Evaluation of Methods Used from 1965 Through 1982 to Determine Inorganic Constituents in Water Samples

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Evaluation of Methods Used from 1965 Through 1982 to Determine Inorganic Constituents in Water Samples

By LINDA C. FRIEDMAN and
MARVIN J. FISHMAN

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ABBREVIATIONS USED

Although many of the methods have lengthy names, abbreviations have been limited to those methods that are in common use among chemists, to avoid having the reader constantly refer to a list of abbreviations.

AAS = atomic absorption spectrometry.

APDC-MIBK = chelation with ammonium pyrrolidine dithiocarbamate followed by extraction with methyl isobutyl ketone.

°C = degrees Celsius.

C.I. = Confidence interval.

DCP = direct-current plasma.

Emission = atomic emission spectrometry.

ICP = inductively coupled plasma.

mg/L = milligrams per liter.

μg/L = micrograms per liter.

μS/cm = microsiemens per centimeter (formerly micromhos per centimeter).

n = number of laboratories that analyzed a sample.

PDCA-$CHCl_3$ = chelation-extraction with pyrrolidine dithiocarbamic acid in chloroform.

r = correlation coefficient

SD = overall precision, in appropriate units (either mg/l, μg/L, or μS/cm at 25 °C), determined from a regression equation, or determined by pooling the standard deviations over the applicable range of the data.

Significant difference = statistically significant difference at $\alpha = 0.05$.

SPADNS = sodium 2-(parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonate.

SRWS = Standard Reference Water Samples.

X = concentration of constituents in appropriate units (either mg/L, μg/L, or μS/cm at 25 °C), corresponding to *SD*.

Evaluation of Methods Used from 1965 Through 1982 to Determine Inorganic Constituents in Water Samples

By Linda C. Friedman and Marvin J. Fishman

Abstract

Since 1962, the U.S. Geological Survey has prepared and distributed Standard Reference Water Samples (SRWS) to participating laboratories in order to alert them to possible analytical deficiencies. This report marks the first time that a concentrated effort has been made to examine and compare the SRWS data for each constituent by the analytical method that was used to obtain the data.

Unlike laboratories that participate in interlaboratory studies that are designed to determine the precision and accuracy of a particular analytical method, laboratories that participate in the SRWS program are allowed to select the method used to analyze a reference sample and are requested to report the method used. Data for a particular method could not be compared with a "true" value because the data were obtained from analyses of reference samples that were prepared using natural waters; however, where possible a comparison was made between the mean concentrations obtained by the various analytical methods that were used to determine each constituent. Where enough information is available, models for predicting the precisions of the methods have been developed, and the precisions have been compared. In addition to the data presented in the reports, this evaluation provides a good indication of methods that were used routinely to analyze water samples during the 18 years of study.

INTRODUCTION

The U.S. Geological Survey collects more data on the Nation's water resources than any other government agency. Its involvement in water-quality activities dates back to 1879 (Durum, 1978). Over the years, many analytical methods have been used to obtain water-quality data, both within and outside the U.S. Geological Survey. Use of data obtained from more than one method raises the possibility of data-interpretation problems because analytical precision and bias may vary with analytical method. The number of new analytical methods, such as atomic absorption spectrometry, used to obtain water-quality data began to increase rapidly in the 1960's; therefore, the possibility of data-interpretation problems also increased.

The information in this paper is based on 18 years of results from interlaboratory analyses of reference materials. The authors hope that the information provided herein can aid in the interpretation of water-quality data.

As part of its water-quality effort, the U.S. Geological Survey has prepared and distributed reference materials since 1962. Information concerning this program can be found in publications by Skougstad and Fishman (1975), Schroder and others (1980), and Friedman and Erdmann (1982). The Standard Reference Water Samples (SRWS) of the U.S. Geological Survey are stabilized, homogeneous waters that contain ambient or working-level concentrations of primarily inorganic constituents, thus meeting Uriano and Gravatt's (1977) general definition of reference materials. These samples, which are distributed semiannually, serve as a quality-control tool to alert participating laboratories to possible analytical problems. Data from interlaboratory analyses are statistically evaluated; outlying values are rejected based on the *T* value (Grubbs test) as described in the American Society for Testing and Materials (ASTM) Standard E-178-80 (1980); and the mean, standard deviation, range, and 95-percent confidence interval are calculated and reported for each constituent for each sample. Publications by Janzer (1983) and Janzer and Latal (1984) provide examples of the type of reports that are produced.

Methods

Unlike laboratories that participate in interlaboratory studies that are designed to determine the precision and accuracy of a particular analytical method, laboratories that participate in the SRWS program are allowed to select the method used to analyze a reference sample, and are requested to report that method. This report is the first in which a concentrated effort has been made to examine and compare the SRWS data for inorganic constituents by the analytical method that was used to obtain that data. Although the SRWS program has been expanded to include reference samples on water-sediment mixtures and trace organic constituents, the methods used to analyze these samples are not evaluated here; however, pilot programs for these samples have been reported elsewhere (Fishman and others, 1984; Friedman and others, 1984). For the purpose of this report, several minor variations may be included in a "method." For example, when determining chromium by atomic absorption spectrometry, one laboratory may add ammonium chloride to suppress iron interference and another laboratory may add a different suppressor or may not add anything; all data are included under "atomic absorption spectrometry, direct." Thus, the data reported in this paper are not necessarily those that would be obtained if the same laboratories were to follow a specified set of instructions for a particular method (such as would be done in participating in an ASTM "round robin"). However, the data in this report should be useful to someone who knows the general method used (for example, atomic absorption) to obtain data without knowing the precise details about the method and its expected precision. This evaluation should be particularly useful to someone who wishes to compare data being obtained today (or in the future) to data obtained in the past by analytical methods that may no longer be in use. It also provides a good indication of what methods were used in routine analyses of water samples during the 18 years of study.

Data from a particular method cannot be compared with a "true" value because these data were obtained from analyses of samples that had been prepared using surface waters rather than deionized water. Instead, where possible, the different analytical procedures used to determine a particular constituent are compared to each other, with no attempt made to say which is "correct." Because SRWS were prepared in deionized water prior to October 1965, data from analyses of samples prepared from 1962 through 1964 are not included in this report. Furthermore, if a laboratory did not report the method used, the value has been ignored.

References are given for the methods that were used. However, because data may be from many variations of a method, only references that are, or were, commonly used in selecting methods to analyze water samples are cited (for example, the American Public Health Association's Standard Methods for the Examination of Water and Wastewater (15 ed.), 1980). Other methods, such as "neutron activation" are widely known, but no standard references may be available that specifically describe how to use the methods for water analyses. In general, older editions of references are used only if a method cannot be found in a new edition; thus, if a method is in both the 12th and 15th editions of Standard Methods, only the 15th edition is used.

Calculation, Presentation, and Evaluation of Data

We have assumed that, if the concentration of a constituent being determined is greater than the analytical detection limit and if systematic errors are not present, results obtained by any one method should be normally distributed. For each constituent determined in each SRWS, the mean and standard deviation were calculated for each method if used by at least three laboratories. Outlying values were rejected using the same criteria applied in the original interlaboratory study (that is, by using the T values previously mentioned); however, because the data are now divided by method, some cases occur where values that were rejected in the original SRWS study are now included, and other cases occur where values that were included in the original SRWS study are now rejected.

Except for a few constituents where data are very limited and the information is presented only in the text, histograms are presented to depict the methods that were used to determine each constituent and the number of laboratories using each method. The mean concentration and standard deviation obtained by each method also are shown on the histograms; however, if only two laboratories used a particular method, then only the mean concentration is given, and, if only one laboratory used a particular method, then only the single concentration is given. Note that, because there is no way to really determine an "outlier" if only one or two laboratories used a method, such a value always is included on the histogram, even if it appears to be far from the mean values obtained by all other methods. Although this may lead to some discrepancies because outlier-rejection criteria are applied if three or more laboratories used a method, data collected over a long time likely will represent the method. Nevertheless, caution needs to be used in looking at the histograms, particularly because one or two laboratories could have been the only ones to use a particular method throughout the period of study, and these laboratories always could have performed poorly or well.

If a specific method was used by three or more laboratories to determine a specific constituent in five or more SRWS, standard deviations were calculated and a mathematical model was developed to predict the precision (standard deviation) of the method at a given concentration. If the standard deviation varied with concentration, then a regression equation was calculated and is presented graphically. In almost all instances, the regression equations that are given are linear; a nonlinear model rarely seemed to increase the "fit" of a line significantly. The regressions are weighted for each method, with the weight of each point used to determine the equations (and line) proportional to the number of laboratories that used that particular method. For example, 45 laboratories used atomic absorption spectrometry to determine calcium in SRWS 80, whereas only 3 laboratories used atomic absorption spectrometry to determine calcium in SRWS 16; 15 times more weight is given to the point represented by SRWS 80 than to the point represented by SRWS 16.

If the standard deviations were independent of the concentrations (determined by testing the slope and correlation coefficient at the 1-percent level), a "pooled" standard deviation was calculated and a line representing the pooled value was drawn on the graph. The pooled value and its corresponding 95-percent confidence interval also are indicated.

If a specific method was not used by three or more laboratories to determine a specific constituent in five or more SRWS, either the means and standard deviations are given only in the text or the points representing the means and standard deviations (and not a line) are plotted on the graphs. In all cases, the number of SRWS and the total number of values represented by the points for each method are indicated on the graphs. If a precision model is given, the length of the line represents the concentration range for which the model was developed.

The reader is cautioned that points for different methods plotted at roughly the same concentration may not represent the same SRWS. In fact, a point that represents analysis by one method may be near a point that represents analysis by another method that was used years before and it is only a coincidence that both points appear to represent similar concentrations.

In addition to the information presented on the histograms and graphs, the various methods have been compared, where possible, both in terms of their concentration and their precision. The comparisons of concentrations were made by assuming that mean concentrations were dependent on both the particular SRWS sample and the analytical method and then by using analysis of variance techniques to examine differences caused by the method. Because the data showed a lack of homoscedasticity, logarithms of the data were taken before making the comparisons. Koch and Link (1971, 1980) have pointed out that, when the coefficient of variation is less than 120 percent, such transformations can introduce severe bias without gaining efficiency. However, comparisons were made for several constituents both before and after the data were transformed and the comparisons made using the logarithmically transformed data were judged to be more "logical." For example, data for four methods that were used to determine boron between October 1979 and April 1982 are depicted in figure 1; if data are compared after logarithms are taken, a statistically significant difference exists between the concentrations obtained by the colorimetric, carmine method and the other three methods, whereas, if the untransformed data are compared, no significant difference exists between the colorimetric, carmine method and the other three methods. An examination of figure 1 indicates that a difference does appear to exist; the changing variance of the colorimetric, carmine method (see figure 19) apparently masks the difference when the untransformed data are used.

Comparisons for precision were made by assuming that the standard deviation was dependent on both the mean concentration and the analytical method and then by examining differences caused by the method. If an inspection of the histograms indicated that mean concentrations or standard deviations of a method were not reported for a particular period of time or for a particular concentration range, further comparisons were made on more limited data sets.

If a regression equation is given, the intercept was tested (at the 5-percent level) to see if it might be zero. Unless otherwise stated in the discussion of each constituent, the intercept may be zero; because the intercept is approached as the concentration approaches zero, this information is important for establishing the analytical detection limit of a method and for interpreting data that are near the detection limit.

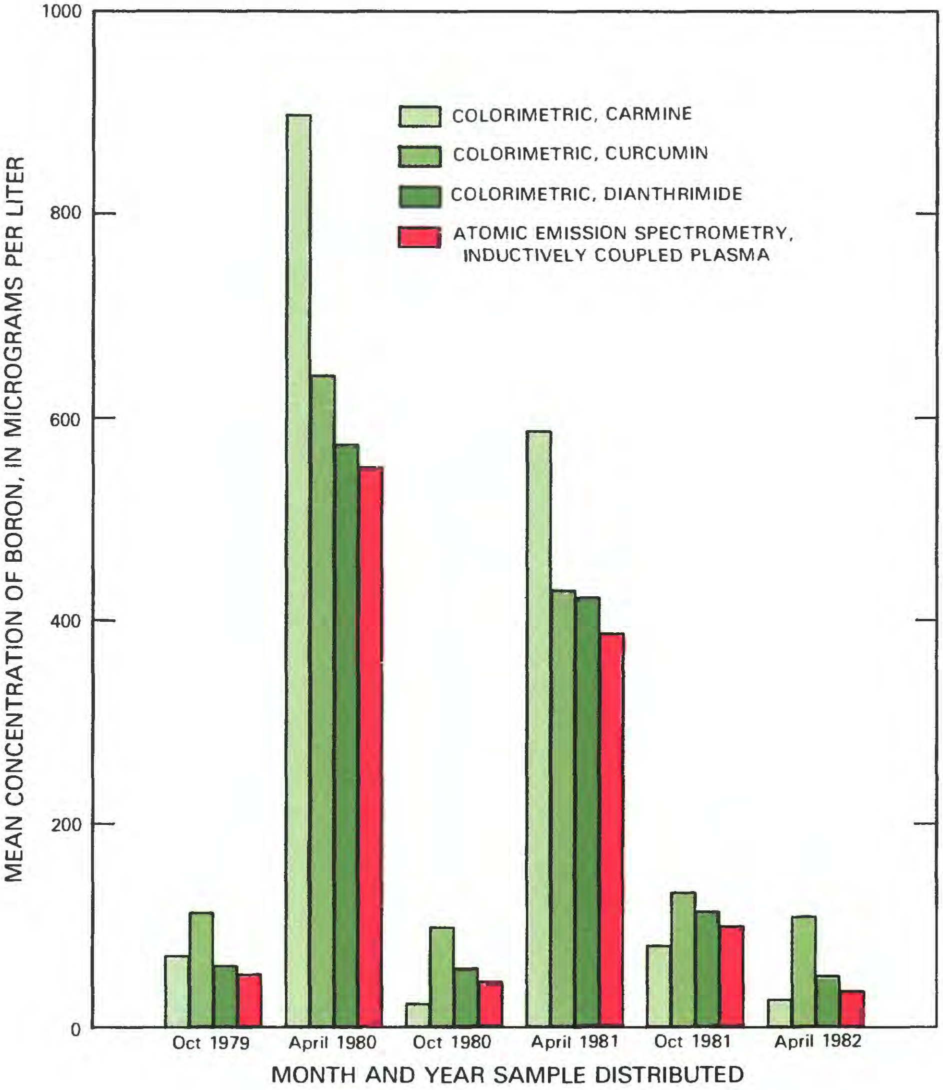

Figure 1. Comparison of four methods used to determine boron.

ACIDITY

Acidity was determined in only two SRWS. Twenty-one laboratories in 1968 and 13 laboratories in 1982 analyzed the SRWS by electrometric titration (Skougstad and others, 1979; U.S. Environmental Protection Agency, 1979a; American Public Health Association and others, 1980; American Society for Testing and Materials, 1983). In each case, the mean concentration was 26 mg/L as H^+ and the relative standard deviation was 3 percent.

ALKALINITY AS CALCIUM CARBONATE

Four methods were used to determine alkalinity although the majority of the data collected during the 18 years were from the titration, electrometric method (fig. 2). The concentrations reported for the titration, electrometric, automated method are significantly different from the concentrations reported for the titration, electrometric method or titration, indicator method. Except for those differences, no other significant difference exists between the concentrations reported for the methods.

The titration, indicator procedure has a significantly different precision than the automated and manual electrometric titration procedures (fig. 3). No significant difference exists between the precisions for the automated and manual electrometric titration procedures, even though the standard deviation obtained for the manual titration appears to vary with concentration, whereas the standard deviation obtained for the automated procedure does not. A less than 5-percent chance exists that the intercept of the model for the titration, indicator method is equal to zero.

The correlation coefficient, *r*, of the model for the precision of the titration, electrometric procedure is only 0.5308. Even if the point representing the rather large standard deviation of 26 mg/L is deleted, the correlation coefficient would only increase to 0.5807 (and the line would change to $SD=0.026x+2.06$). However, a less than 1-percent chance of obtaining a slope this great exists if the standard deviations do not vary with concentration.

References to the methods are given below:

Method	*Reference*
Colorimetric, methyl orange, automated	U.S. Environmental Protection Agency, 1979a
Titration, electrometric	American Public Health Association and others, 1980
	American Society for Testing and Materials, 1983
	Skougstad and others, 1979
	U.S. Environmental Protection Agency, 1979a
Titration, electrometric, automated	Skougstad and others, 1979
Titration, indicator	American Public Health Association and others, 1980
	American Society for Testing and Materials, 1983

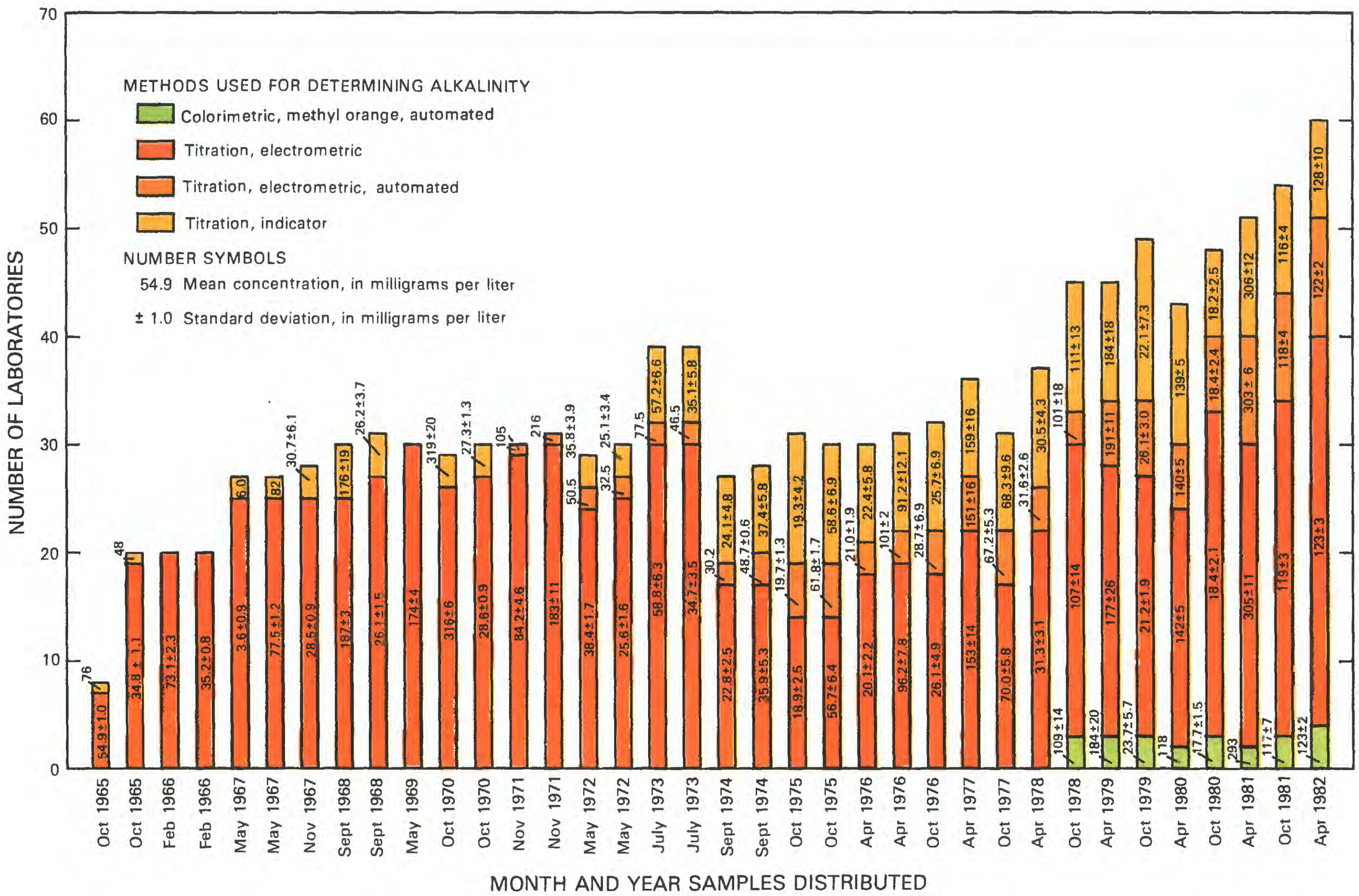

Figure 2. Mean concentrations and standard deviations for alkalinity as calcium carbonate in 36 Standard Reference Water Samples.

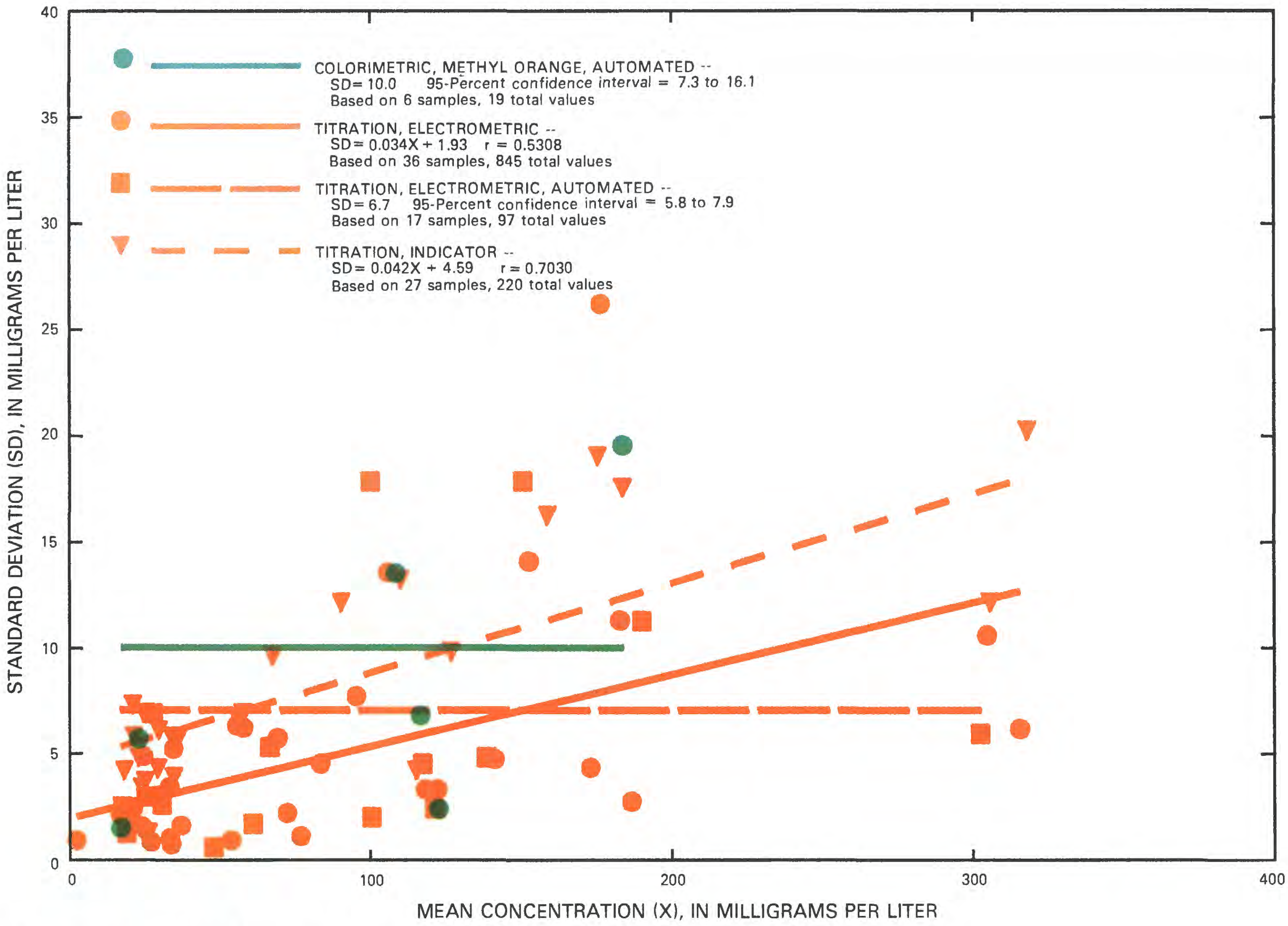

Figure 3. Interlaboratory precision of four methods used to determine alkalinity as calcium carbonate.

ALUMINUM

Twelve methods were used to determine aluminum (fig. 4). However, from 1965 to 1972, most of the data were from the colorimetric, ferron-orthophenanthroline method. After 1972, most of the data were from the AAS, chelation-extraction (8-hydroxyquinoline methyl isobutyl ketone) method; the AAS, direct method; the AAS, graphite-furnace method; and, beginning in 1979, the emission, ICP method.

With the possible exception of the colorimetric, aluminon method, no significant difference exists between the concentrations of aluminum determined by the different methods. The data for the colorimetric, aluminon method are so limited that little reliance can be placed on the fact that a difference was found.

