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Analytical precision of One-Sixth Order Semiquantitative Spectrographic analysis

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By J. M. Motooka and D. J. Grimes

G E O L O G I C A L S U R V E Y C I R C U L A R 738

*Superimposed frequency diagrams represent the
precision for low, medium, and high concentrations
of the thirty elements routinely determined by the
Denver-based mobile spectrographic laboratories*

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ABSTRACT

Over 2,700 separate analyses were made on 22 different geologic samples selected to cover wide concentration ranges for the 30 elements studied. The precision for low, medium, and high concentrations of each element determined is represented by superimposed frequency diagrams and displays the frequency of reported values occurring within one-sixth order reporting intervals about the mean. Results are derived from mixed analyst and instrument conditions with no controls enforced other than randomization of samples. The precision of the six-step (one-sixth order) semiquantitative spectrographic analysis utilized by the Denver-based mobile laboratories exceeds that which is necessary for exploration geochemistry. Disallowing results obtained near the detection levels, the repeatability of the method, in general, is shown to be within one adjoining reporting interval on each side of the mean, 83 percent of the time, and within two adjoining reporting intervals on each side of the mean 96 percent of the time.

INTRODUCTION

Spectrochemical analysis is one of the most widely used analytical systems in geochemical exploration. In the six-step semiquantitative spectrographic method commonly used in the U.S. Geological Survey and first described by Myers, Havens, and Dunton (1961), and later by Ward, Lakin, Canney, and others (1963), and Grimes and Marranzino (1968), the light emitted at specific wavelengths by excited atoms of an unknown sample is photographed and results are obtained by visually comparing line densities of the unknown sample to the densities of known standard concentrations. The principal advantages, not found simultaneously in other types of analysis, are: a rapid multi-element analysis, adequate detection levels, relatively inexpensive cost per determination, and utilization of small sample sizes (10 milligrams or less). The mobile laboratories (Canney and others, 1957) also provide geologic field crews a

means of "on-site" analytical support which results in a more efficient planning of sampling programs by day-to-day evaluation of analytical data.

The basis of this report is a graphic illustration of the precision of each element at three concentration levels (low, medium, and high) evaluated according to occurrence within one-sixth order intervals about the respective mean values. The results of this investigation indicate a level of precision in excess of that required for geological exploration needs. In general, the repeatability within one (one-sixth order) reporting interval of the mean is approximately 83 percent and approximately 96 percent within two (one-sixth order) reporting intervals of the mean.

The primary reason for initiating this study was to provide information on the precision of the six-step semiquantitative spectrographic method, thereby determining the degree of confidence that can be placed on the reported values of the 30 elements chosen for analysis. In order to provide the necessary information to set a confidence level, the authors felt it important to design the study to investigate the sources of variation that affect precision. The study was also designed to simulate the variations of normal routine conditions.

The data were collected over a 3-year period and were generated by 7 analysts using 6 spectrographic instruments located in both field oriented laboratories and "in-house" laboratories. Because of the design of the study, it should be noted that the precision results shown here are representative of the spectrographic laboratory as a whole. Any one individual, under controlled conditions, would be expected to produce better results.

This report summarizes the efforts of numerous U.S. Geological Survey personnel. Special mention is given of the contributions made by A. T. Miesch for his initial consultation in setting up the study; by R. J. Smith and L. O. Wilch for handling the computer aspects; and by K. J. Curry, G. W. Day, J. A. Domenico, C. L. Forn, R. T. Hopkins, Jr., and D. F. Siems for performing the analytical work.

SPECTROGRAPHIC STANDARDS

In the six-step method used by the Denver-based mobile laboratories, synthetic standards are prepared from spectrographically pure compounds (usually oxides and some carbonates) and are diluted in one-third-order intervals, thereby providing three steps per order of magnitude. In order to obtain six steps per order of magnitude, the intermediate steps are visually interpolated.

Appropriate quantities of the sought-after elements are added and thoroughly mixed with an average rock matrix consisting of major elements (31 percent Si, 5 percent Al, 7 percent Fe, 2 percent Ca, 0.6 percent Mg, 1.6 percent Na, 1.1 percent K). Standards containing successively lower amounts of the elements are made by use of a dilution factor equal to the reciprocal of the cube root 10 (0.464). Analytical results are reported as six steps per order of magnitude (10, 7, 5, 3, 2, 1.5, or powers of 10 of these numbers) which are approximate geometric midpoints of concentration ranges whose boundaries are as follows:

<i>Reported value</i>	<i>Interval</i>
10	8.3-12
7	5.6-8.3
5	3.8-5.6
3	2.6-3.8
2	1.8-2.6
1.5	1.2-1.8

Details on the technique of preparing spectrographic standards are further described by Grimes and Marranzino (1968).

EXPERIMENTAL DESIGN

The study was designed to simulate normal routine conditions for analyses of the test samples. The routine procedure for the Denver-

based mobile spectrographic laboratories is to analyze all silicate samples by the same analytical method and to employ the same set of spectrographic standards for obtaining results—that is, no distinction for modification of procedure is used for different types of rocks, soils, or stream sediments. Thirty elements, each of whose concentrations may range widely, are routinely determined in the six-step spectrographic method. As detection levels are approached, precision of the analysis is greatly diminished. To provide the various concentration levels of all elements reported, 15 geologic samples were originally selected, and 7 “geochemical exploration reference samples” were added later to fill some of the missing concentration levels (Allcott and Lakin, 1974). The samples were selected according to the concentration of a certain element or elements without regard to geologic material types. Therefore, several types of sample media were included, such as stream sediments, soils, drill cores, and various rock types. The detectable gold in two samples is in the micrometre to sub- μ m particle size. They were specifically selected because of their homogeneity and should not be considered as characteristic of all gold-bearing geologic materials. Gold samples of larger particle size would not be expected to produce such precise results when using 10-milligram sample sizes.

The original 15 samples were not given any special preparation prior to analysis, whereas the “geological reference samples” were prepared under well-defined conditions, specifically to insure homogeneity (Allcott and Lakin, 1975).

The 22 study samples were split into 600 subsamples. Random numbers were assigned and the 600 subsamples were divided into groups of 40 samples each for distribution and rotation among the analysts. A coded number was assigned to each split, to distinguish sample, spectrographer, spectrographic instrument, “in-house” or field laboratory, and the year in which the work was performed. The purpose of this report is not to provide individual breakdowns but to determine the precision of the entire laboratory under the combined influence of precision-affecting variables.

The study samples were analyzed along with routine samples at the rate of approximately 1 split to every 20 routine samples. At periodic intervals the groups of 40 splits were rotated

among the spectrographers so that all the original 22 test samples were analyzed numerous times (approximately 20) by all 7 spectrographers utilizing different spectrographic instruments both "in-house" and in field laboratories. Over a 3-year period, each study sample was analyzed a minimum of 83 times, and some as many as 154 times, resulting in over 2,700 separate analyses. The data were stored in a computer-storage system for easy retrieval.

EXPLANATION OF GRAPHS AND TABLES

GRAPHS

The line graphs (figs. 1-30) are frequency diagrams of histograms obtained from a computer program designed to generate graphical displays. Each figure is representative of a single element, and most contain three superimposed graphs representative of the precision of the element at a low, medium, and high concentration level. Where two or more of the same concentration levels were present, among the 22 test samples, selection was made on an arbitrary basis. The concentration level of each graph is indicated. Elements having only two line graphs are Au, Cd, Nb, Sc, and W, where only two distinct concentration levels could be found in the 22 test samples. Note that each line graph is representative of a concentration level of an element in only 1 of 22 test samples and is identified by sample number in the tables so that comparisons of different elements within a sample can be made.

The frequency diagrams for the same element are superimposed to display the variable skewness at different concentration ranges. Since each line graph is a different concentration range, in order to superimpose them the mean value is set at zero (abscissa axes). Variations in the analysis from the mean (reported as geometric midpoints of the spectrographic reporting intervals) are then designated +1, -1, +2, -2, and so forth, with respect to the mean value at zero, and plotted according to frequency. The interval frequencies are rounded to whole numbers, and the sums of the plot-points on the diagrams are within 1 percent of 100.

In the six-step semiquantitative spectrographic method, if a spectrographic line is

detected but is less than the lowest discernible standard line, the value is designated as L (less than amount shown); if no line is detected, the value is designated as N (not detected); and if the line is greater than the highest standard, the value is designated as G (greater than). These values (L, N, and G) are termed "qualified values." Inasmuch as only unqualified values can be used for calculations, in this report, all L's were assigned the next lowest reporting value, and all remaining qualified values (N and G) were dropped from the calculation of the mean values. Where N's and G's occur, the histograms end abruptly with the symbol \square in their respective spectrographic interval.

TABLES

The tables are capsule summaries of the frequency diagrams. Each test sample is identified by a number, and the mean value (set to zero on the diagram) of the chosen concentration ranges is shown. The columns of percent frequency include (1) the values of the mean interval plus one adjacent interval on each side, and (2) the mean plus two adjacent intervals on each side. Qualified values of G within two intervals of the mean are included in the frequency calculations, whereas qualified values of N within two intervals of the mean are not. A final column denotes the total number of analyses of a particular sample.

DISCUSSION

The frequencies of analytical values (not including those at the lower limit of detection) within the reporting interval containing the mean value plus or minus one and two adjoining intervals have respective norm values of approximately 83 percent and 96 percent. These values are consistent for a variety of geologic materials and show no appreciable difference between elements or their concentration ranges regardless of the variation apparent in some of the histograms. Some of the more extreme outlying values and some of the consequent variation may be due to misplaced decimals, inadvertent zeros, or errors made in transcribing the more than 81,000 determinations included in the study.

