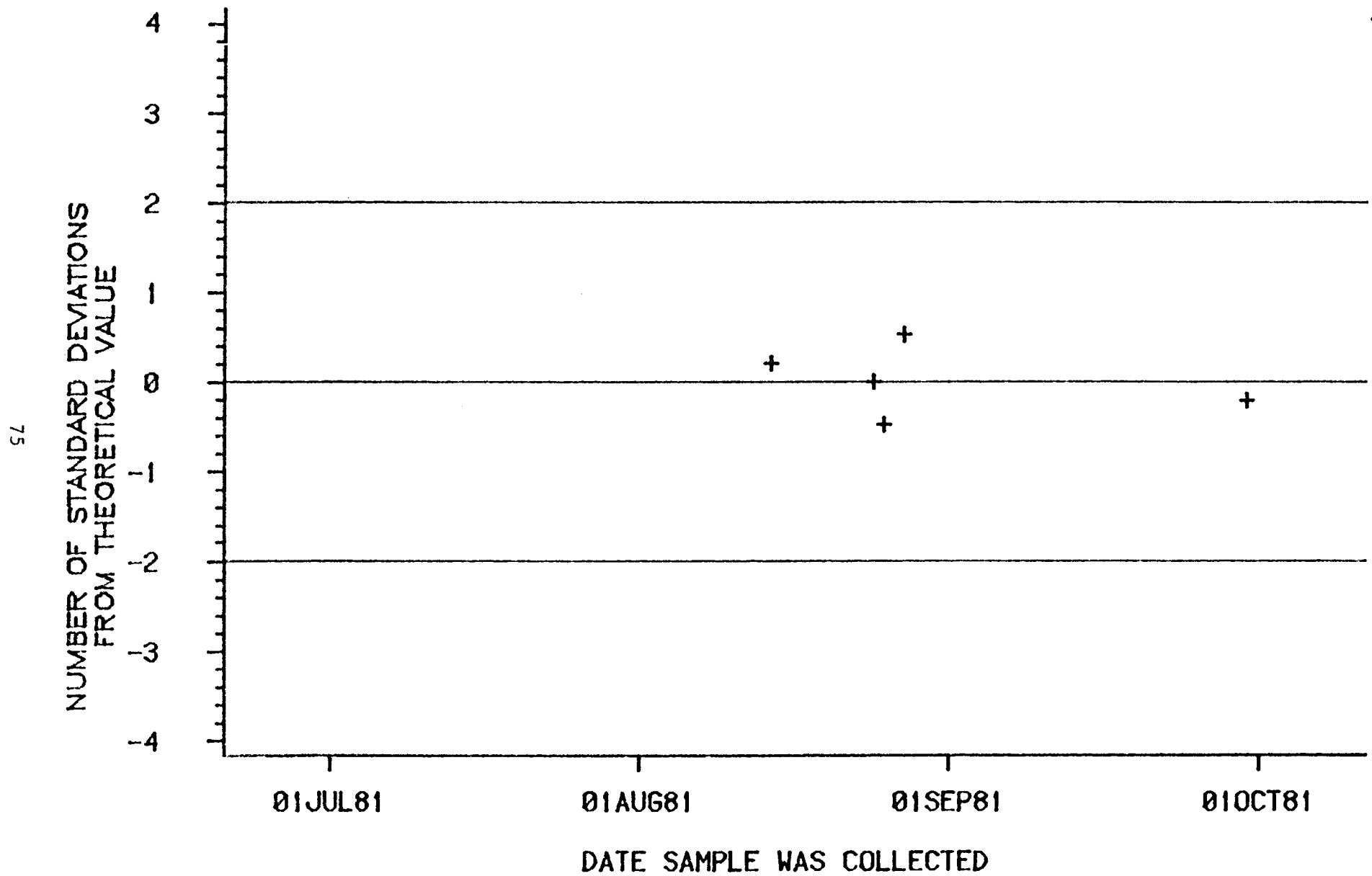


Figure A1.2.7.--Beryllium data for the Denver Laboratory.

LAB=DENVER

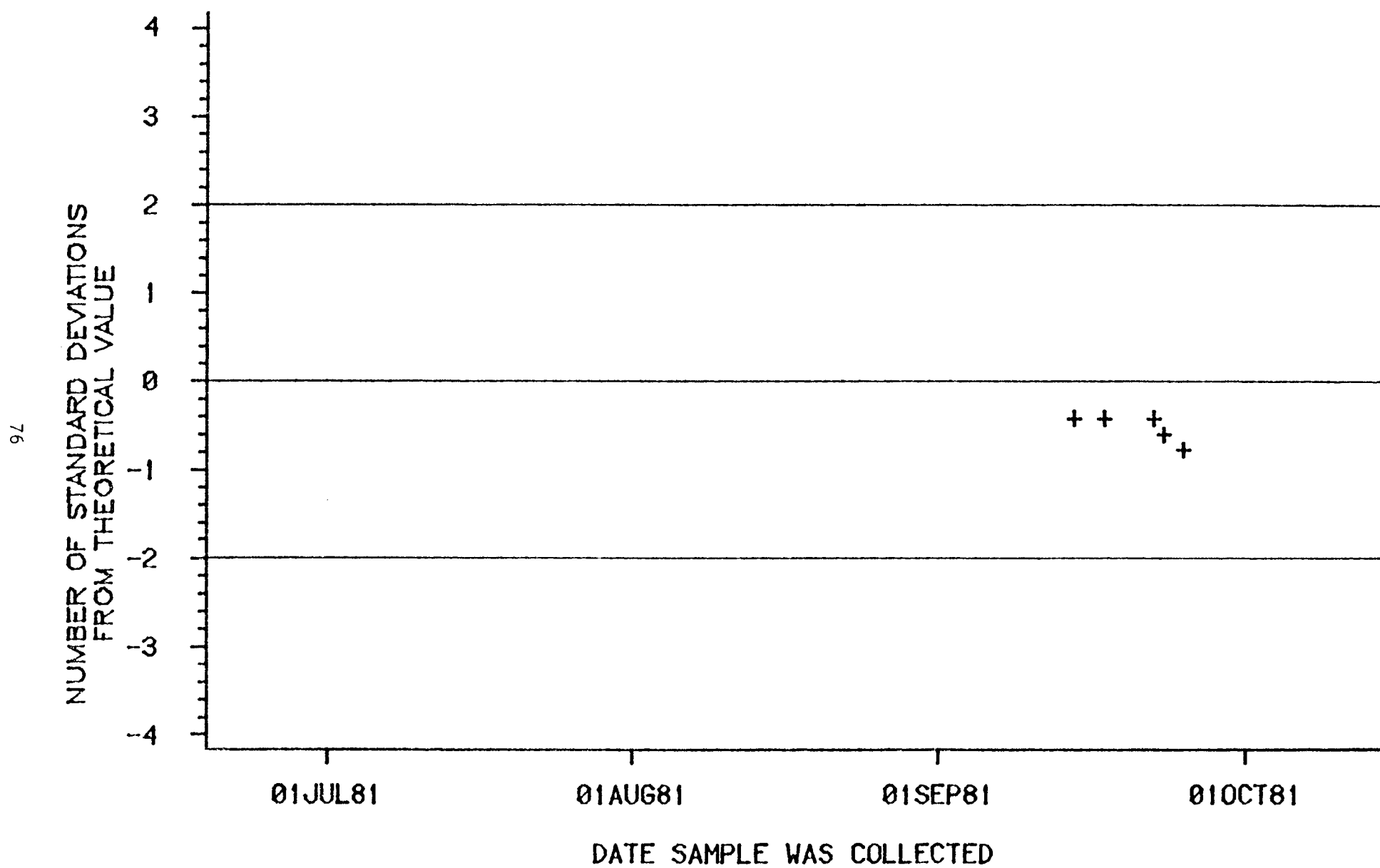


Figure A1.2.8.--Boron data for the Denver Laboratory.

LAB=DENVER

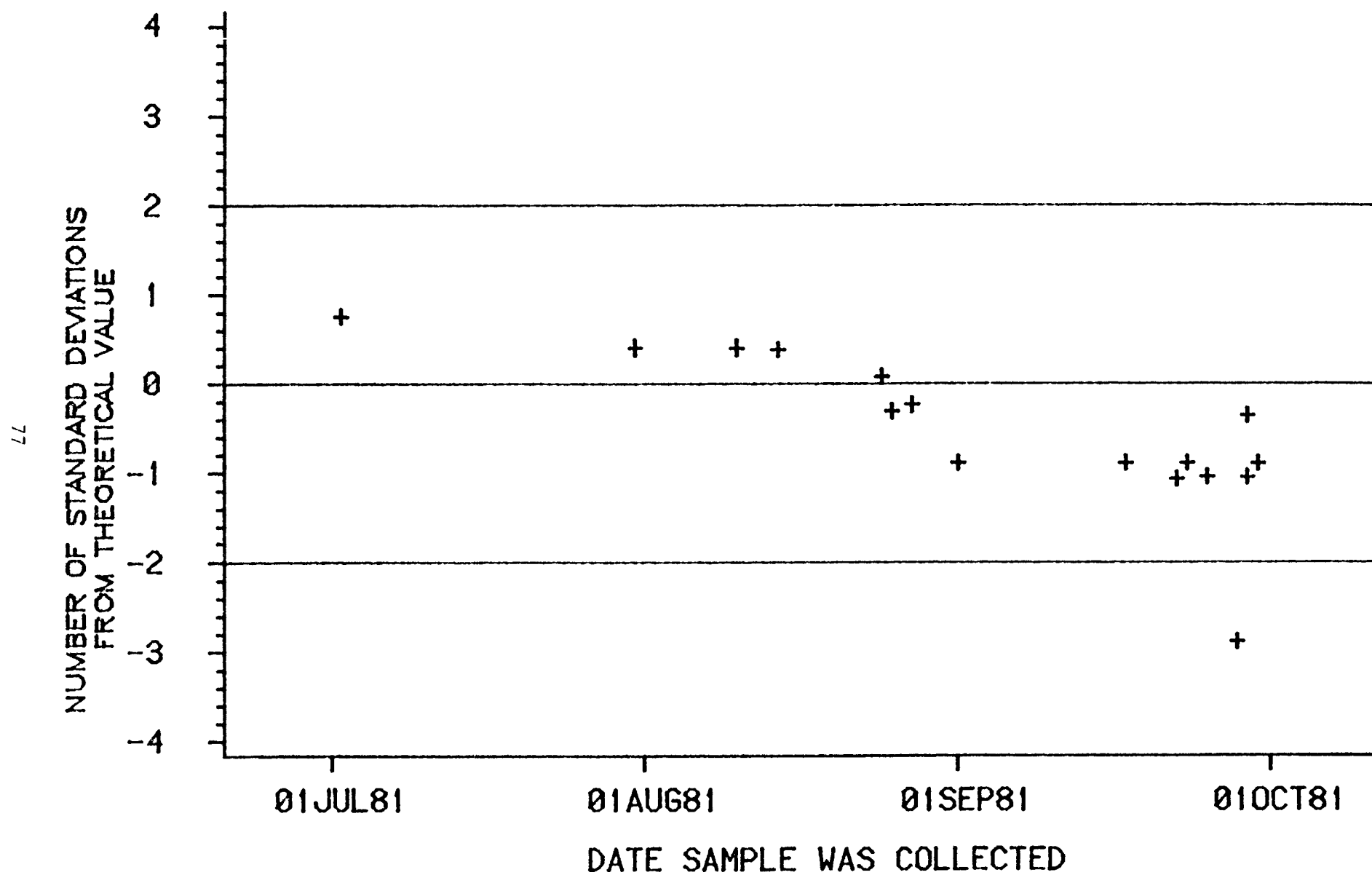


Figure A1.2.9.--Cadmium data for the Denver Laboratory.

LAB=DENVER

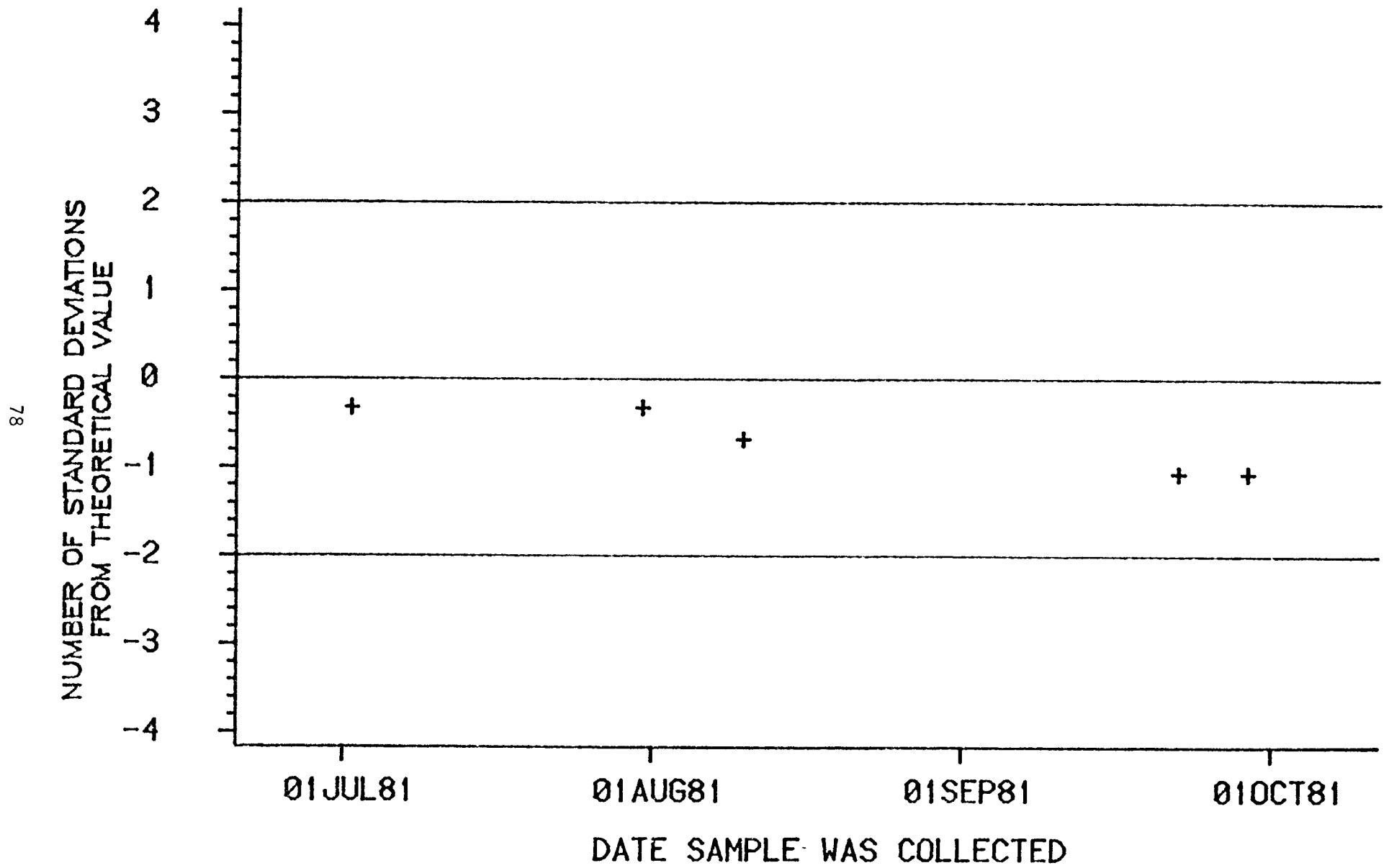


Figure A1.2.10.--Cadmium, total recoverable data for the Denver Laboratory.

LAB=DENVER

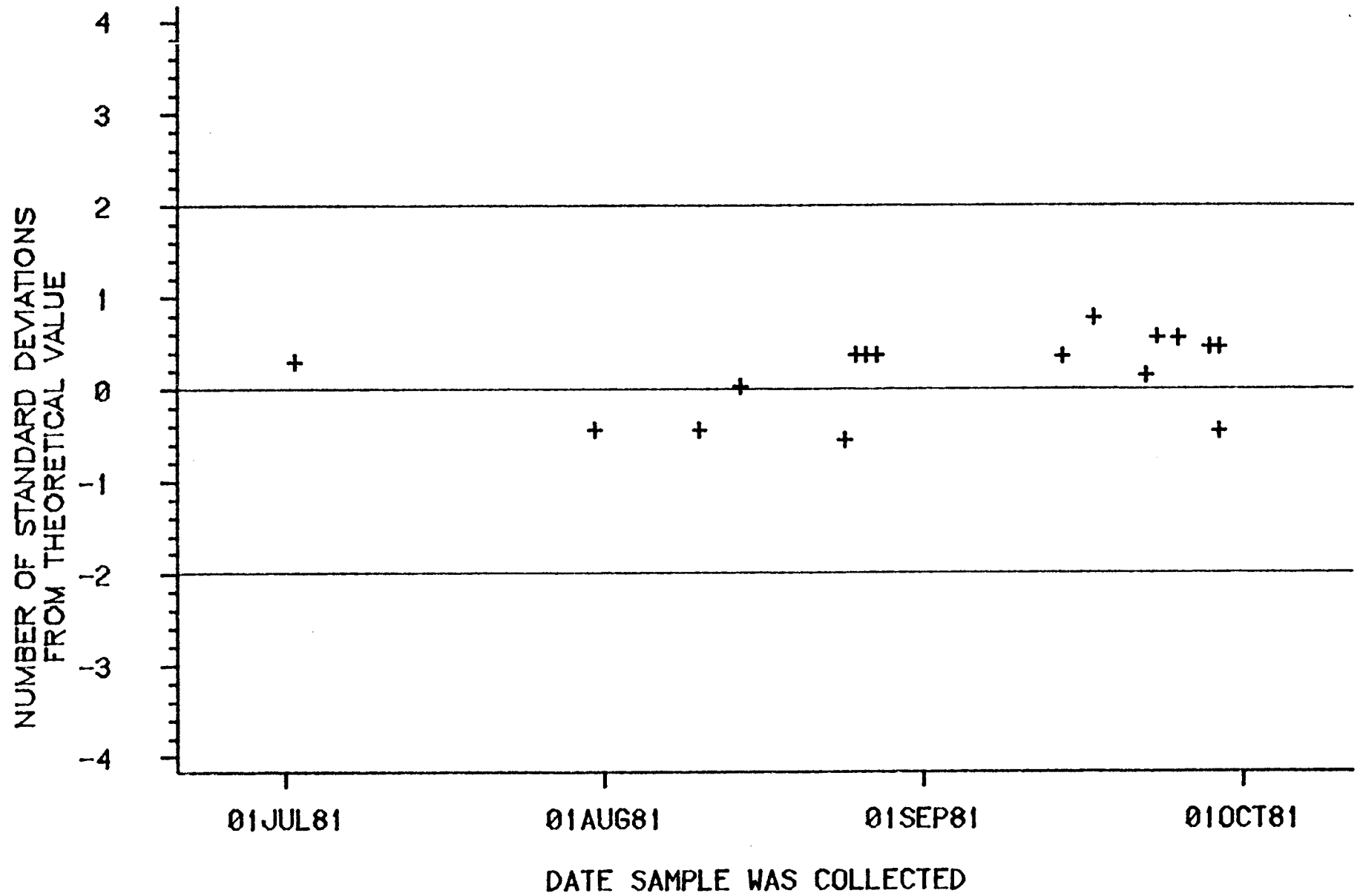


Figure A1.2.11.--Calcium data for the Denver Laboratory.