The precision reported for the AAS, graphite-furnace method is significantly different, and generally worse, than the precision for the other methods (fig. 5). However, if just the AAS, direct; AAS, graphite-furnace; and emission, ICP methods are compared for SRWS distributed in or after October 1979 (the SRWS for which the emission, ICP method first was reported), no significant difference is found in the precisions (nor, for that matter, in the concentrations).

The precision for the colorimetric, ferron-orthophenanthroline method is significantly different and appears generally better than those from both the AAS, graphite-furnace and the emission, ICP methods, but the precision is not different than the precisions of the AAS, chelation-extraction (8-hydroxyquinoline methyl isobutyl ketone) and AAS, direct methods. However, the data for the precision model for the colorimetric procedure were collected from reference samples distributed before 1973, whereas the data for the other three methods were collected from reference samples distributed after 1973. A less than 5-percent chance exists that the intercept of the model for the colorimetric, ferron-orthophenanthroline method is equal to zero.

References to the methods are given below:

Method	*Reference*
Atomic absorption spectrometry, chelation-extraction with 8-hydroxyquinoline and methyl isobutyl ketone	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979
Atomic absorption spectrometry, direct	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a
Atomic absorption spectrometry, graphite-furnace	U.S. Environmental Protection Agency, 1979a
Atomic emission spectrometry, arc-spark	Barnett and Mallory, 1971
Atomic emission spectrometry, direct-current plasma	American Society for Testing and Materials, 1983
Atomic emission spectrometry, flame	—
Atomic emission spectrometry, inductively coupled plasma	U.S. Environmental Protection Agency, 1979b
Colorimetric, aluminon	American Public Health Association and others, 1965
Colorimetric, erichrome cyanine-R	American Public Health Association and others, 1980
Colorimetric, ferron-orthophenanthroline	American Society for Testing and Materials, 1983 Skougstad and others, 1979
Colorimetric, 8-quinolinol extraction	American Society for Testing and Materials, 1983
Neutron activation	—

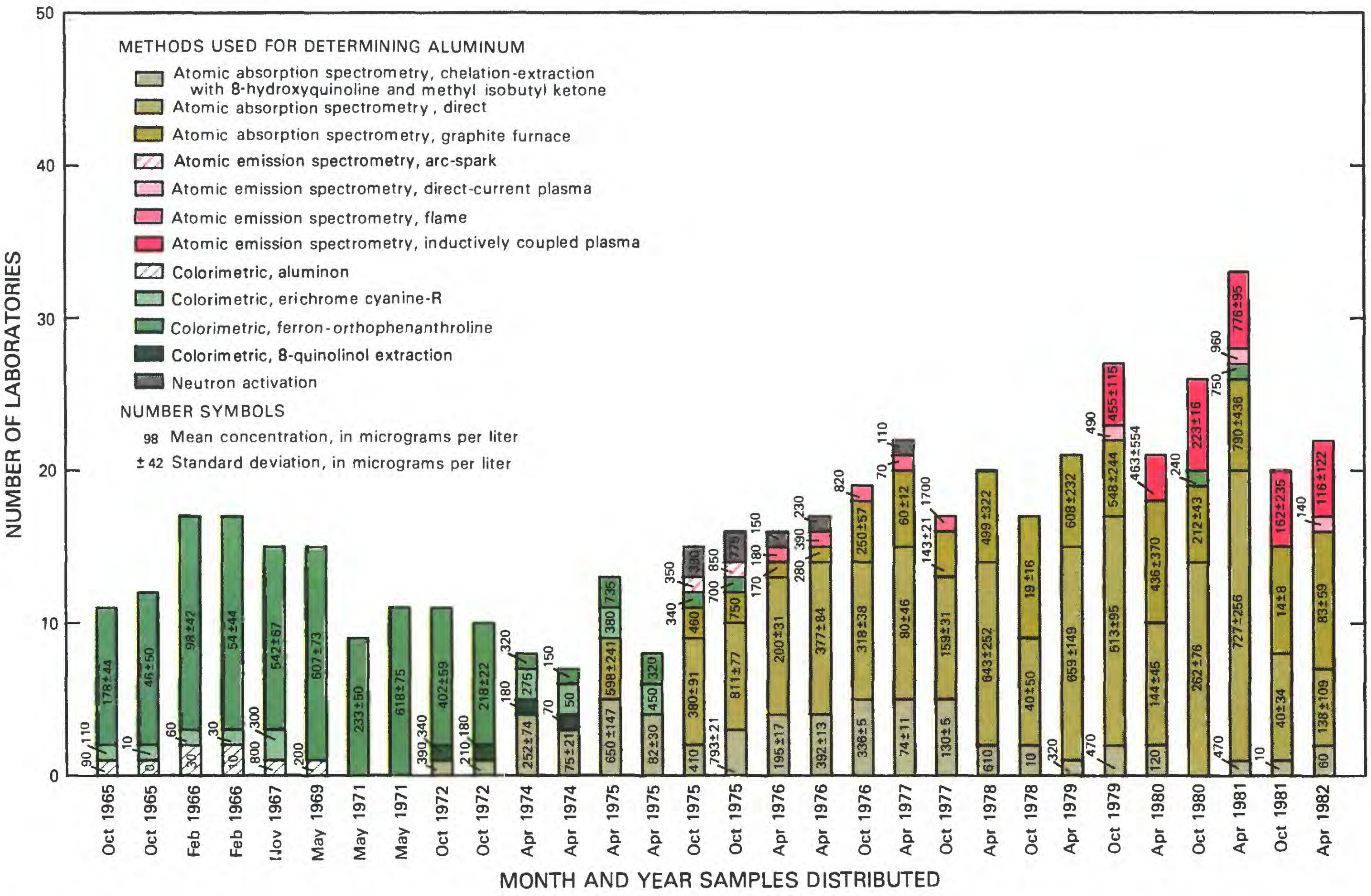

Figure 4. Mean concentrations and standard deviations for aluminum in 30 Standard Reference Water Samples.

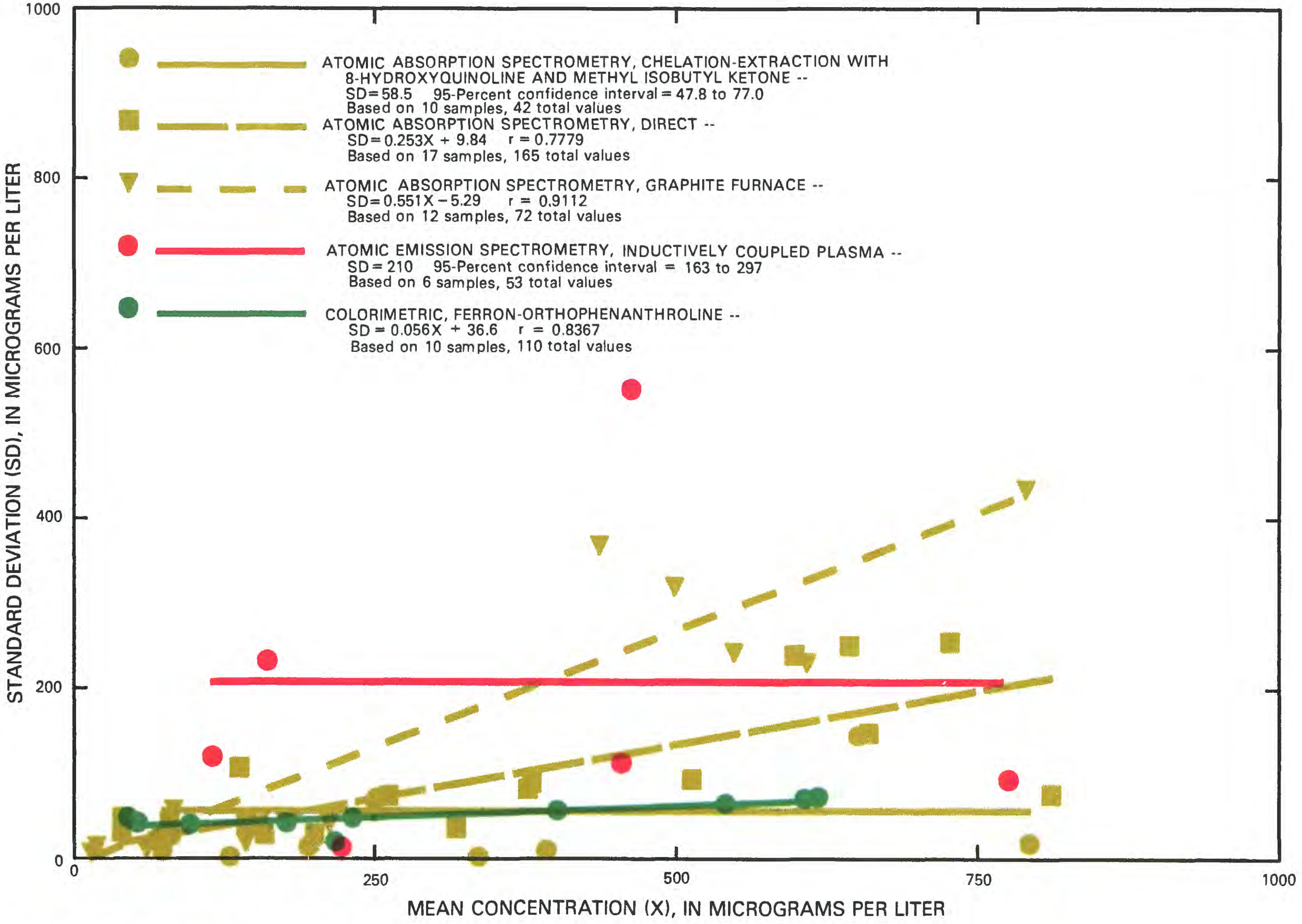

Figure 5. Interlaboratory precision of five methods used to determine aluminum.

AMMONIA NITROGEN

Three methods were used to determine ammonia (fig. 6). However, data are rather limited because only nine SRWS were distributed.

No significant difference is found in the concentrations reported for the three methods. Significant differences are observed in the precisions of the colorimetric, indophenol, automated and the distillation-plus-nesslerization-or-titration methods (fig. 7); however, neither method has a significant difference in precision compared to the potentiometric, ion-selective-electrode method. A less than 5-percent chance exists that the intercept of the model for the colorimetric, indophenol, automated method is equal to zero.

References to the methods are given below:

Method	*Reference*
Colorimetric, indophenol, automated	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a
Distillation plus nesslerization or titration	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a
Potentiometric, ion-selective electrode	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a

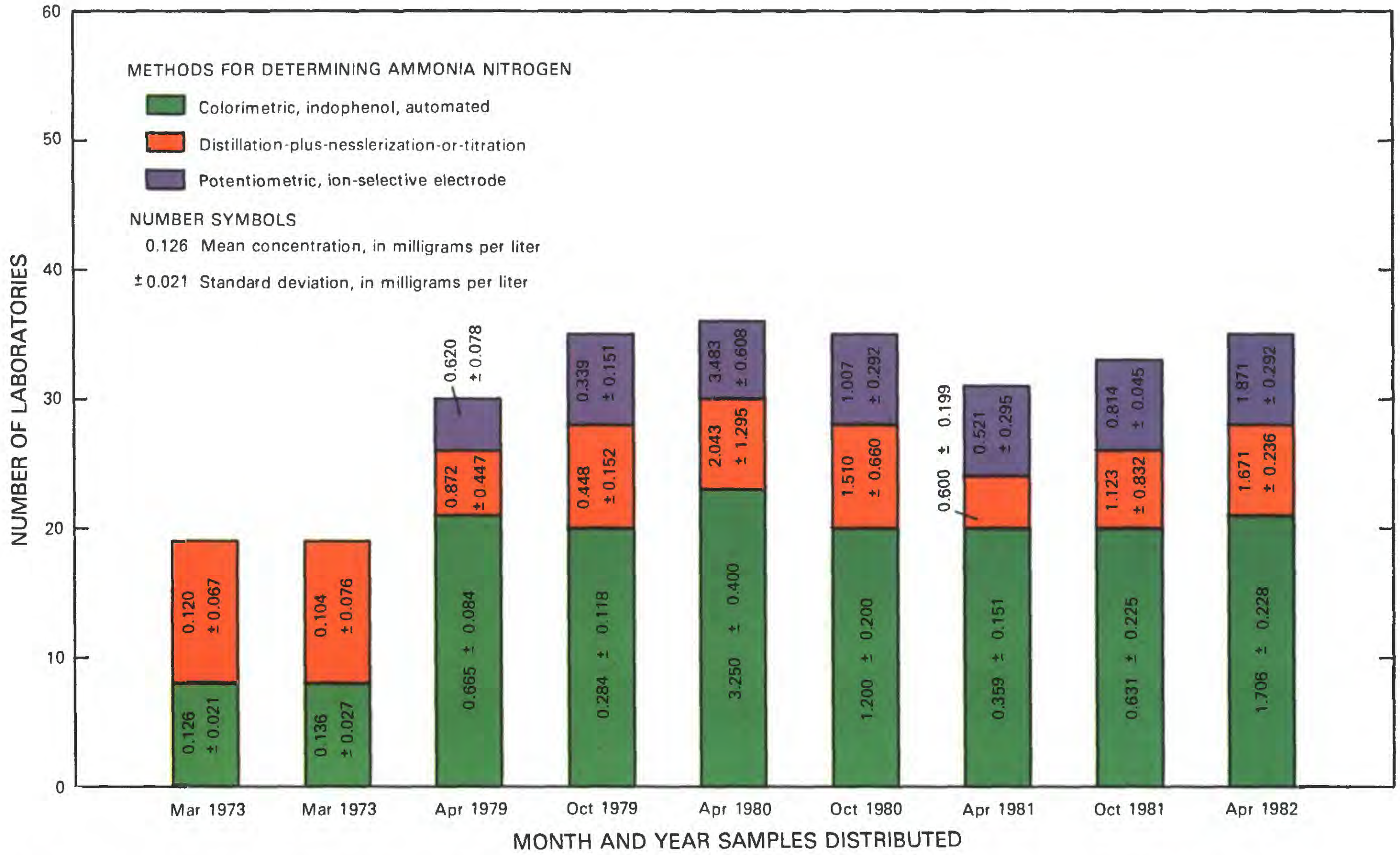

Figure 6. Mean concentrations and standard deviations for ammonia nitrogen in nine Standard Reference Water Samples.

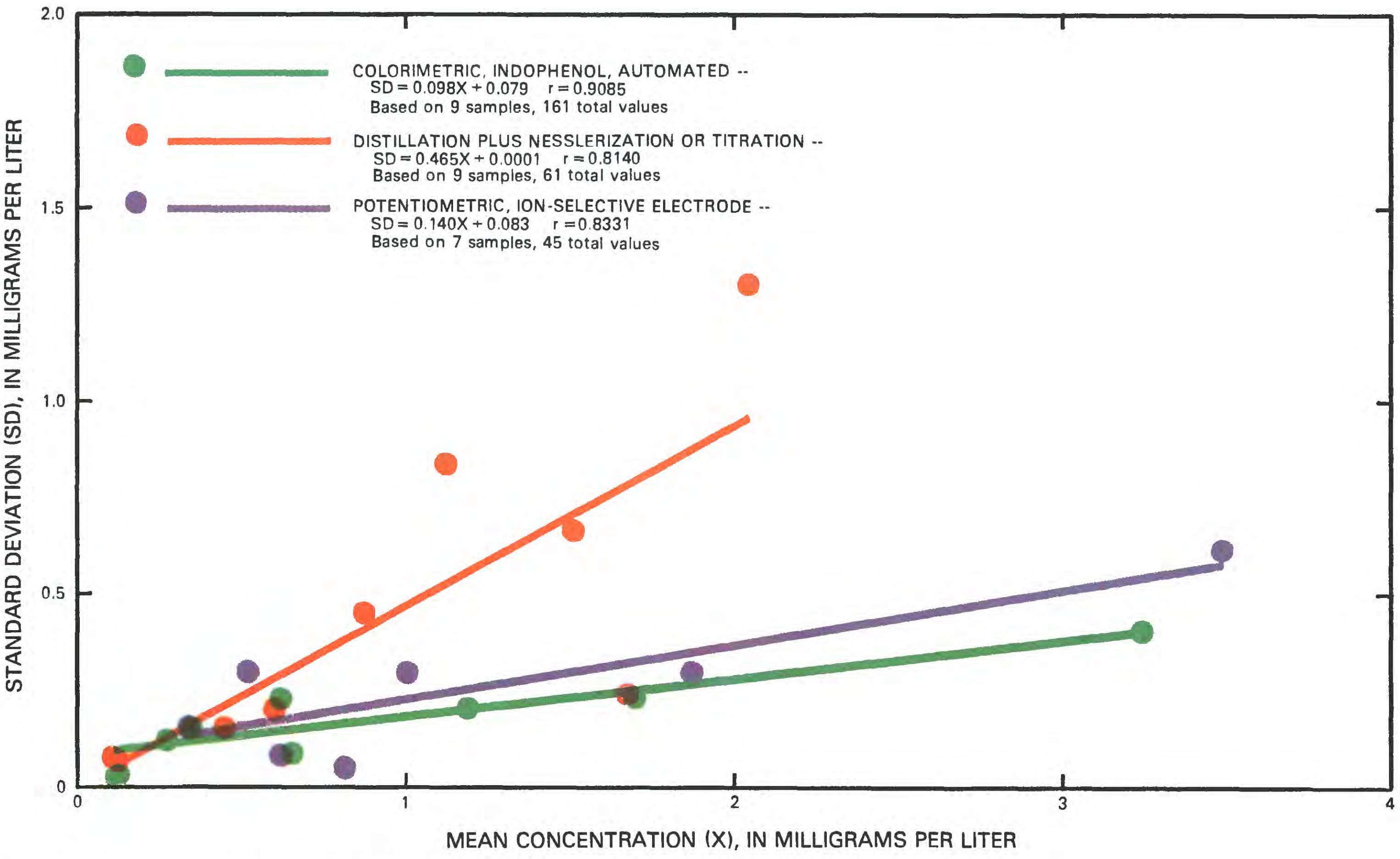

Figure 7. Interlaboratory precision of three methods used to determine ammonia nitrogen.

AMMONIA PLUS ORGANIC NITROGEN

Laboratories participating in the interlaboratory tests were requested to report "ammonia" and "organic" nitrogen. However, we believe that many laboratories determined "ammonia nitrogen" and "ammonia plus organic nitrogen" and then subtracted the ammonia to obtain the "organic nitrogen"; there is no way to determine this information from the data.

Four methods were identified (fig. 8). To look at the data for these methods, each separate ammonia and organic nitrogen result was added prior to taking the logarithms or computing the mean concentration and standard deviation. No significant difference exists in the concentrations or precisions for the four methods (figs. 8 and 9).

Because data used in the evaluation were obtained by combining data from the determination of ammonia nitrogen with data from the determination of organic nitrogen, also refer to the discussions for those constituents. Note that the precision models for the methods described here indicate that precision does not vary with concentration even though the precisions for the methods to determine ammonia nitrogen do appear to change with concentration (fig. 7).

References to the methods are given below:

Method	*Reference*
Kjeldahl digestion plus nesslerization or titration	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a
Kjeldahl digestion plus colorimetric, indophenol, automated	Skougstad and others, 1979
Kjeldahl digestion plus colorimetric, salicylate, automated	Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a
Kjeldahl digestion, continous plus colorimetric, indophenol, automated	U.S. Environmental Protection Agency, 1979a

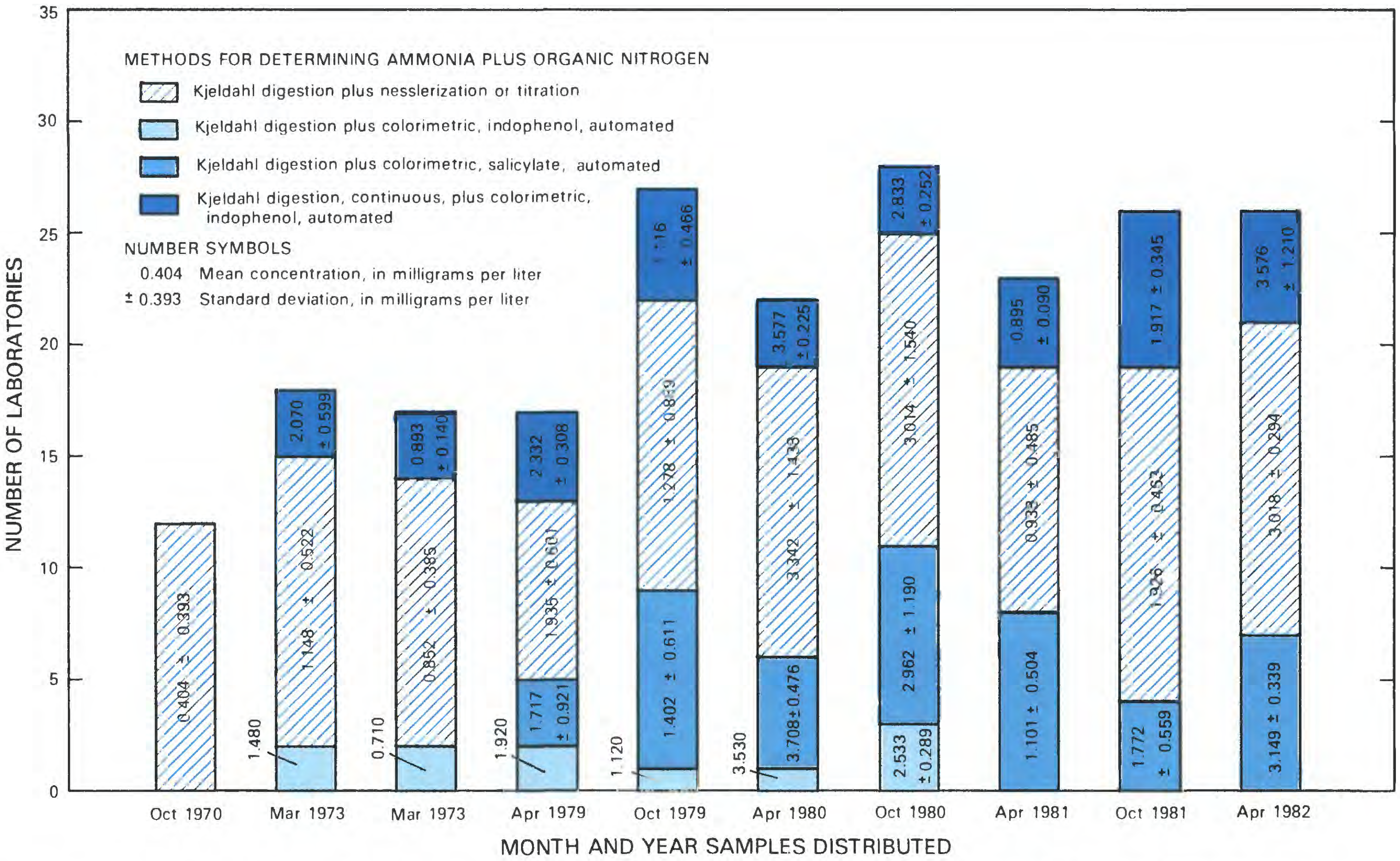

Figure 8. Mean concentrations and standard deviations for ammonia plus organic nitrogen in 10 Standard Reference Water Samples.