When the concentration levels of the elements are at or near the detection limit of the method, the precision tends to be lower. Much of this can

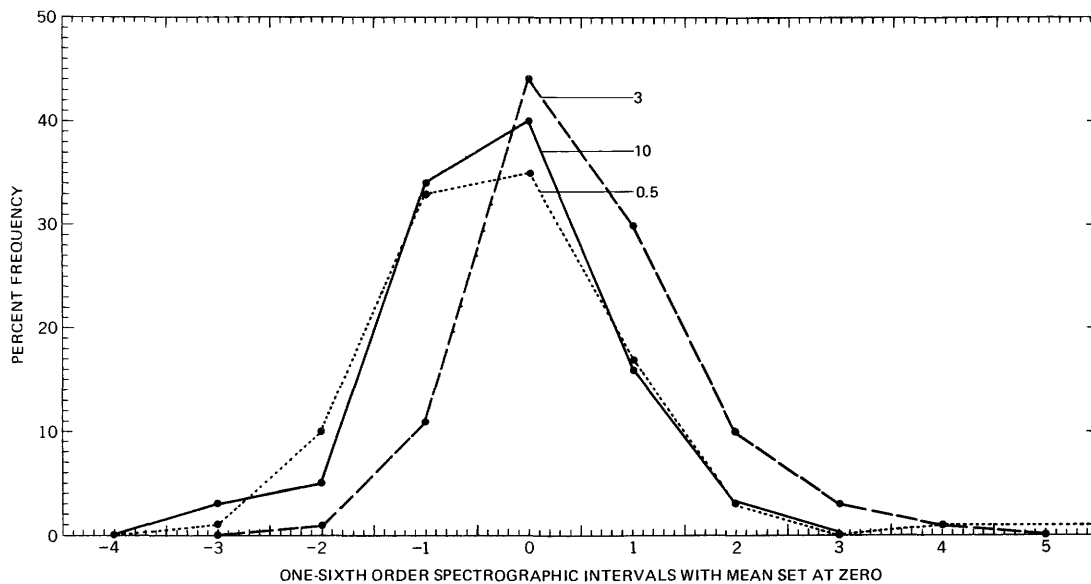
be attributed to N (not detected) values being reported for the low concentration levels. For concentration levels at or near the detection level, such elements as As, La, Nb, Sn, Sr, Zn, and Zr were not detected by the analyst more than 25 percent of the time. Factors causing this could be (1) differences in instrumentation, (2) inconsistencies in the analytical procedure, (3) inexperienced spectrographers, or, possibly more important, (4) detection levels set too low for these elements. Four elements—Mn, Ag, As, and Cu — show a distinct bimodal distribution in the frequency diagrams at the low-concentration levels. These bimodal distribution patterns are indicative of an analyst's inability to visually distinguish between concentration steps in the spectrographic standards at the lower levels.

The precision of the six-step semiquantitative spectrographic method is equal to and even exceeds in certain instances the precision of other studies (Myers and others, 1961; Barnett, 1961) developed under more stringent laboratory conditions. The authors feel the precision of the method is more than adequate for the intended purpose of the procedure. Until newer or more sensitive multielement methods are developed, the six-step semiquantitative spectrographic method holds a unique position as

one of the most useful and effective data-gathering reconnaissance tools in geochemical exploration.

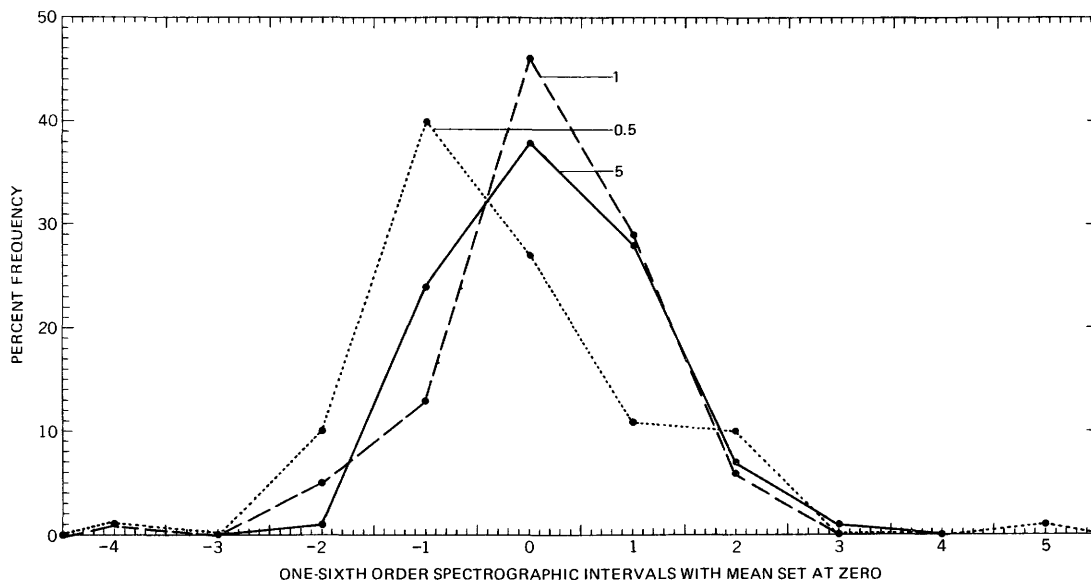
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Sample number	Concentration (percent)	Percent frequency		Total analyses
		One interval	Two intervals	
6	0.5	85	98	147
11	3	85	96	136
4	10	90	98	152

FIGURE 1. — Frequency diagram and tabular summary for iron in selected experimental samples; Fe detection level (0.05) in percent.



Sample number	Concentration (percent)	Percent frequency		Total analyses
		One interval	Two intervals	
7	0.5	78	98	126
17	1	88	99	102
11	5	90	97	136

FIGURE 2.—Frequency diagram and tabular summary for magnesium in selected experimental samples; Mg detection level (0.02) in percent.

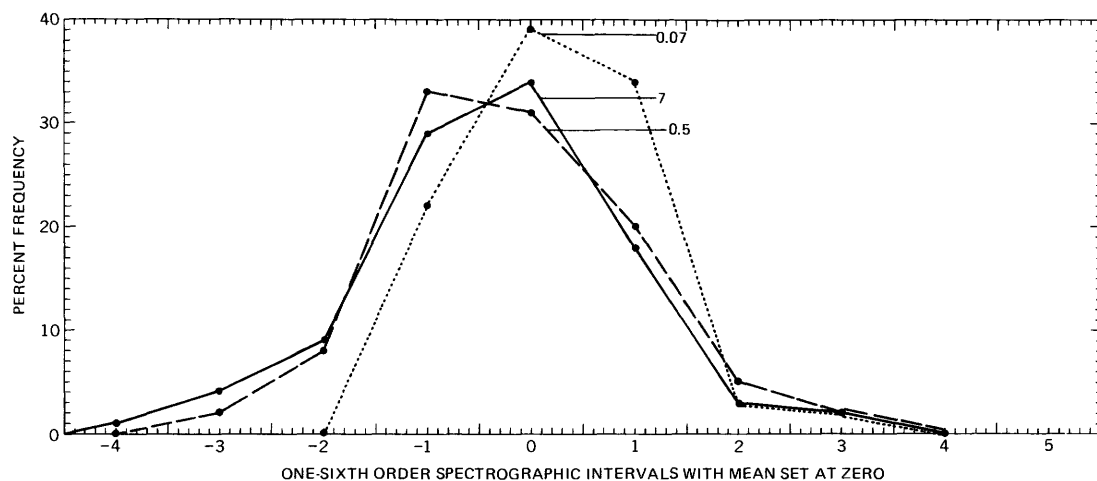


FIGURE 3.—Frequency diagram and tabular summary for calcium in selected experimental samples; Ca detection level (0.05) in percent.

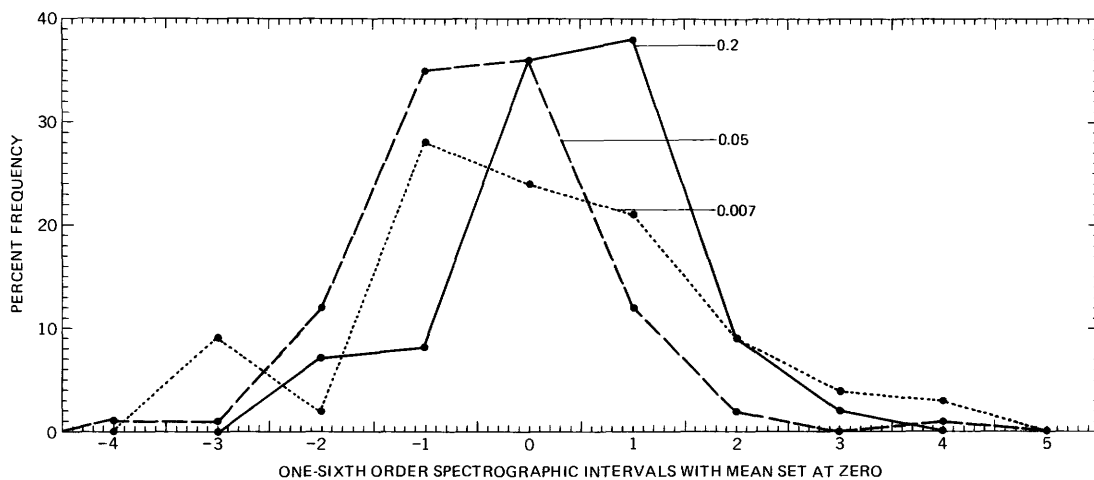
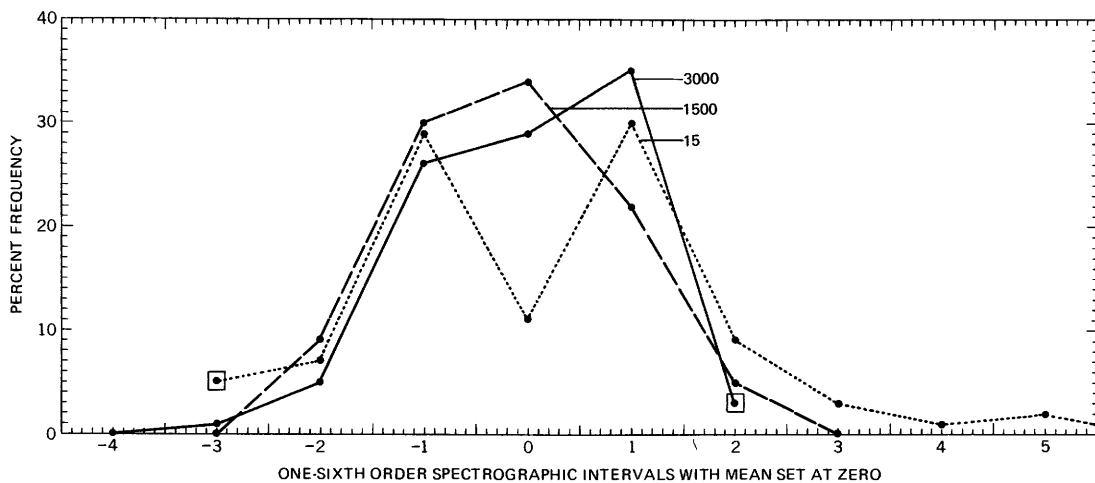
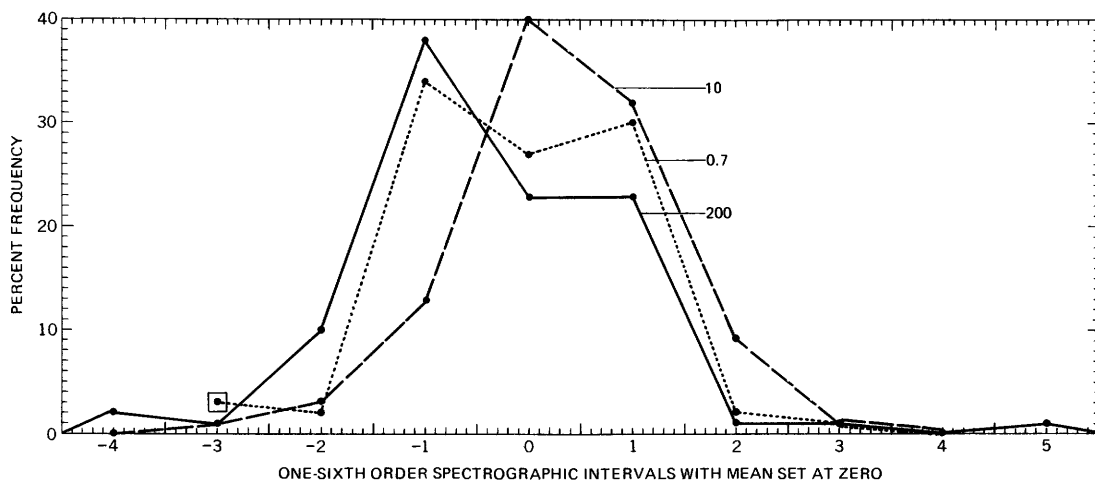