LAB=DENVER

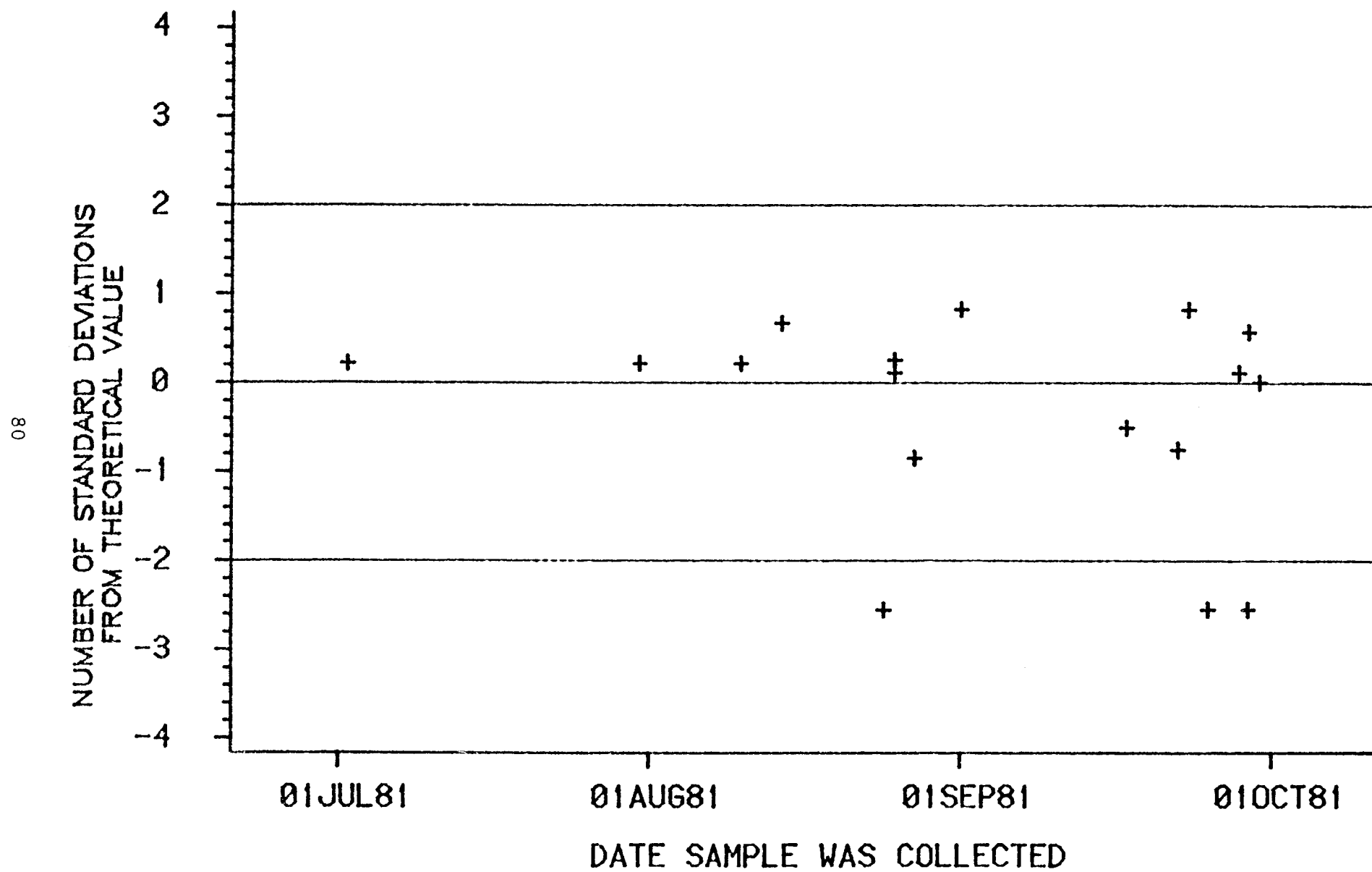


Figure A1.2.12.--Chromium data for the Denver Laboratory.

LAB=DENVER

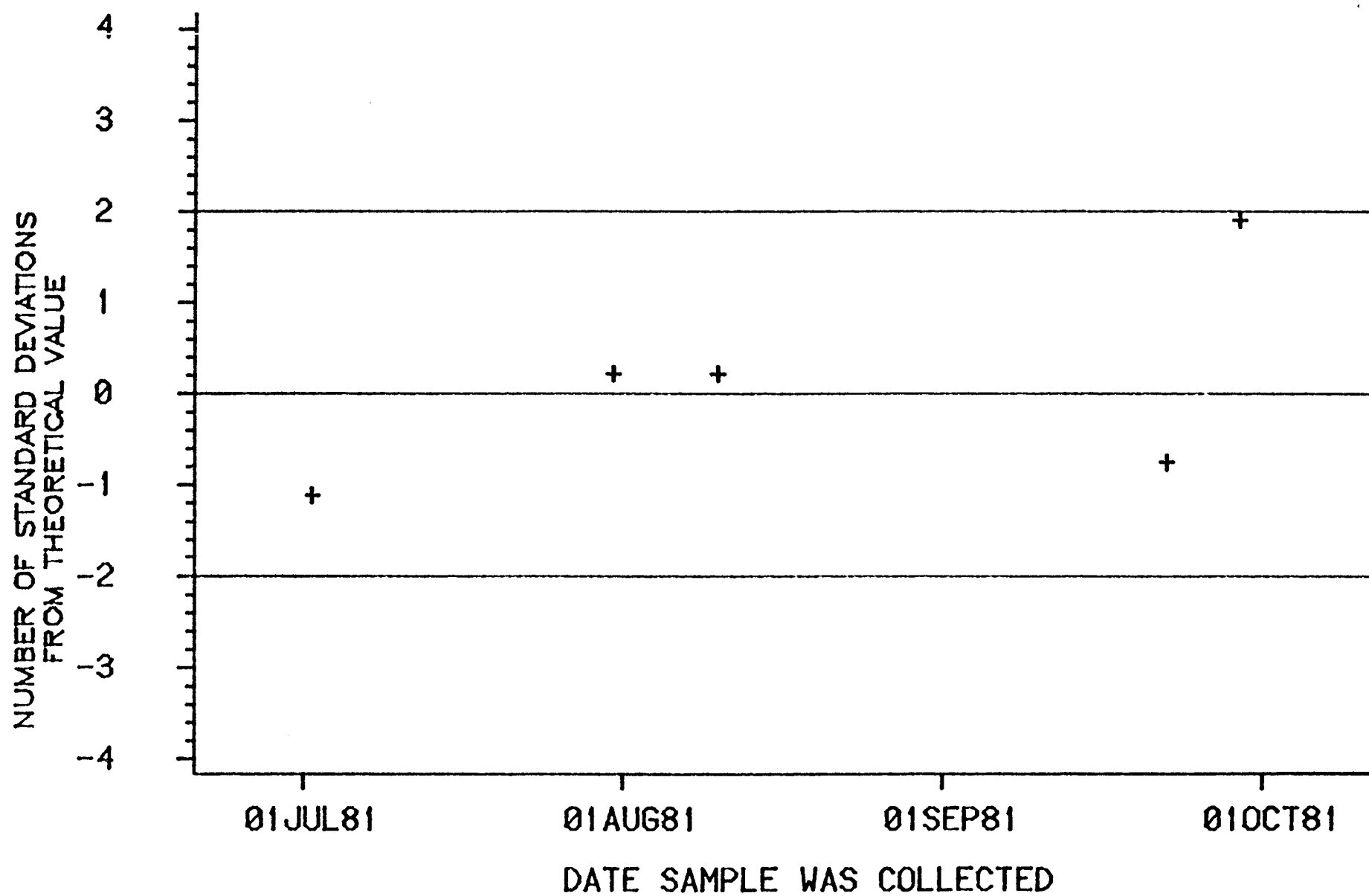


Figure A1.2.13.--Chromium, total recoverable data for the Denver Laboratory.

LAB=DENVER

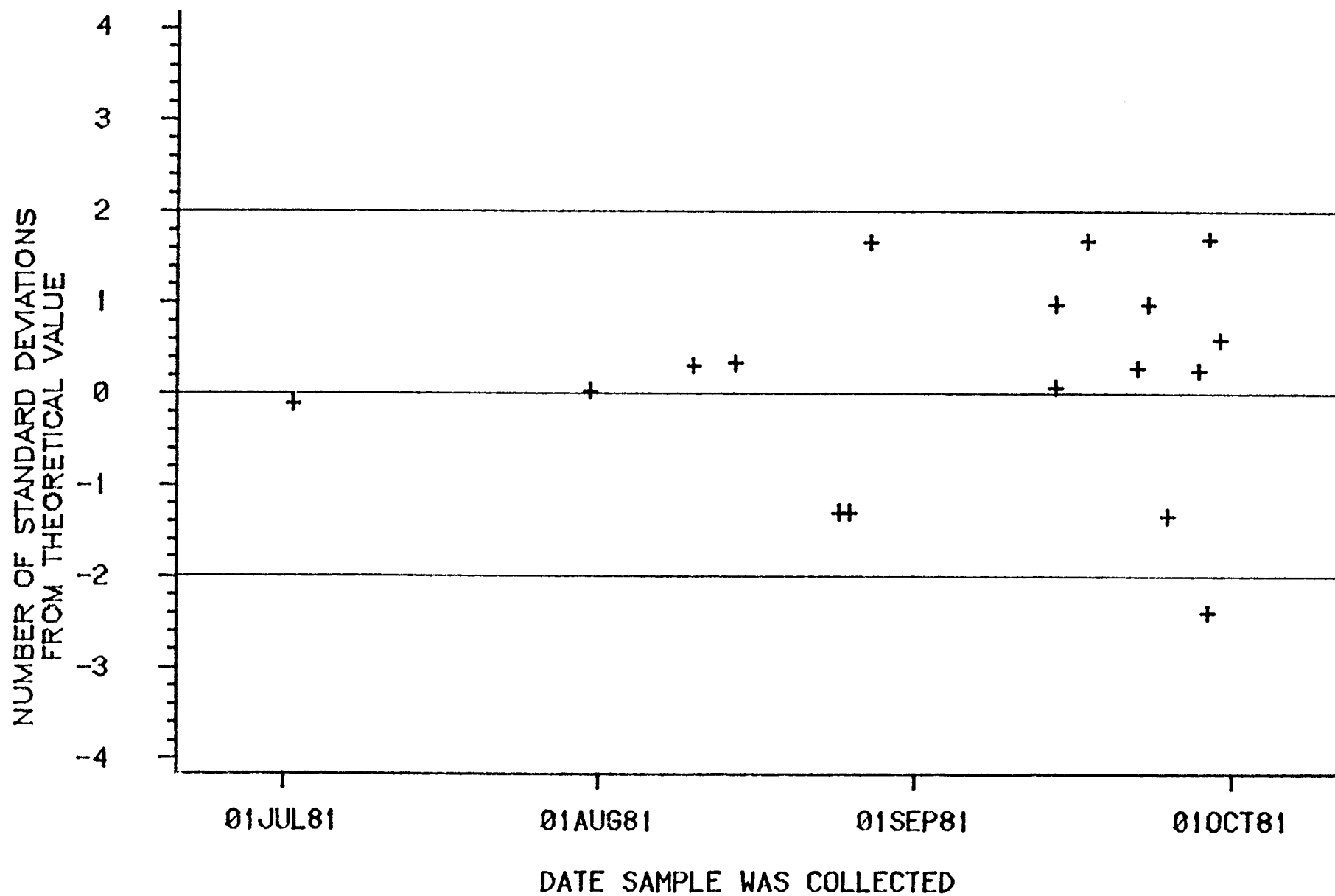


Figure A1.2.14.--Chloride data for the Denver Laboratory.
(Two observations were out of range.)

LAB=DENVER

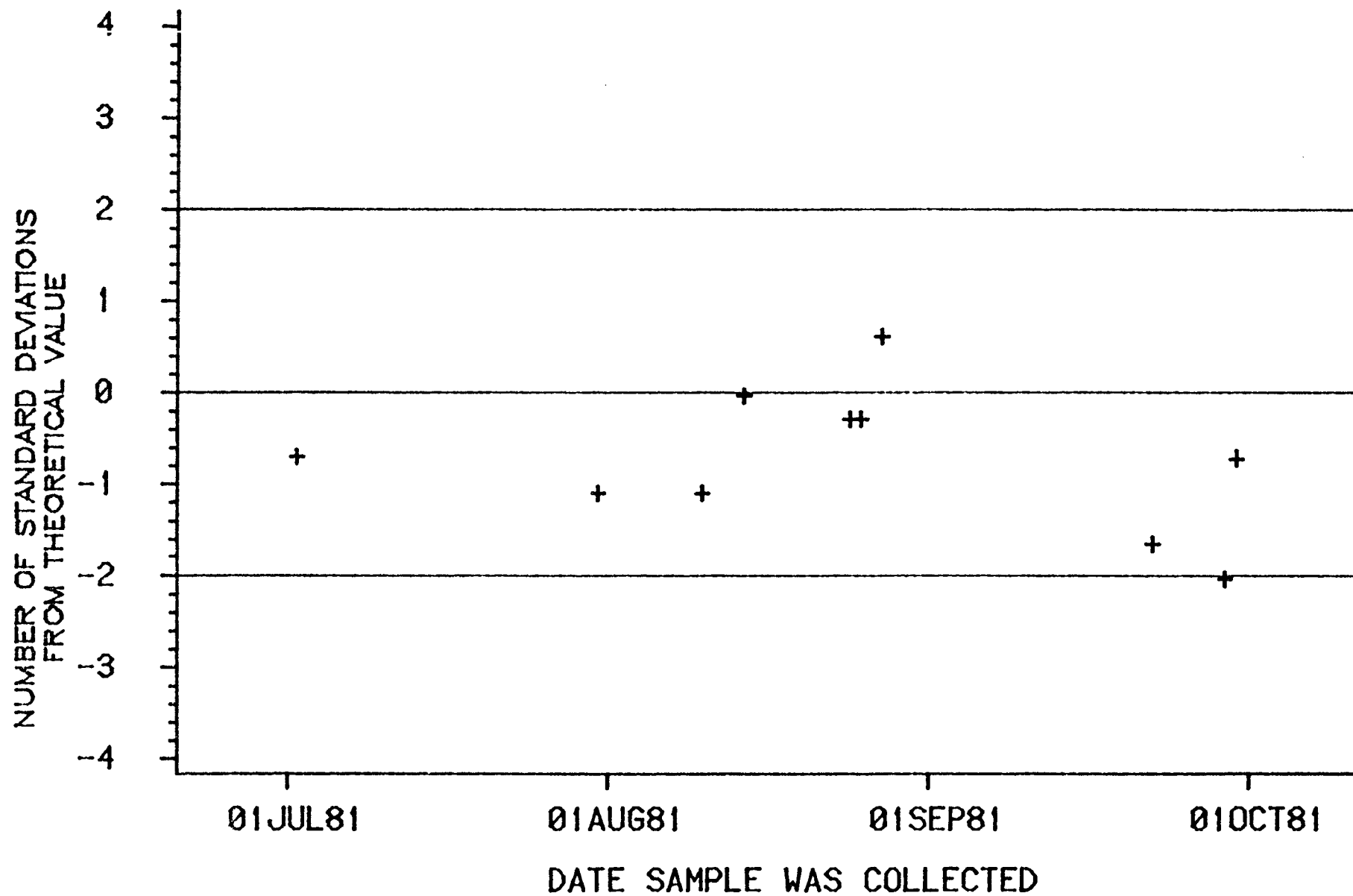


Figure A1.2.15.--Cobalt data for the Denver Laboratory.

LAB=DENVER

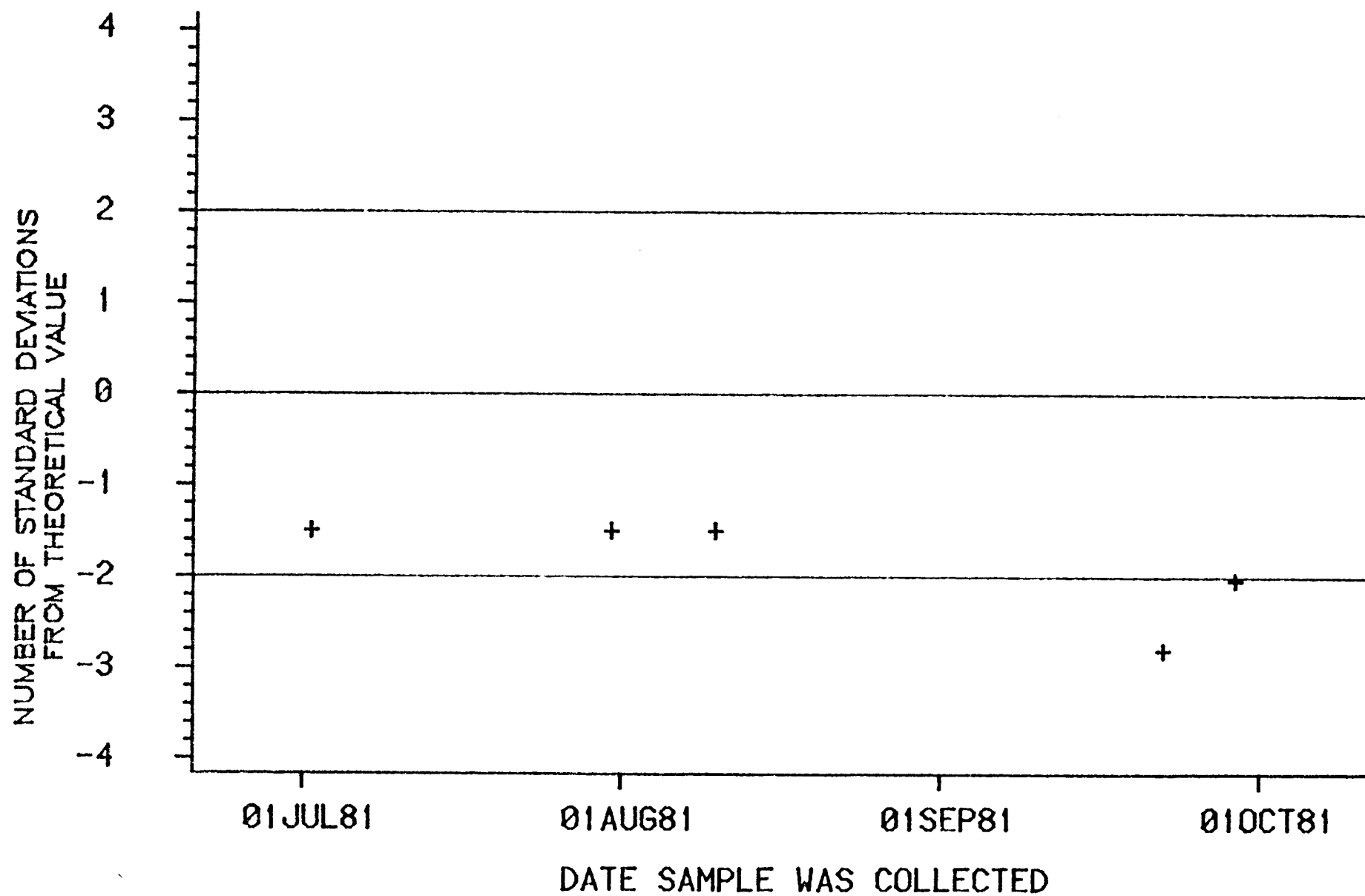


Figure A1.2.16.--Cobalt, total recoverable data for the Denver Laboratory.