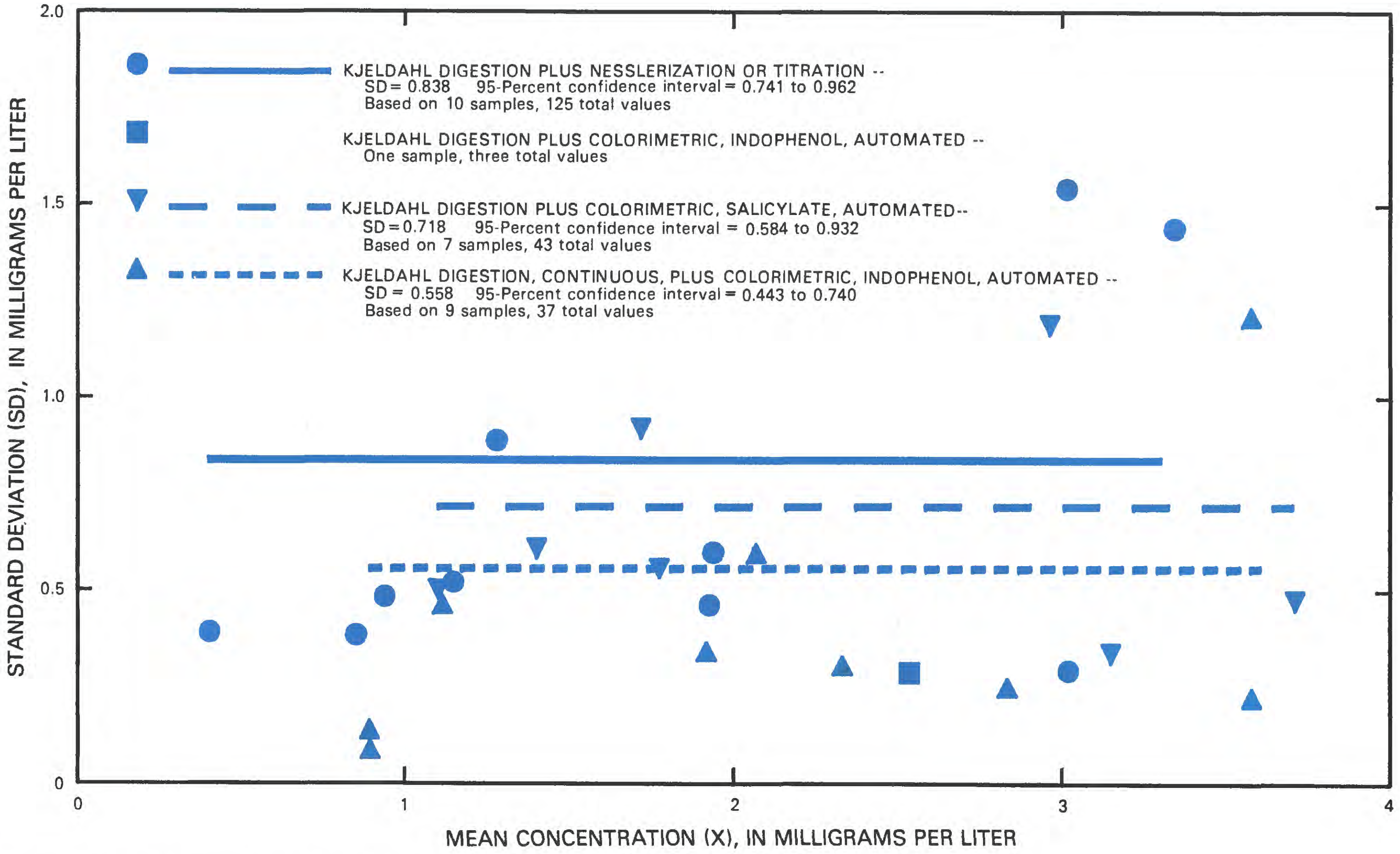

Figure 9. Interlaboratory precision of four methods used to determine ammonia plus organic nitrogen.

ANTIMONY

Only a few laboratories determined antimony in the 10 SRWS that were distributed. Three methods were used (fig. 10). From the relatively few data available, no significant difference is apparent between the concentrations obtained by the three methods.

The precision data were even more limited (fig. 11). Based on the analysis of 7 SRWS (a total of 22 values), the precision, *SD*, that can be obtained using the AAS, hydride ($NaBH_4$) procedure between 2.0 and 8.0 μg/L is ±0.88 μg/L. Because of the extremely limited precision data available for the AAS, graphite-furnace method, the precisions for the two methods are not compared.

References to the methods are given below:

Method	*Reference*
Atomic absorption spectrometry, graphite-furnace	U.S. Environmental Protection Agency, 1979a
Atomic absorption spectrometry, hydride (sodium borohydride)	American Society for Testing and Materials, 1983 Skougstad and others, 1979
Neutron activation	—

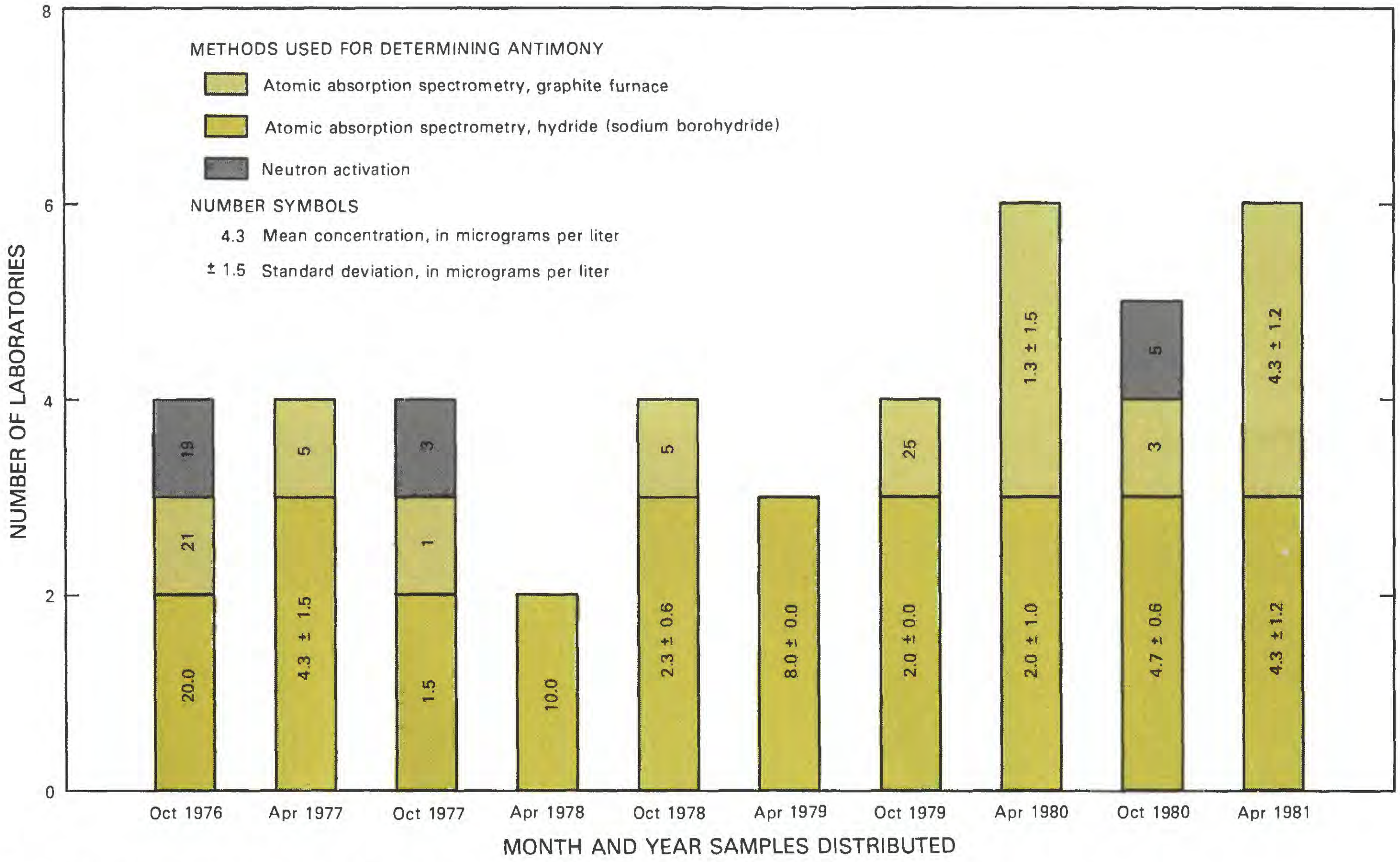

Figure 10. Mean concentrations and standard deviations for antimony in 10 Standard Reference Water Samples.

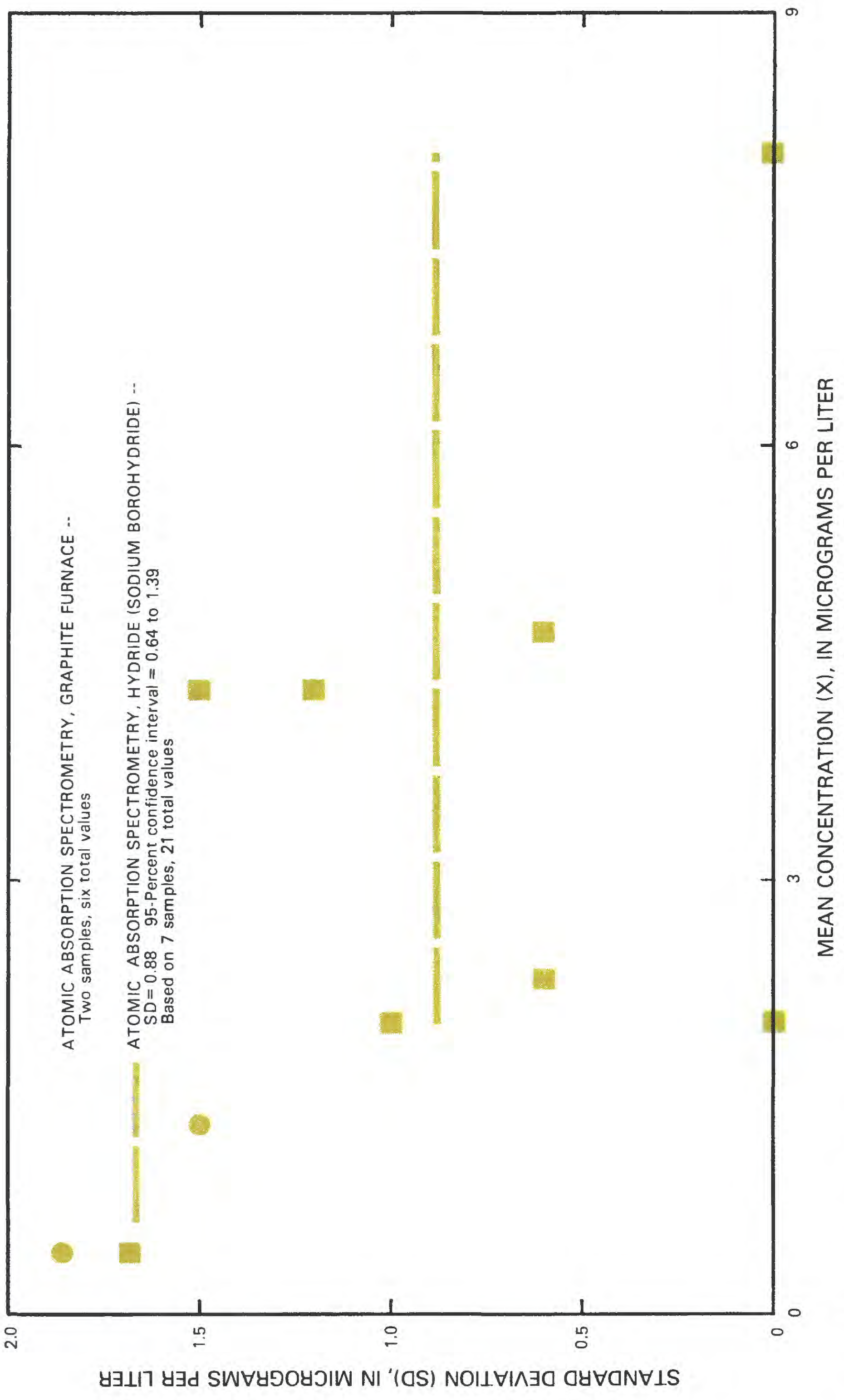

Figure 11. Interlaboratory precision of two methods used to determine antimony.

ARSENIC

Seven methods were used to determine arsenic (fig. 12). Prior to 1973, almost all data were from the colorimetric, silver diethyldithiocarbamate procedure. In 1973, the hydride procedures began to be used to analyze the SRWS. The AAS, hydride, $NaBH_4$ method appears to be gradually replacing the initial AAS, hydride, zinc method. The AAS, graphite-furnace method began to be used in 1976; beginning in 1980, this method was reported as used by more than one half the laboratories analyzing SRWS.

No significant difference exists in reported concentrations for the different analytical methods. Limiting the comparisons to the automated and manual AAS, hydride, $NaBH_4$ methods for data from samples distributed in or after April 1979 (when the automated method first began to be used) still indicates no significant difference between concentrations.

No significant difference exists among the precisions reported for the different methods (fig. 13). A less than 5-percent chance exists that the intercept of the model for the colorimetric, silver diethyldithiocarbamate method is equal to zero.

References to the methods are given below:

Method	*Reference*
Atomic absorption spectrometry, graphite-furnace	U.S. Environmental Protection Agency, 1979a
Atomic absorption spectrometry, hydride (sodium borohydride)	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983
Atomic absorption spectrometry, hydride (sodium borohydride), automated	Skougstad and others, 1979
Atomic absorption spectrometry, hydride (zinc)	American Society for Testing and Materials, 1983 Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a
Colorimetric, silver diethyldithiocarbamate	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a
Neutron activation	—
Titration, gutzeit	Rainwater and Thatcher, 1960

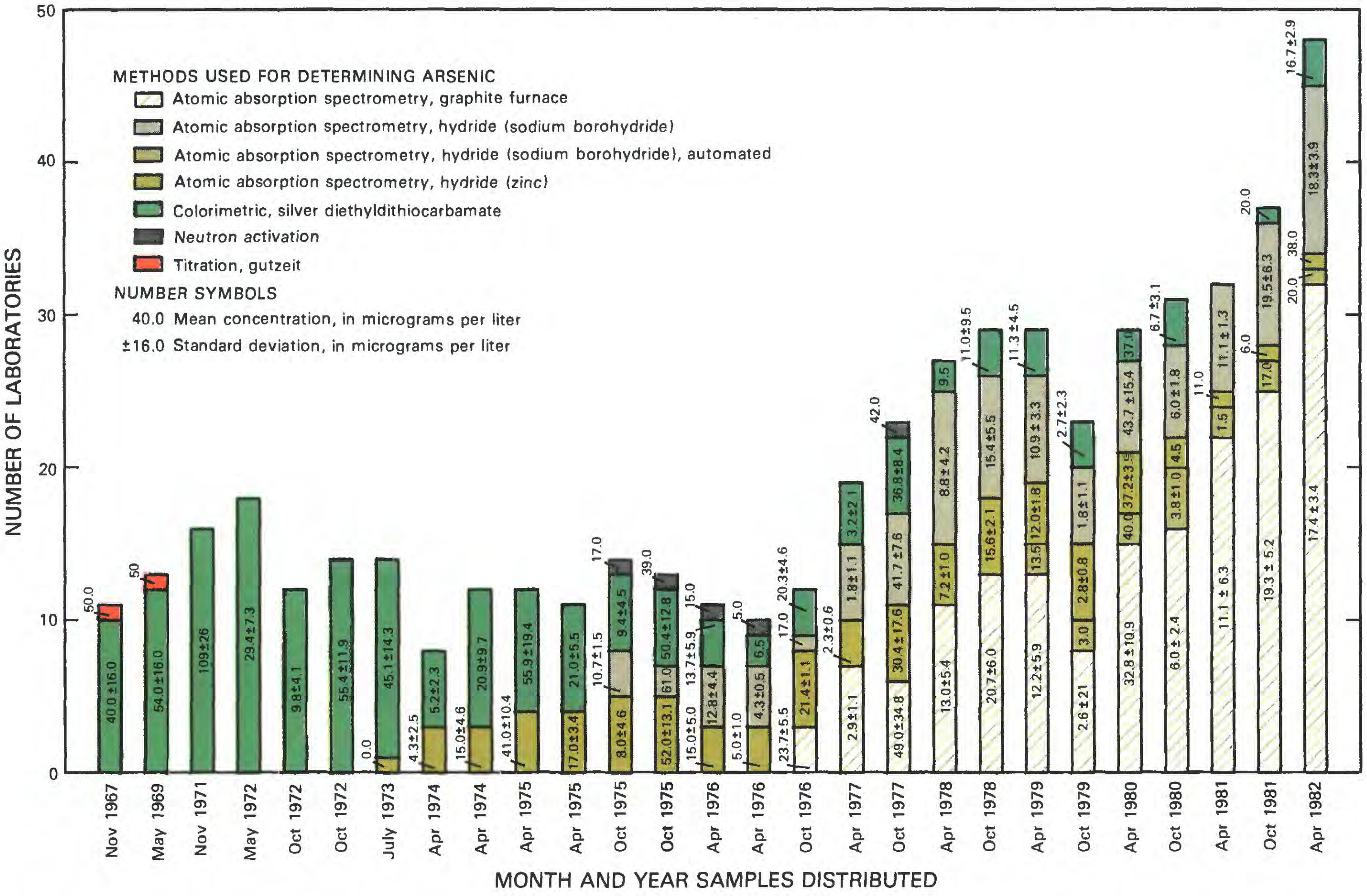

Figure 12. Mean concentrations and standard deviations for arsenic in 27 Standard Reference Water Samples.

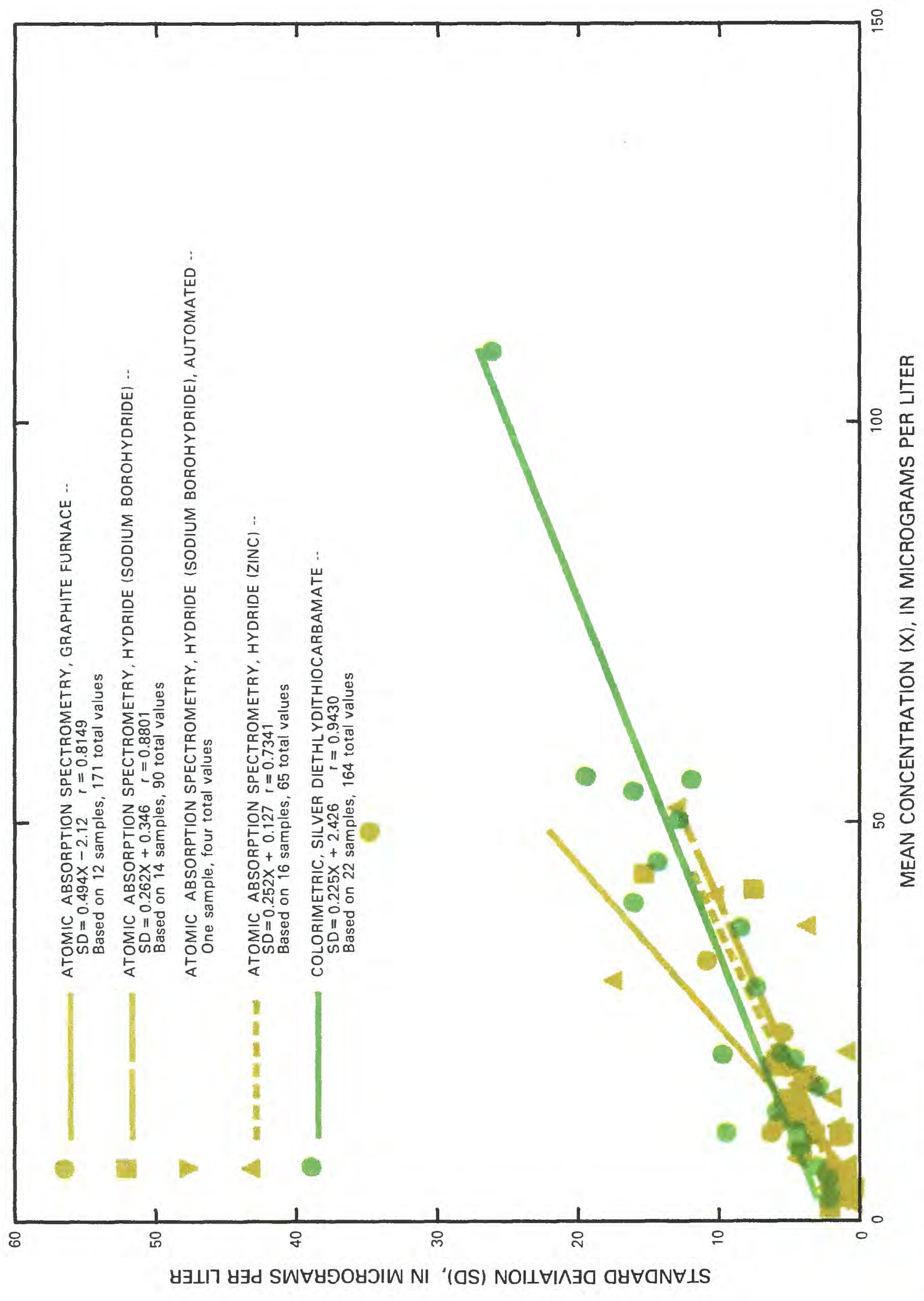

Figure 13. Interlaboratory precision of five methods used to determine arsenic.

BARIUM

Seven methods were used to determine barium although only the AAS, direct method was used on all samples (fig. 14). When data are compared from SRWS issued in or after October 1976 (when the AAS, graphite-furnace method first began to be used), a significant difference exists in the concentrations of barium reported by using the AAS, direct and AAS, graphite-furnace methods. However, when data are further limited to those from SRWS issued in or after April 1978 (when at least three laboratories reported data using the AAS, graphite-furnace method), no significant difference is observed in the reported concentrations for any of the methods.

No significant difference exists between the precisions for the AAS, direct and AAS, graphite-furnace methods despite the fact that the precision of the AAS, graphite-furnace method appears to vary with concentration and the precision of the AAS, direct method does not (fig. 15). This is true even if the data from the AAS, direct method are limited to concentrations less than 300 μg/L (that is, to concentrations that are in the range covered by the other methods). Even when only those concentrations less than 300 μg/L are used to compute the precision model for the AAS, direct method, the model still indicates that the precision does not vary with concentration; however, the standard deviation then would be 83.0 instead of 95.3 μg/L.

The precision for the emission, ICP method is significantly different from that for the AAS, direct method and from that for the AAS, graphite-furnace method (data for SRWS distributed in or after October 1979, when emission, ICP first began to be used, were used for the comparison). Reported concentrations are not significantly different.

The data from the emission, DCP; emission, arc-spark; and neutron-activation methods are really too limited to be compared. However, these data indicate that the concentrations reported using the emission, DCP method are not significantly different from the concentrations reported for the AAS, direct and emission, ICP methods; they also give no indication that the emission, arc-spark or neutron-activation methods give significantly different concentrations than does the AAS, direct method.

References to the methods are given below:

Method	*Reference*
Atomic absorption spectrometry, direct	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a
Atomic absorption spectrometry, graphite-furnace	U.S. Environmental Protection Agency, 1979a
Atomic emission spectrometry, direct-current plasma	—
Atomic emission spectrometry, arc-spark	Barnett and Mallory, 1971
Atomic emission spectrometry, flame	—
Atomic emission spectrometry, inductively coupled plasma	Fishman and Bradford, 1982
Neutron activation	—

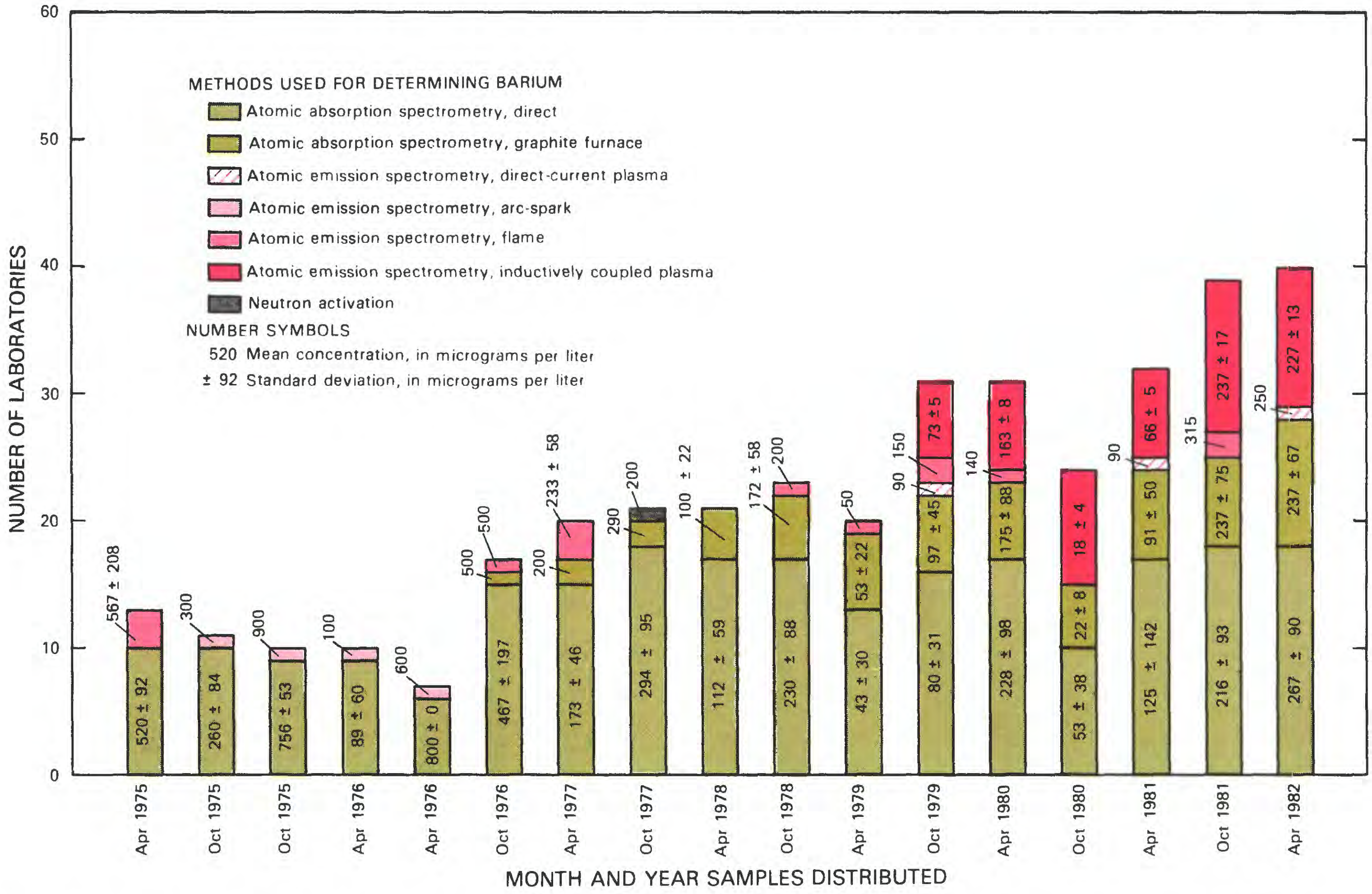

Figure 14. Mean concentrations and standard deviations for barium in 17 Standard Reference Water Samples.