FIGURE 4.—Frequency diagram and tabular summary for titanium in selected experimental samples; Ti detection level (0.002) in percent.



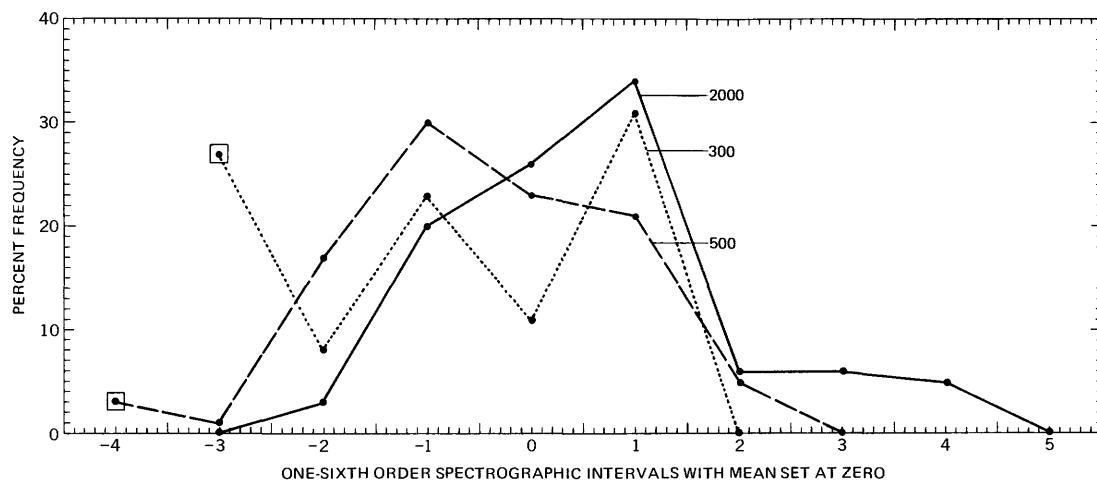
Sample number	Concentration (ppm)	Percent frequency		Total analyses
		One interval	Two intervals	
6	15	70	86	149
14	1,500	86	100	113
2	3,000	90	98	152

FIGURE 5.—Frequency diagram and tabular summary for manganese in selected experimental samples; Mn detection level (10) in ppm. Box indicates qualified value N or G.



Sample number	Concentration (ppm)	Percent frequency		Total analyses
		One interval	Two intervals	
20	0.7	91	95	88
11	10	85	97	136
13	200	84	95	134

FIGURE 6.—Frequency diagram and tabular summary for silver in selected experimental samples; Ag detection level (0.5) in ppm. Box indicates qualified value N or G.



Sample number	Concentration (ppm)	Percent frequency		Total analyses
		One interval	Two intervals	
21	300	65	73	88
6	500	74	96	149
5	2,000	80	88	141

FIGURE 7.—Frequency diagram and tabular summary for arsenic in selected experimental samples; As detection level (200) in ppm. Box indicates qualified value N or G.

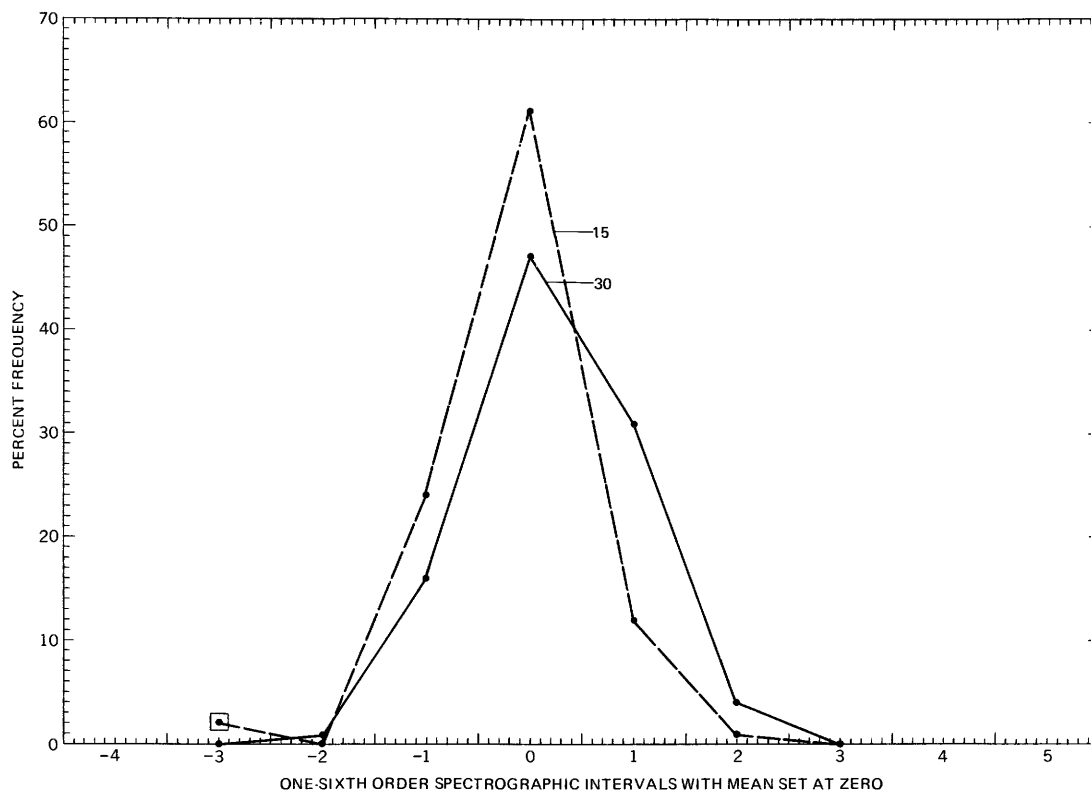
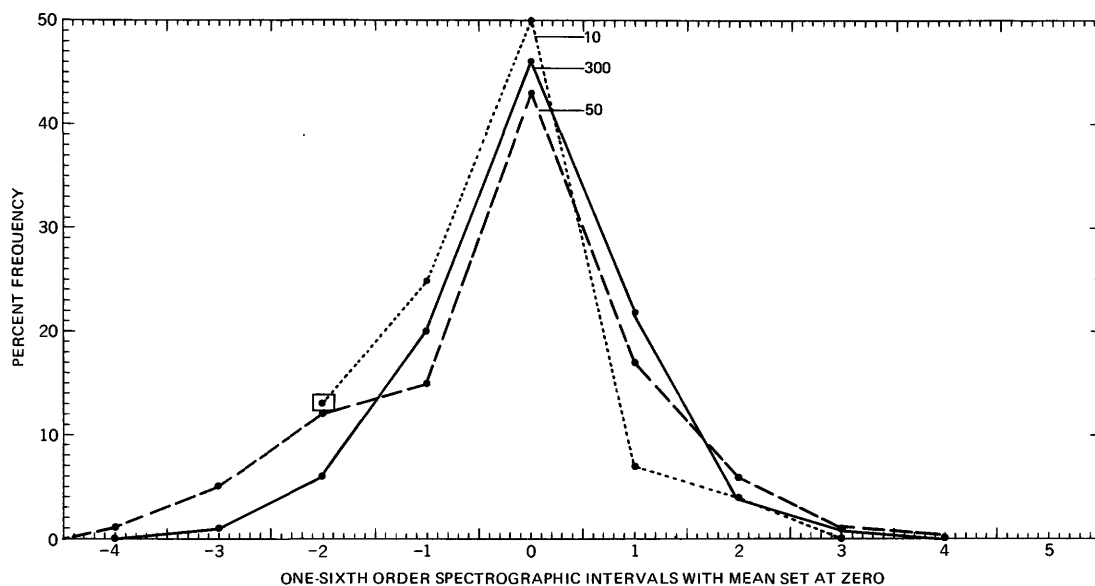


FIGURE 8.—Frequency diagram and tabular summary for gold in selected experimental samples; Au detection level (10) in ppm. Box indicates qualified value N or G.



Sample number	Concentration (ppm)	Percent frequency		Total analyses
		One interval	Two intervals	
19	10	82	86	99
11	50	75	93	136
12	300	88	98	140

FIGURE 9.—Frequency diagram and tabular summary for boron in selected experimental samples; B detection level (10) in ppm. Box indicates qualified value N or G.