LAB=DENVER

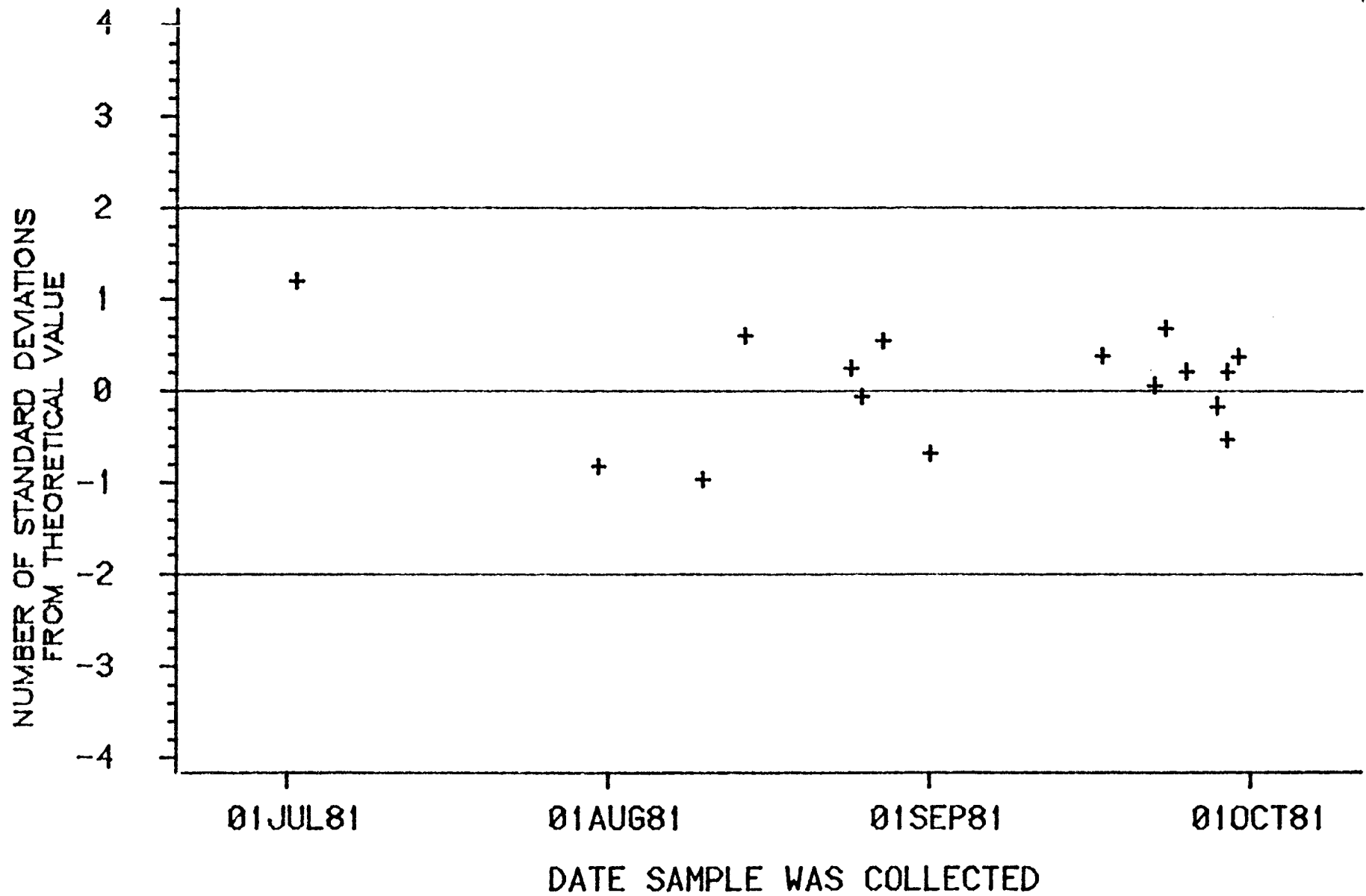


Figure A1.2.17.--Copper data for the Denver Laboratory.

LAB=DENVER

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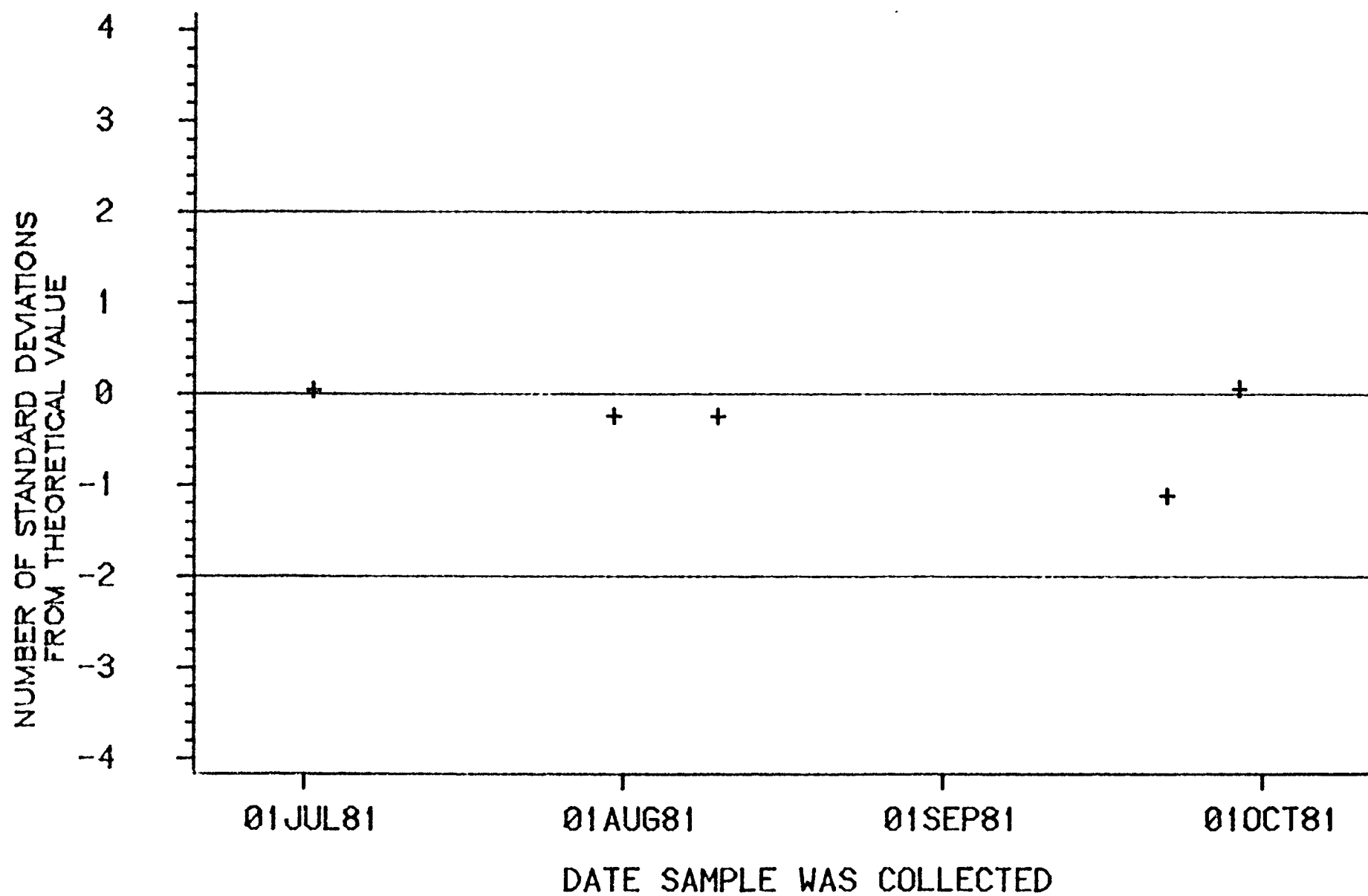


Figure A1.2.18.--Copper, total recoverable data for the Denver Laboratory.

LAB=DENVER

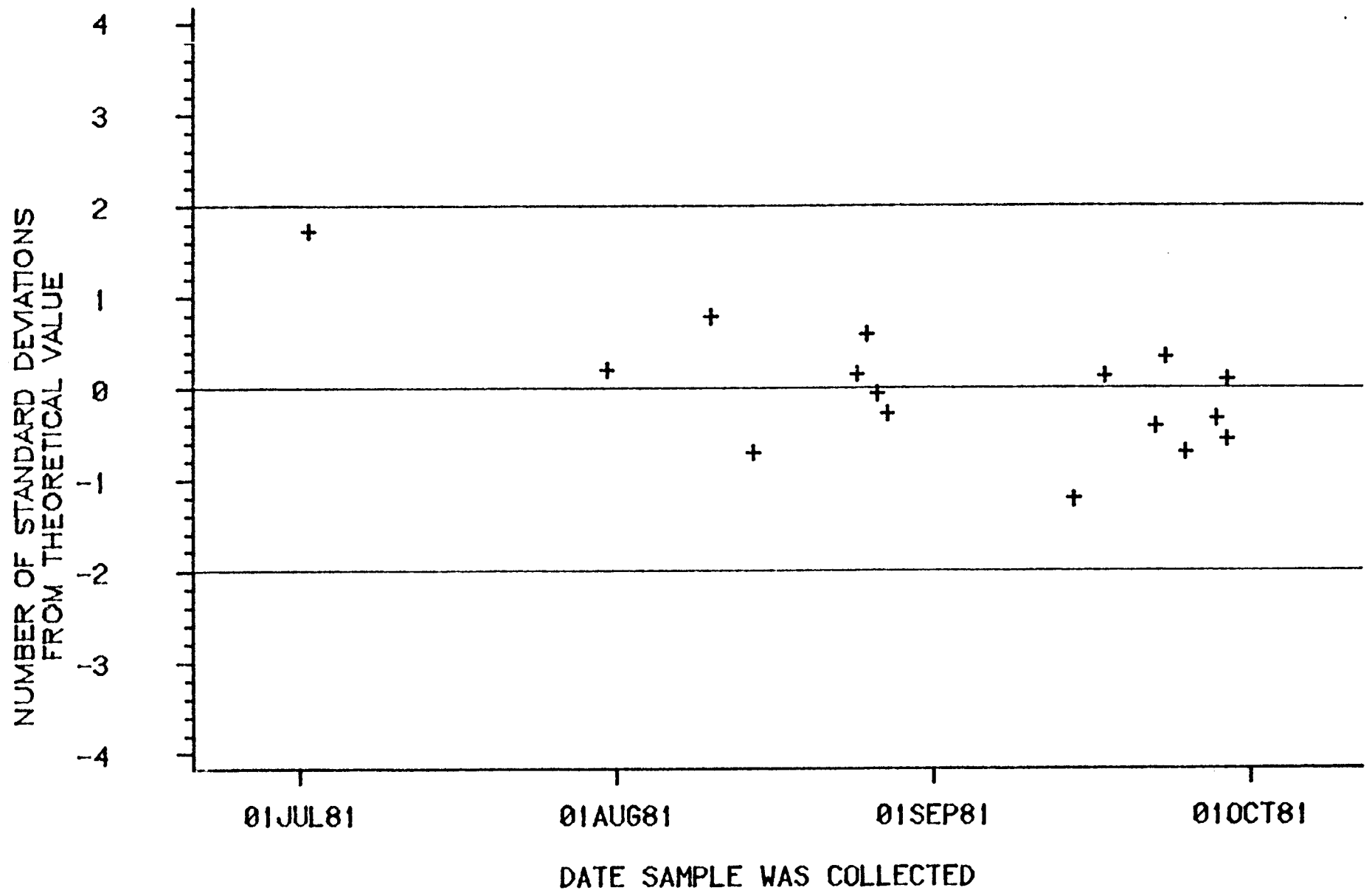


Figure A1.2.19.--Dissolved solids data for the Denver Laboratory.

LAB=DENVER

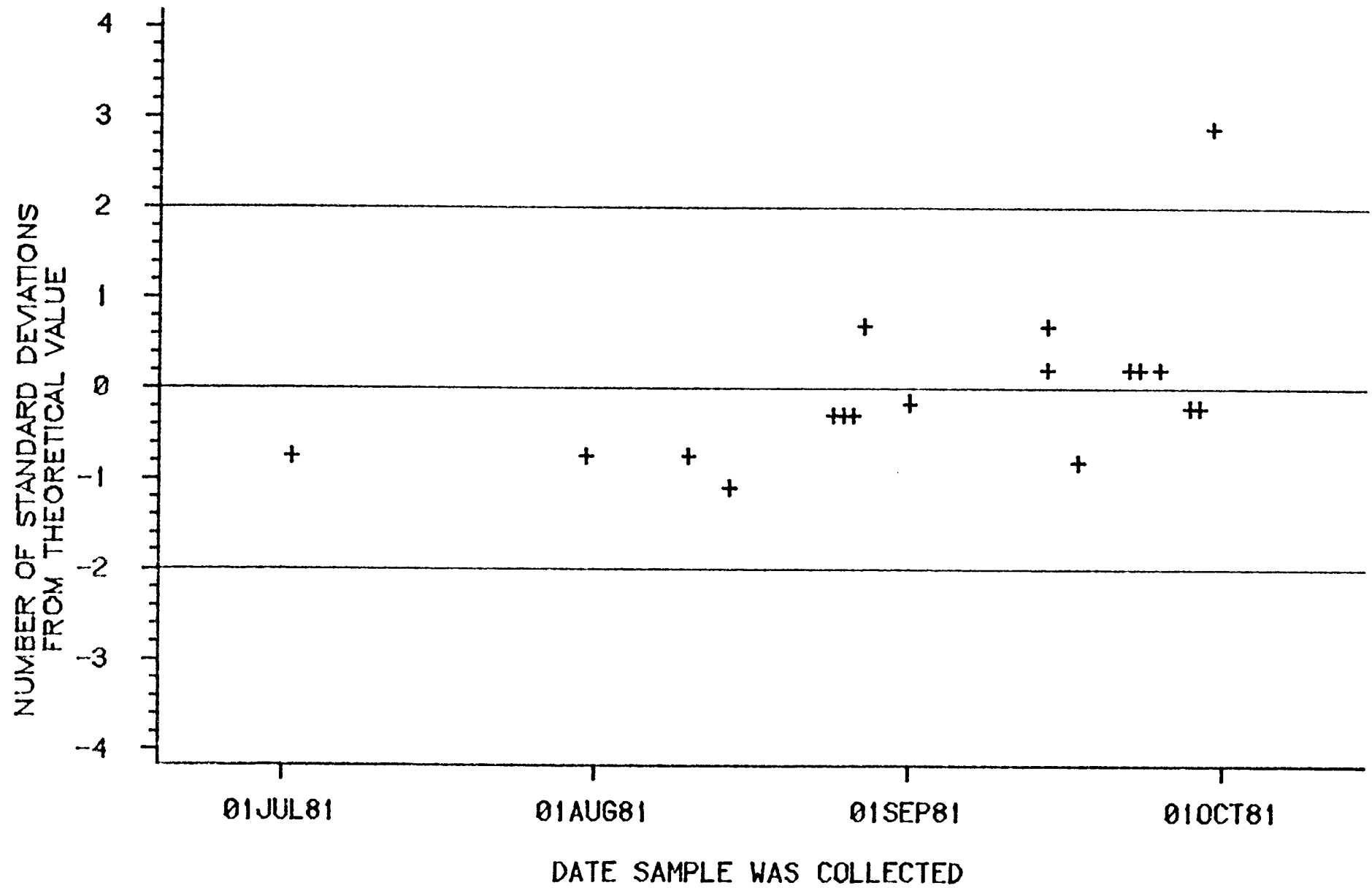


Figure A1.2.20.--Fluoride data for the Denver Laboratory.
(One observation was out of range.)