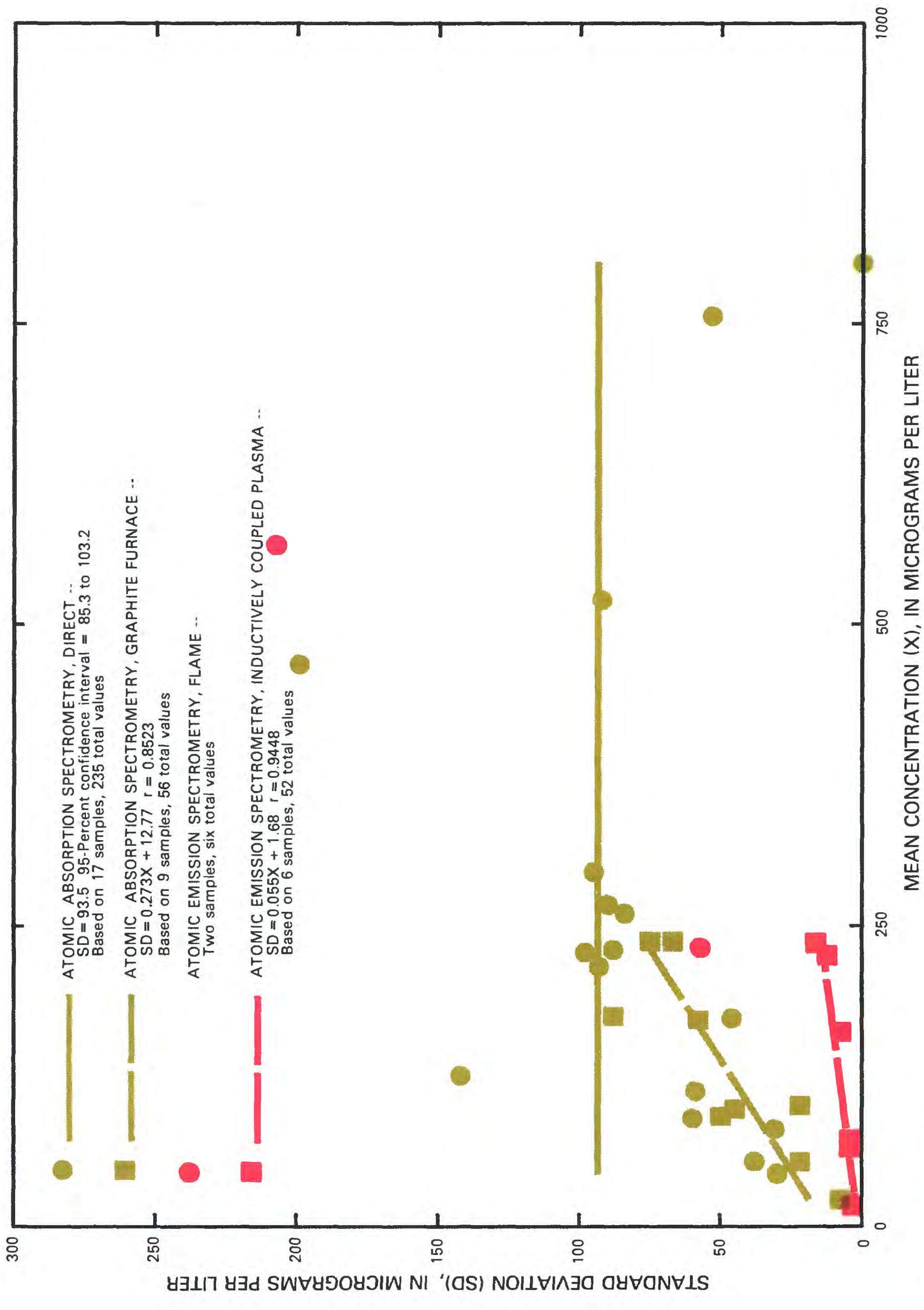

Figure 15. Interlaboratory precision of four methods used to determine barium.

BERYLLIUM

Five methods were used to determine beryllium (fig. 16) although only the AAS, direct method was used for all samples. The data indicate no significant difference in the concentrations reported for the different methods. If the data set is limited to concentrations reported for the AAS, direct; AAS, graphite-furnace; and emission, ICP methods on SRWS distributed in or after October 1979 (when emission, ICP data first were collected), there are still no significant differences in concentrations.

Data from 17 SRWS (a total of 97 values) indicate that the precision of the AAS, direct method does not vary with concentration (fig. 17). Data for the AAS, graphite-furnace and emission, ICP methods are much more limited, and the overall precision model for the AAS, graphite-furnace method obviously is influenced by a concentration that is almost 100 μg/L (fig. 17). If this value is ignored, the pooled standard deviation would be 4.21 μg/L instead of the equation, $SD=0.671x-7.19$, given in figure 16; however, this standard deviation then would be based on the analyses of only 4 SRWS and, as indicated in the introduction, we have chosen to provide models only for those methods in which the standard deviation has been determined on at least 5 SRWS.

References to the methods are given below:

Method	*Reference*
Atomic absorption spectrometry, chelation-extraction (8-hydroxyquinoline-methyl isobutyl ketone)	American Public Health Association and others, 1980
Atomic absorption spectrometry, direct	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a
Atomic absorption spectrometry, graphite-furnace	U.S. Environmental Protection Agency, 1979a
Atomic emission spectrometry, arc-spark	Barnett and Mallory, 1971
Atomic emission spectrometry, inductively coupled plasma	U.S. Environmental Protection Agency, 1979b

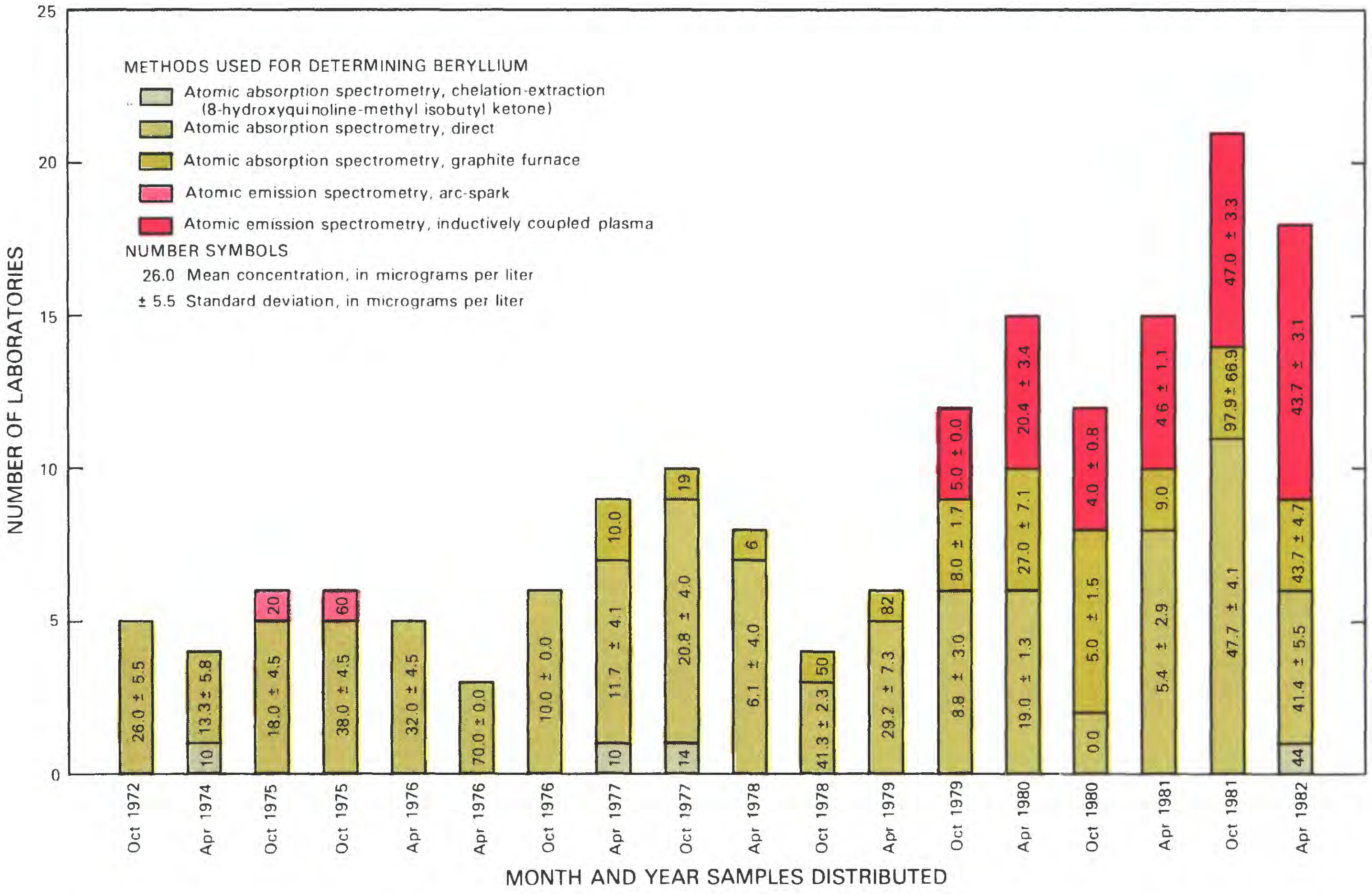

Figure 16. Mean concentrations and standard deviations for beryllium in 18 Standard Reference Water Samples.

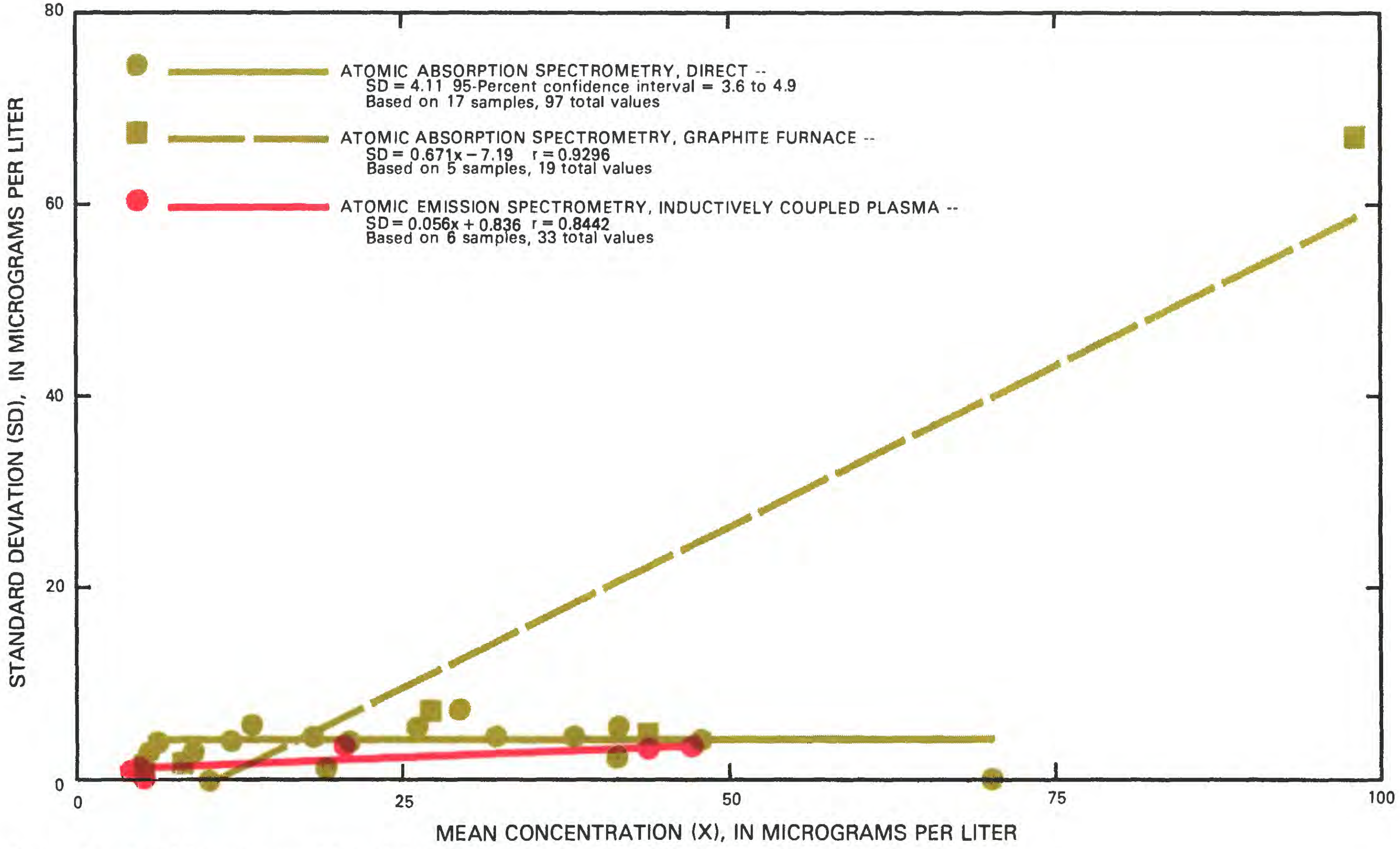

Figure 17. Interlaboratory precision of three methods used to determine beryllium.

BORON

Seven methods were used to determine boron (fig. 18). Most of the data are from analyses by one of three colorimetric methods (carmine, curcumin, and dianthrimide). When data from these three methods are considered apart from all others, the carmine method yields data with concentrations that are significantly different from the dianthrimide method. When data for these three colorimetric methods are considered along with the emission, ICP method for those SRWS distributed in or after October 1979 (when emission, ICP data are first recorded), the colorimetric, carmine method gives significantly different concentrations from the other three methods, but no other differences in concentrations are reported for the methods (see also fig. 1).

The precision of the carmine method is significantly different from those of both the curcumin and dianthrimide methods, and also from the emission, ICP method—the only other method to be used by three or more laboratories to analyze several samples. Note (fig. 19) that the colorimetric, carmine method is the only method in which the standard deviation increases with increasing concentration. Interestingly, if data are limited to only those from the curcumin and dianthrimide methods, the two methods have significantly different precisions.

References to the methods are given below:

Method	*Reference*
Atomic emission spectrometry, direct-current plasma	American Society for Testing and Materials, 1983
Atomic emission spectrometry, inductively coupled plasma	—
Colorimetric, carmine	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979
Colorimetric, carmine, automated	—
Colorimetric, curcumin	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a
Colorimetric, dianthrimide	Skougstad and others, 1979
Potentiometric, mannitol	American Public Health Association and others, 1971 American Society for Testing and Materials, 1983

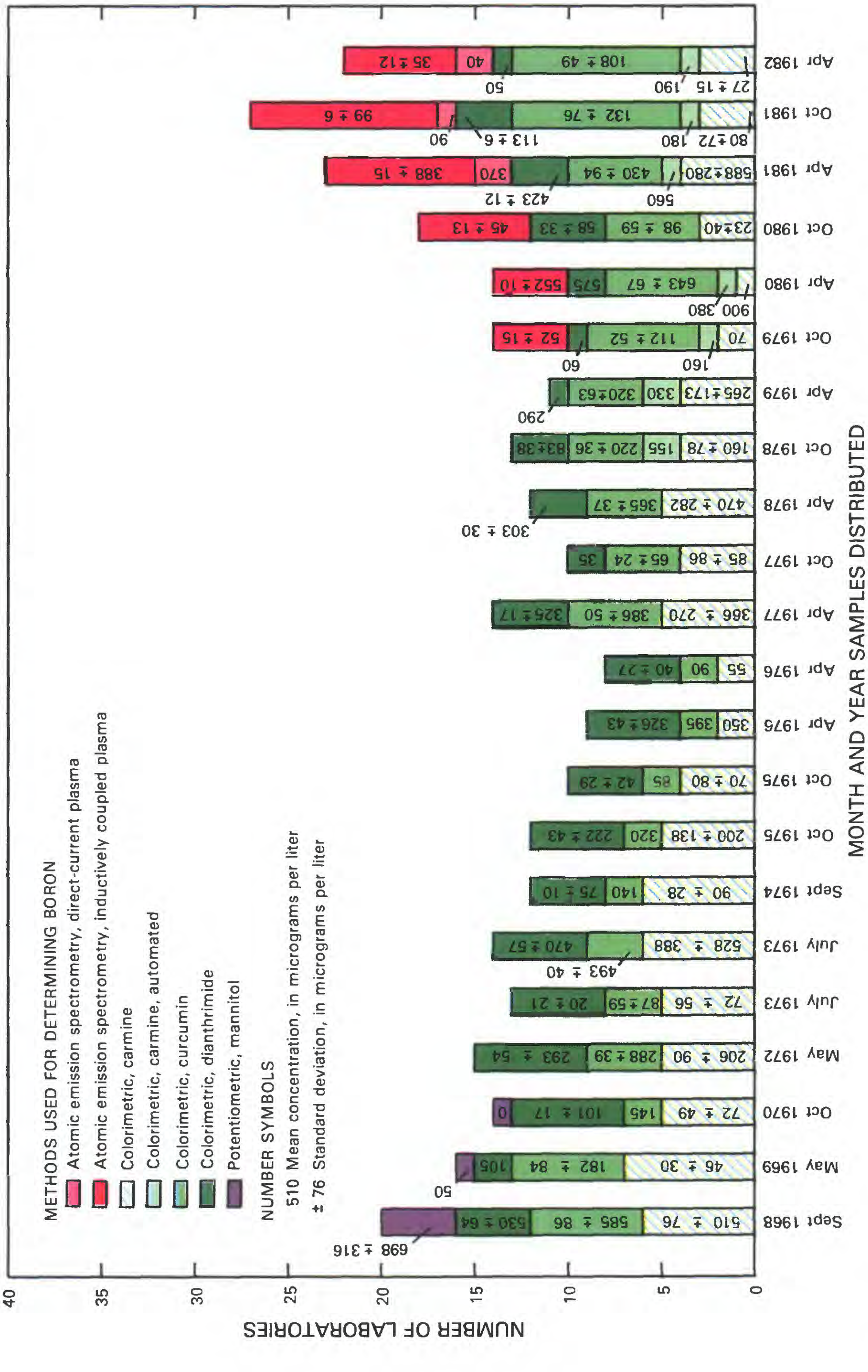

Figure 18. Mean concentrations and standard deviations for boron in 27 Standard Reference Water Samples.

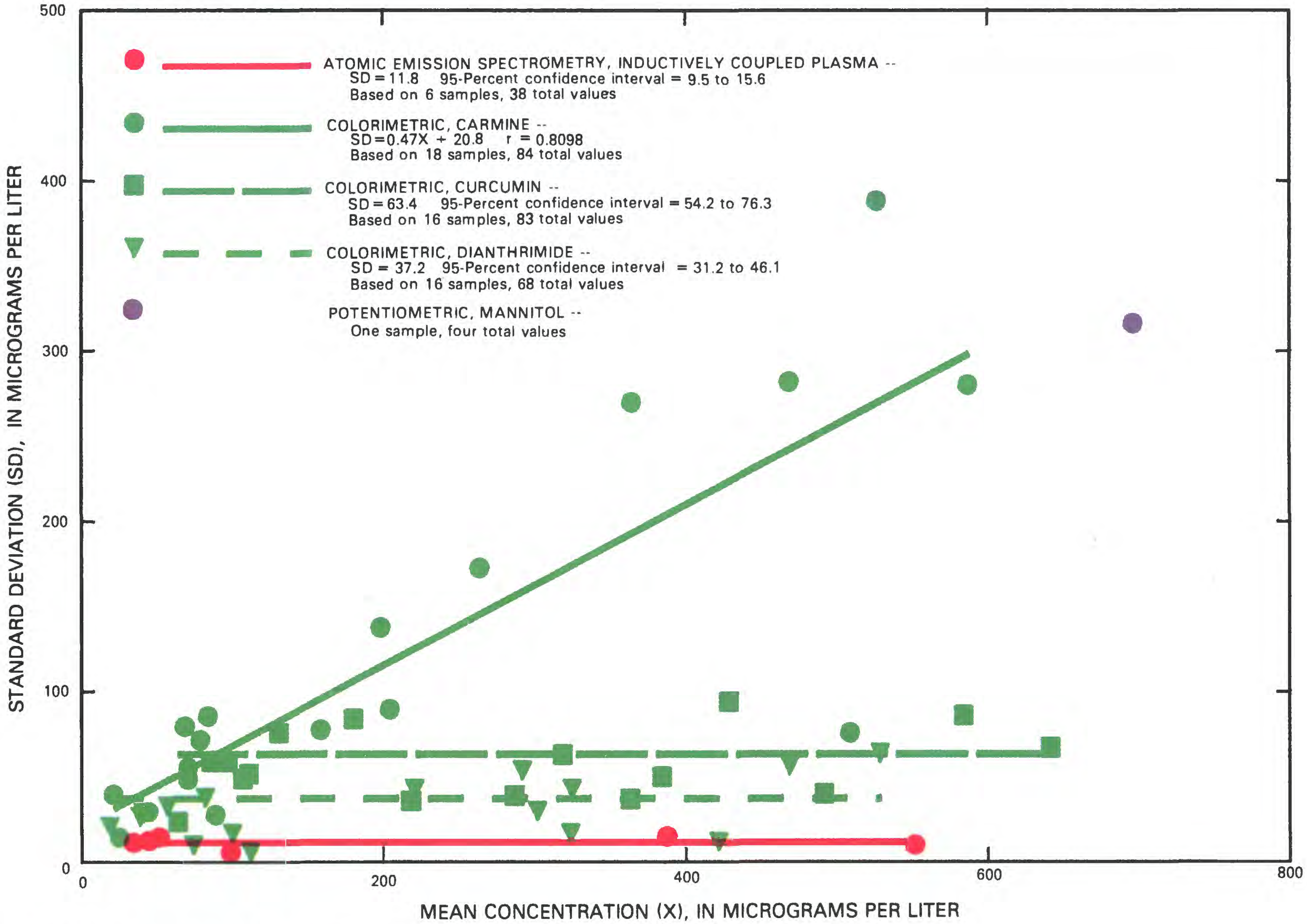

Figure 19. Interlaboratory precision of five methods used to determine boron.

BROMIDE

Data for bromide were extremely limited. The colorimetric, catalytic oxidation method (American Society for Testing and Materials, 1983; Skougstad and others, 1979) was used to determine bromide in six SRWS. For three of these, the reported mean concentrations and standard deviations were 0.216±0.201 mg/L (5 laboratories); 0.450±0.493 mg/L (6 laboratories); and 0.507±0.440 mg/L (3 laboratories). Only two results were reported for each of the other three SRWS; the reported concentrations were 0.33 and 0.40 mg/L; 0.30 and 0.40 mg/L; and 0.70 and 0.93 mg/L.

CADMIUM

Seven methods were used to determine cadmium (fig. 20). Prior to 1975, the majority of the data were from the AAS, APDC-MIBK method; however, use of that method to analyze SRWS appears to be decreasing. The AAS, direct; AAS, graphite-furnace; and emission, ICP methods were the main methods used in the last few years of this study with the AAS, graphite-furnace method accounting for more than one-half of the data in 1982.

Concentrations determined by the AAS, direct method are significantly different from those determined by the AAS, APDC-MIBK method. No other significant difference exists in concentrations. If data are limited to SRWS distributed in or after October 1979 (when emission, ICP data were first recorded) and a comparison is made of concentrations obtained using the AAS, direct; AAS, APDC-MIBK; AAS, graphite-furnace; and emission, ICP methods, no significant difference is observed between concentrations determined by the different methods. Furthermore, a comparison between concentrations determined by the AAS, PDCA-CHCL$_3$ and AAS, APDC-MIBK methods indicates no significant difference.

If all data are examined, the precisions for the AAS, direct and AAS, APDC-MIBK methods are significantly different. There is no significant difference between the precisions of the other methods shown in figure 21 when all data are examined. If only data from SRWS distributed from October 1975 (when more than those two methods were first reported) to October 1979 (when the emission, ICP data were first recorded) are considered, no significant difference exists among the precisions of any of the methods. However, if data from SRWS distributed in or after October 1979 are considered, the precisions for the AAS, direct and AAS, APDC-MIBK methods are significantly different.