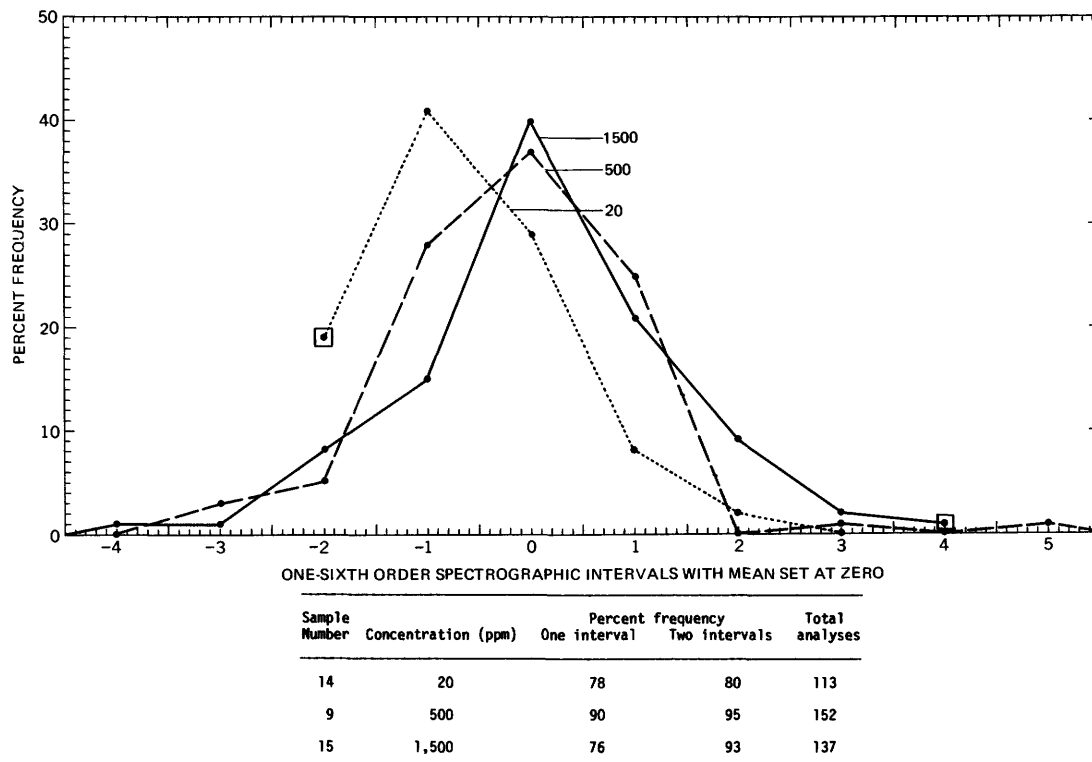
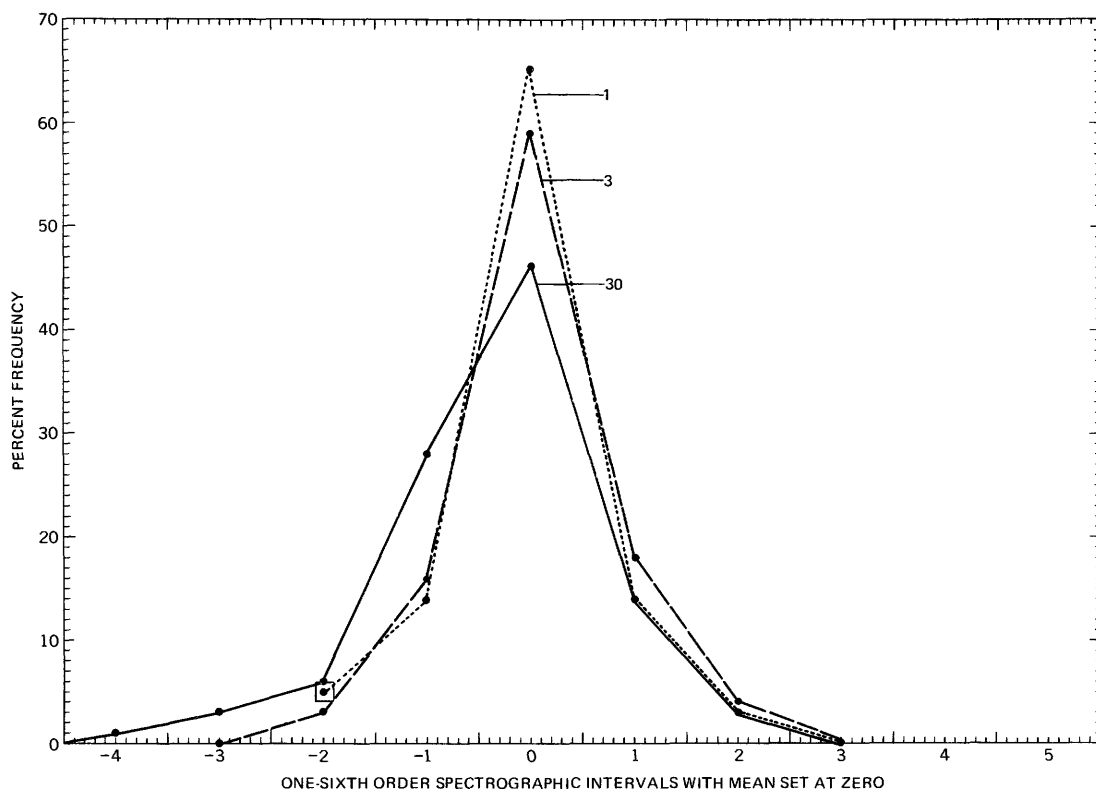


FIGURE 10.—Frequency diagram and tabular summary for barium in selected experimental samples; Ba detection level (20) in ppm. Box indicates qualified value N or G.



Sample number	Concentration (ppm)	Percent frequency		Total analyses
		One interval	Two intervals	
16	1	93	96	96
5	3	93	100	141
3	30	88	97	151

FIGURE 11.—Frequency diagram and tabular summary for beryllium in selected experimental samples; Be detection level (1) in ppm. Box indicates qualified value N or G.

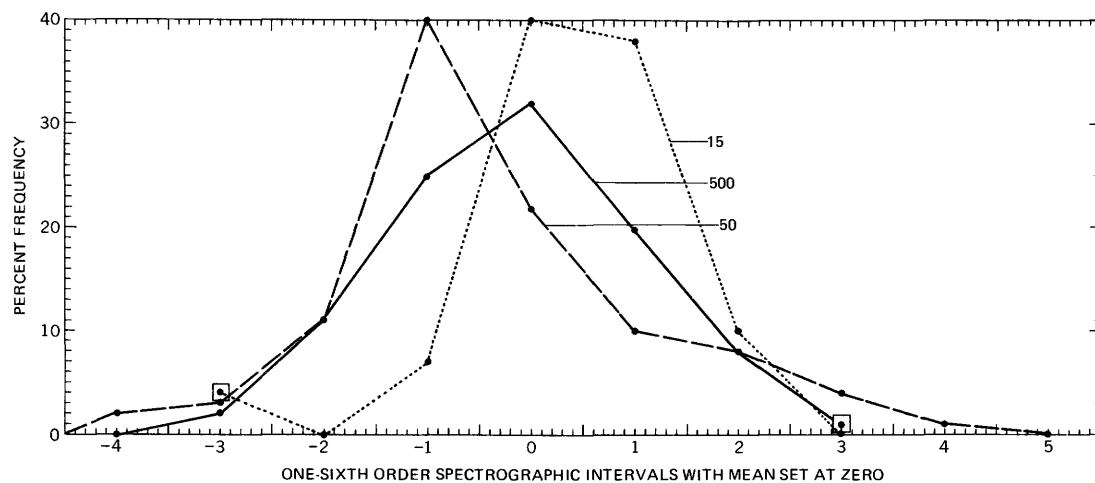


FIGURE 12.—Frequency diagram and tabular summary for bismuth in selected experimental samples; Bi detection level (10) in ppm. Box indicates qualified value N or G.

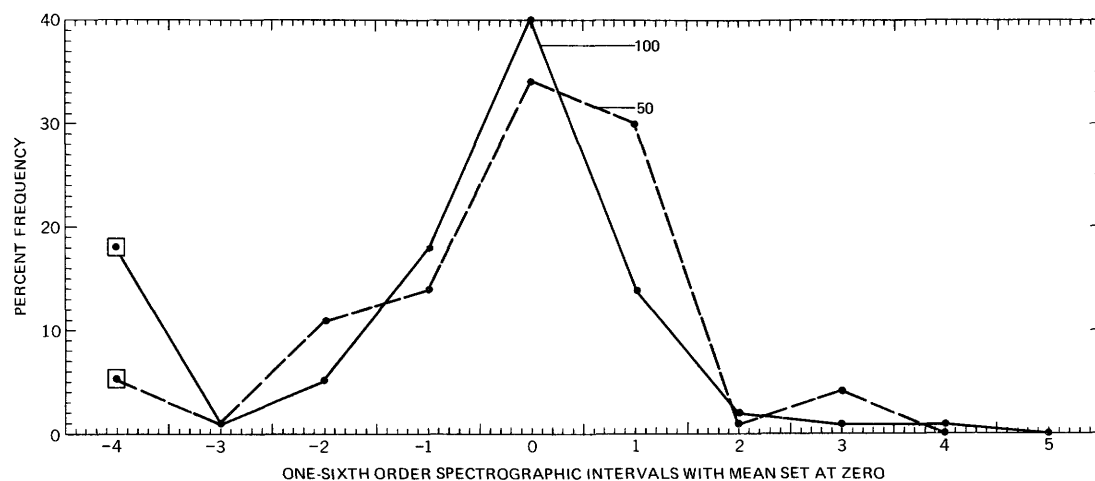


FIGURE 13.—Frequency diagram and tabular summary for cadmium in selected experimental samples; Cd detection level (20) in ppm. Box indicates qualified value N or G.