LAB=DENVER

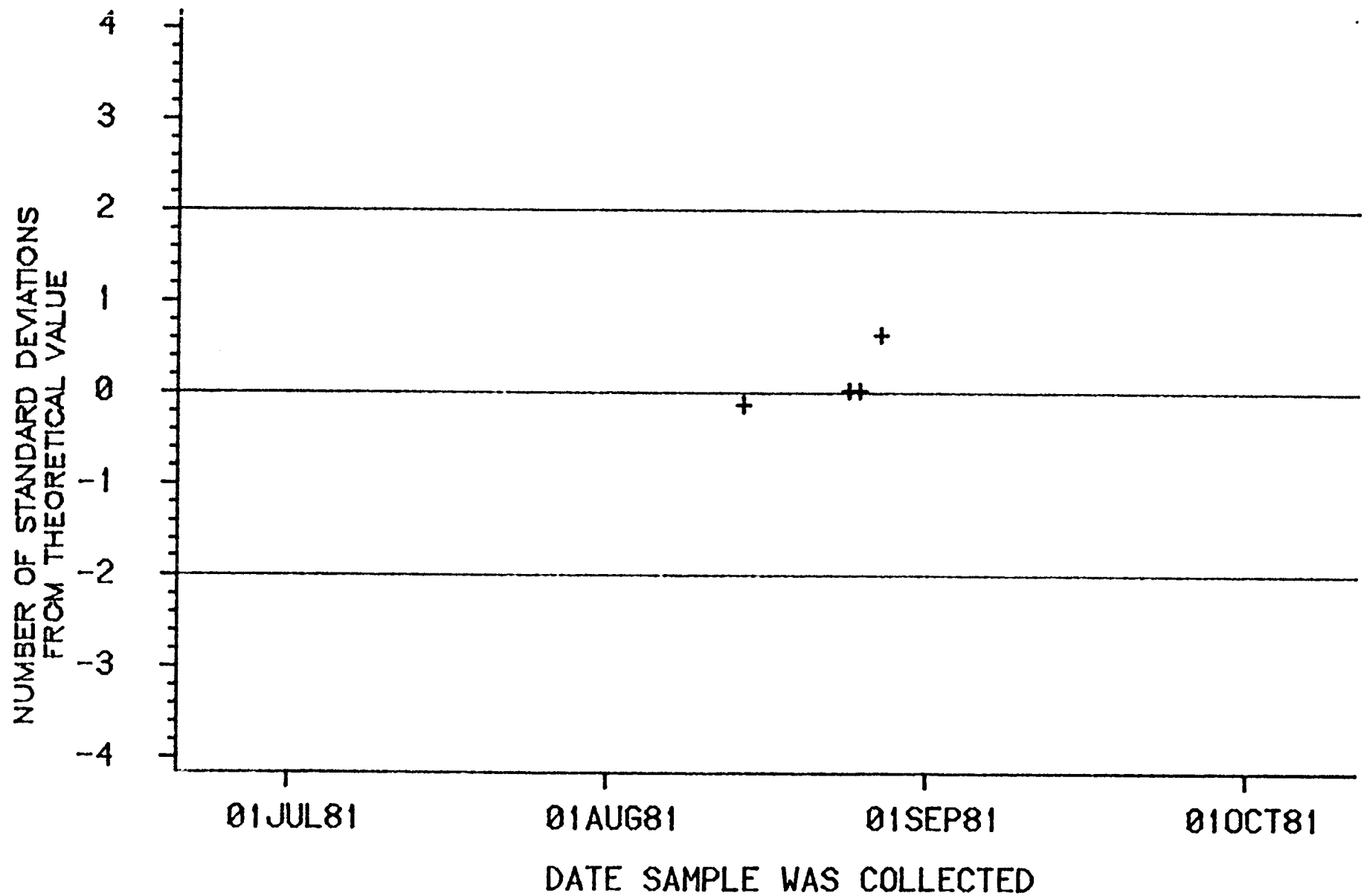


Figure A1.2.21.--Iron data for the Denver Laboratory.
(Three observations were out of range.)

LAB=DENVER

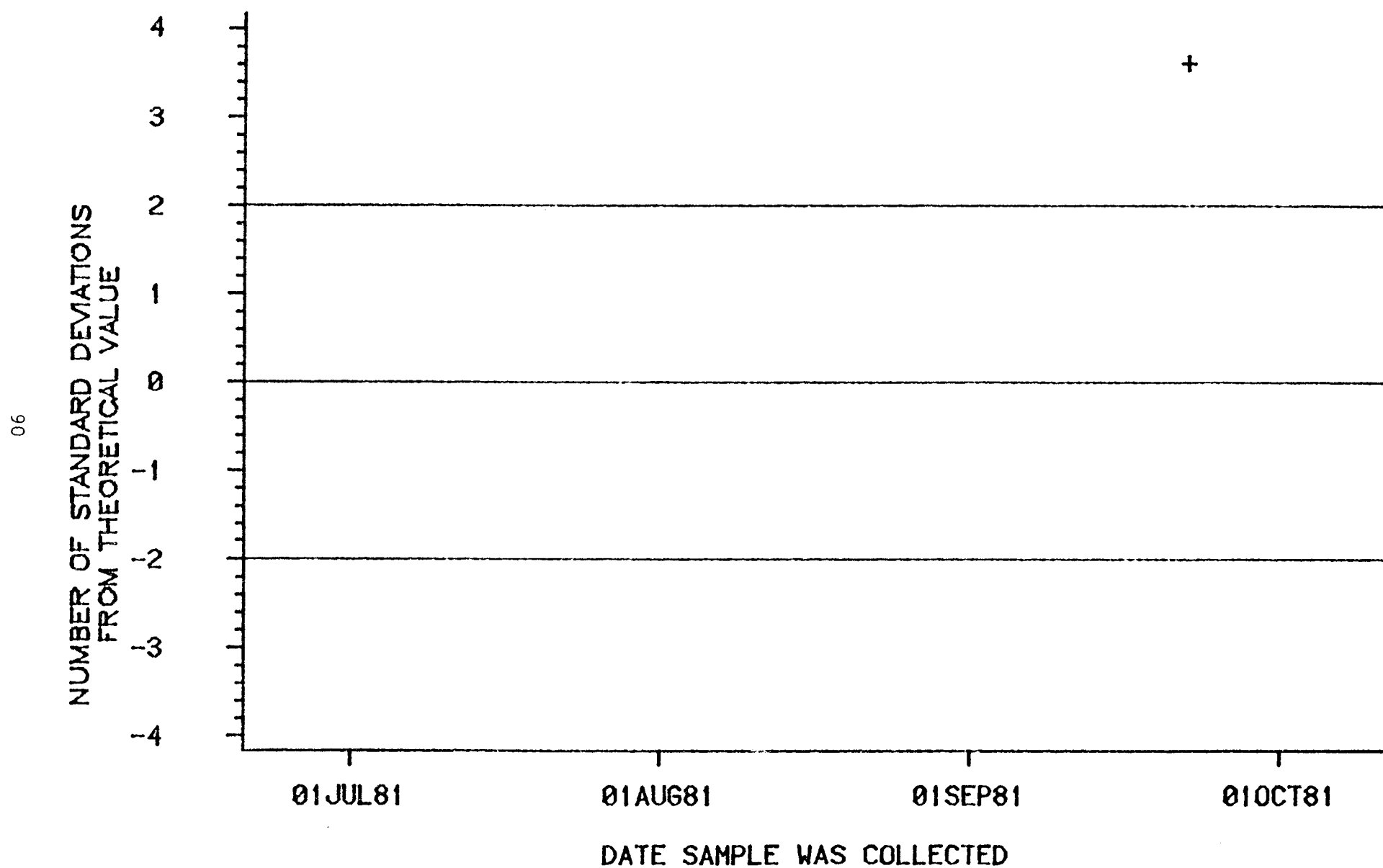


Figure A1.2.22.--Iron, total recoverable data for the Denver Laboratory.
(Two observations were out of range, see Discussion.)

LAB=DENVER

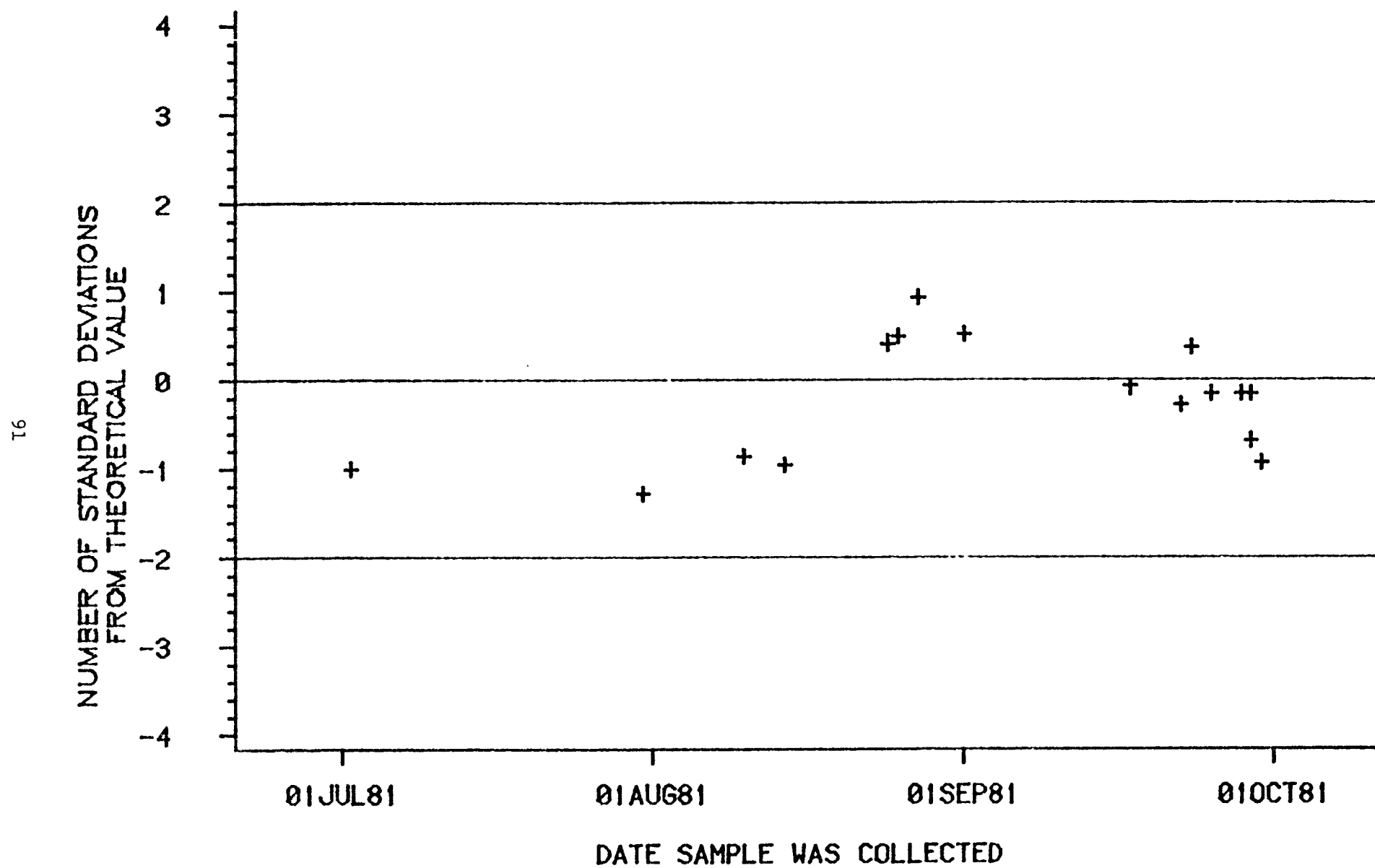


Figure A1.2.23.--Lead data for the Denver Laboratory.

LAB=DENVER

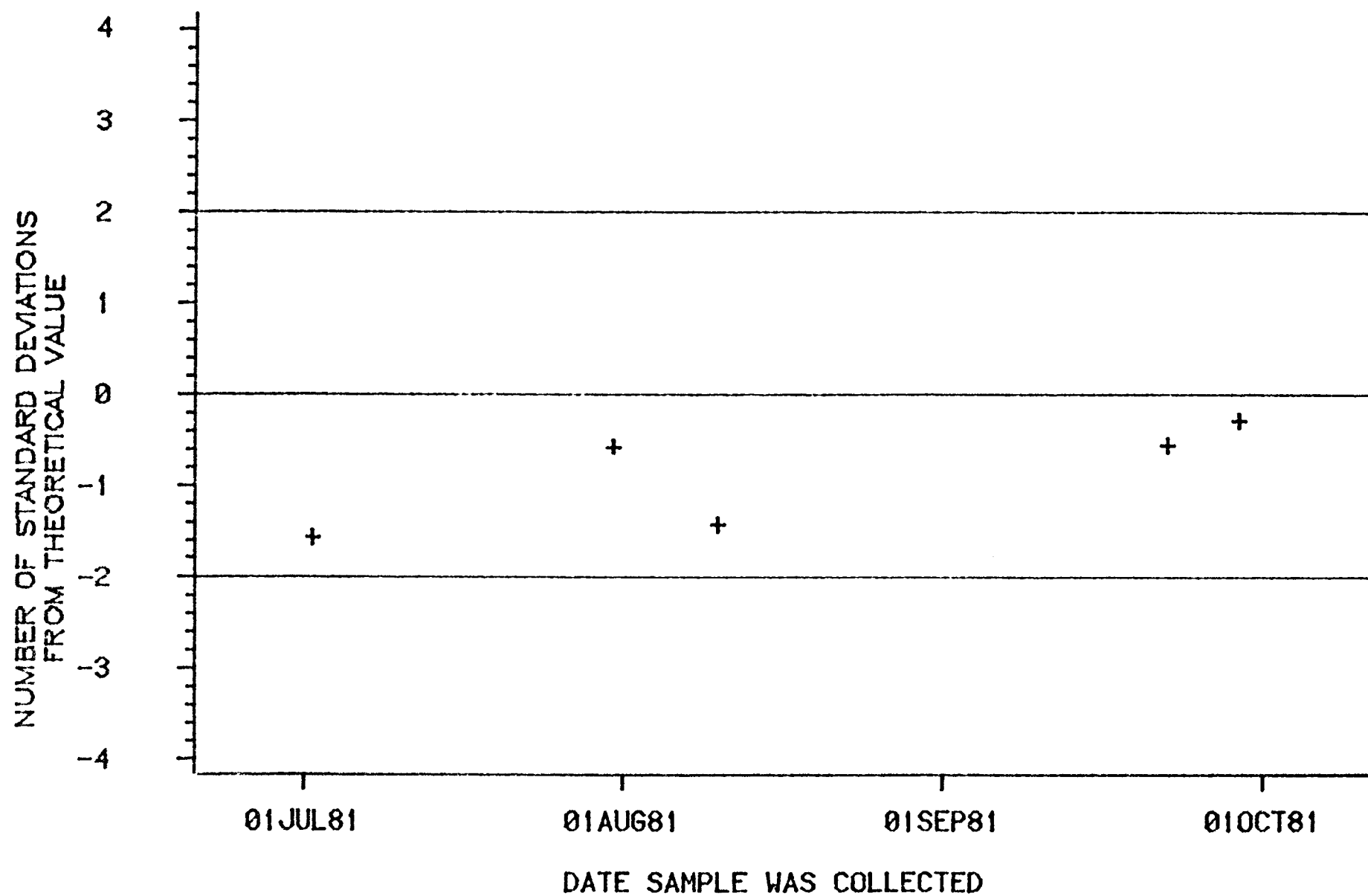


Figure A1.2.24.--Lead, total recoverable data for the Denver Laboratory.

LAB=DENVER

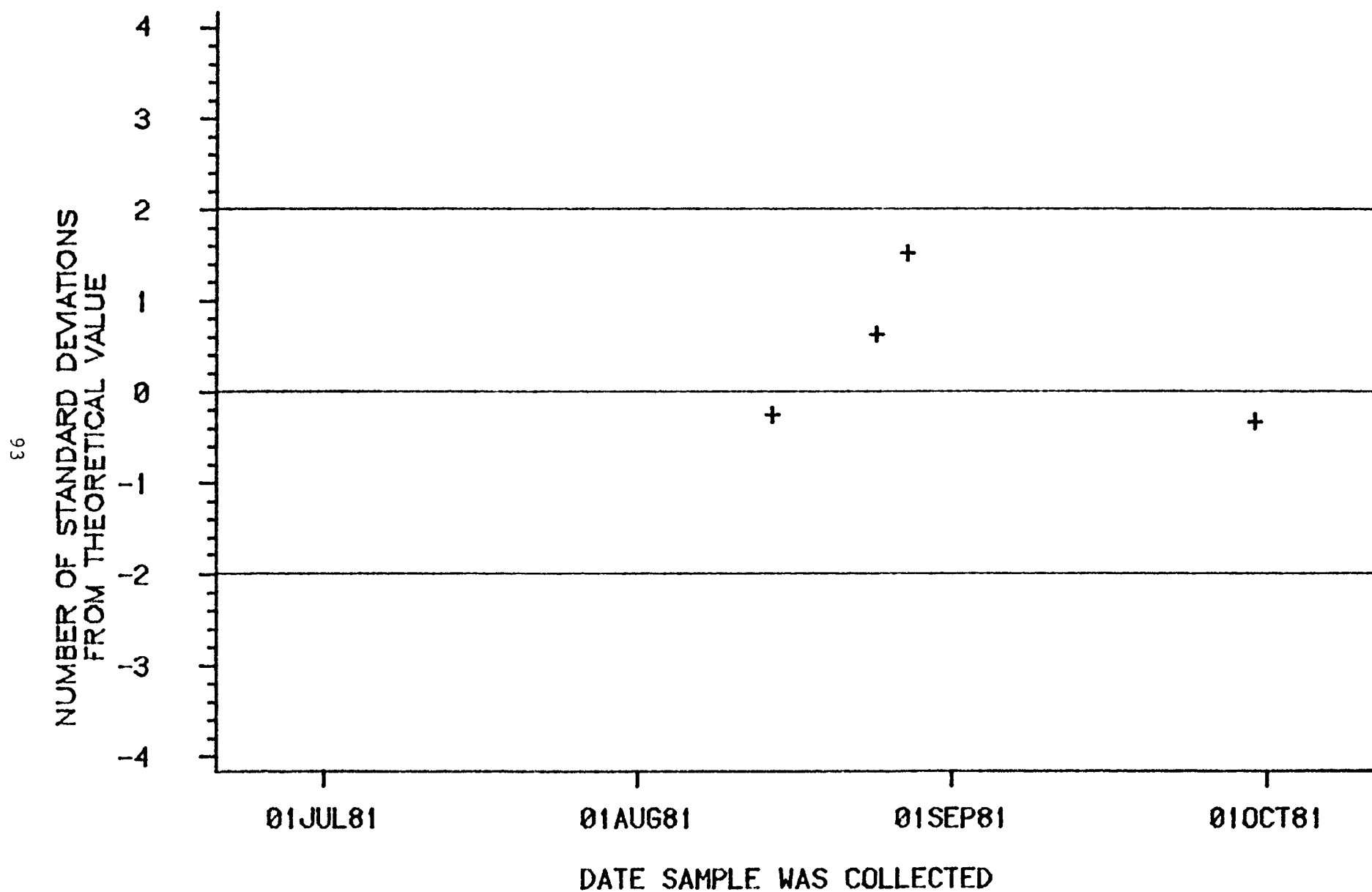


Figure A1.2.25.--Lithium data for the Denver Laboratory.
(One observation was out of range.)