References to the methods are given below:

Method	*Reference*
Atomic absorption spectrometry, chelation-extraction with ammonium pyrrolidine dithiocarbamate and methyl isobutyl ketone	American Public Health Association and others, 1980 Skougstad and others, 1979
Atomic absorption spectrometry, chelation-extraction with pyrrolidine dithiocarbamic acid in chloroform	American Society for Testing and Materials, 1983 U.S. Environmental Protection Agency, 1979a
Atomic absorption spectrometry, direct	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a
Atomic absorption spectrometry, graphite-furnace	U.S. Environmental Protection Agency, 1979a
Atomic emission spectrometry, direct-current plasma	American Society for Testing and Materials, 1983
Atomic emission spectrometry, inductively coupled plasma	Fishman and Bradford, 1982 U.S. Environmental Protection Agency, 1979b
Voltammetry, anodic stripping	American Society for Testing and Materials, 1983

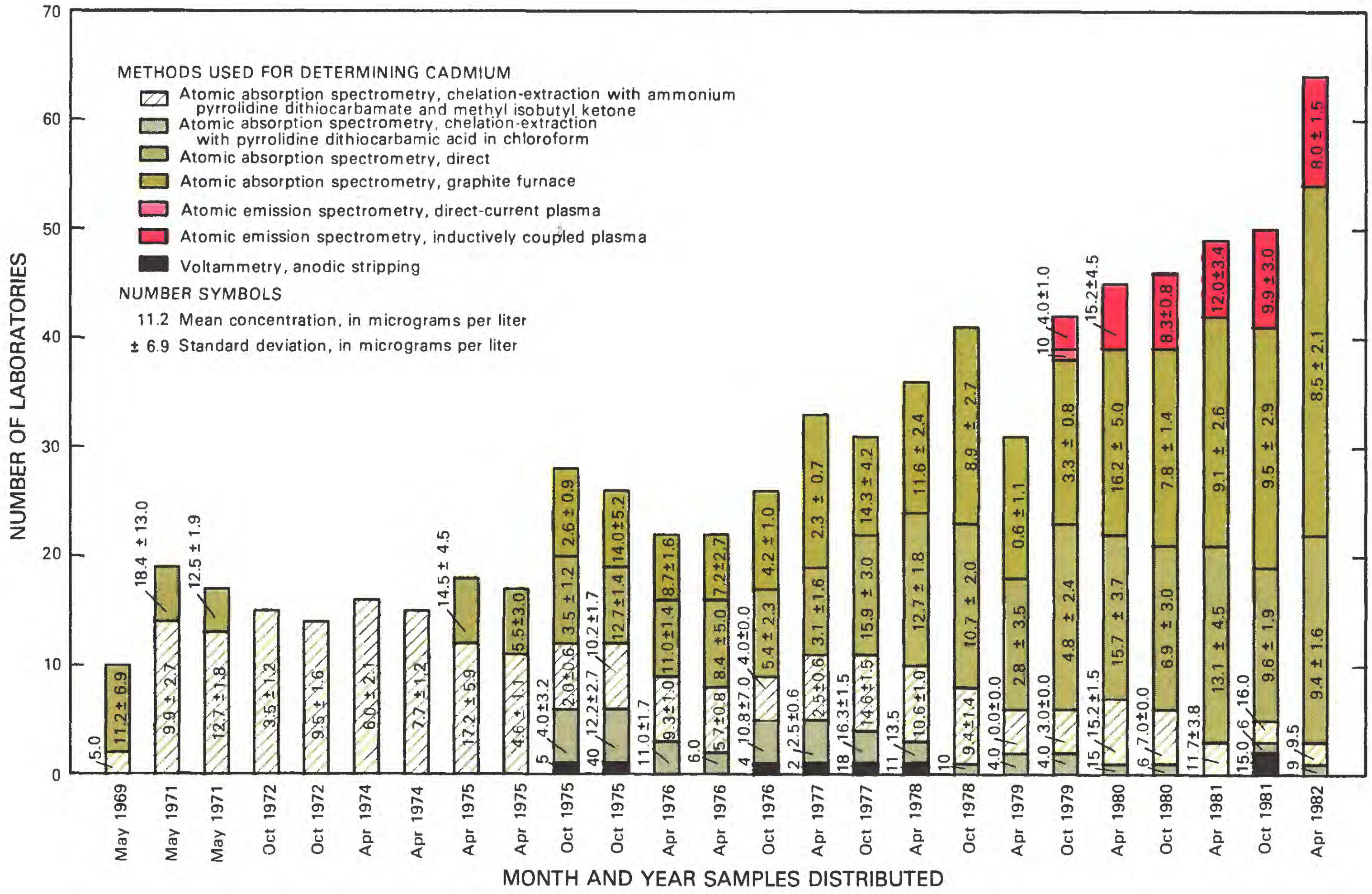

Figure 20. Mean concentrations and standard deviations for cadmium in 21 Standard Reference Water Samples.

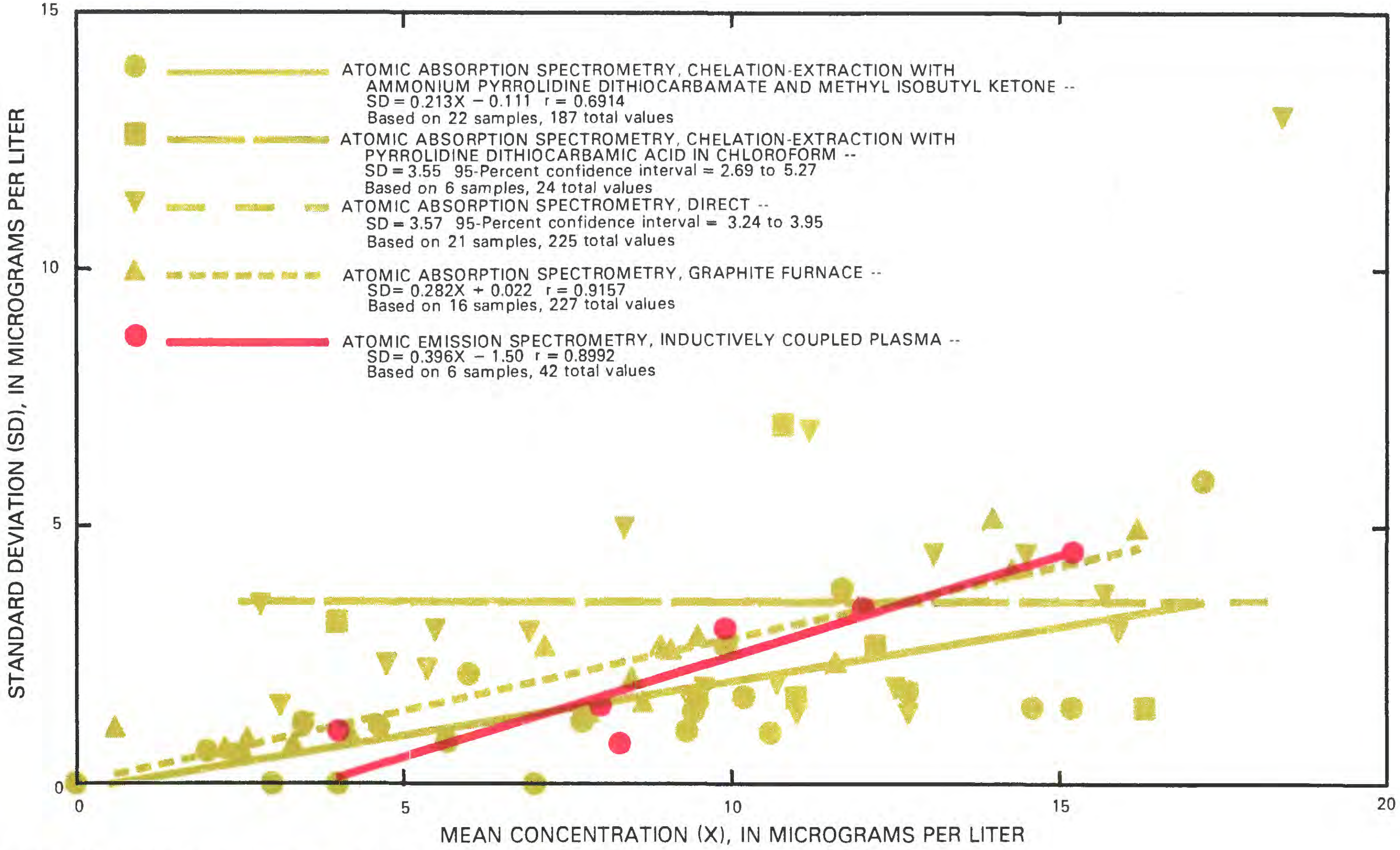

Figure 21. Interlaboratory precision of five methods used to determine cadmium.

CALCIUM

Six methods were used to determine calcium during the period of record (fig. 22). The AAS, direct and complexometric-titration methods were used throughout the period with the majority of data being obtained from the AAS, direct method.

The determination of calcium by AAS, direct and by complexometric titration gave values that have significantly different concentrations and precisions. This is true when all of the data are considered, when only data with an *n* greater than two are considered, or when just the two methods are considered. The mean concentration values obtained by complexometric titration are generally slightly greater than those obtained by AAS, direct; for example, 21.0 mg/L compared to 20.0 mg/L, 11.1 mg/L compared to 10.8 mg/L, and 115.6 mg/L compared to 110.4 mg/L.

In general, the complexometric-titration method is apparently more precise except at small concentrations (fig. 23). Interestingly, neither the AAS, direct nor complexometric-titration methods show significant differences in concentration or precision when compared to the determination of calcium by emission, ICP (the only other method that had at least three values submitted for an SRWS), although many fewer values are available for data analysis.

References to the methods are given below:

Method	*Reference*
Atomic absorption spectrometry, direct	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a
Atomic emission spectrometry, direct-current plasma	—
Atomic emission spectrometry, flame	—
Atomic emission spectrometry, inductively coupled plasma	Fishman and Bradford, 1982
Neutron activation	—
Titration, complexometric, ethylenediaminetetraacetic acid	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Brown and others, 1970 U.S. Environmental Protection Agency, 1979a

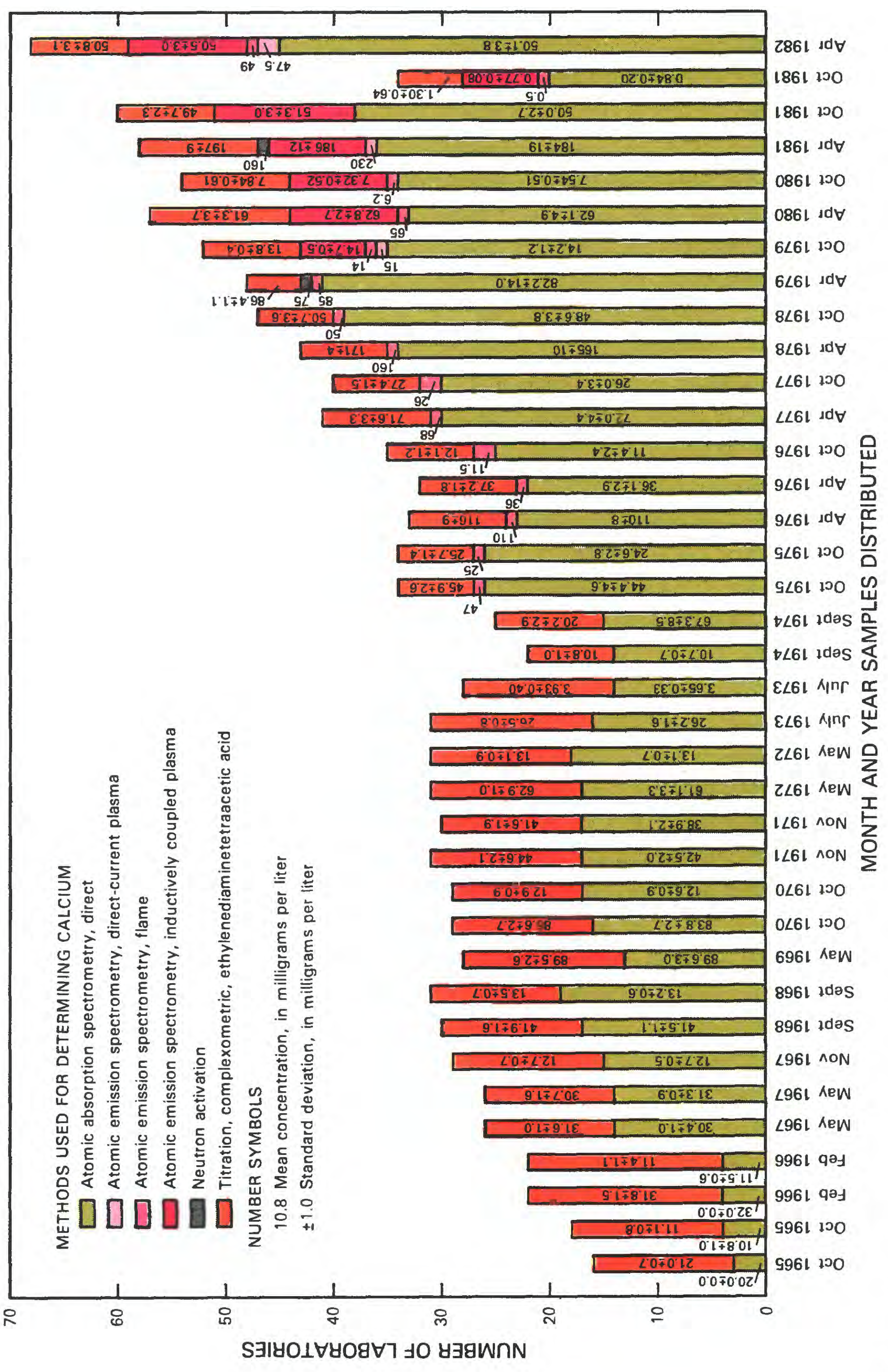

Figure 22. Mean concentrations and standard deviations for calcium in 37 Standard Reference Water Samples.

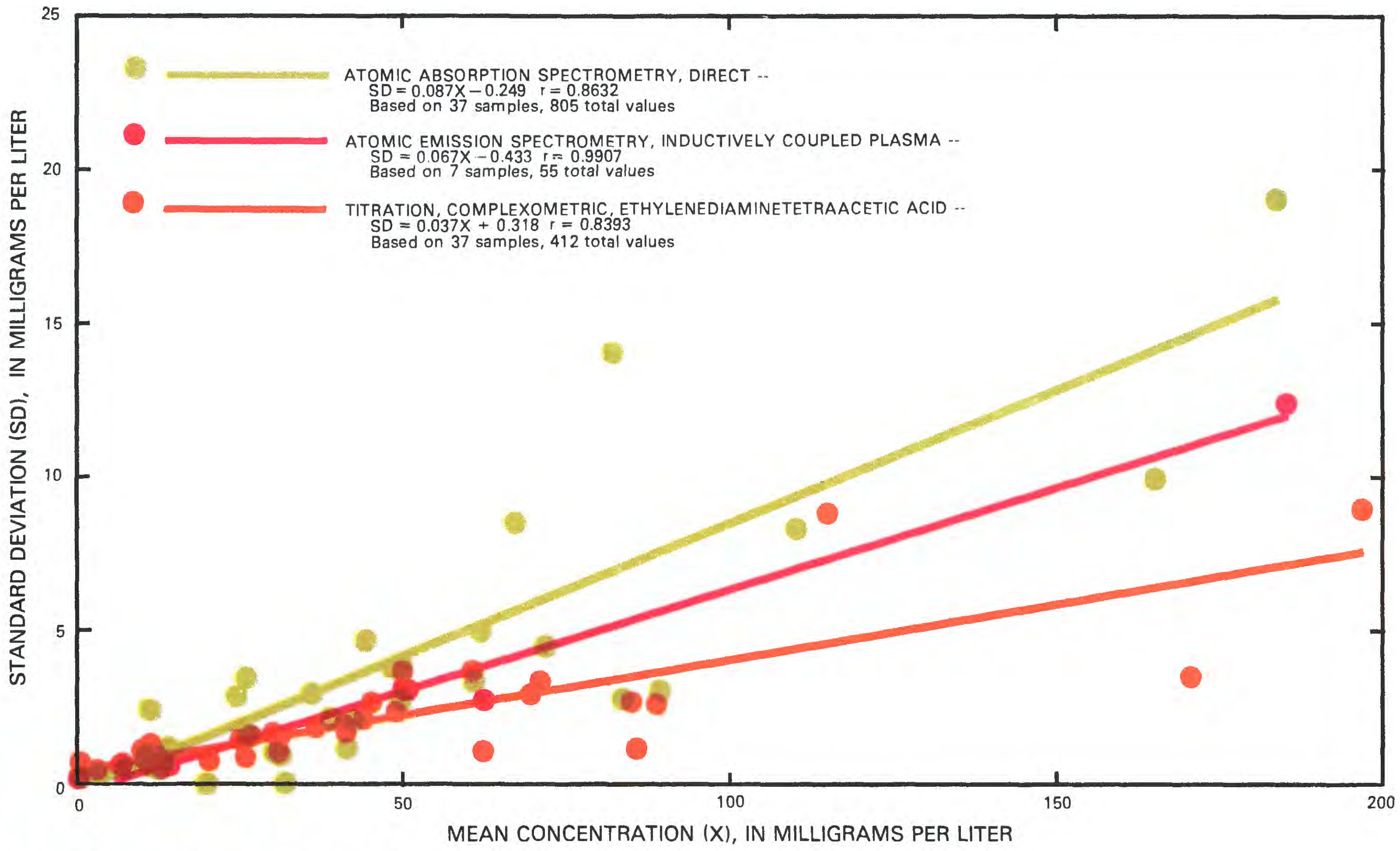

Figure 23. Interlaboratory precision of three methods used to determine calcium.

CHLORIDE

Six methods were used to determine chloride (fig. 24). Data from the gravimetric method are too limited to use in any valid comparisons. If all other methods are considered, the chance is 5-percent that the concentrations determined by the titration, silver nitrite method are the same as the concentrations determined by the titration, mercuric nitrite method. If data are limited to SRWS distributed in or after October 1975 (when the potentiometric, ion-selective-electrode method was first reported), concentrations for the two methods are significantly different; however, no other significant difference is found between the methods with respect to the reported concentrations.

The precision for the ion-selective-electrode method is significantly different from the precision for the colorimetric, mercuric thiocyanate, automated method (fig. 25). It also is significantly different from the precision for the titration, silver nitrate method if all available standard-deviation values are considered. However, if only data from SRWS distributed in or after October 1975 are considered, no significant difference exists between the precisions for the ion-selective-electrode and titration, silver nitrate methods, but a significant difference exists between the precisions of the colorimetric, mercuric thiocyanate, automated and the titration, mercuric nitrate methods. No other significant differences exist in the analytical precisions for the various methods. Also, a less than 5-percent chance exists that the intercept for the precision model of the colorimetric, mercuric thiocyanate, automated method is equal to zero.

References to the methods are given below:

Method	*Reference*
Colorimetric, mercuric thiocyanate, automated	American Public Health Association and others, 1980 Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a
Gravimetric	Rainwater and Thatcher, 1960
Potentiometric, ion-selective electrode	American Society for Testing and Materials, 1983
Potentiometric, titration	American Public Health Association and others, 1980
Titration, mercuric nitrate	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a
Titration, silver nitrate	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979

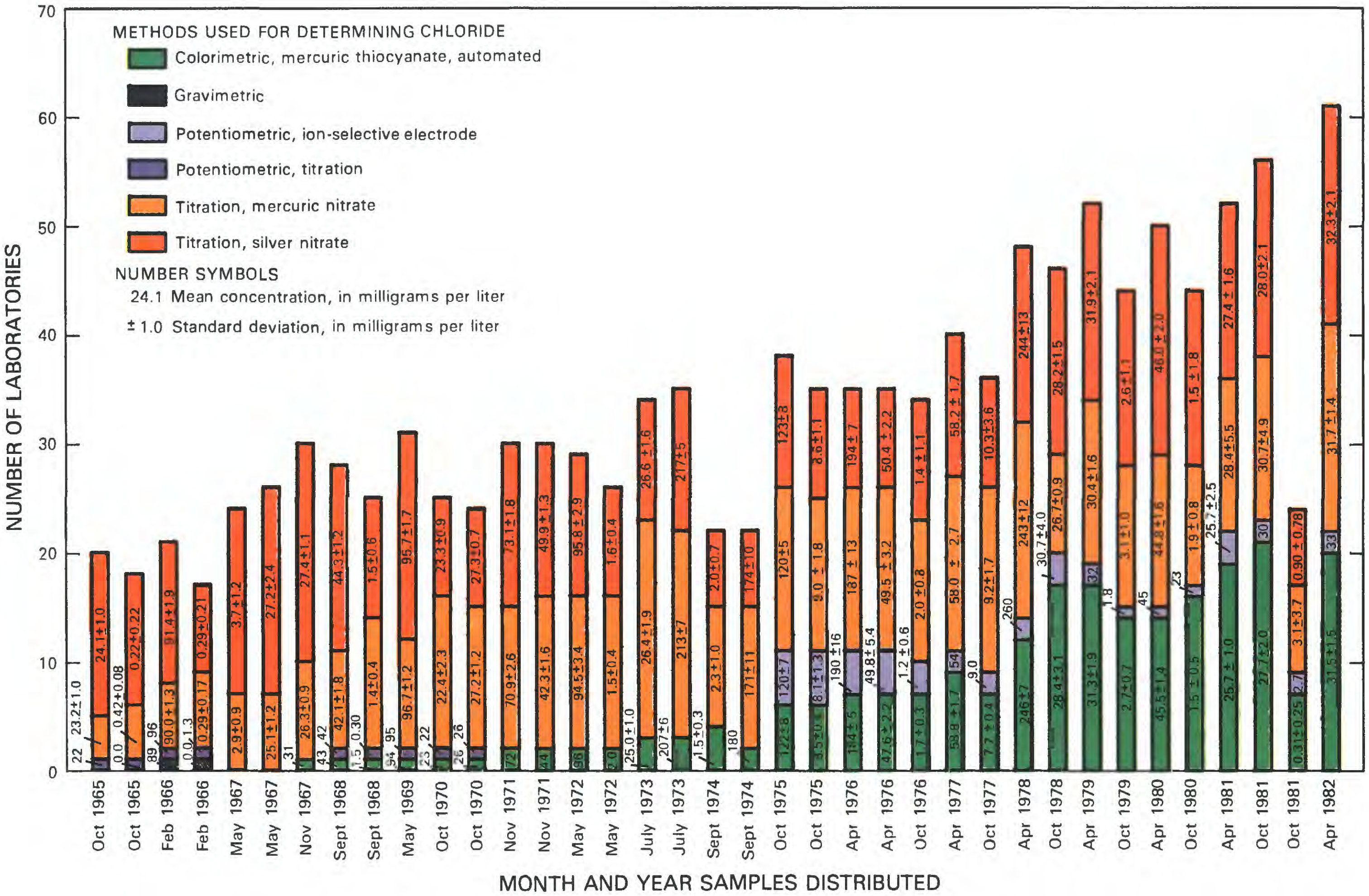

Figure 24. Mean concentrations and standard deviations for chloride in 37 Standard Reference Water Samples.