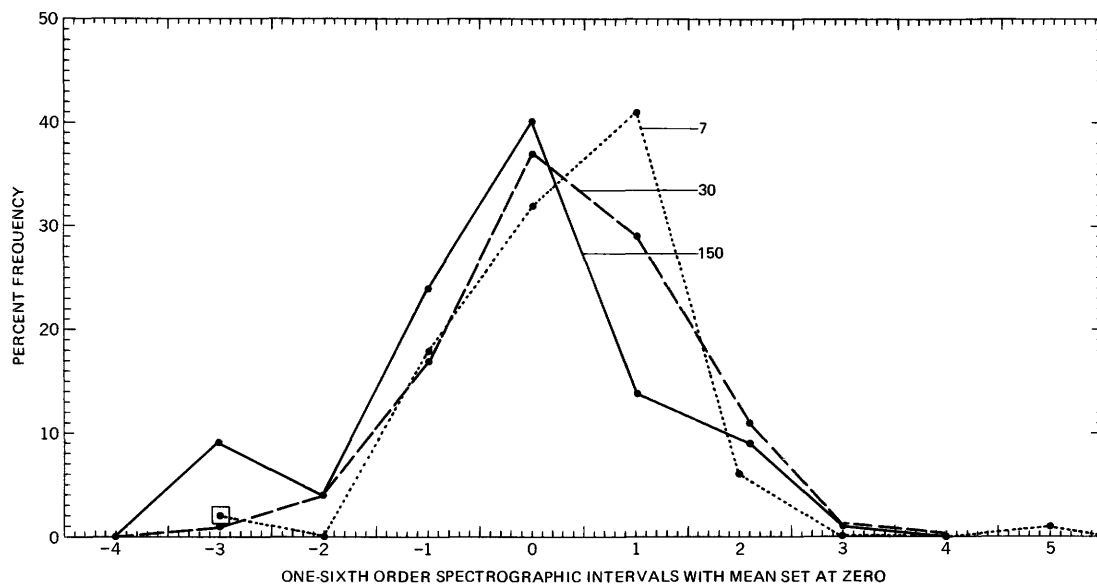
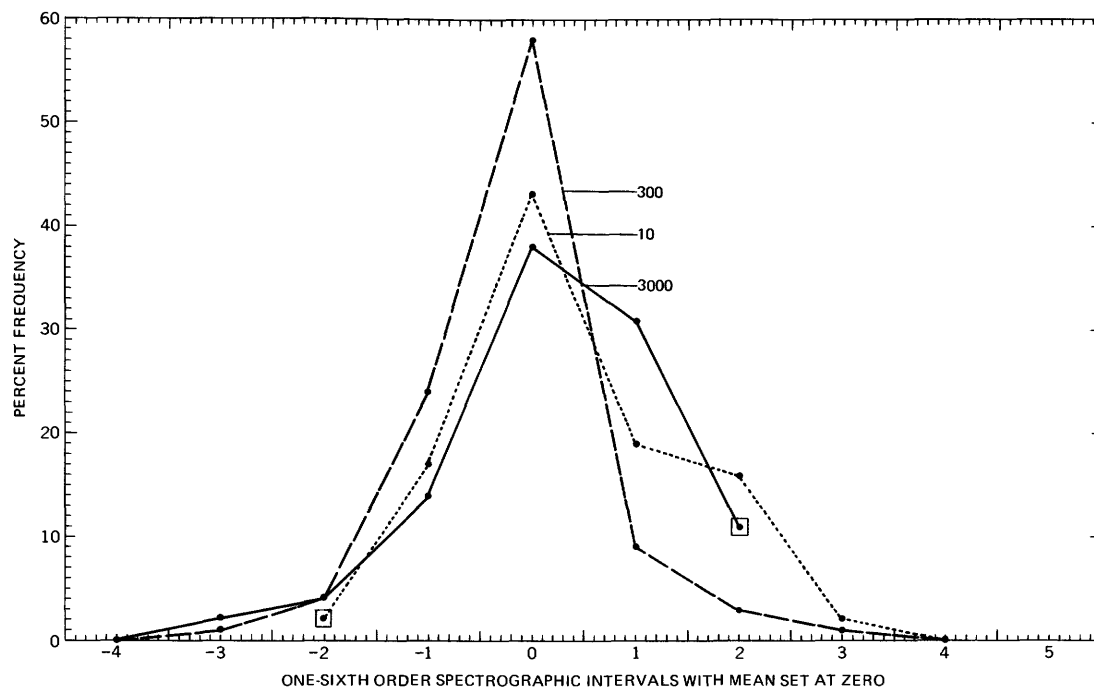
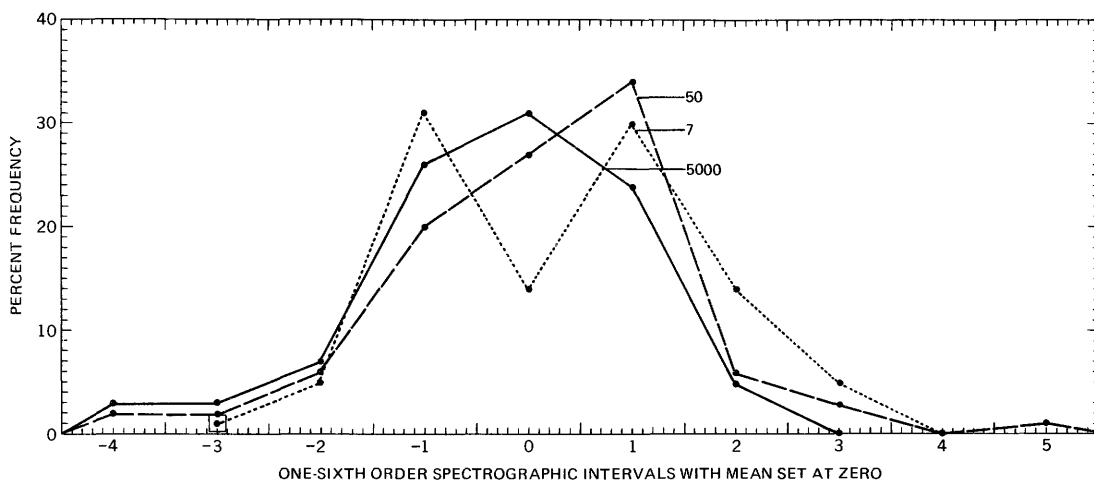


FIGURE 14.—Frequency diagram and tabular summary for cobalt in selected experimental samples; Co detection level (5) in ppm. Box indicates qualified value N or G.



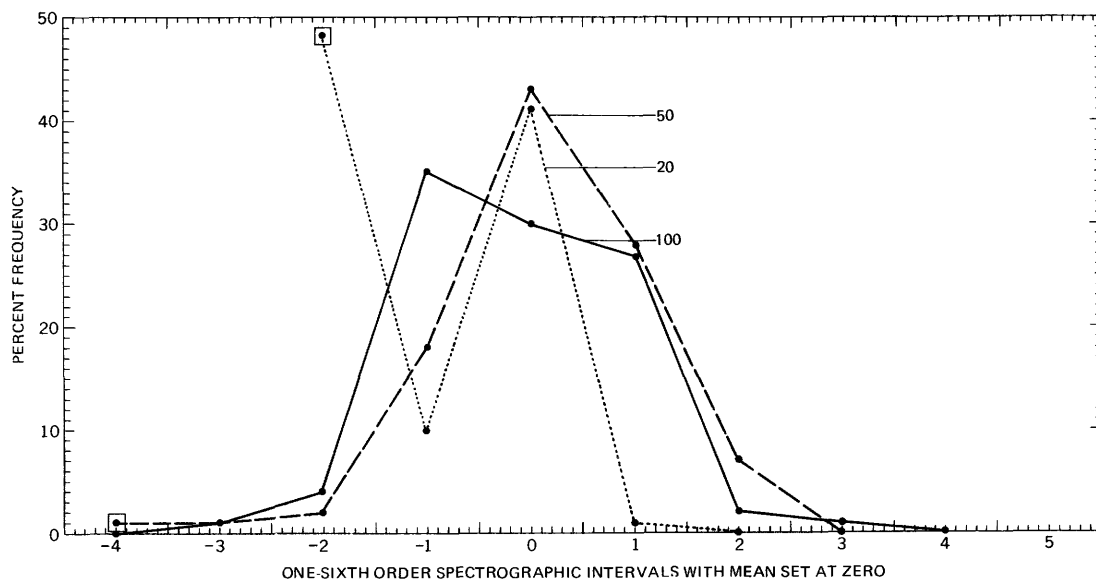
Sample number	Concentration (ppm)	Percent frequency		Total analyses
		One interval	Two intervals	
22	10	79	95	83
11	300	91	98	136
14	3,000	83	98	113

FIGURE 15.—Frequency diagram and tabular summary for chromium in selected experimental samples; Cr detection level (10) in ppm. Box indicates qualified value N or G.



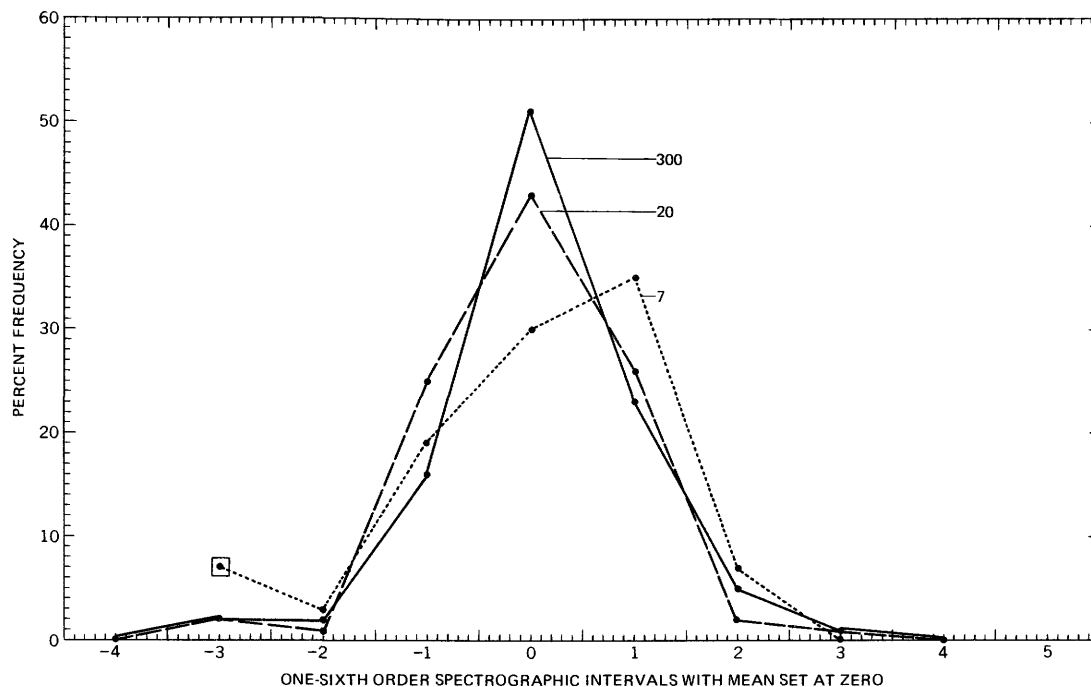
Sample number	Concentration (ppm)	Percent frequency		Total analyses
		One interval	Two intervals	
18	7	75	94	103
9	50	81	93	152
13	5,000	81	93	134

FIGURE 16.—Frequency diagram and tabular summary for copper in selected experimental samples; Cu detection level (5) in ppm. Box indicates qualified value N or G.