LAB=DENVER

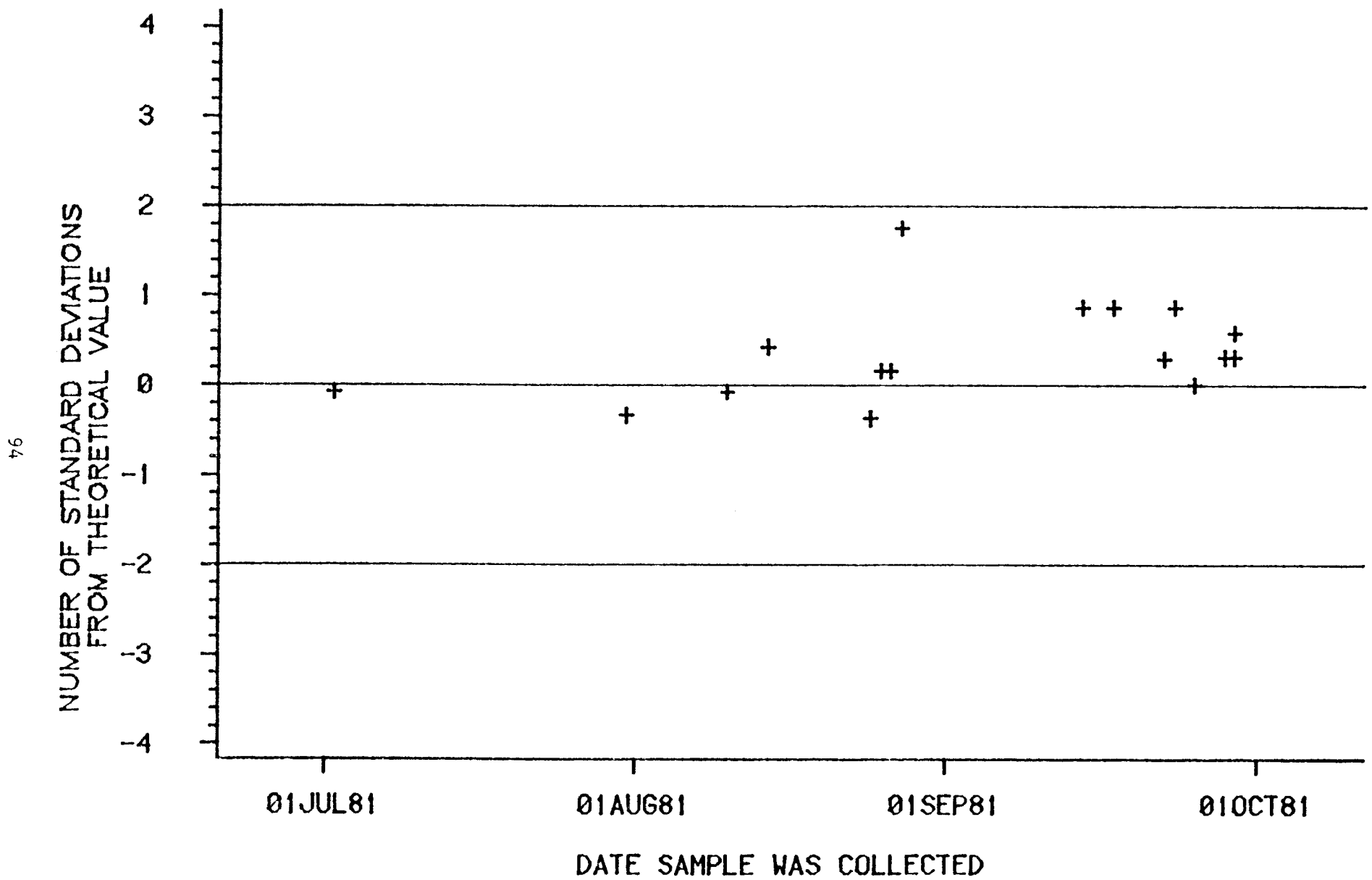


Figure A1.2.26.--Magnesium data for the Denver Laboratory.

LAB=DENVER

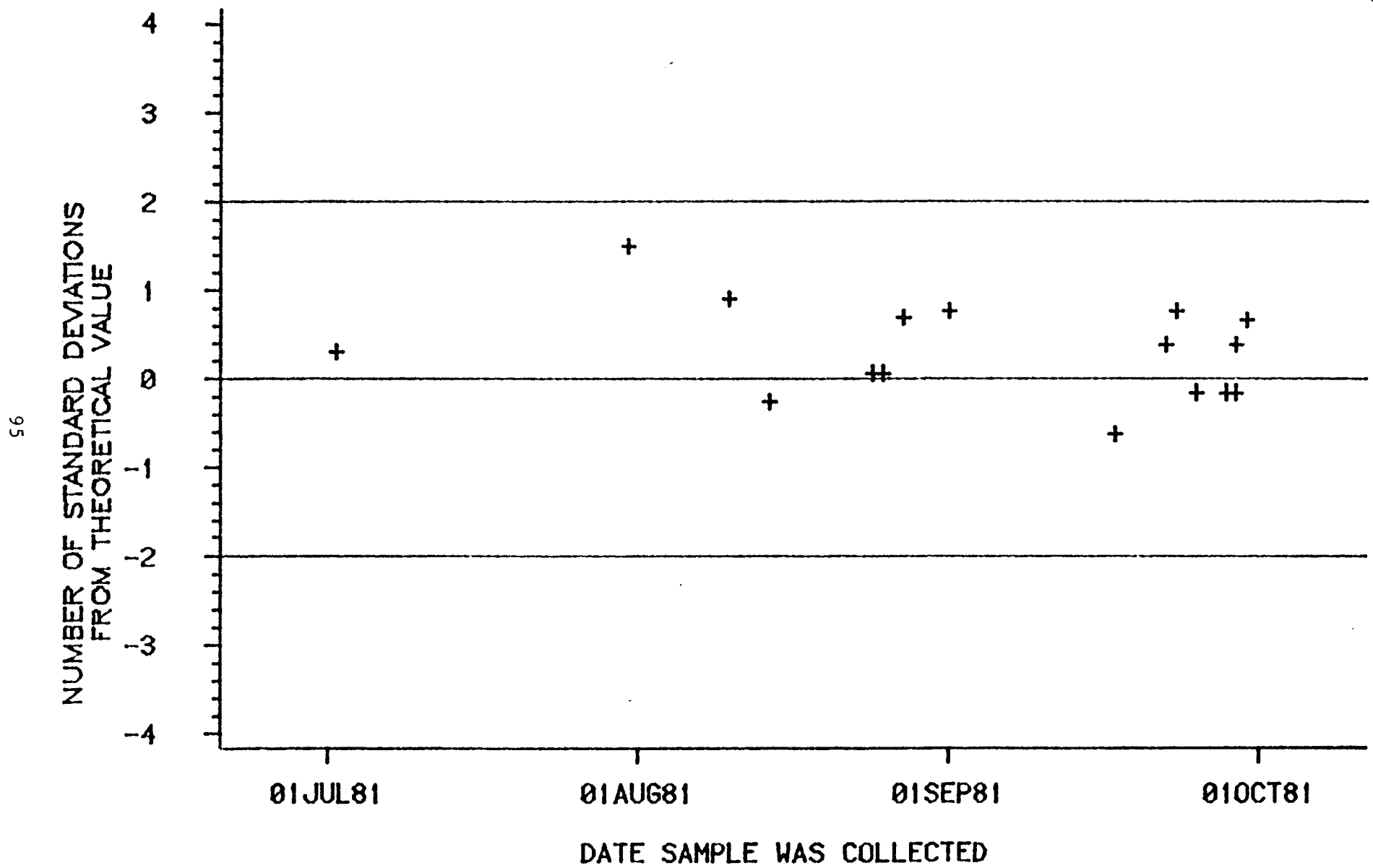


Figure A1.2.27.--Manganese data for the Denver Laboratory.

LAB=DENVER

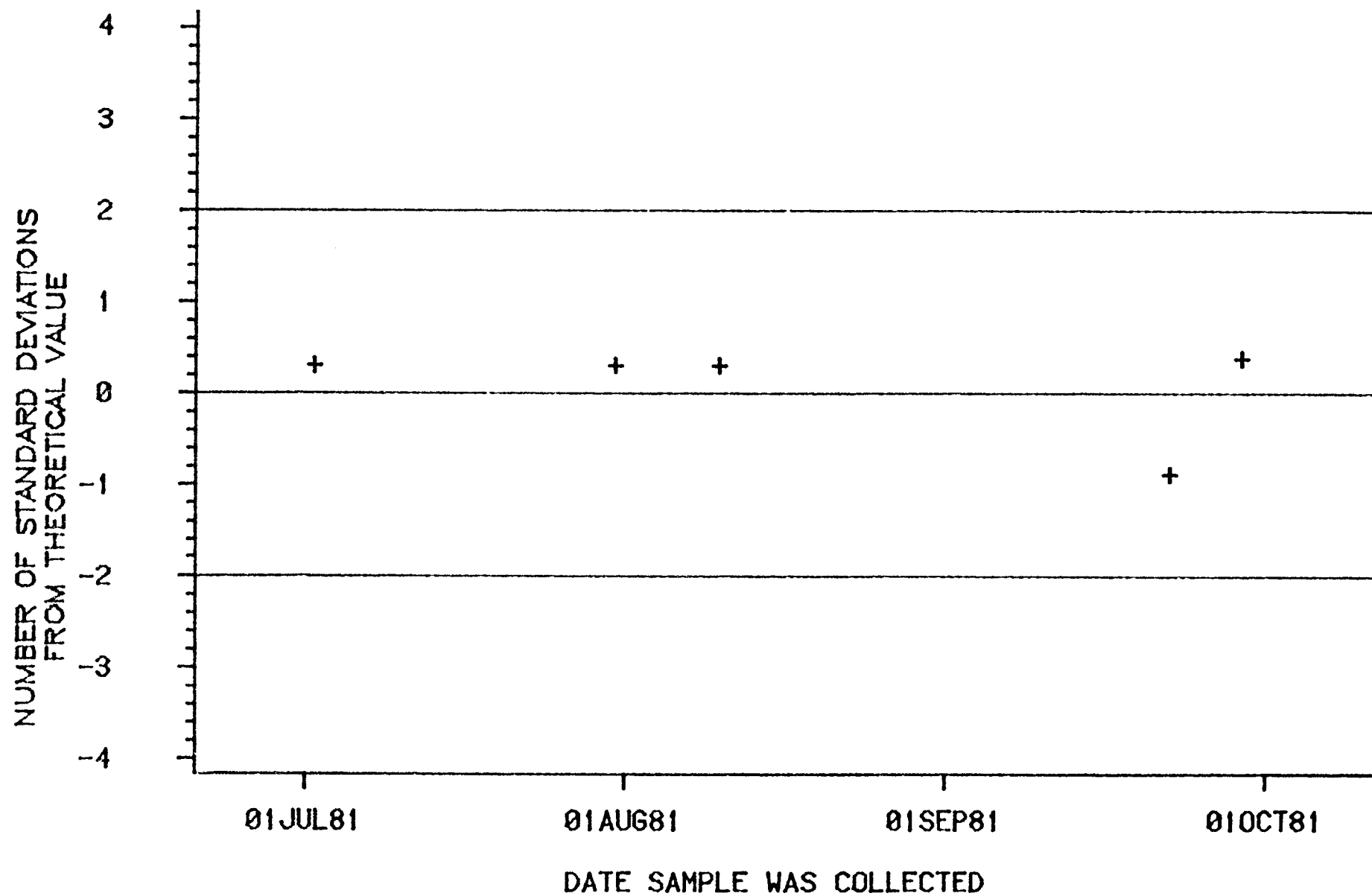


Figure A1.2.28.--Manganese, total recoverable data for the Denver Laboratory.

LAB=DENVER

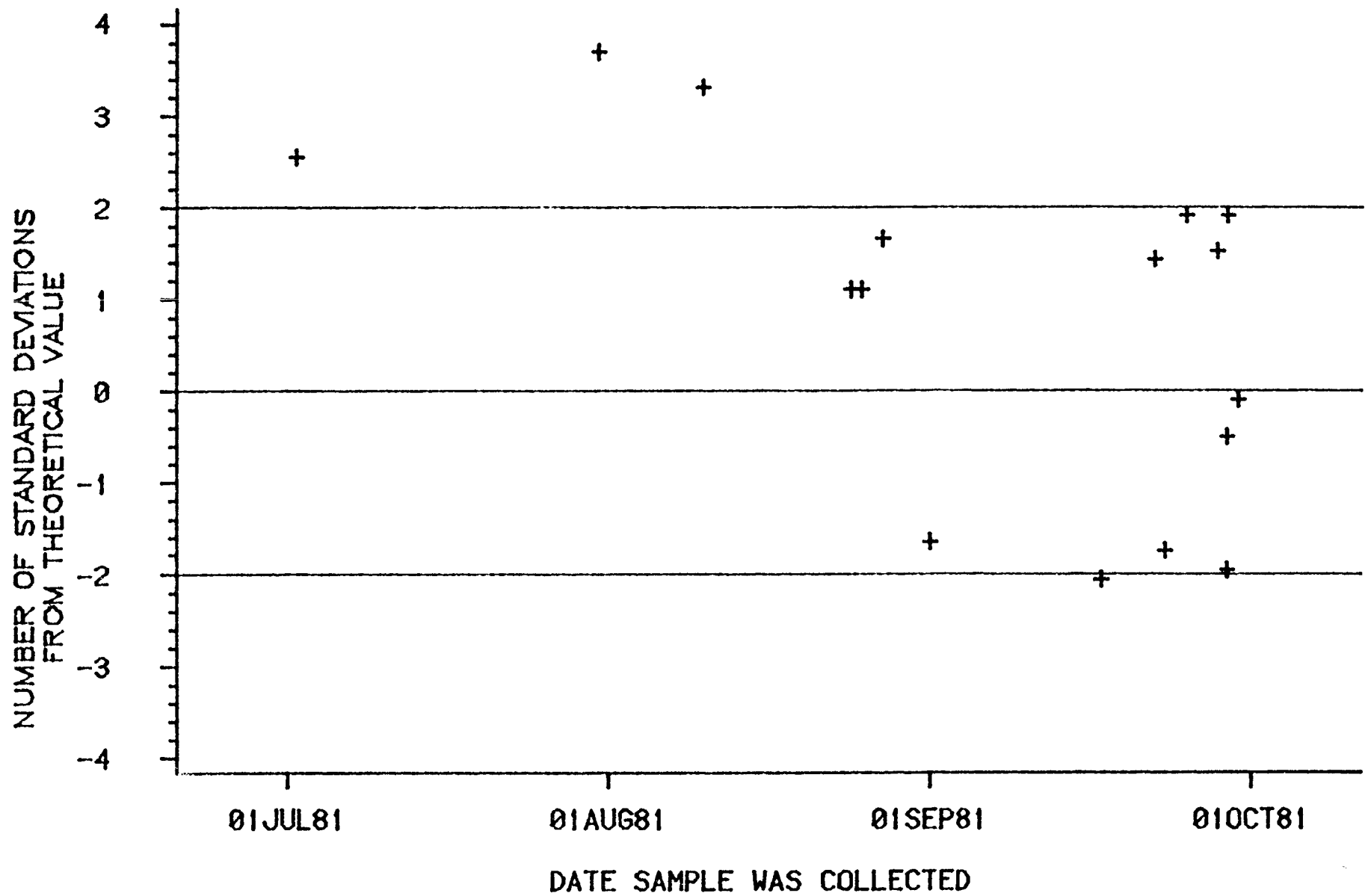


Figure A1.2.29.--Mercury data for the Denver Laboratory.
(Four observations were out of range.)

LAB=DENVER

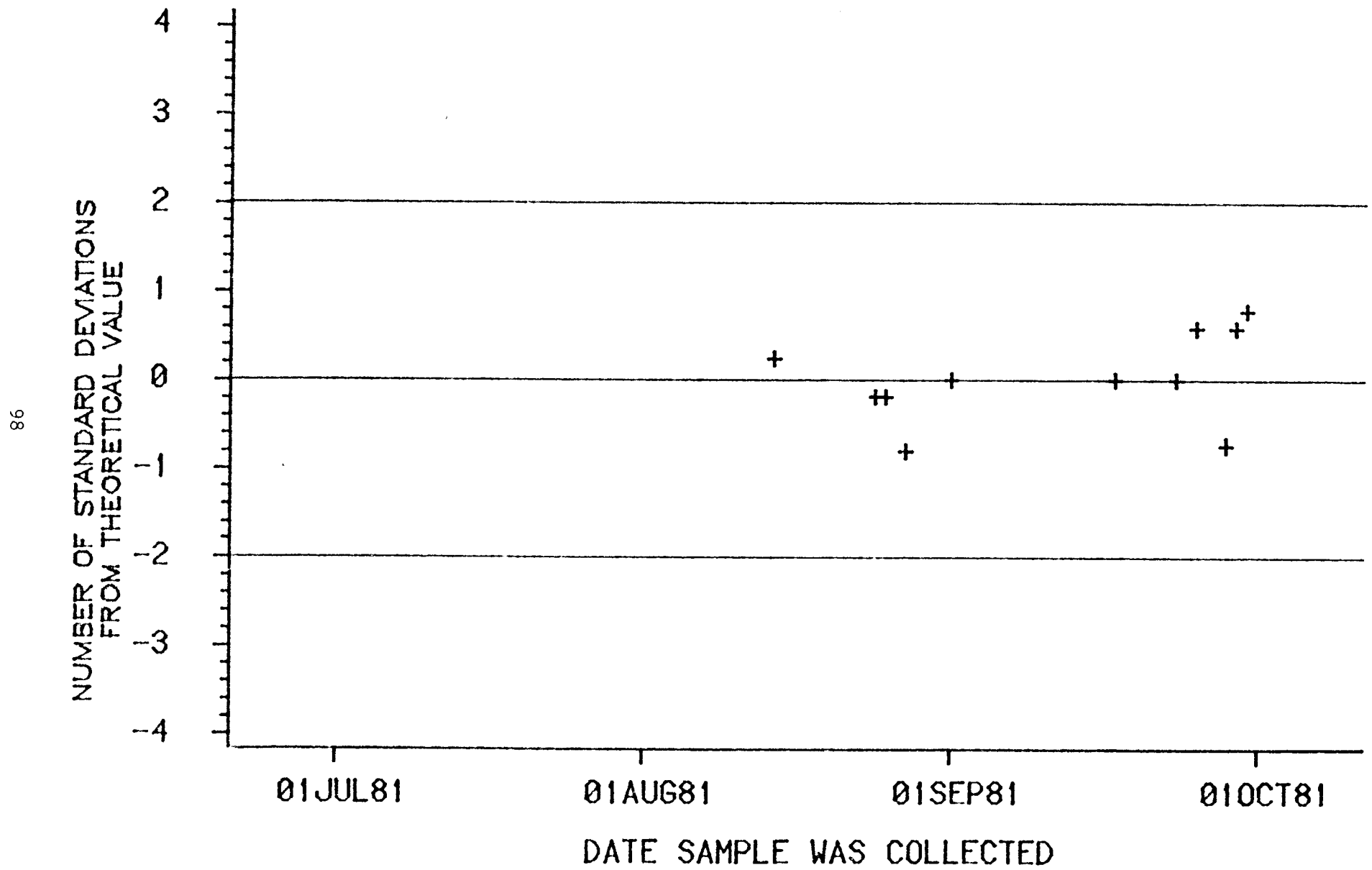


Figure A1.2.30.--Molybdenum data for the Denver Laboratory.