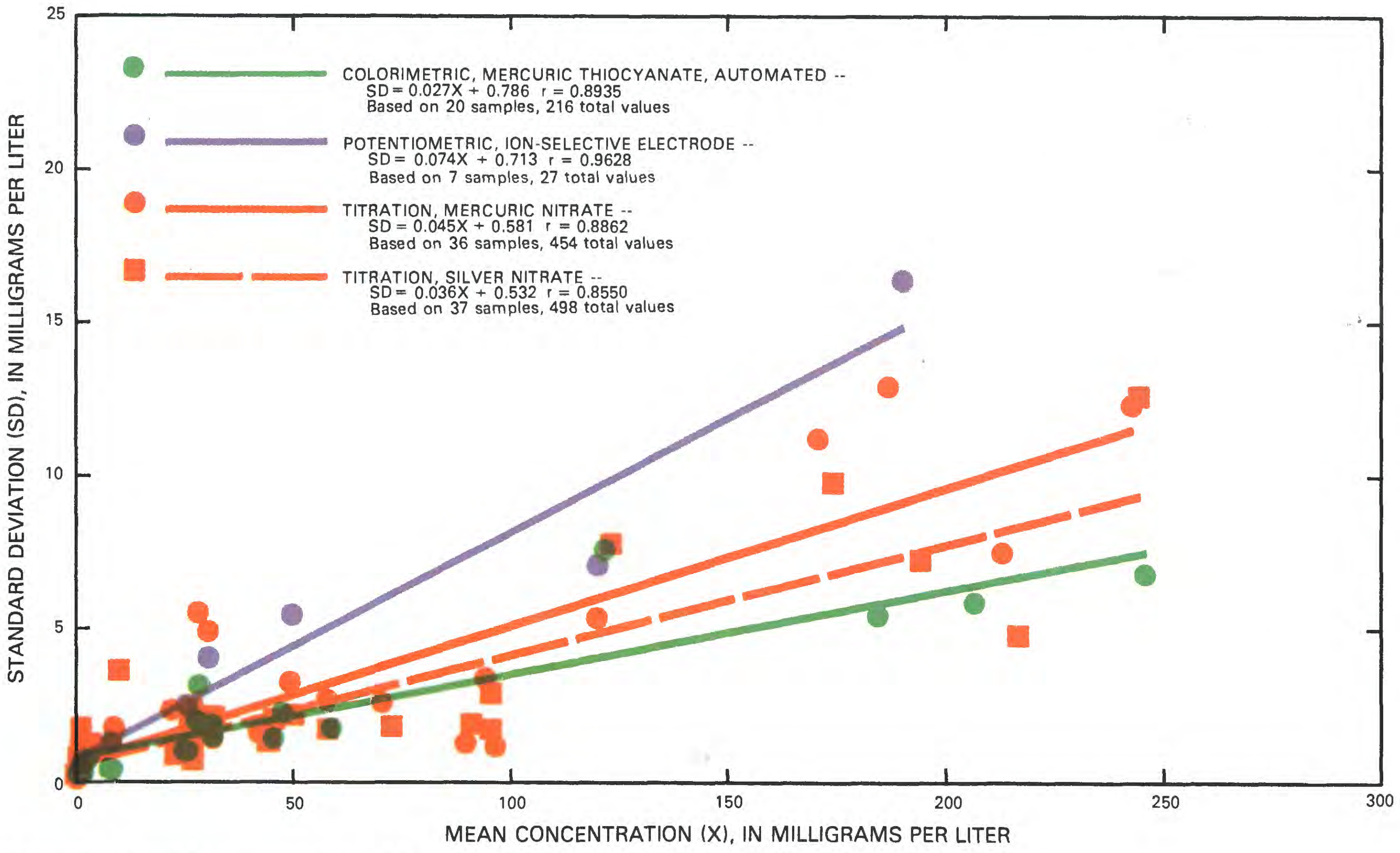

Figure 25. Interlaboratory precision of four methods used to determine chloride.

CHROMIUM

Nine methods were used to determine chromium (fig. 26). If all data, or data limited to SRWS distributed in or after October 1975 (when AAS, graphite-furnace data were first reported), or data further limited to SRWS distributed in or after October 1979 (when emission, ICP data were first recorded) are considered, then the concentrations for the AAS, direct method are significantly different from the concentrations for the AAS, graphite-furnace method. No other significant difference is found in concentrations reported for the methods.

Precision data were available for five of the nine methods, with sufficient data to develop a model available for four of the methods (fig. 27). If all data are examined, the precision for the AAS, oxidation, APDC-MIBK method is significantly different from those of the AAS, direct; AAS, graphite-furnace; and emission, ICP methods. The precision for the AAS, graphite-furnace method is significantly different from those for the AAS, direct; AAS, oxidation, APDC-MIBK; and the colorimetric, oxidation, permanganate-azide methods. The precision for the colorimetric, oxidation, permanganate-azide method is significantly different from the precision for the AAS, graphite-furnace and emission, ICP methods.

If only data from SRWS distributed in or after October 1979 are examined, the AAS, direct and emission, ICP methods yield significantly different precisions. If only data from SRWS distributed in or before October 1978 are examined, the AAS, direct and AAS, APDC-MIBK methods show no significant difference in precisions.

References to the methods are given below:

Method	*Reference*
Atomic absorption spectrometry, oxidation, chelation extraction with ammonium pyrrolidine dithiocarbamate and methyl isobutyl ketone	American Public Health Association and others, 1980 Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a
Atomic absorption spectrometry, oxidation, chelation extraction with pyrrolidine dithiocarbamic acid in chloroform	U.S. Environmental Protection Agency, 1979a
Atomic absorption spectrometry, direct	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a
Atomic absorption spectrometry, graphite-furnace	U.S. Environmental Protection Agency, 1979a.
Atomic emission spectrometry, arc-spark	Barnett and Mallory, 1971
Atomic emission spectrometry, direct-current plasma	American Society for Testing and Materials, 1983
Atomic emission spectrometry, inductively coupled plasma	U.S. Environmental Protection Agency, 1979b
Colorimetric, oxidation, permanganate azide	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979
Neutron activation	—

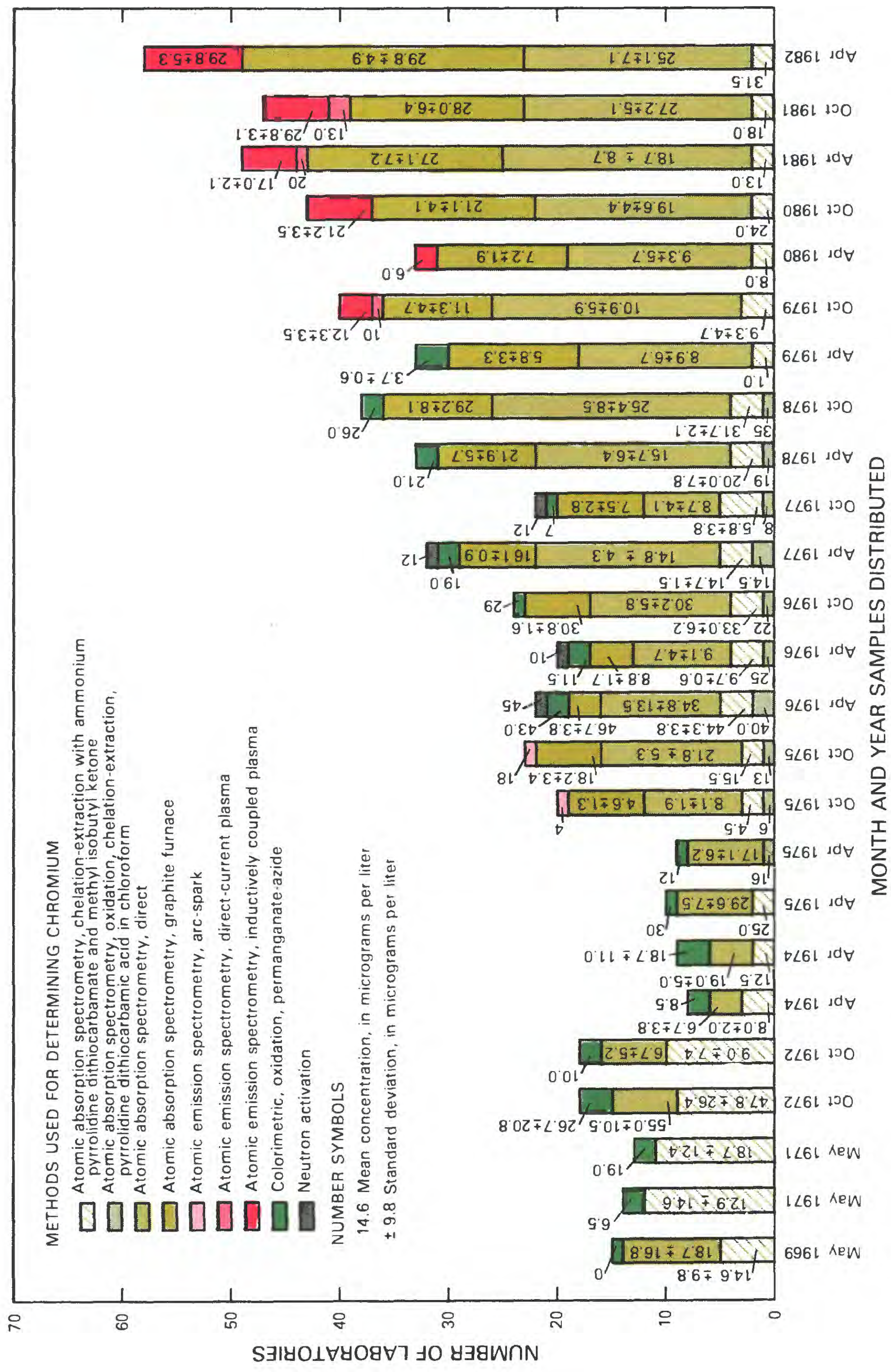

Figure 26. Mean concentrations and standard deviations for chromium in 25 Standard Reference Water Samples.

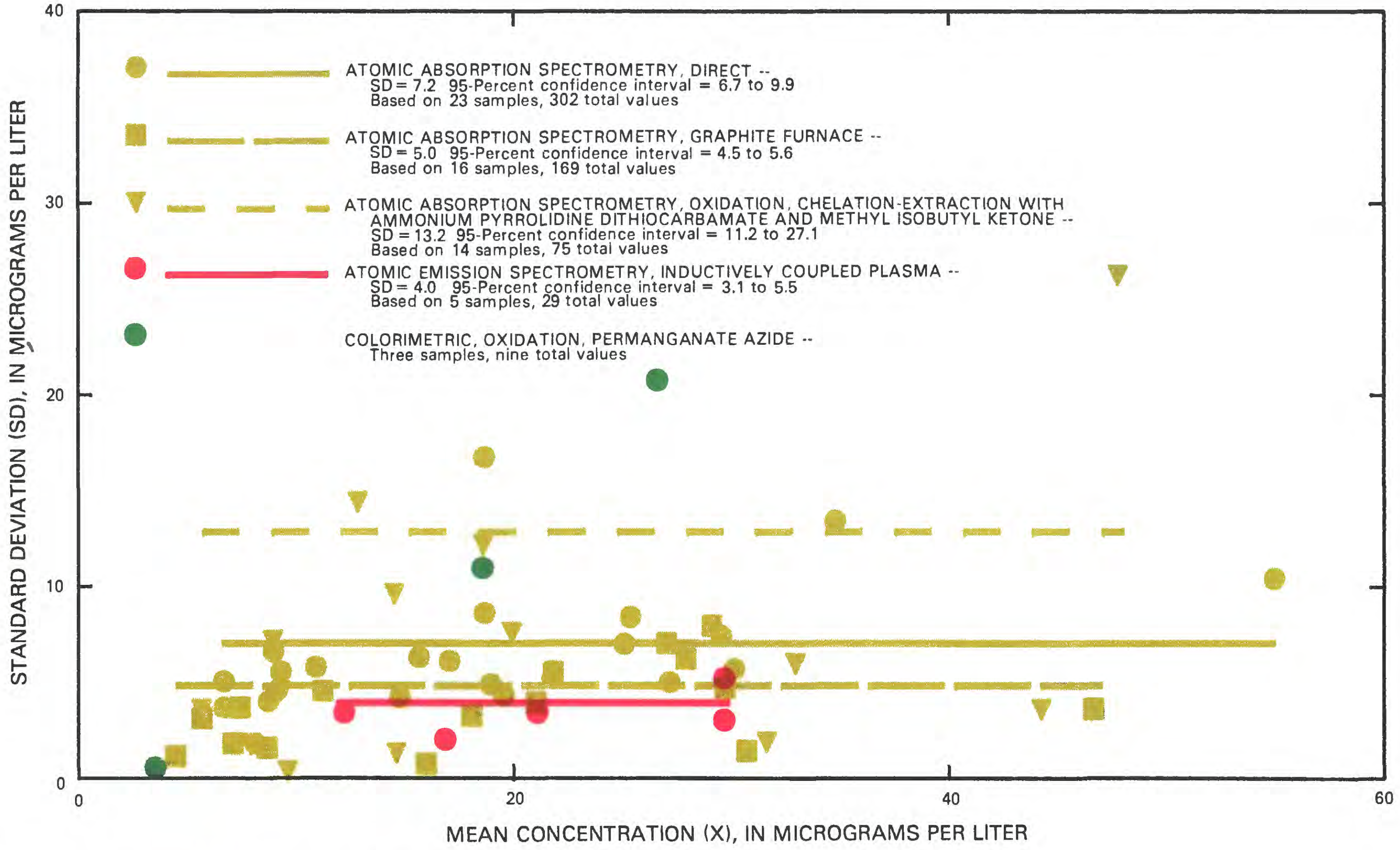

Figure 27. Interlaboratory precision of five methods used to determine chromium.

COBALT

Eight methods were used to determine cobalt (fig. 28). Initially, all data were from the AAS, APDC-MIBK method; however, the use of that method appears to have been quite limited in the past few years with the increased use of the AAS, graphite-furnace; and emission, ICP methods. No significant difference is found in the concentrations reported for the methods.

In developing precision models, the analytical standard deviation did not vary with the reported concentration (fig. 29) in any of the four methods for which enough data were available. Although the difference in the absolute values for the precisions of the methods does not appear very great, the precision for the AAS, APDC-MIBK method is significantly different (and appears better) than those for the AAS, direct; AAS, graphite-furnace; and emission, ICP methods. In addition, a significant difference exists between the precisions of the AAS, direct and AAS, graphite-furnace methods.

References to the methods are given below:

Method	*Reference*
Atomic absorption spectrometry, chelation-extraction with ammonium pyrrolidine dithiocarbamate and methyl isobutyl ketone	American Public Health Association and others, 1980 Skougstad and others, 1979
Atomic absorption spectrometry, chelation-extraction with pyrrolidine dithiocarbamic acid in chloroform	American Society for Testing and Materials, 1983 U.S. Environmental Protection Agency, 1979a
Atomic absorption spectrometry, direct	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a
Atomic Absorption spectrometry, graphite-furnace	U.S. Environmental Protection Agency, 1979a
Atomic emission spectrometry, direct-current plasma	American Society for Testing and Materials, 1983
Atomic emission spectrometry, inductively coupled plasma	Fishman and Bradford, 1982 U.S. Environmental Protection Agency, 1979b
Atomic emission spectrometry, arc-spark	Barnett and Mallory, 1971
Neutron activation	—

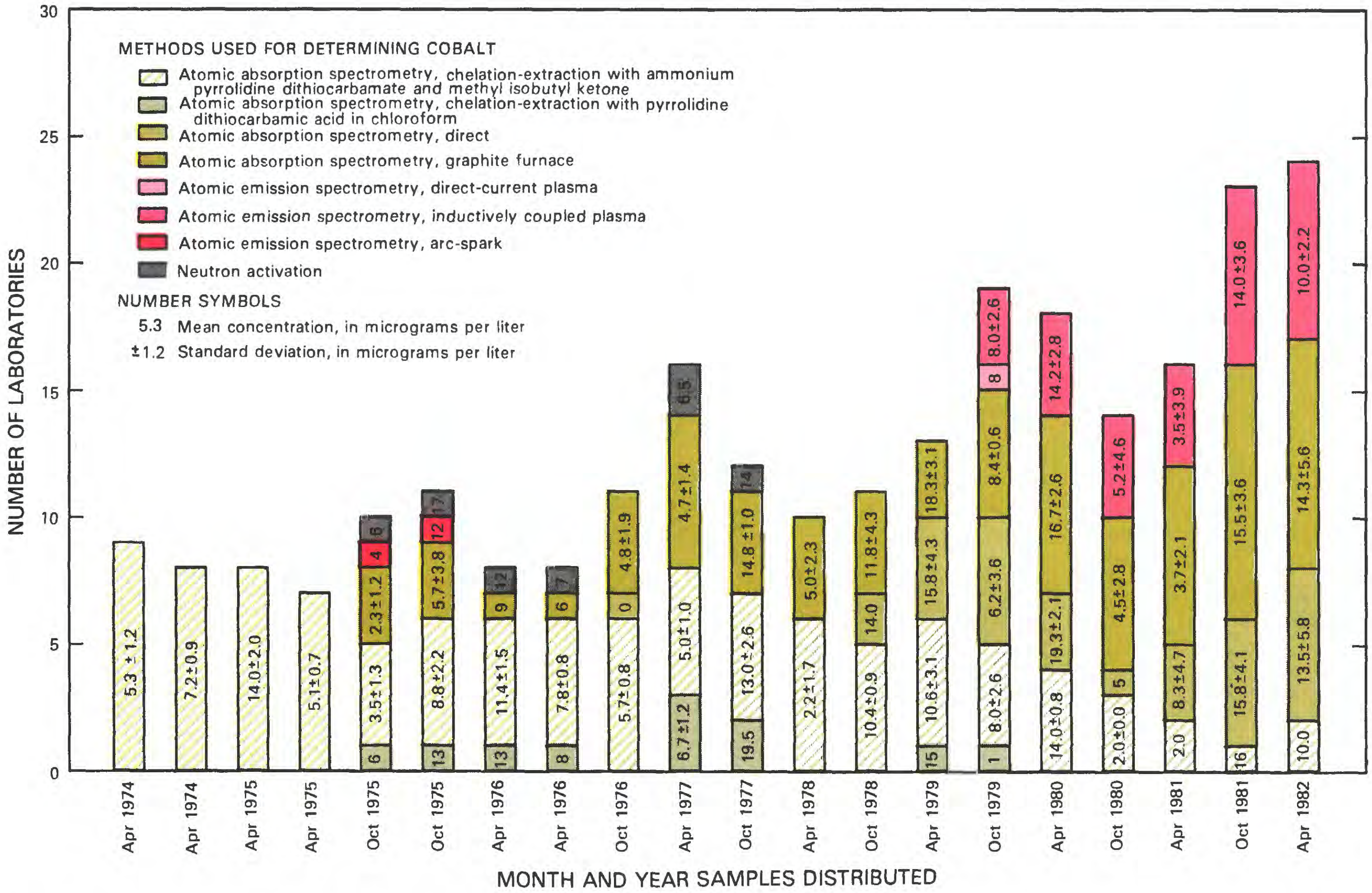

Figure 28. Mean concentrations and standard deviations for cobalt in 20 Standard Reference Water Samples.

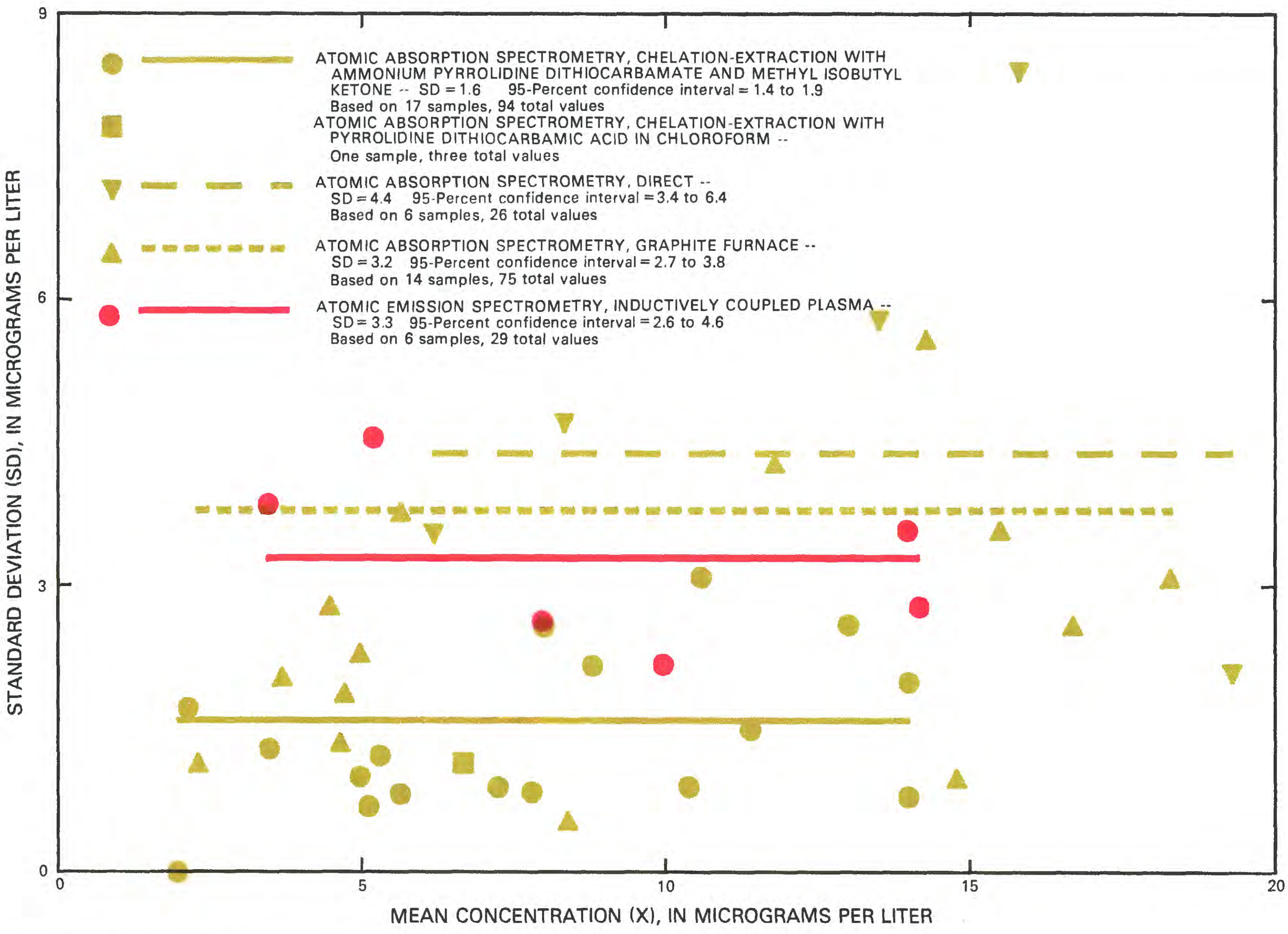

Figure 29. Interlaboratory precision of five methods used to determine cobalt.

COPPER

Ten methods were used to determine copper (fig. 30). Most of the data are from the AAS, direct method, although the AAS, APDC-MIBK method also was used for most of the period of record and the AAS, graphite-furnace and emission, ICP methods show increasing use in the last few years. When data for all SRWS are considered, no significant difference is found in the concentrations reported for the various methods. However, when data are limited to SRWS distributed in or after October 1975 (when the AAS, graphite-furnace method was first reported), a significant difference exists between concentrations reported for the AAS, direct and AAS, graphite-furnace methods. If data are limited further to SRWS distributed in or after October 1979 (when the emission, ICP method was first recorded), no significant difference is found in concentrations.

Precision models for four methods were determined and are given in figure 31, along with three standard deviations for the colorimetric method. When all data are considered, or when only data from SRWS distributed in or after October 1975 are considered, a significant difference exists between the precisions reported for the AAS, graphite-furnace and AAS, direct methods, with the standard deviations for the AAS, graphite-furnace method generally being larger. However, no significant difference is found in the precisions reported for the other methods. When only data from SRWS distributed in or after October 1979 are considered, no significant difference is found among the precisions for any of the methods. A less than 5-percent chance exists that the intercept for the precision models for either the AAS, direct or emission, ICP methods is equal to zero.

References to the methods are given below:

Method	*Reference*
Atomic absorption spectrometry, chelation-extraction with ammonium pyrrolidine dithiocarbamate and methyl isobutyl ketone	American Public Health Association and others, 1980 Skougstad and others, 1979
Atomic absorption spectrometry, direct	American Public Health Assocation and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a
Atomic absorption spectrometry, graphite-furnace	U.S. Environmental Protection Agency, 1979a
Atomic emission spectrometry, arc-spark	Barnett and Mallory, 1971
Atomic emission spectrometry, direct-current plasma	American Society for Testing and Materials, 1983
Atomic emission spectrometry, inductively coupled plasma	Fishman and Bradford, 1982
Colorimetric, cuprethol	American Public Health Association and others, 1971 American Society for Testing and Materials, 1983 Rainwater and Thatcher, 1960
Colorimetric, dithizone	—
Neutron activation	—
Voltammetry, anodic stripping	—

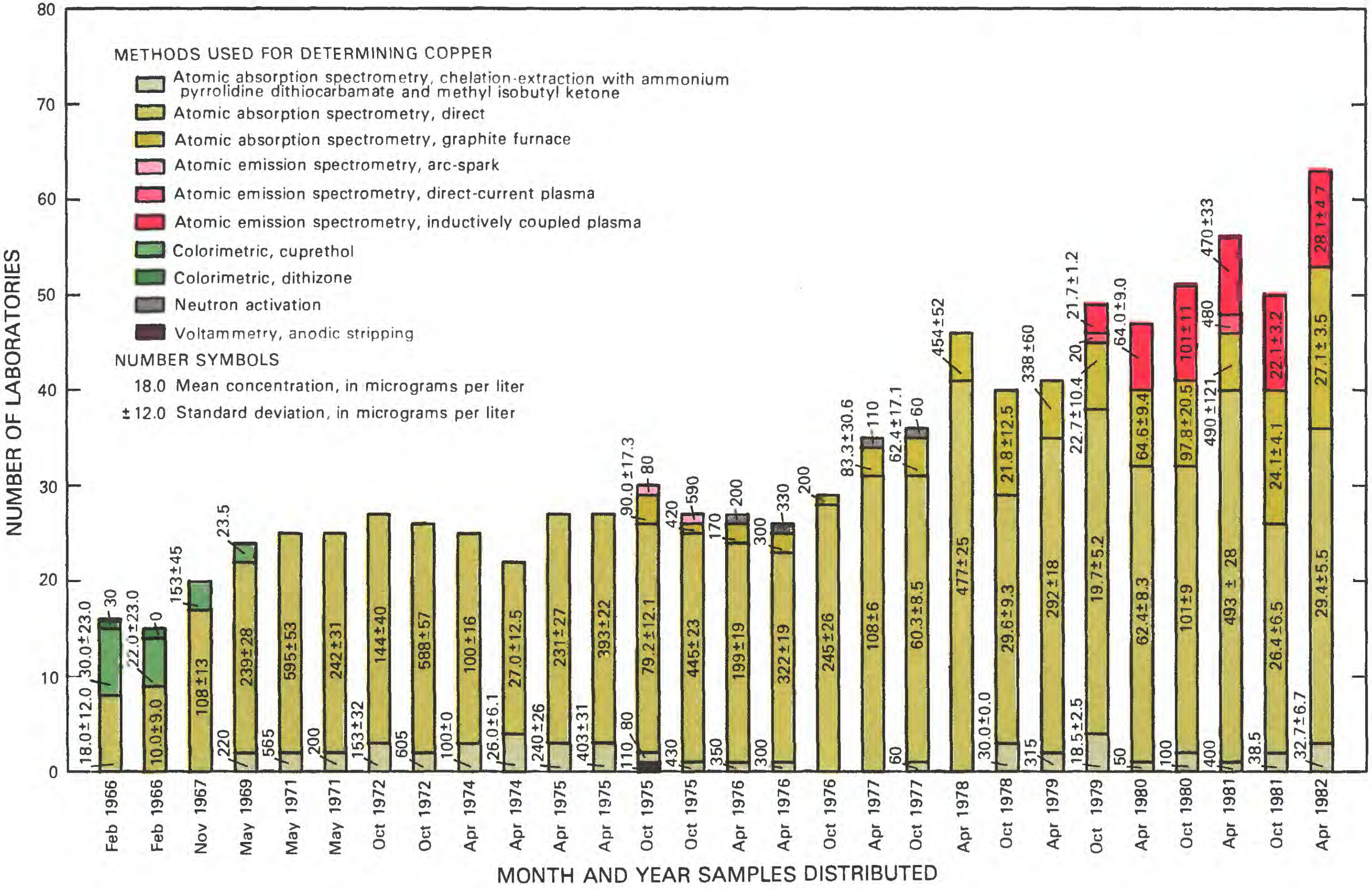

Figure 30. Mean concentrations and standard deviations for copper in 28 Standard Reference Water Samples.