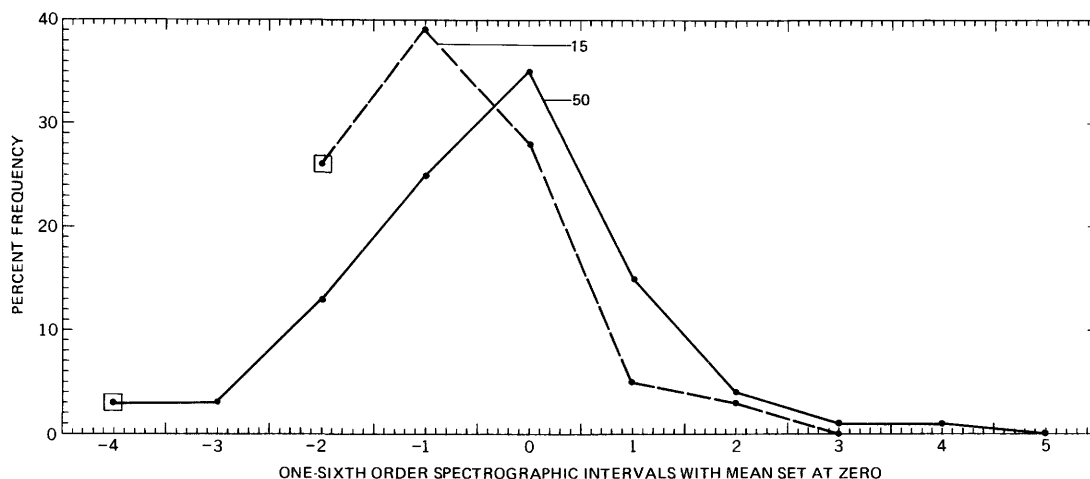
Sample number	Concentration (ppm)	Percent frequency		Total analyses
		One interval	Two intervals	
6	20	52	52	88
9	50	89	98	152
11	100	92	98	136

FIGURE 17.—Frequency diagram and tabular summary for lanthanum in selected experimental samples; La detection level (20) in ppm. Box indicates qualified value N or G.



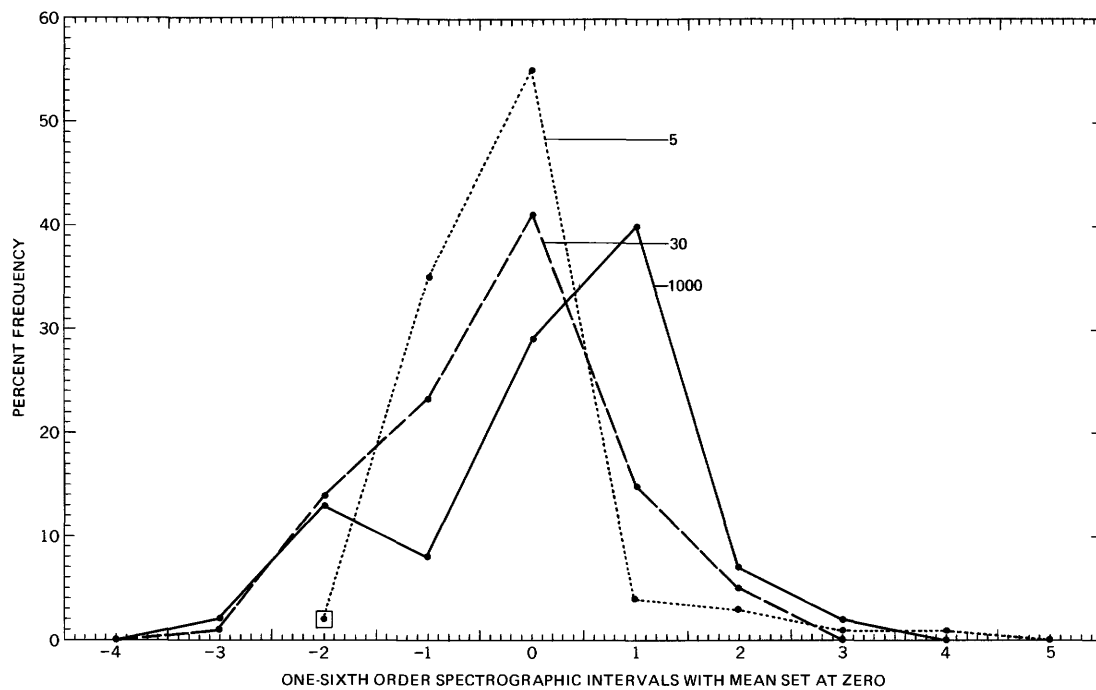
Sample number	Concentration (ppm)	Percent frequency		Total analyses
		One interval	Two intervals	
9	7	84	94	152
15	20	94	97	136
5	300	90	97	97

FIGURE 18.—Frequency diagram and tabular summary for molybdenum in selected experimental samples; Mo detection level (5) in ppm. Box indicates qualified value N or G.



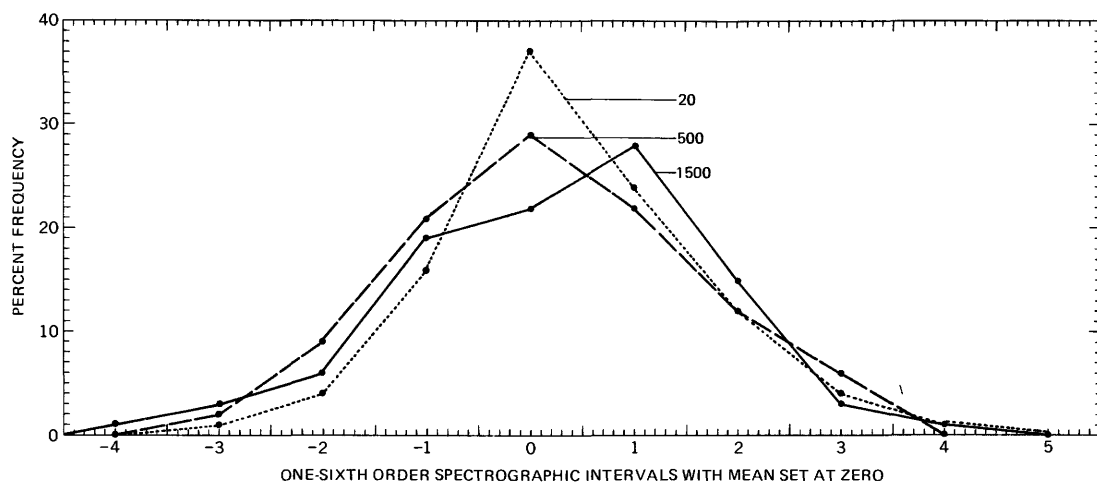
Sample Number	Concentration (ppm)	Percent frequency		Total analyses
		One interval	Two intervals	
9	15	72	75	152
2	50	75	92	153

FIGURE 19.—Frequency diagram and tabular summary for niobium in selected experimental samples; Nb detection level (10) in ppm. Box indicates qualified value N or G.



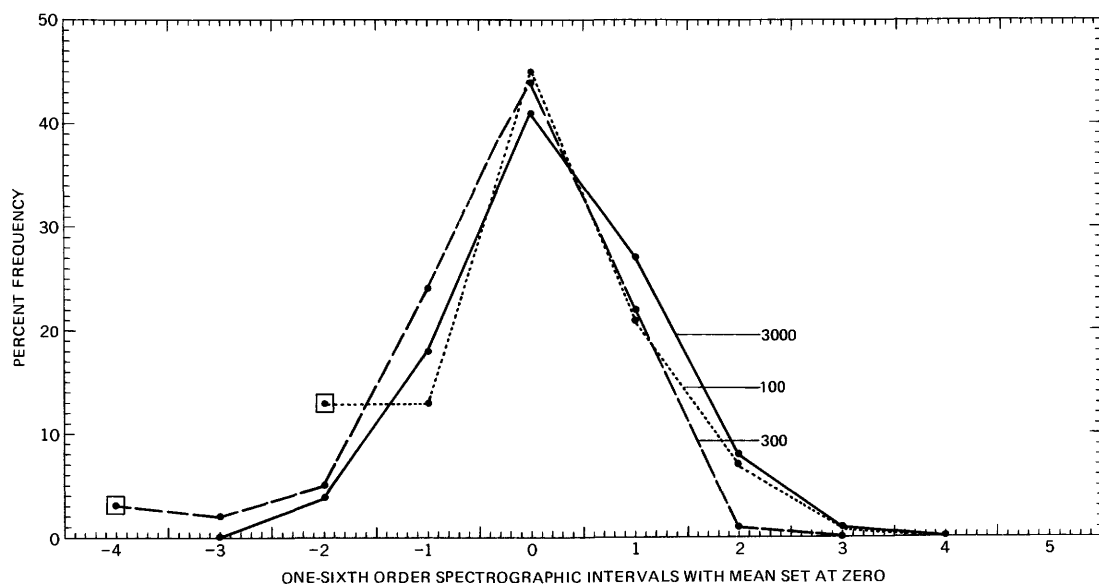
Sample number	Concentration (ppm)	Percent frequency		Total analyses
		One interval	Two intervals	
15	5	94	97	136
3	30	79	98	151
14	1,000	77	97	112

FIGURE 20.—Frequency diagram and tabular summary for nickel in selected experimental samples; Ni detection level (5) in ppm. Box indicates qualified value N or G.