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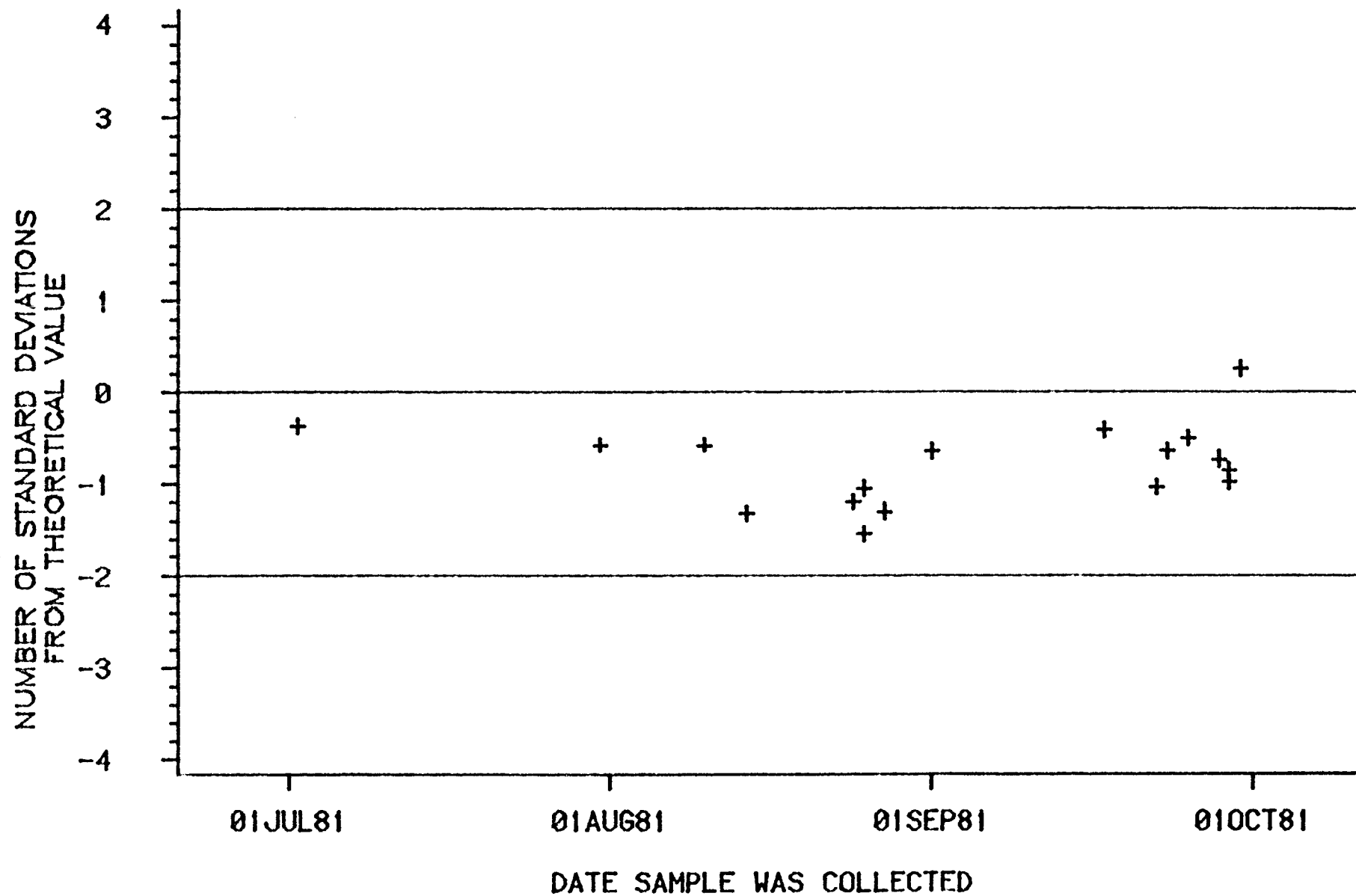


Figure A1.2.31.--Nickel data for the Denver Laboratory.

LAB=DENVER

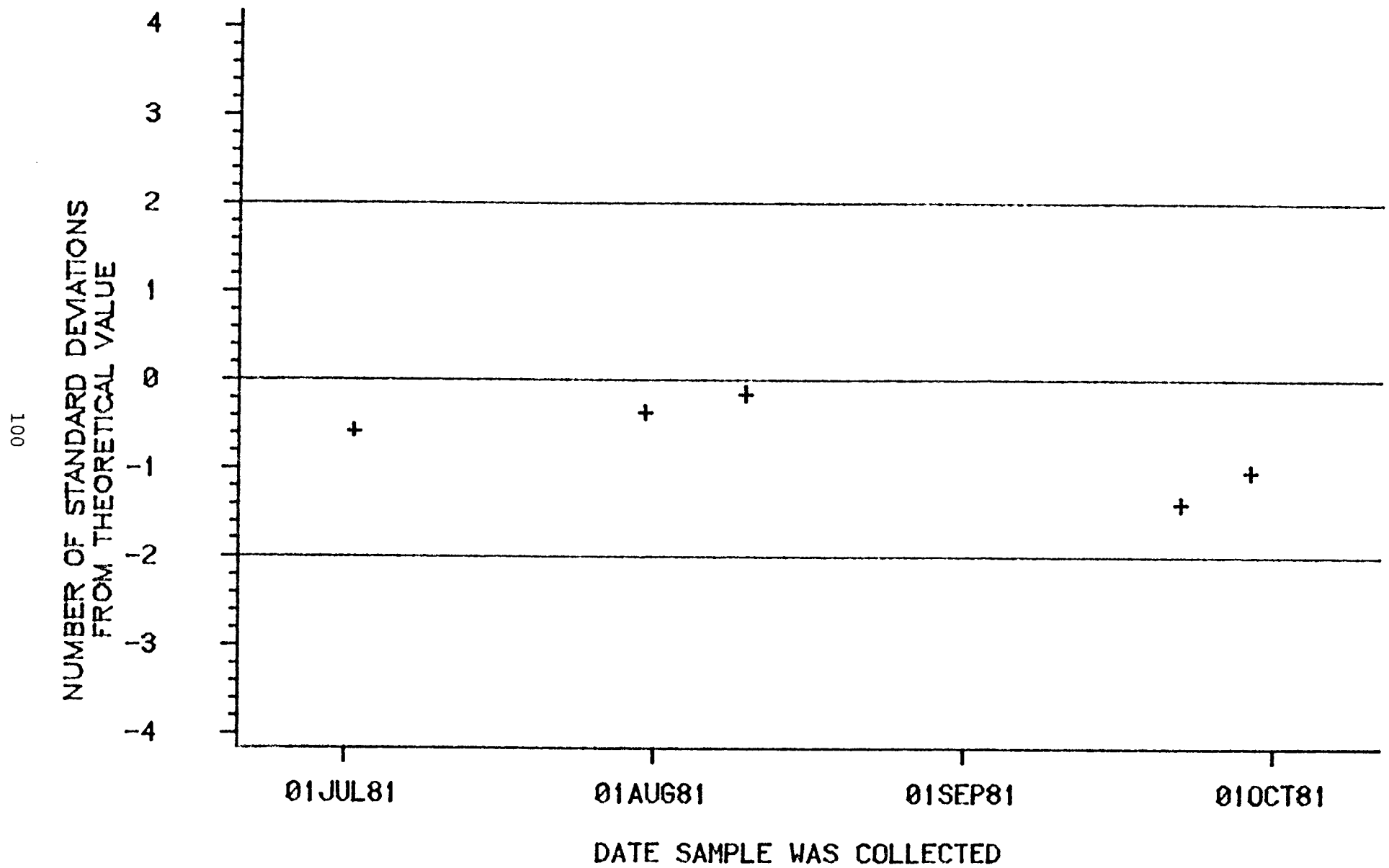


Figure A1.2.32.--Nickel, total recoverable data for the Denver Laboratory.

LAB=DENVER

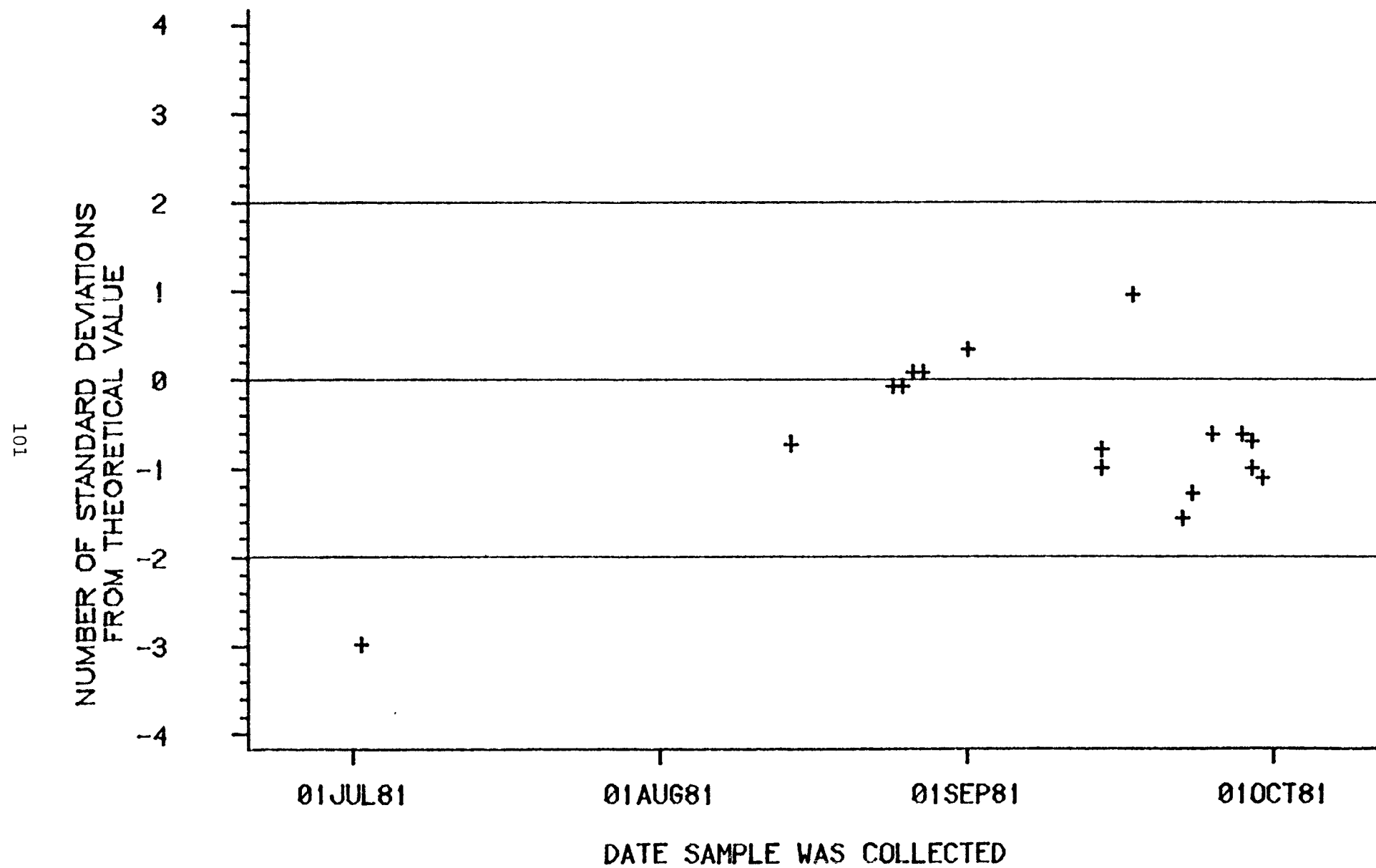


Figure A1.2.33.--Nitrate plus nitrite-nitrogen data for the Denver Laboratory.
(Two observations were out of range.)

LAB=DENVER

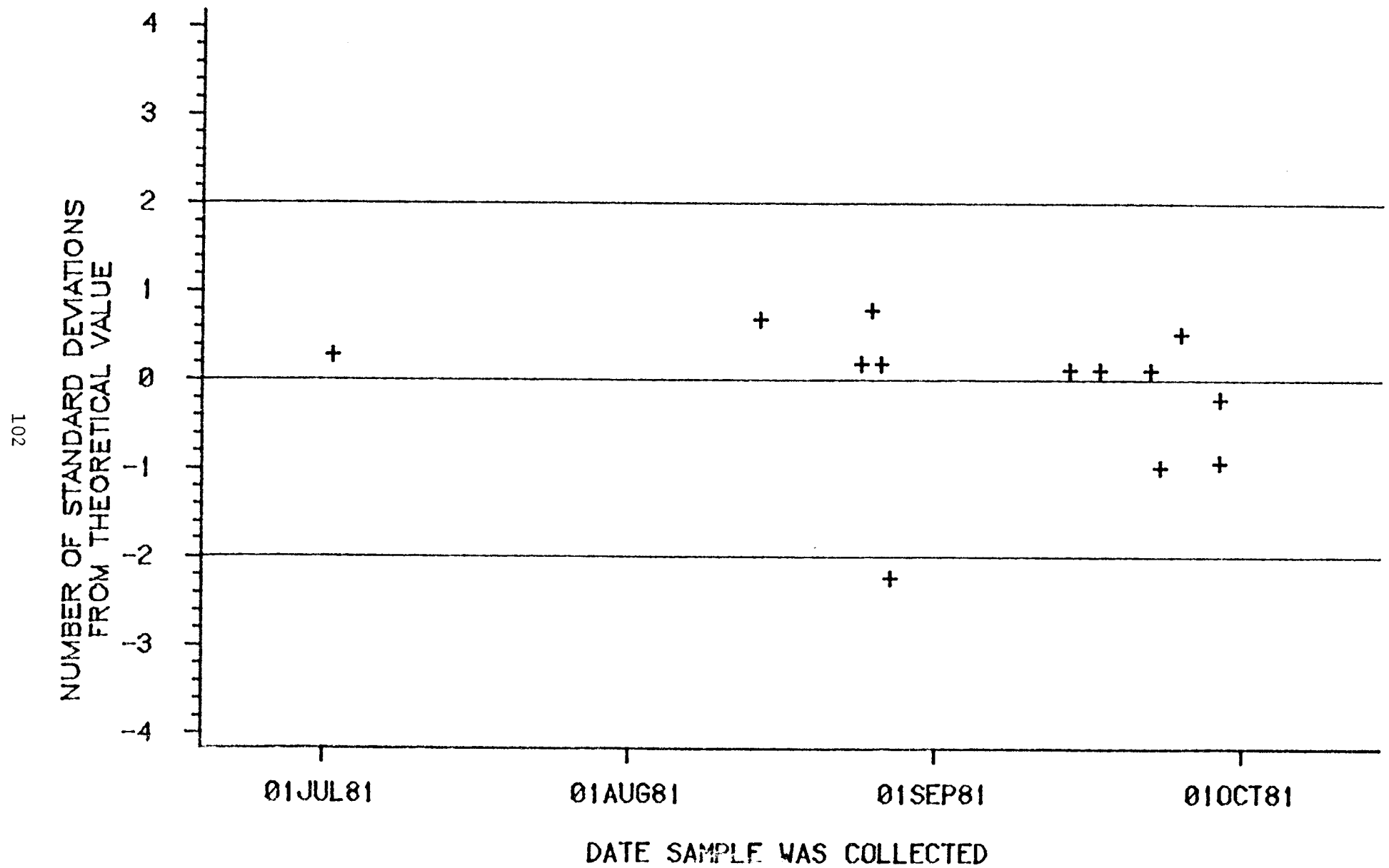


Figure A1.2.34.--Phosphorus data for the Denver Laboratory.
(Three observations were out of range.)

LAB=DENVER

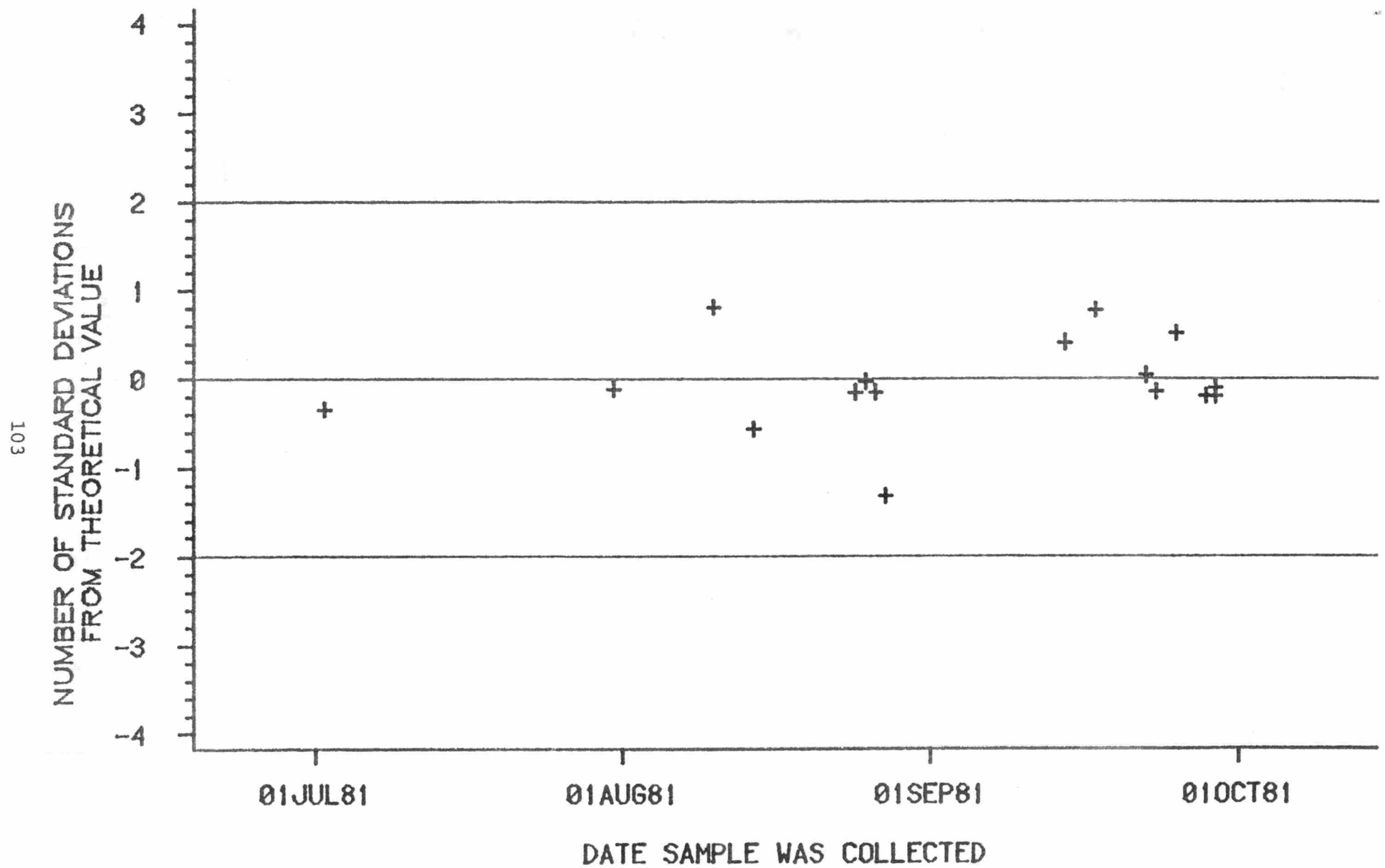


Figure A1.2.35.--Potassium data for the Denver Laboratory.