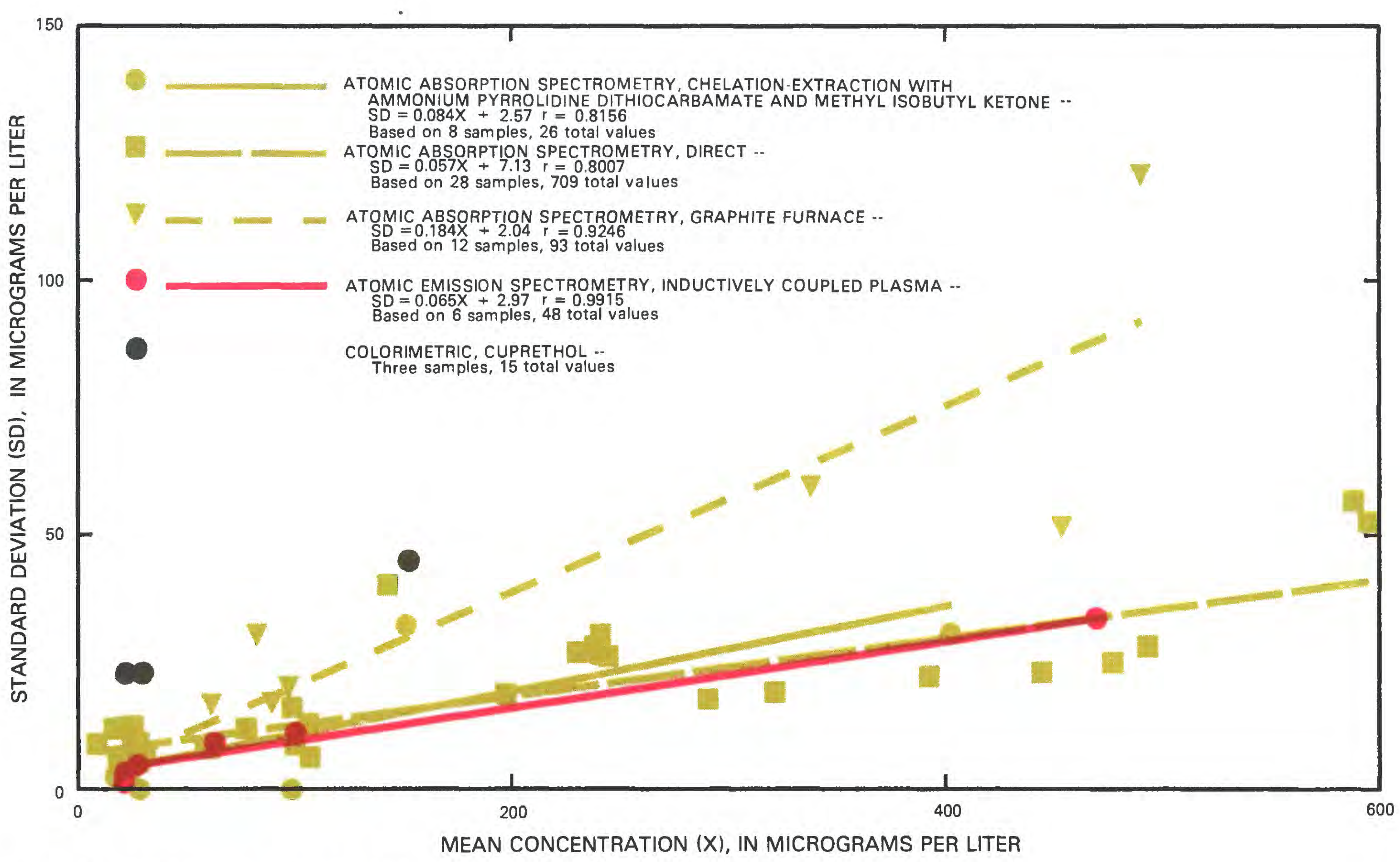

Figure 31. Interlaboratory precision of five methods used to determine copper.

DISSOLVED SOLIDS

Participants in the SRWS interlabortory studies were requested to use 108 °C for drying the evaporated sample residue for the dissolved solids determination (American Public Health Association and others, 1980; Skougstad and others, 1979; U.S. Environmental Protection Agency, 1979a). The dissolved solids concentration was determined on 22 SRWS (769 values total). The model for estimating the precision between 59.2 and 1761 mg/L is given in figure 32.

It is worth noting that a less than 5-percent chance exists that the intercept of this model is equal to zero; however, the lowest reported mean concentration was 59.2 mg/L, and analysis of samples with less dissolved solids could greatly affect the intercept.

FLUORIDE

Eight methods were used to determine fluoride; as is obvious in figure 33, the colorimetric procedures showed a steady decline in use and, by the end of the period of study, had been largely replaced by the potentiometric, ion-selective-electrode method. No significant difference in concentrations is reported for the methods. This is true if all data are considered, if data are limited to SRWS distributed in or after September 1968 (when the potentiometric method was first reported), or if data are limited to SRWS distributed in or after October 1975 (when the automated potentiometric method was first reported).

Concentrations greater than 3.0 mg/L were not included in the precision models shown in figure 34. If they were included, the model for the colorimetric, zirconium eriochrome cyanine-R method would be $SD=0.118x+0.006$, $r=0.8046$; the model for the colorimetric, SPADNS method would be $SD=0.350x-0.169$, $r=0.8465$; and the model for the potentiometric, ion-selective-electrode method would be $SD=0.15$ mg/L. These data imply that standard deviations for the colorimetric, zirconium eriochrome cyanine-R method did vary with concentration; standard deviations for the potentiometric, ion-selective-electrode method did not vary with concentration; and standard deviations for the colorimetric, SPADNS method might have been found to vary with concentration if more data were available.

If only concentrations less than 3 mg/L are included in the data set, no significant difference is observed in the precision of the methods. However, if all data are considered, the precision of the colorimetric, SPADNS method is significantly different than those of both the manual and automated ion-selective-electrode methods.

References to the methods are given below:

Method	*Reference*
Colorimetric, alizarin, automated	American Public Health Association and others, 1980 U.S. Environmental Protection Agency, 1979a
Colorimetric, alizarin, visual	American Public Health Association and others, 1980 American Society for Testing and Materials, 1970 Rainwater and Thatcher, 1960
Colorimetric, SPADNS	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 U.S. Environmental Protection Agency, 1979a
Colorimetric, SPADNS, automated	—
Colorimetric, zirconium eriochrome cyanine-R	Skougstad and others, 1979
Colorimetric, zirconium xylenol orange	—
Potentiometric, ion-selective electrode	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a
Potentiometric, ion-selective electrode, automated	Skougstad and others, 1979

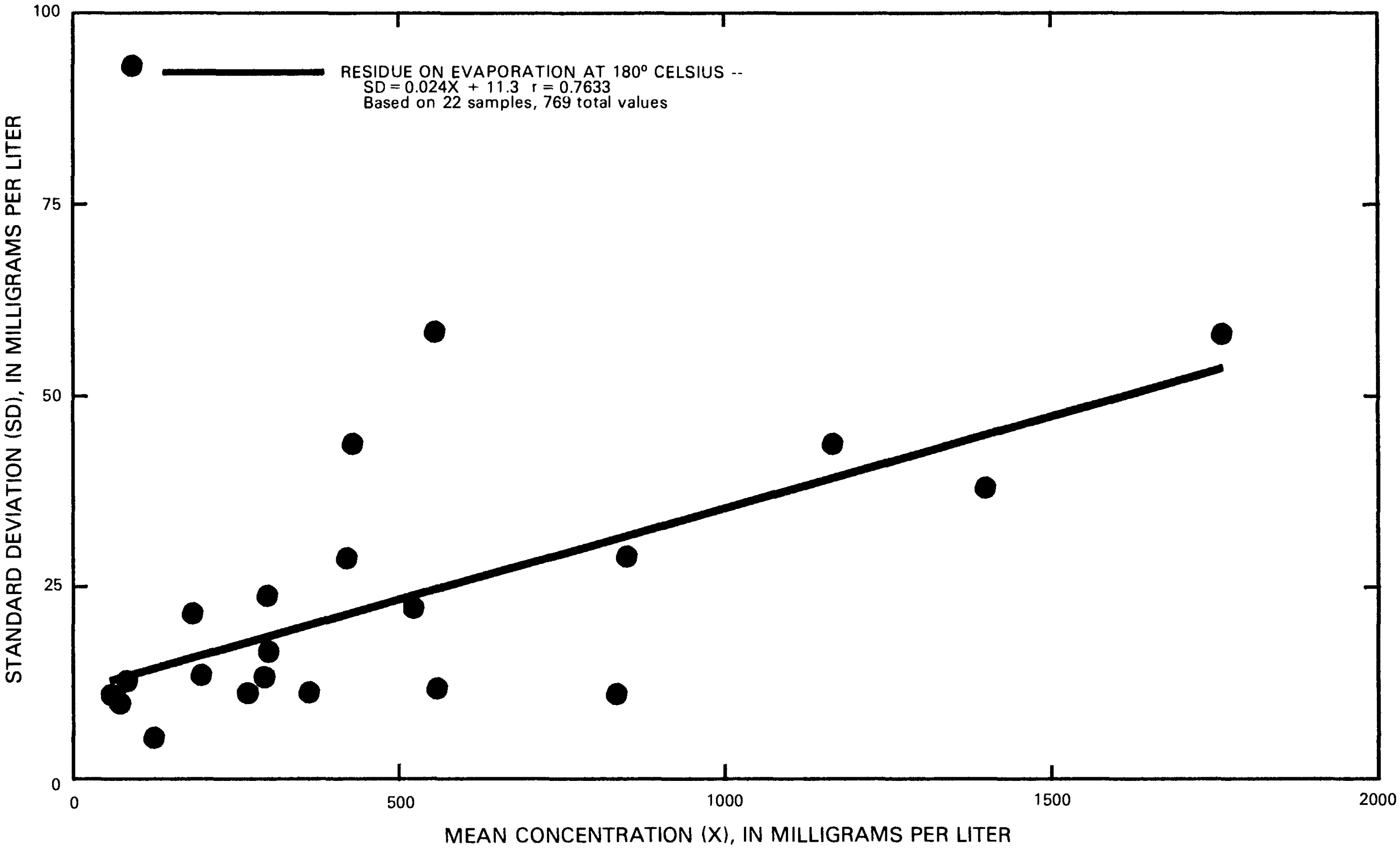

Figure 32. Interlaboratory precision for the determination of dissolved solids residue on evaporation at 180°C.

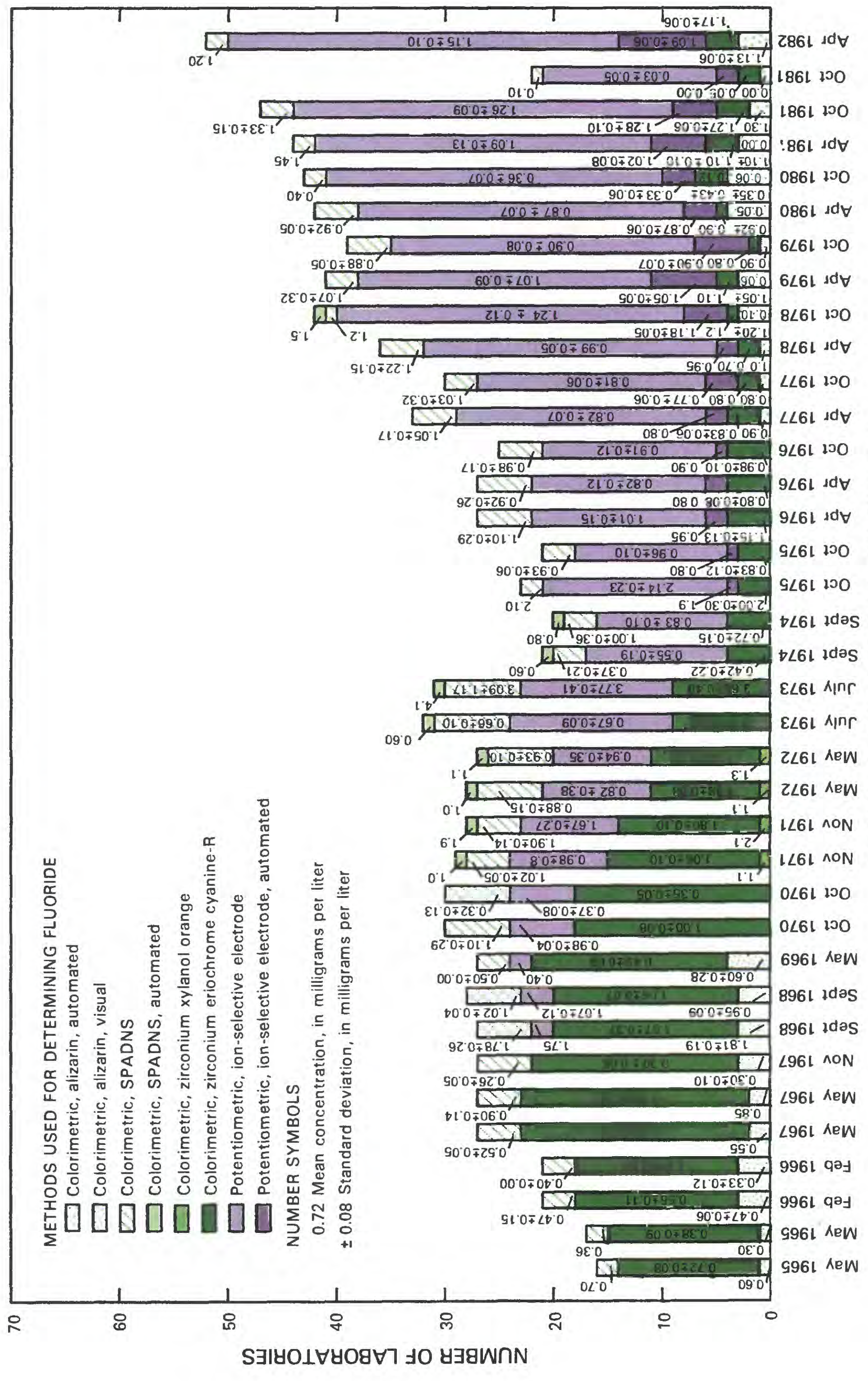

Figure 33. Mean concentrations and standard deviations for fluoride in 37 Standard Reference Water Samples.

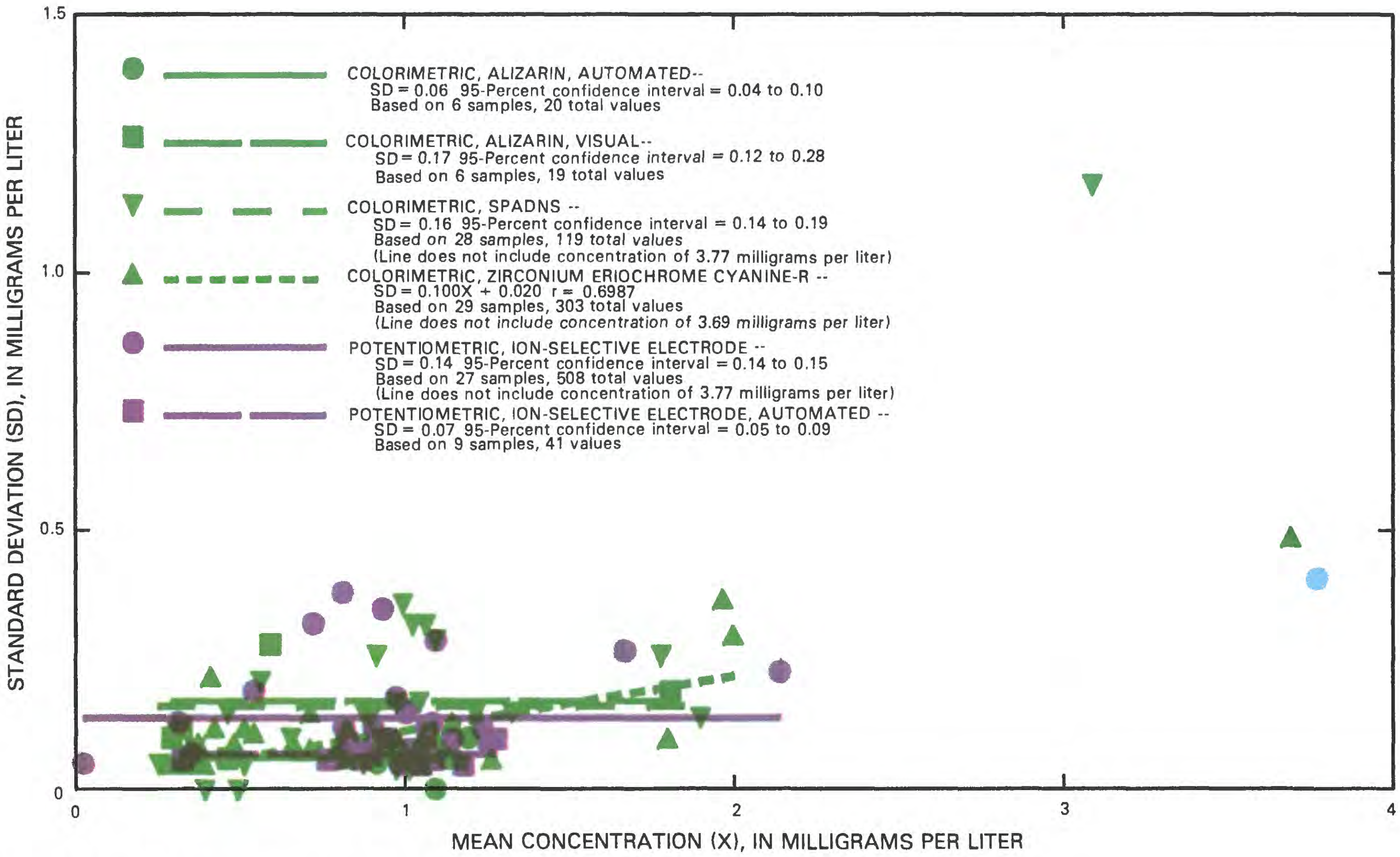

Figure 34. Interlaboratory precision of six methods used to determine fluoride.

HARDNESS

Laboratories analyzing SRWS are not requested to report hardness. However, we have assumed that laboratories reporting magnesium using a titration, complexometric method actually determined hardness and subtracted calcium, and possibly subtracted strontium and barium, before reporting magnesium (American Public Health Association and others, 1980; American Society for Testing and Materials, 1983; Skougstad and others, 1979; U.S. Environmental Protection Agency, 1979a). Therefore, hardness was recalculated and a precision model was developed (fig. 35).

IODIDE

Data for iodide were extremely limited. The colorimetric, ceric arsenious oxidation method (American Public Health Association and others, 1980; American Society for Testing and Materials, 1983; Skougstad and others, 1979) was used to determine iodide in four SRWS. For three of the samples, the reported mean concentrations and standard deviations were 0.023±0.021 mg/L (3 laboratories); 0.034±0.031 mg/L (3 laboratories); and 0.117±0.065 mg/L (3 laboratories). Only two results were reported for the fourth SRWS: 0.050 and 0.054 mg/L.

IRON

Eight methods were used to determine iron (fig. 36) with the AAS, direct method the obvious method of preference beginning in 1971. The concentrations obtained by the colorimetric, bipyridine method are significantly different from the concentrations obtained by the colorimetric, phenanthroline method. No other significant difference is found in the concentrations reported for the different methods.

Models used in estimating the precision were developed for five methods, with the models for the AAS, direct and colorimetric, phenanthroline methods based on analyses of at least twice as many samples as the other three methods (fig. 37). Interestingly, the standard deviation varied with concentrations only for the AAS, direct method. The precision for the AAS, graphite-furnace method is significantly different from those for the AAS, direct; the colorimetric, bipyridine; the colorimetric, phenanthroline; and the emission, ICP methods. In addition, the precision for AAS, direct method is significantly different from those for the colorimetric, bipyridine and emission, ICP methods. However, no significant difference is found in the precisions for the colorimetric, bipyridine; colorimetric, phenanthroline; and emission, ICP methods, and no significant difference is found between in the precision of the AAS, direct and colorimetric, phenanthroline methods. A less than 5-percent chance exists the intercept of the precision model for the AAS, direct method is equal to zero.

References to the methods are given below:

Method	*Reference*
Atomic absorption spectrometry, direct	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a
Atomic absorption spectrometry, graphite-furnace	U.S. Environmental Protection Agency, 1979a
Atomic emission spectrometry, arc-spark	Barnett and Mallory, 1971
Atomic emission spectrometry, direct-current plasma	American Society for Testing and Materials, 1983
Atomic emission spectrometry, inductively coupled plasma	Fishman and Bradford, 1982 U.S. Environmental Protection Agency, 1979b
Colorimetric, bipyridine	Skougstad and others, 1979
Colorimetric, bipyridine, automated	Skougstad and others, 1979
Colorimetric, phenanthroline	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983

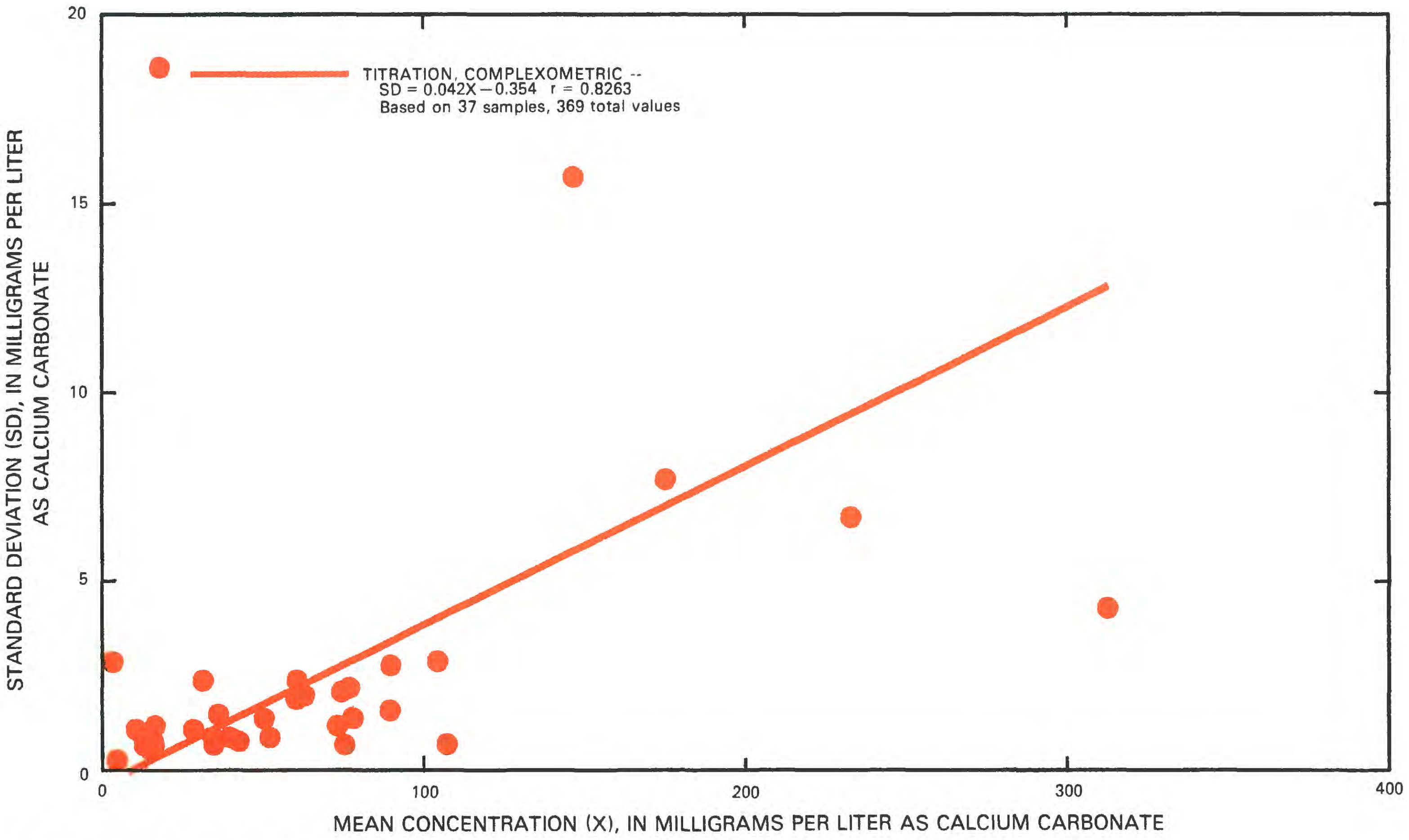

Figure 35. Interlaboratory precision in the determination of hardness.