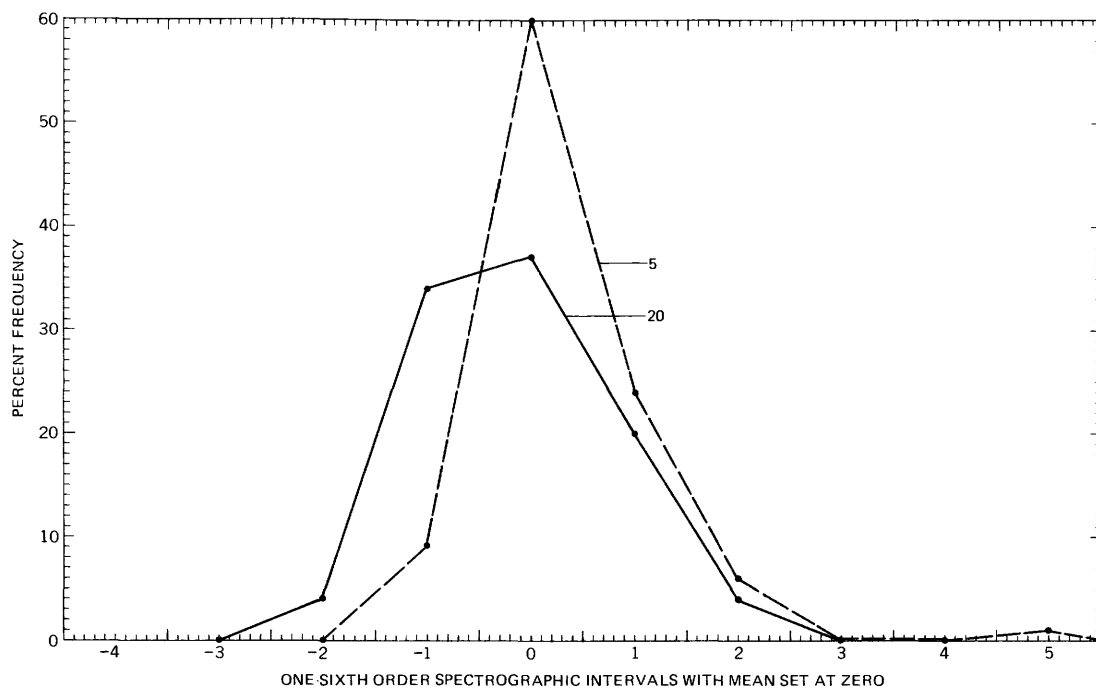
Sample number	Concentration (ppm)	Percent frequency		Total analyses
		One interval	Two intervals	
2	20	77	93	153
10	500	72	93	129
15	1,500	69	90	137

FIGURE 21.—Frequency diagram and tabular summary for lead in selected experimental samples; Pb detection level (10) in ppm.



Sample number	Concentration (ppm)	Percent frequency		Total analyses
		One interval	Two intervals	
5	100	79	86	141
9	300	90	96	152
13	3,000	86	98	134

FIGURE 22.—Frequency diagram and tabular summary for antimony in selected experimental samples; Sb detection level (100) in ppm. Box indicates qualified value N or G.



Sample number	Concentration (ppm)	Percent frequency		Total analyses
		One interval	Two intervals	
1	5	93	99	139
11	20	91	99	135

FIGURE 23.—Frequency diagram and tabular summary for scandium in selected experimental samples; Sc detection level (5) in ppm.

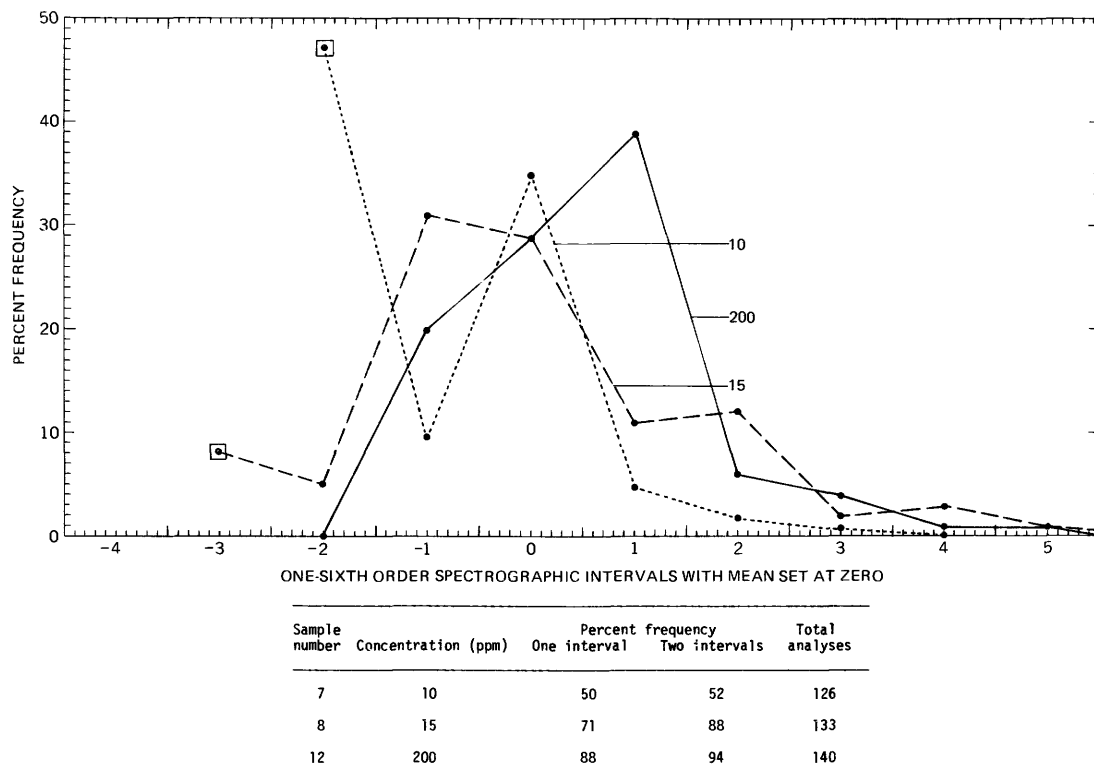
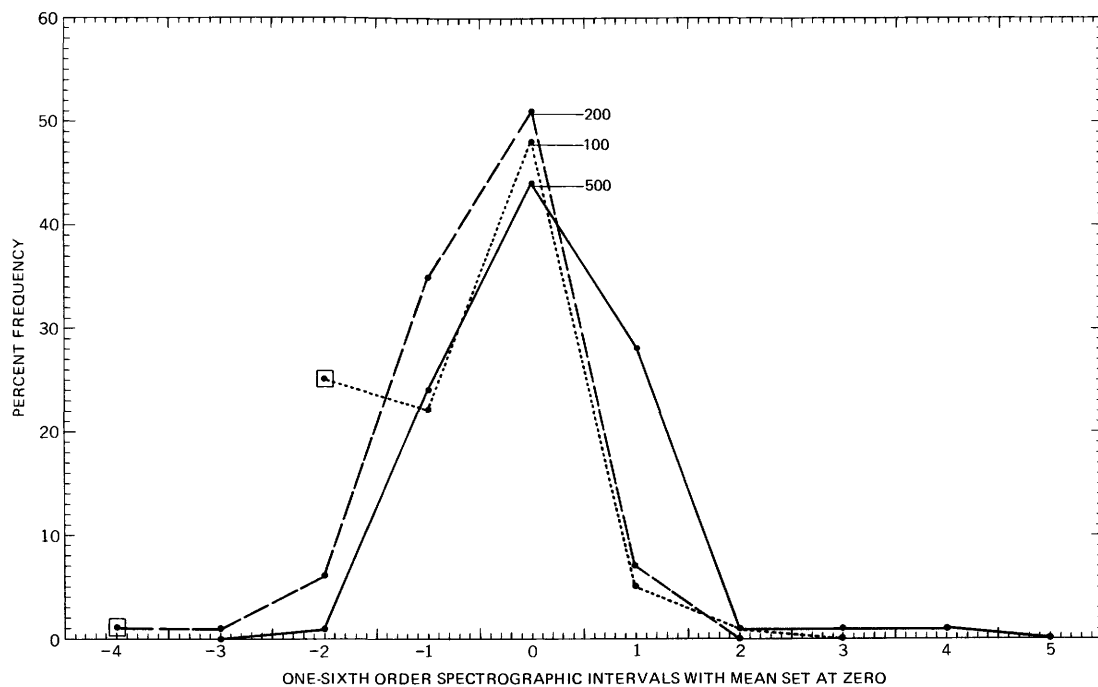
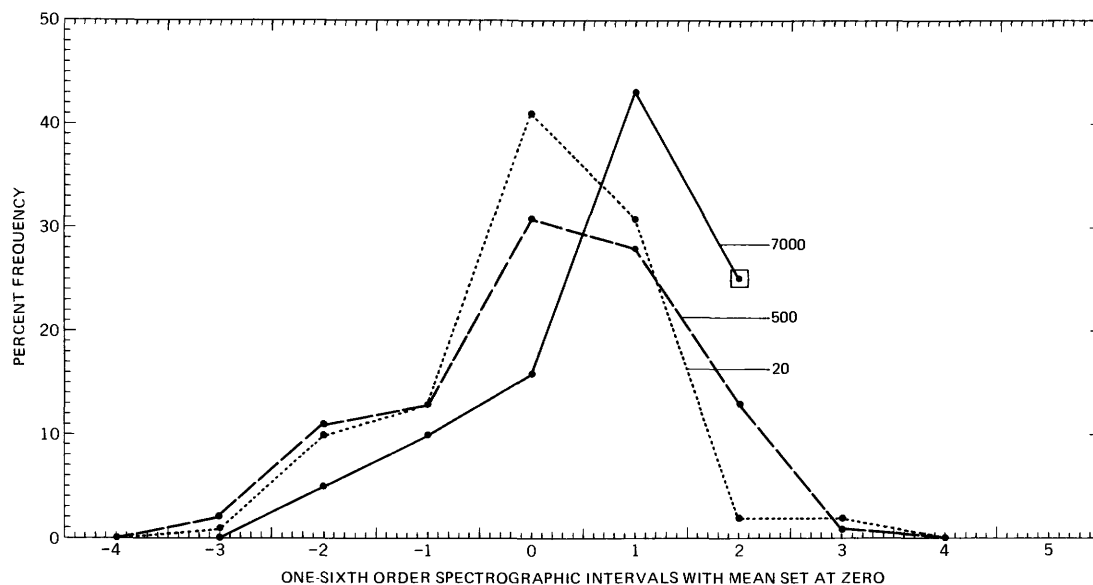


FIGURE 24.—Frequency diagram and tabular summary for tin in selected experimental samples; Sn detection level (10) in ppm. Box indicates qualified value N or G.