LAB=DENVER

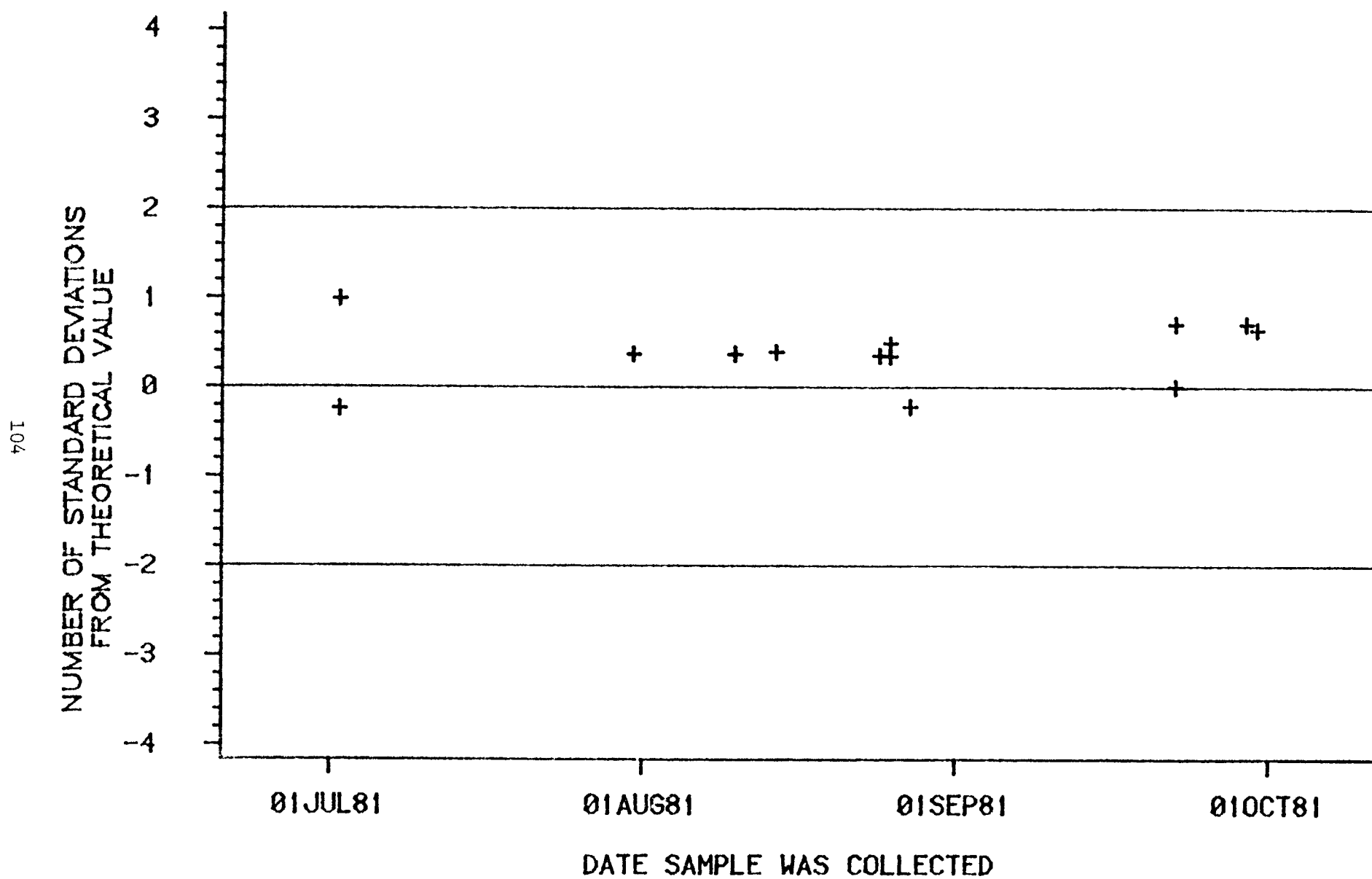


Figure A1.2.36.--Selenium data for the Denver Laboratory.

LAB=DENVER

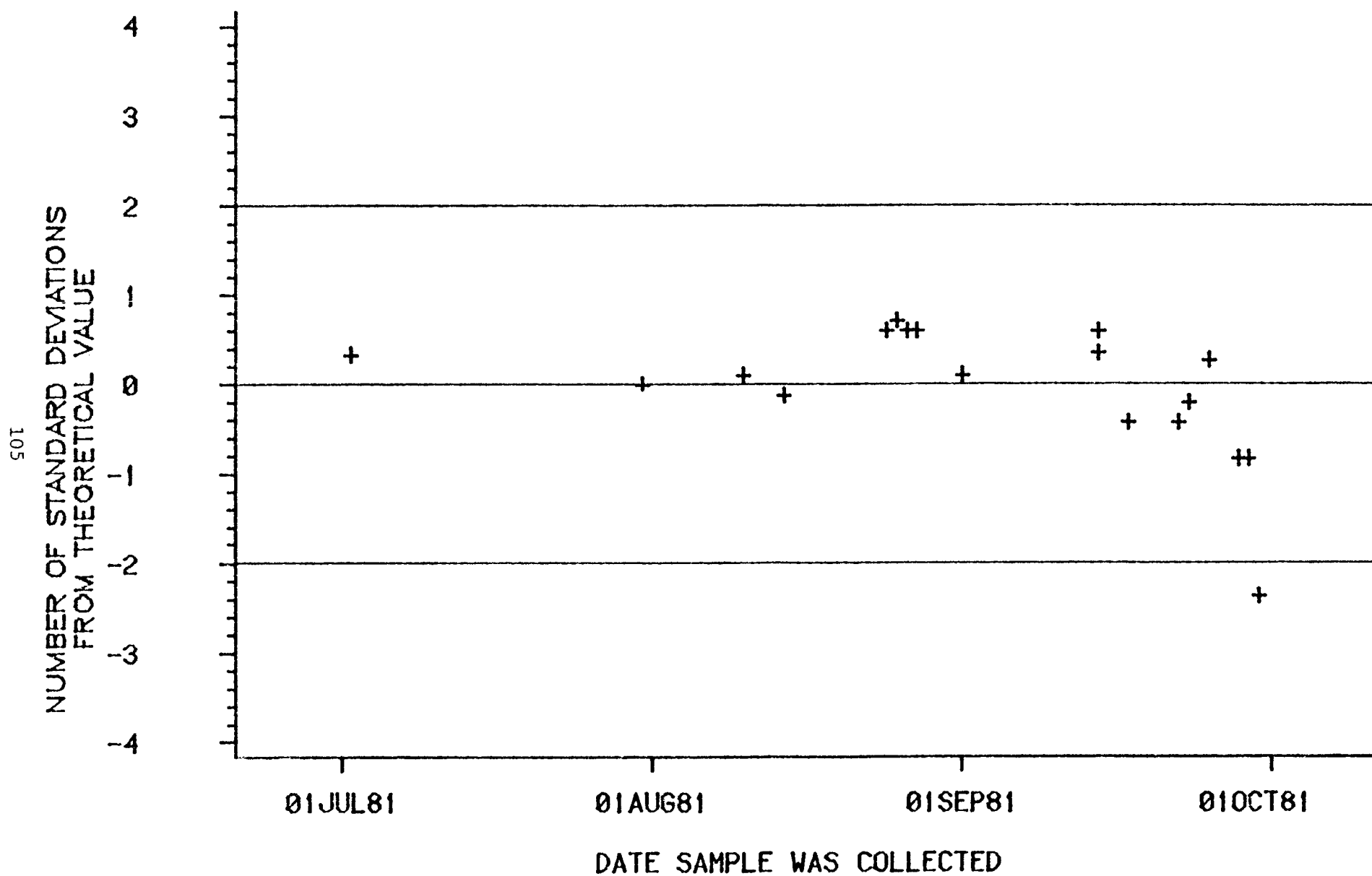


Figure A1.2.37.--Silica data for the Denver Laboratory.

LAB=DENVER

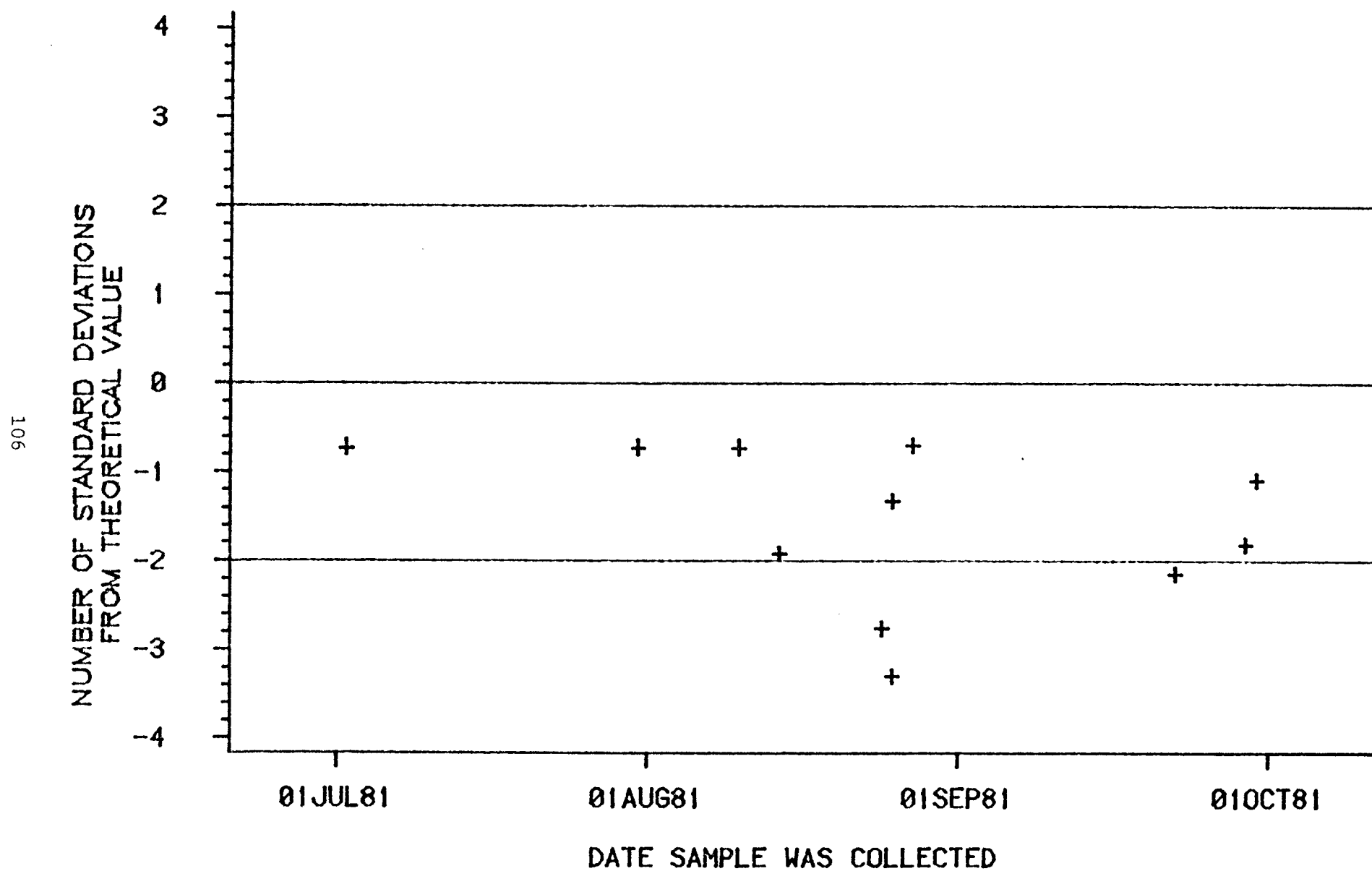


Figure A1.2.38.--Silver data for the Denver Labortory.

LAB=DENVER

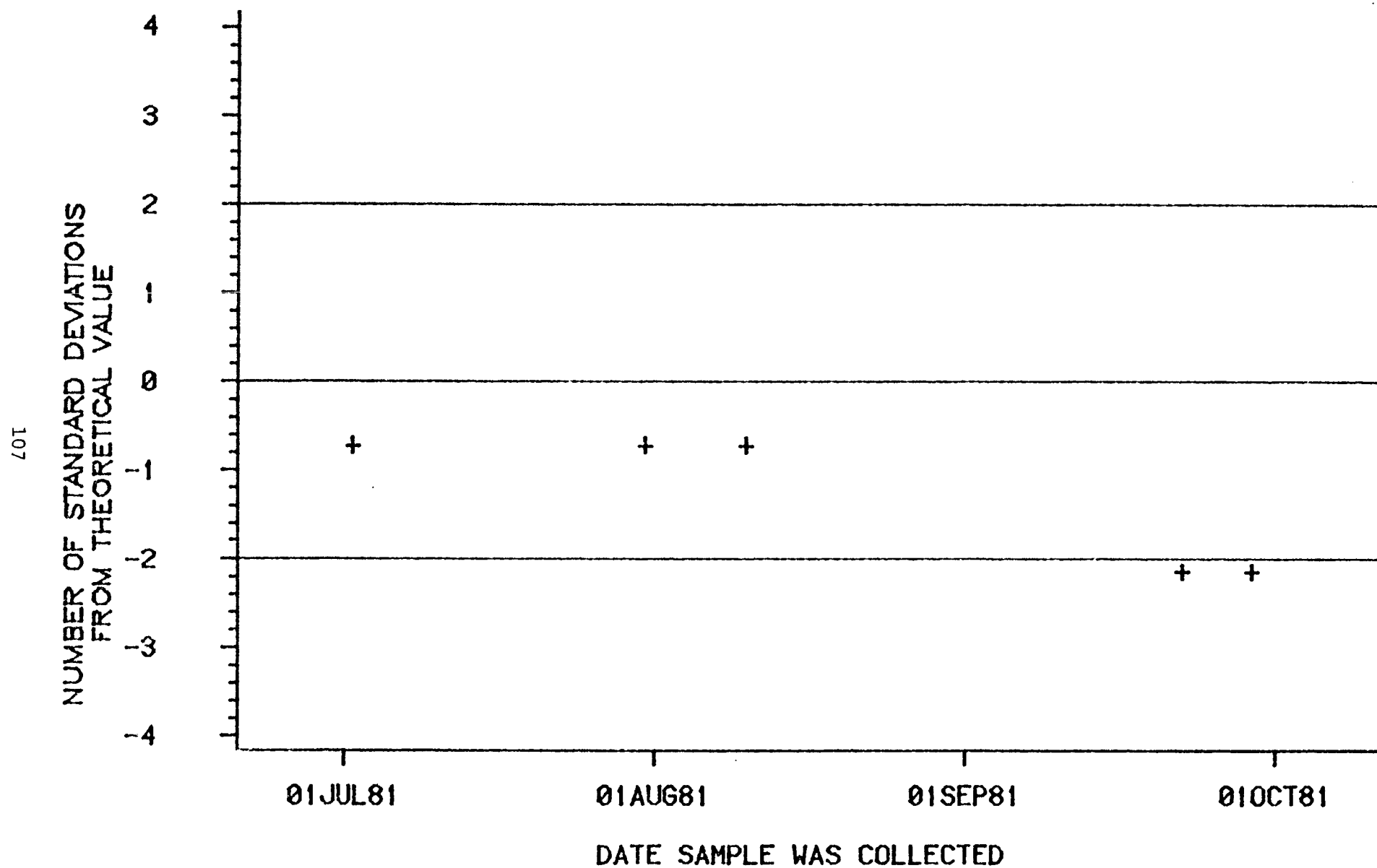


Figure A1.2.39.--Silver, total recoverable data for the Denver Laboratory.

LAB=DENVER

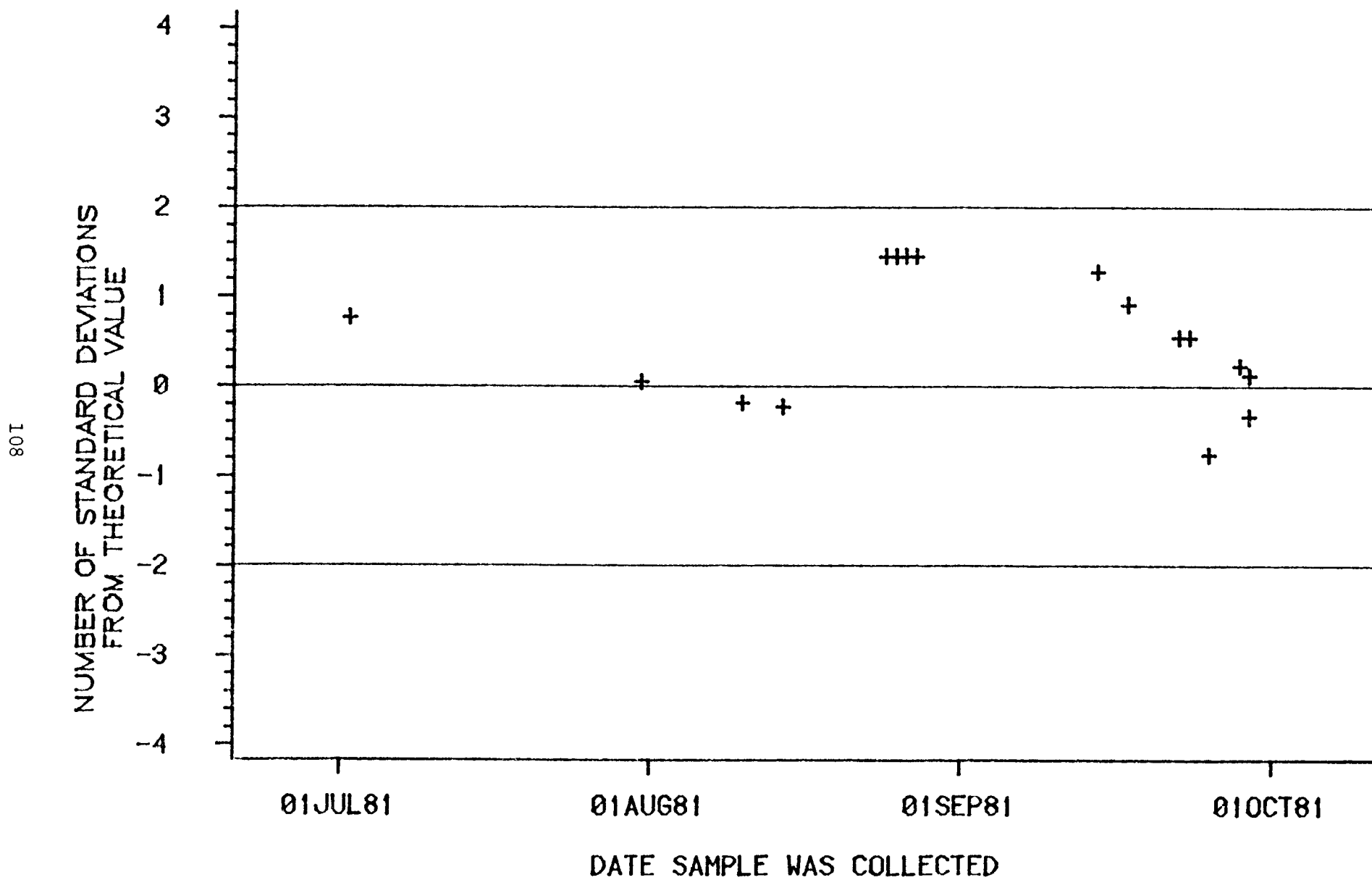


Figure A1.2.40.--Sodium data for the Denver Laboratory.

LAB=DENVER

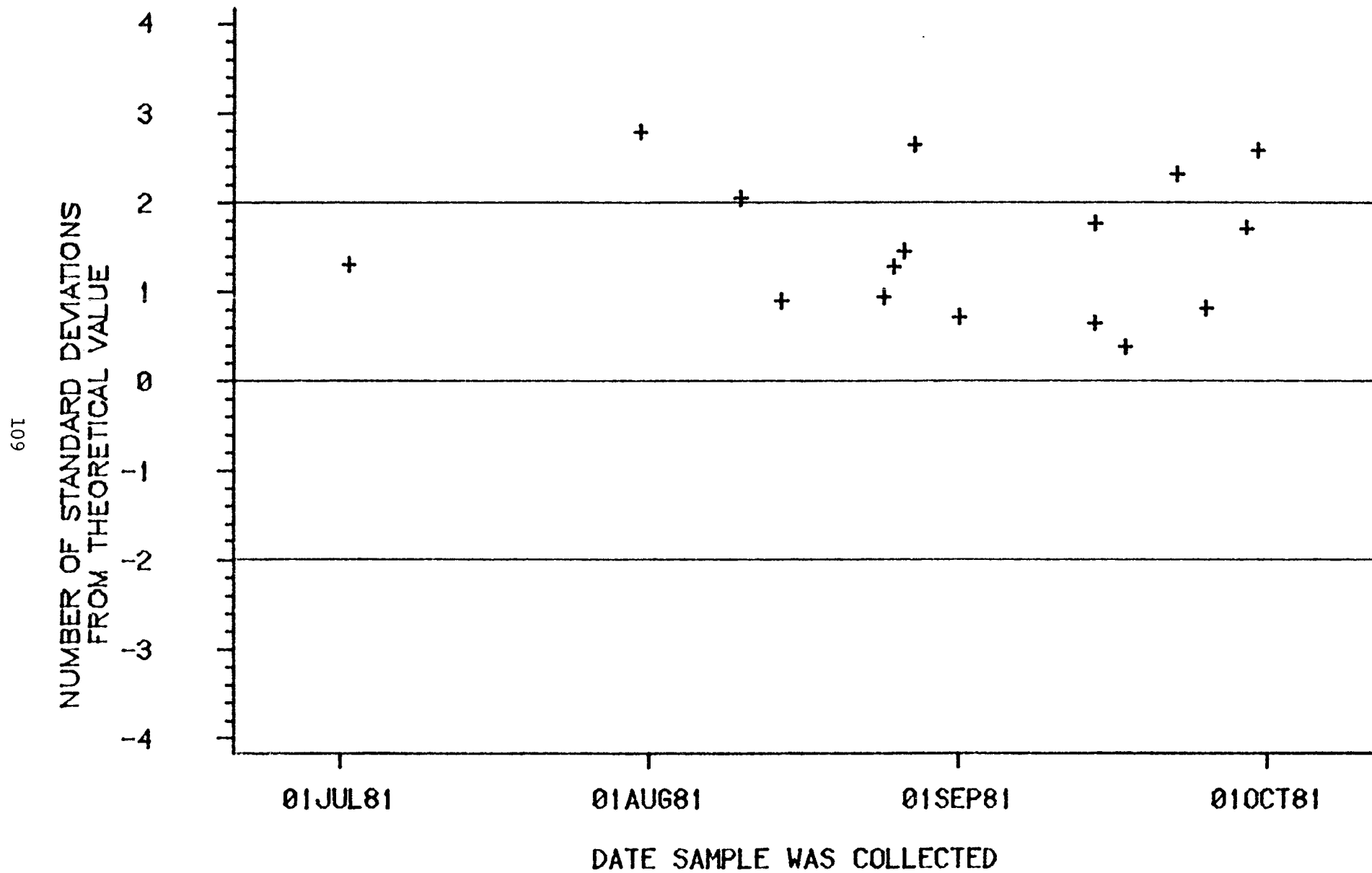


Figure A1.2.41.--Specific conductance data for the Denver Laboratory.
(Three observations were out of range.)

LAB=DENVER

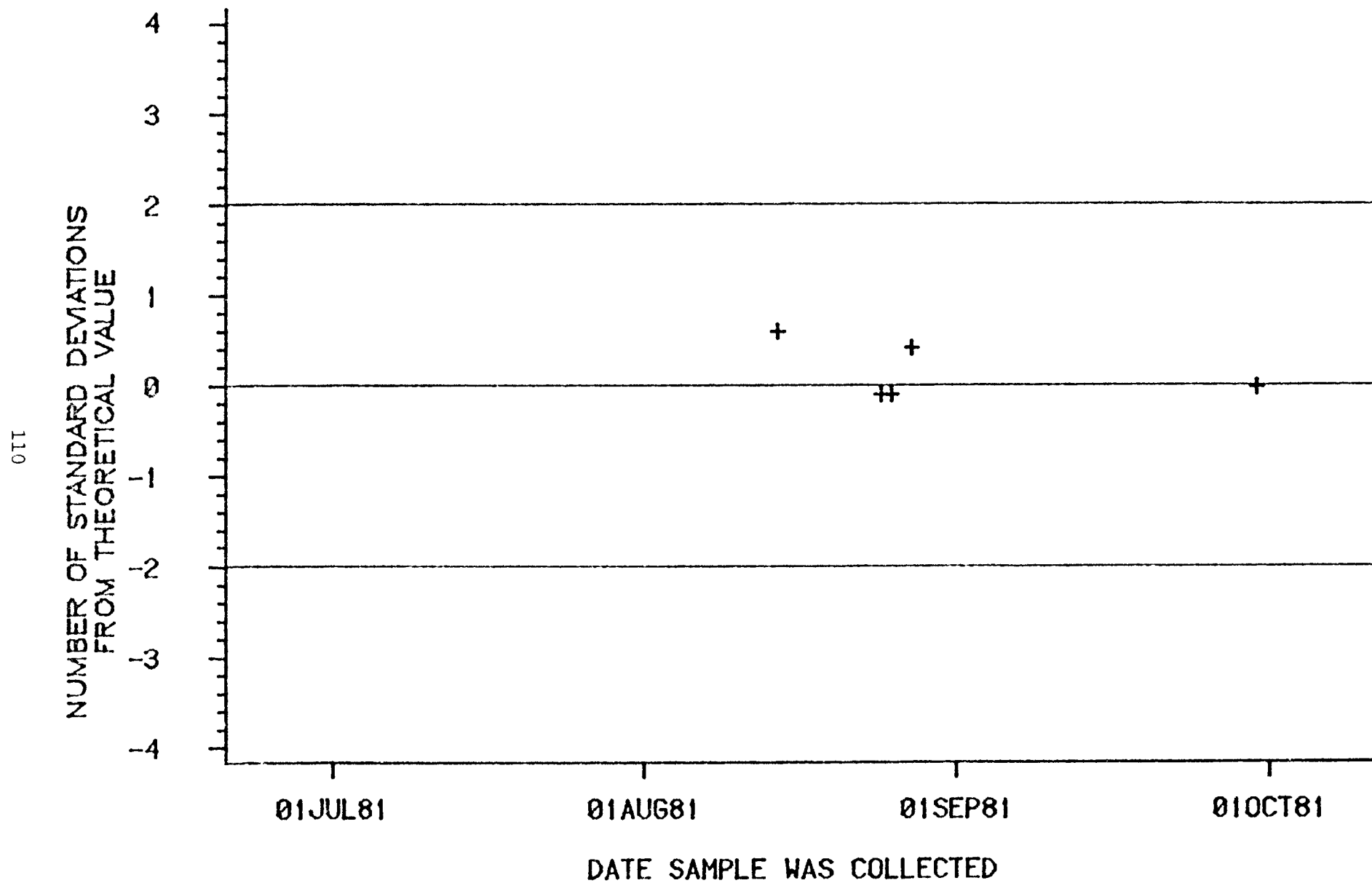


Figure A1.2.42.--Strontium data for the Denver Laboratory.

LAB=DENVER

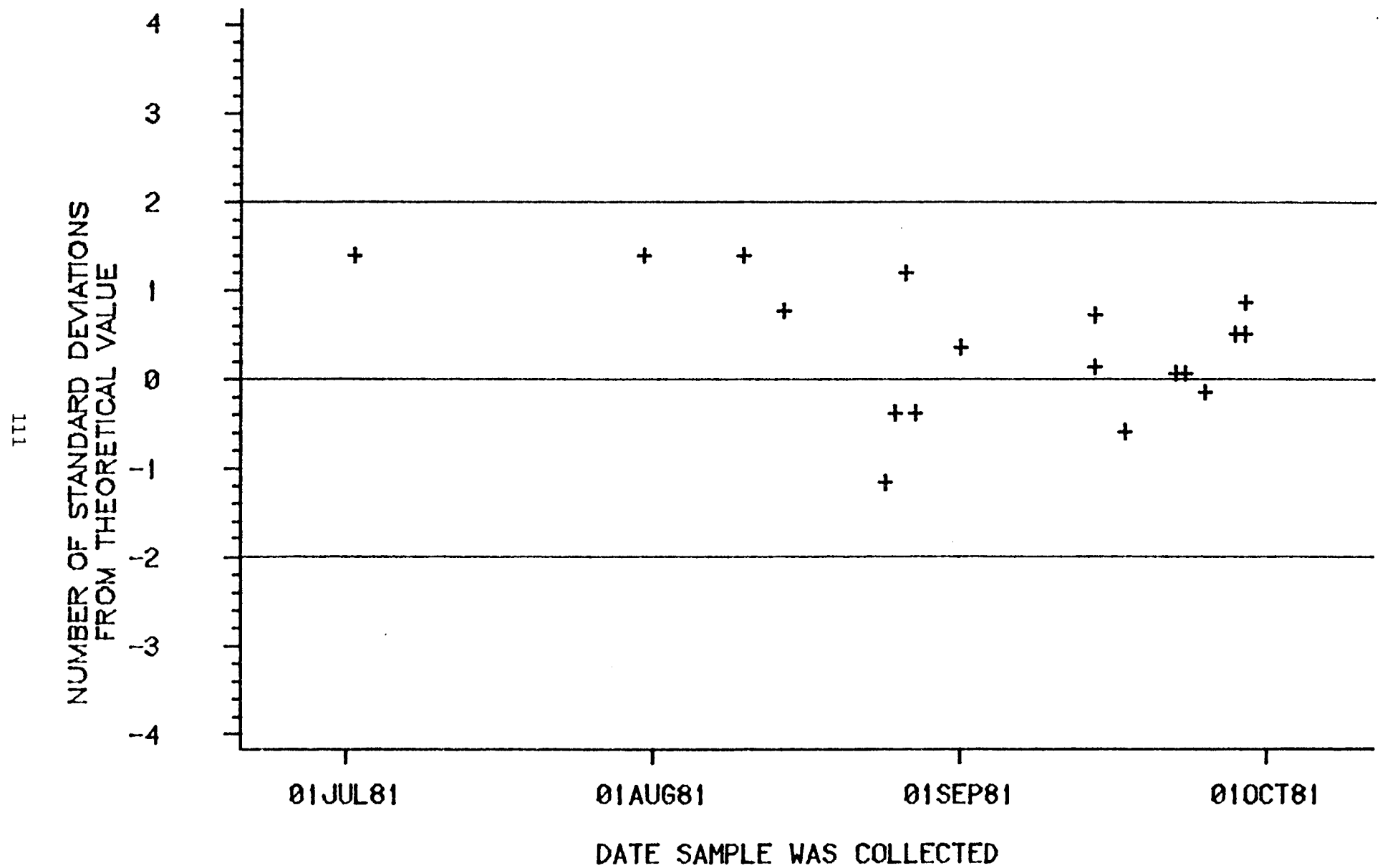


Figure A1.2.43.--Sulfate data for the Denver Laboratory.
(One observation was out of range.)

LAB=DENVER

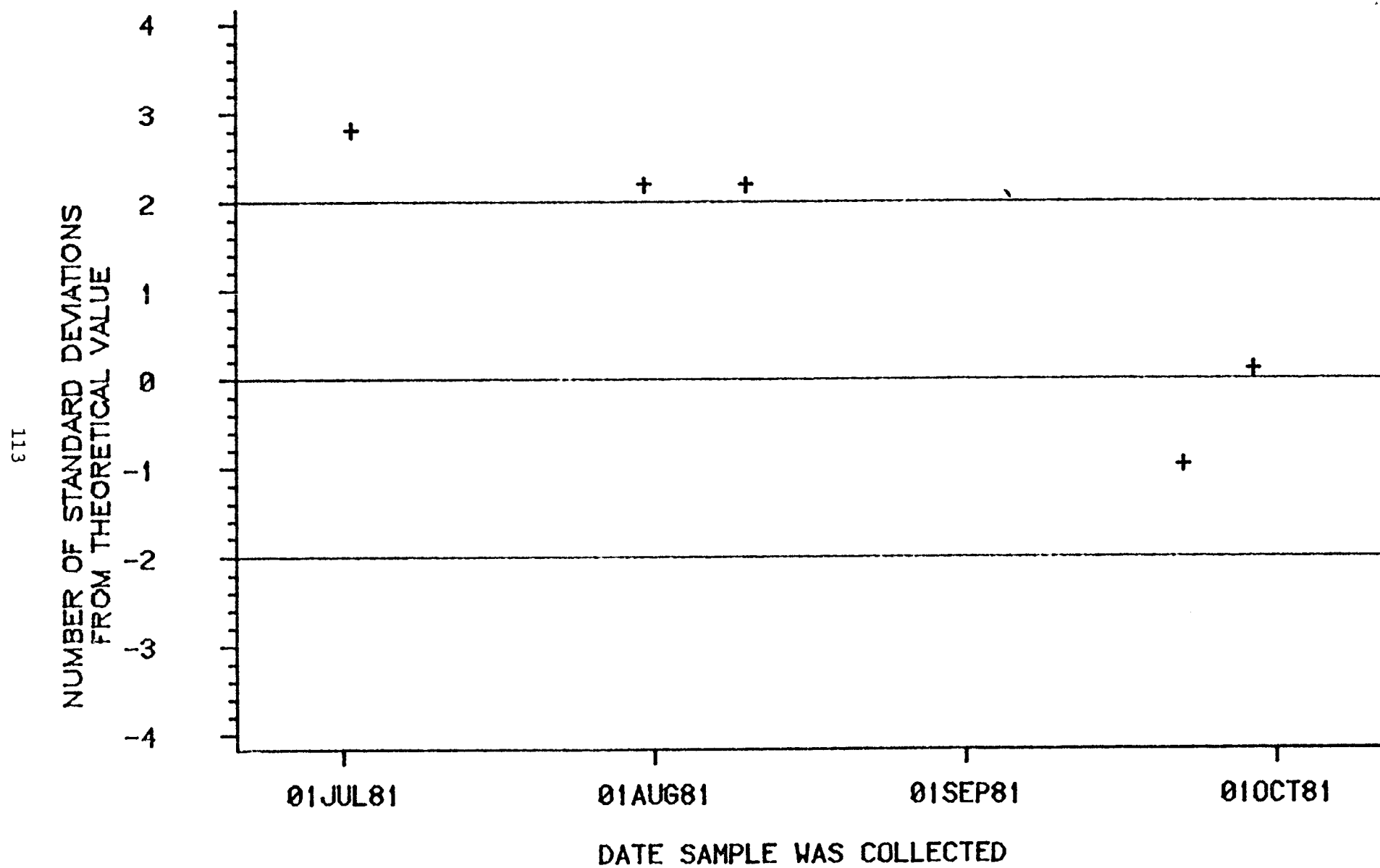


Figure A1.2.45.--Zinc, total recoverable data for the Denver Laboratory.

APPENDIX B

Table B1.1.--Tabulation of results¹ of samples which are
 "split" at time of collection: volatile organics

Determination	Sample	Atlanta (µg/L)	Denver ² (µg/L)
Benzene	1	ND ³	2
	2	ND	2
	3	ND	2
	4	ND	1
Trichloroethylene	1	ND	30
	2	ND	2
	3	ND	1
	4	ND	1
Methylene chloride	1	ND	8
	2	ND	1
	3	ND	1
	4	ND	1

¹All other results were reported as "ND" by the Atlanta Laboratory and "<1" by the Denver Laboratory.

²Analyses performed by the Atlanta Laboratory (see text).

³Not detected.

Table B1.2.--Tabulation of results of samples which are "split"
at time of collection: chlorophyll a

Sample	Atlanta	Denver	Reston ¹
1	19.1	5.3	18.7
2	29.9	12.5	28.6
3	19.8	4.9	18.0
4	4.4	2.1	5.9
5	3.8	1.0	3.0
6	35.9	10.3	37.8
7	21.9	8.3	26.9
	20.5	8.3	26.3
	17.6	8.0	26.4
8	13.3	3.7	13.8
9	7.5	1.1	7.5

¹Potomac Estuary Project Laboratory