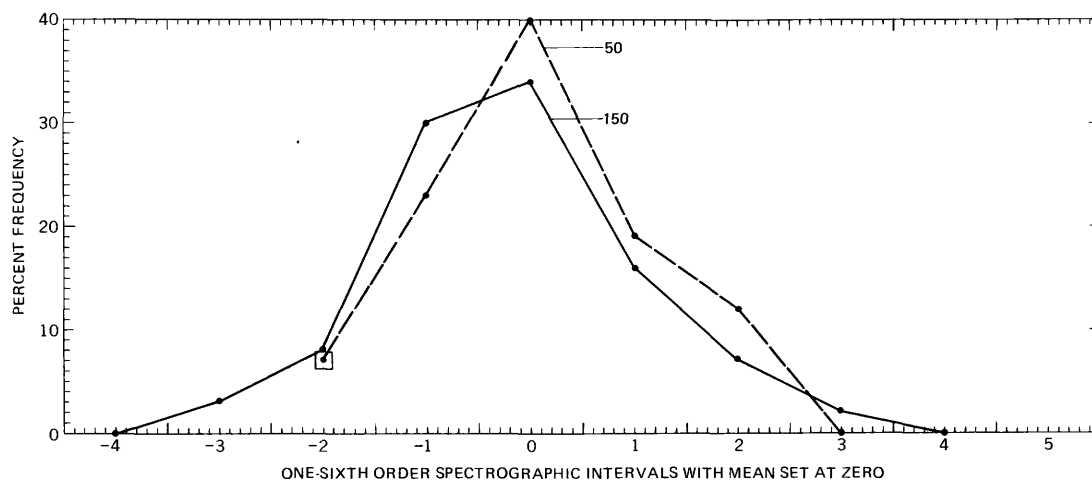
Sample number	Concentration (ppm)	Percent frequency		Total analyses
		One interval	Two intervals	
7	100	75	76	126
1	200	93	99	139
11	500	96	98	136

FIGURE 25.—Frequency diagram and tabular summary for strontium in selected experimental samples; Sr detection level (100) in ppm. Box indicates qualified value N or G.



Sample number	Concentration (ppm)	Percent frequency		Total analyses
		One interval	Two intervals	
15	20	85	97	136
8	500	72	96	134
11	7,000	69	100	136

FIGURE 26.—Frequency diagram and tabular summary for vanadium in selected experimental samples; V detection level (10) in ppm. Box indicates qualified value N or G.



Sample number	Concentration (ppm)	Percent frequency		Total analyses
		One interval	Two intervals	
7	50	82	94	128
9	150	80	95	151

FIGURE 27.—Frequency diagram and tabular summary for tungsten in selected experimental samples; W detection level (50) in ppm. Box indicates qualified value N or G.

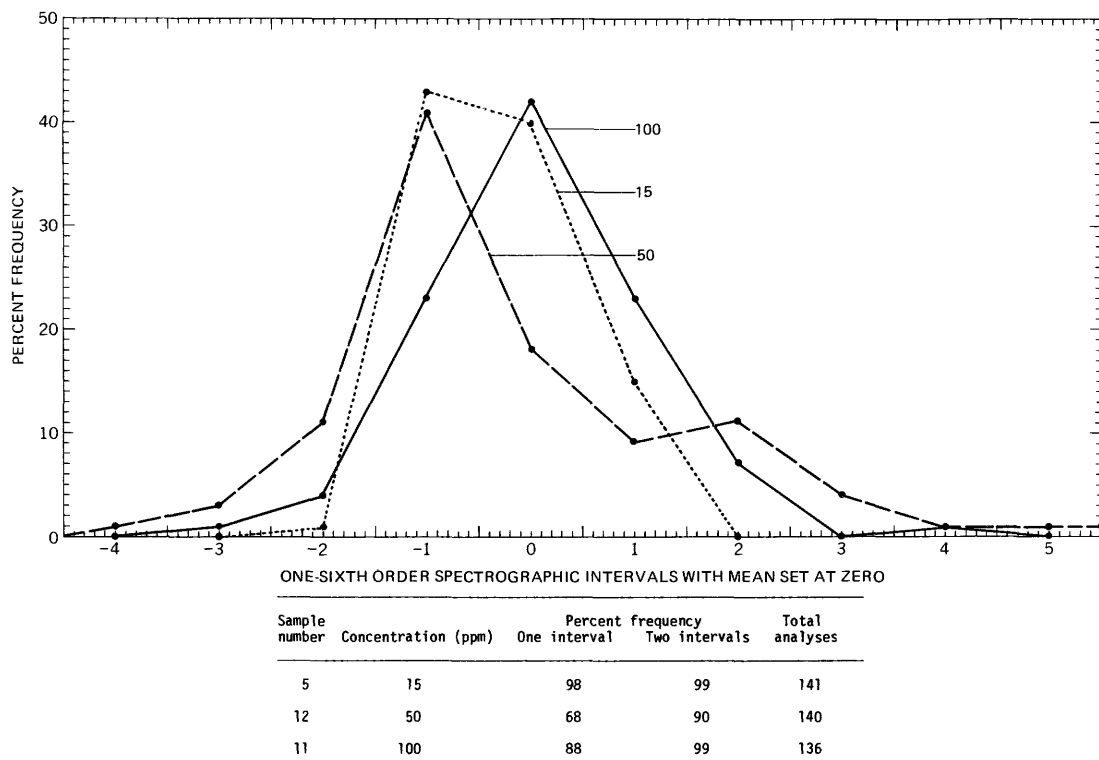


FIGURE 28.—Frequency diagram and tabular summary for yttrium in selected experimental samples; Y detection level (10) in ppm.

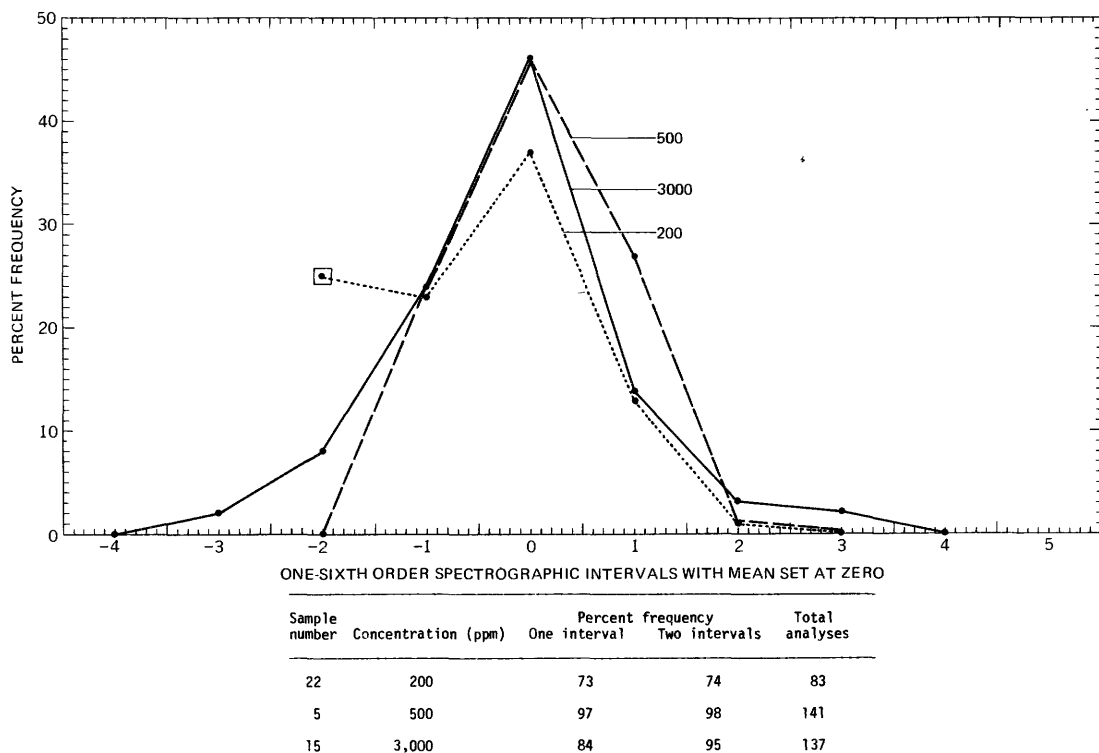
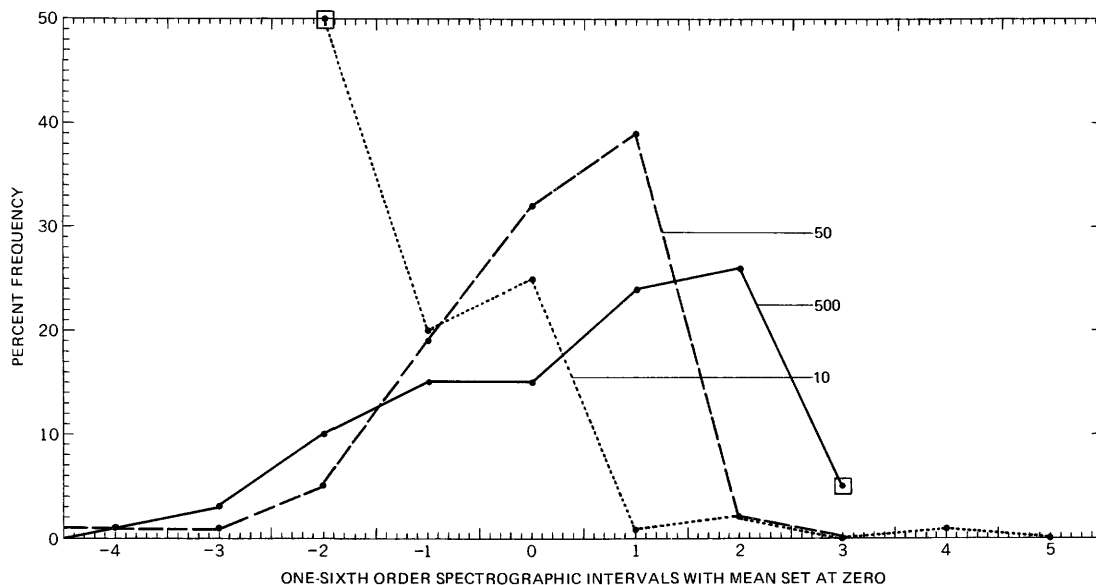


FIGURE 29.—Frequency diagram and tabular summary for zinc in selected experimental samples; Zn detection level (200) in ppm. Box indicates qualified value N or G.



Sample number	Concentration (ppm)	Percent frequency		Total analyses
		One interval	Two intervals	
4	10	46	48	152
10	50	90	97	128
2	500	54	90	153

FIGURE 30.—Frequency diagram and tabular summary for zirconium in selected experimental samples; Zr detection level (10) in ppm. Box indicates qualified value N or G.