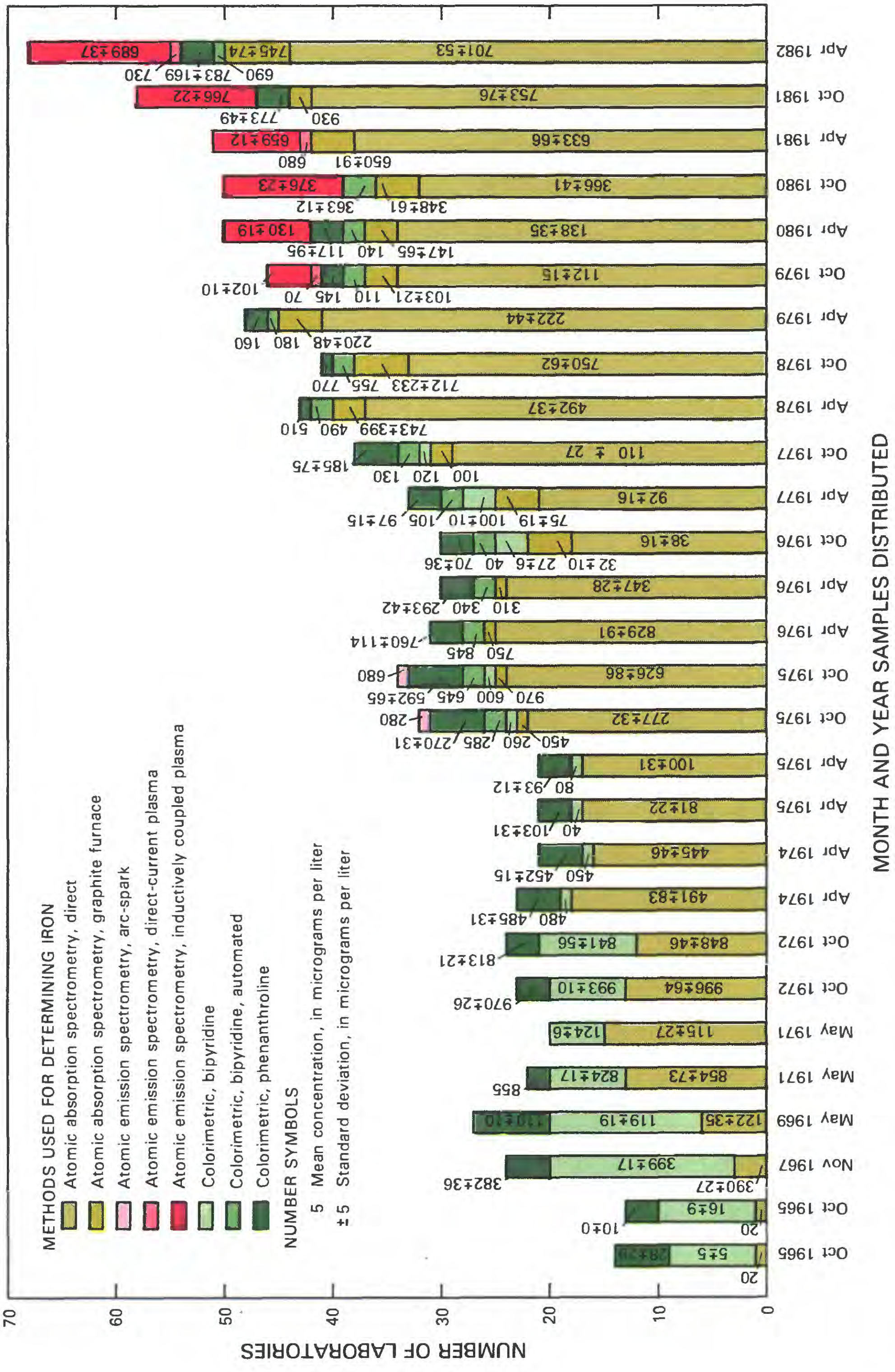

Figure 36. Mean concentrations and standard deviations for iron in 28 Standard Reference Water Samples.

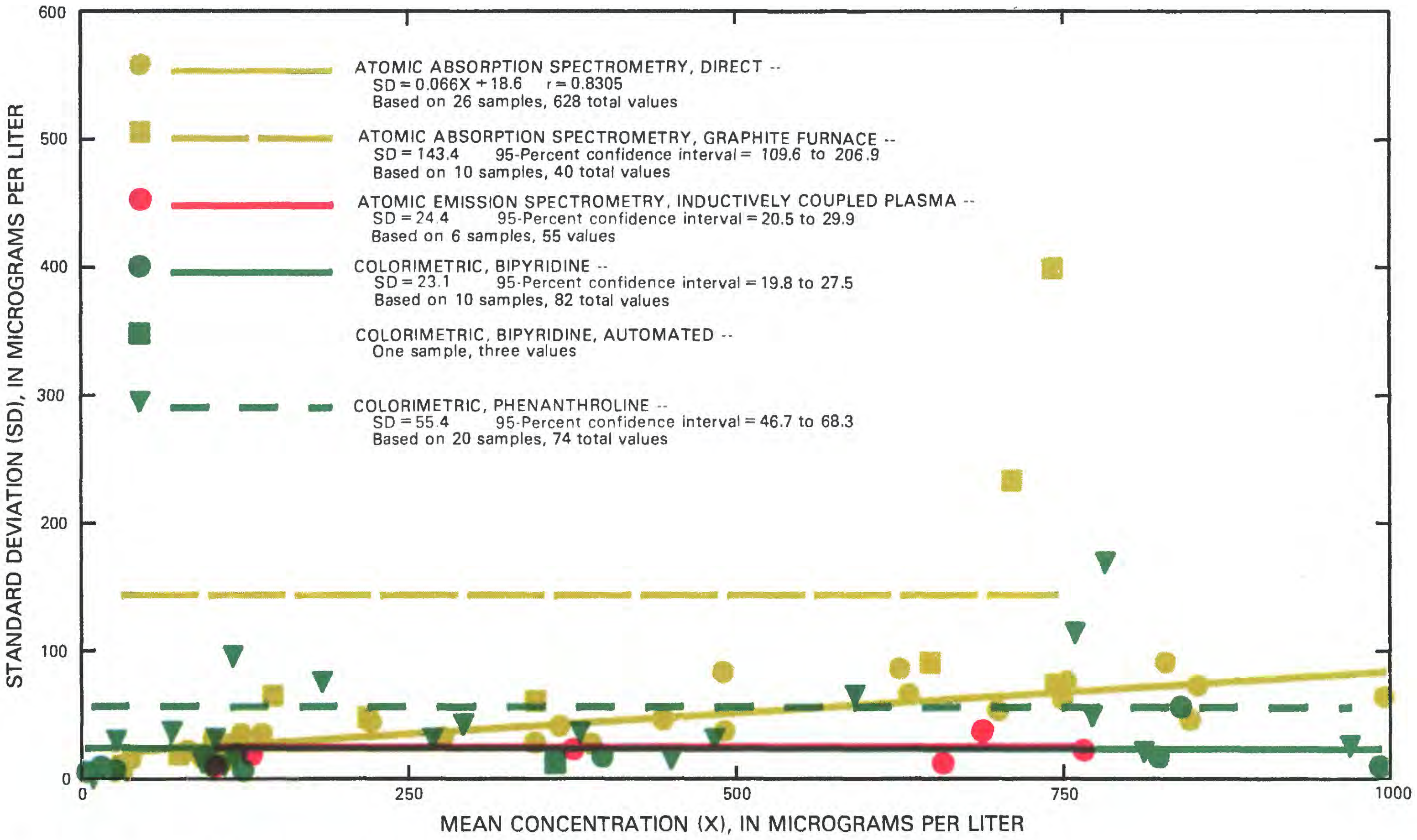

Figure 37. Interlaboratory precision of six methods used to determine iron.

LEAD

Seven methods were used to determine lead (fig. 38). The AAS, APDC-MIBK method was used throughout the period of record but showed a large decrease in use after 1975. On the other hand, the AAS, graphite-furnace method began to be used in 1975 and became the apparent method of choice; more than twice as many laboratories used the AAS, graphite-furnace method in 1982 than all other methods combined.

Significant differences exist in concentrations between the AAS, direct method and those from the AAS, APDC-MIBK; and the AAS, graphite-furnace methods. When data are limited to SRWS distributed in or after October 1979 for the AAS, direct; AAS, APDC-MIBK; AAS, PDCA-CHCL$_3$; and emission, ICP methods, a significant difference exists between the concentrations from the AAS, direct and AAS, graphite-furnace methods, but no other significant differences are found in concentrations for the methods.

The AAS, APDC-MIBK method shows significantly different precision than the precision obtained for the AAS, direct and AAS, graphite-furnace methods, but the precision is not significantly different than those for the AAS, PDCA-CHCL$_3$ or emission, ICP methods or from the single standard deviation reported for the anodic stripping voltammetry method (fig. 39). If only data from SRWS distributed in or after October 1979 are examined, the precision for the AAS, APDC-MIBK method is significantly different from that of the AAS, graphite-furnace method, but is not significantly different from the precisions for the AAS, direct or emission, ICP methods. No statistically significant difference exists in the precisions obtained for the AAS, direct; AAS, graphite-furnace; and emission, ICP methods.

References to the methods are given below:

Method	*Reference*
Atomic absorption spectromtery, chelation-extraction with ammonium pyrrolidine dithiocarbamate and methyl isobutyl ketone	American Public Health Association and others, 1980 Skougstad and others, 1979
Atomic absorption spectrometry, chelation-extraction with pyrrolidine dithiocarbamic acid in chloroform	American Society for Testing and Materials, 1983 U.S. Environmental Protection Agency, 1979a
Atomic absorption spectrometry, direct	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a
Atomic absorption spectrometry, graphite-furnace	U.S. Environmental Protection Agency, 1979a
Atomic emission spectrometry, arc-spark	Barnett and Mallory, 1971
Atomic emission spectrometry, inductively coupled plasma	Fishman and Bradford, 1982 U.S. Environmental Protection Agency, 1979b
Voltammetry, anodic stripping	American Society for Testing and Materials, 1983

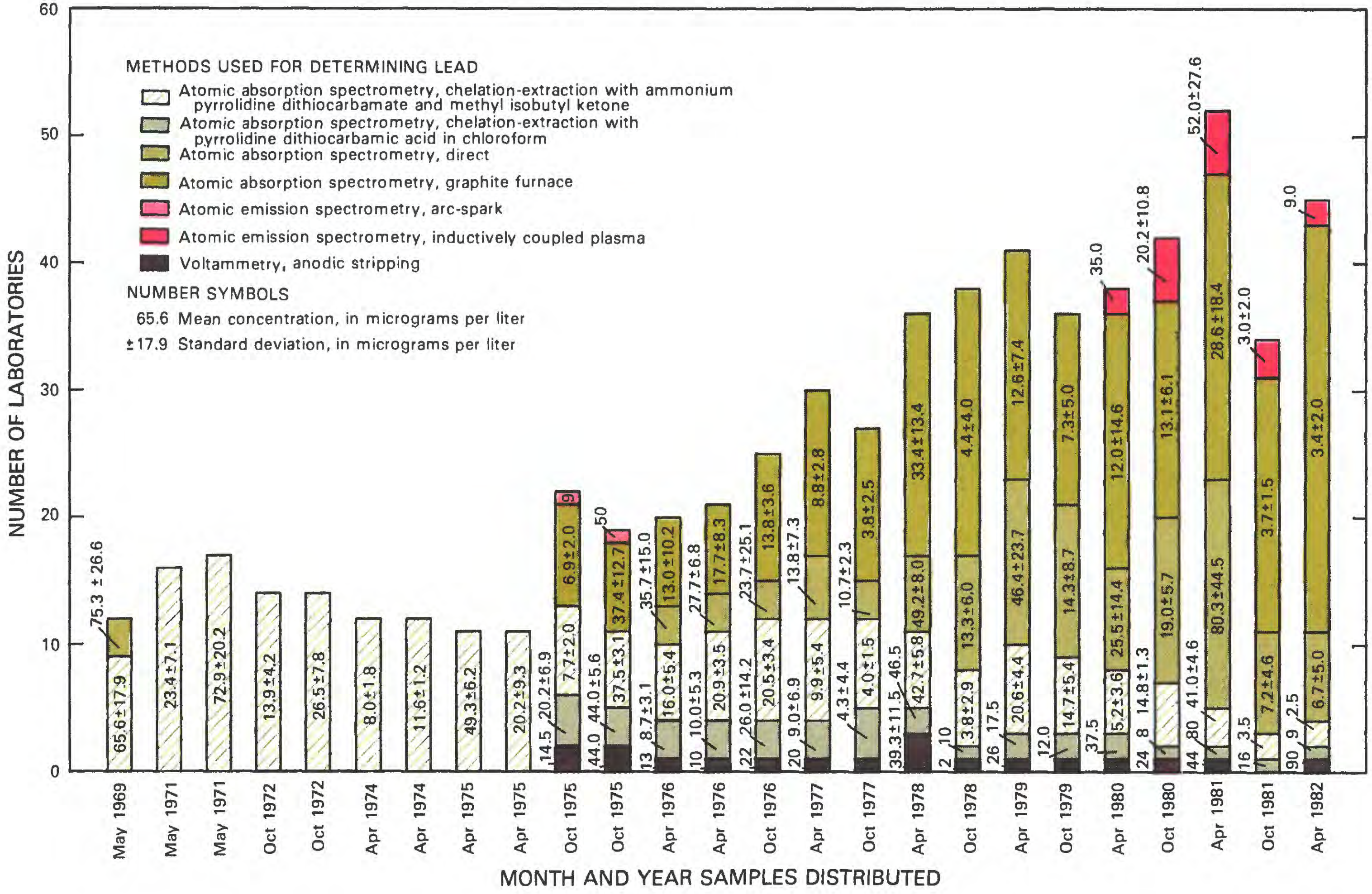

Figure 38. Mean concentrations and standard deviations for lead in 25 Standard Reference Water Samples.

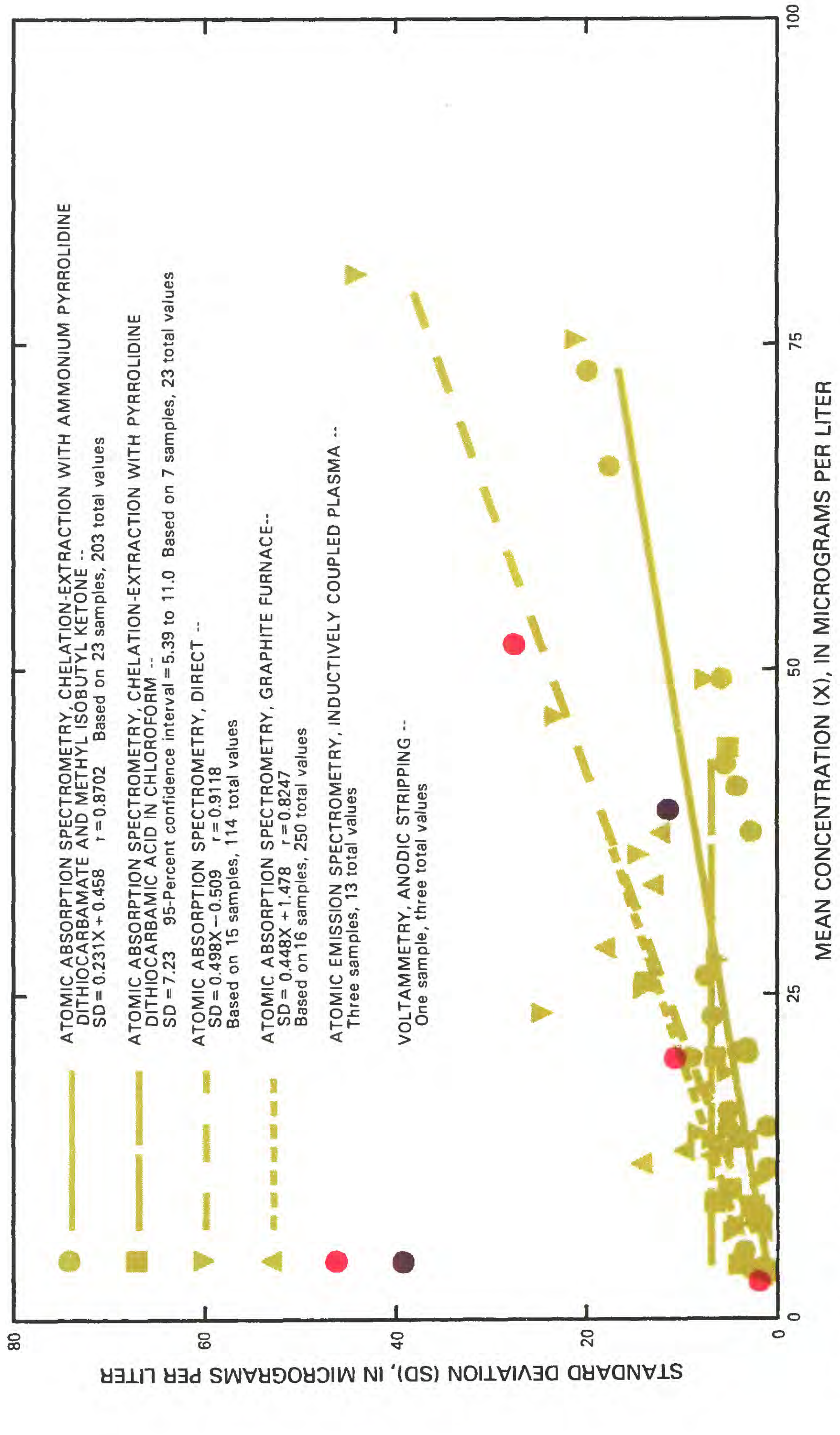

Figure 39. Interlaboratory precision of six methods used to determine lead.

LITHIUM

Five methods were used to determine lithium (fig. 40); however, only one result was reported for the emission arc-spark method and cannot really be used in any valid methods comparison. The majority of the data are from the AAS, direct method, although by 1982 more laboratories used either the emission, flame or emission, ICP methods than the AAS, direct or AAS, graphite-furnace methods. In any case, no significant difference is found in the concentrations reported for the different methods.

The precision for the emission, flame method shows a significant difference from the precision for the AAS, direct method but not from the precision for the emission, ICP method (fig. 41). However, if the standard deviations are compared only for the six SRWS distributed in or after October 1979 (the SRWS for which emission, ICP values were first reported), no significant difference exists in the precisions for the three models. It should be noted that confining the data to those six SRWS, changes the model for the AAS, direct procedure considerably to $SD=0.125x-0.561$ (compared to a model of $SD=0.080x+1.13$ if data are examined from all 19 SRWS for which lithium data are available).

References to the methods are given below:

Method	*Reference*
Atomic absorption spectrometry, direct	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979
Atomic absorption spectrometry, graphite-furnace	—
Atomic emission spectrometry, arc-spark	Barnett and Mallory, 1971
Atomic emission spectrometry, flame	American Public Health Association and others, 1980 Rainwater and Thatcher, 1960
Atomic emission spectrometry, inductively coupled plasma	Fishman and Bradford, 1982

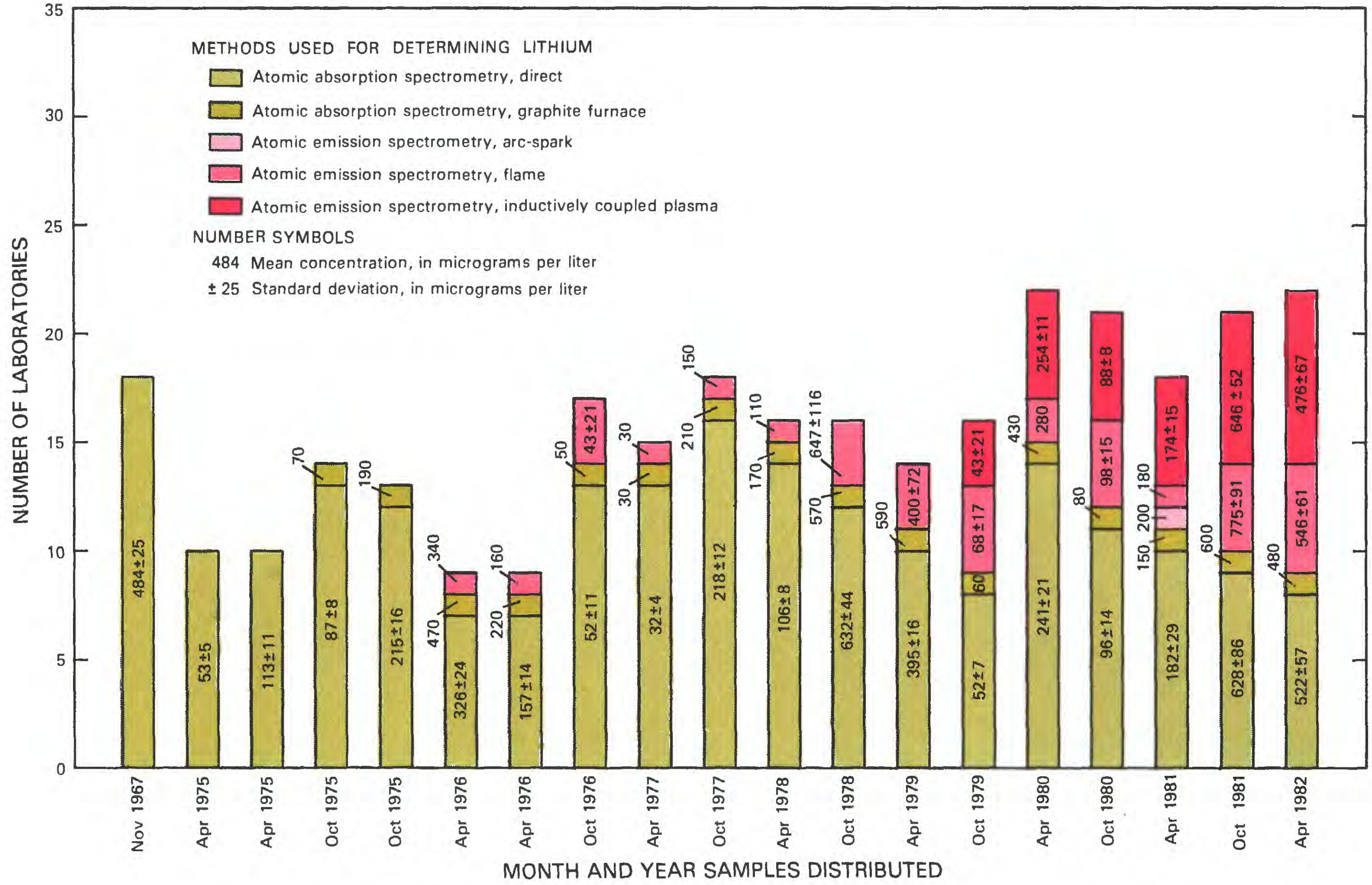

Figure 40. Mean concentrations and standard deviations for lithium in 19 Standard Reference Water Samples.

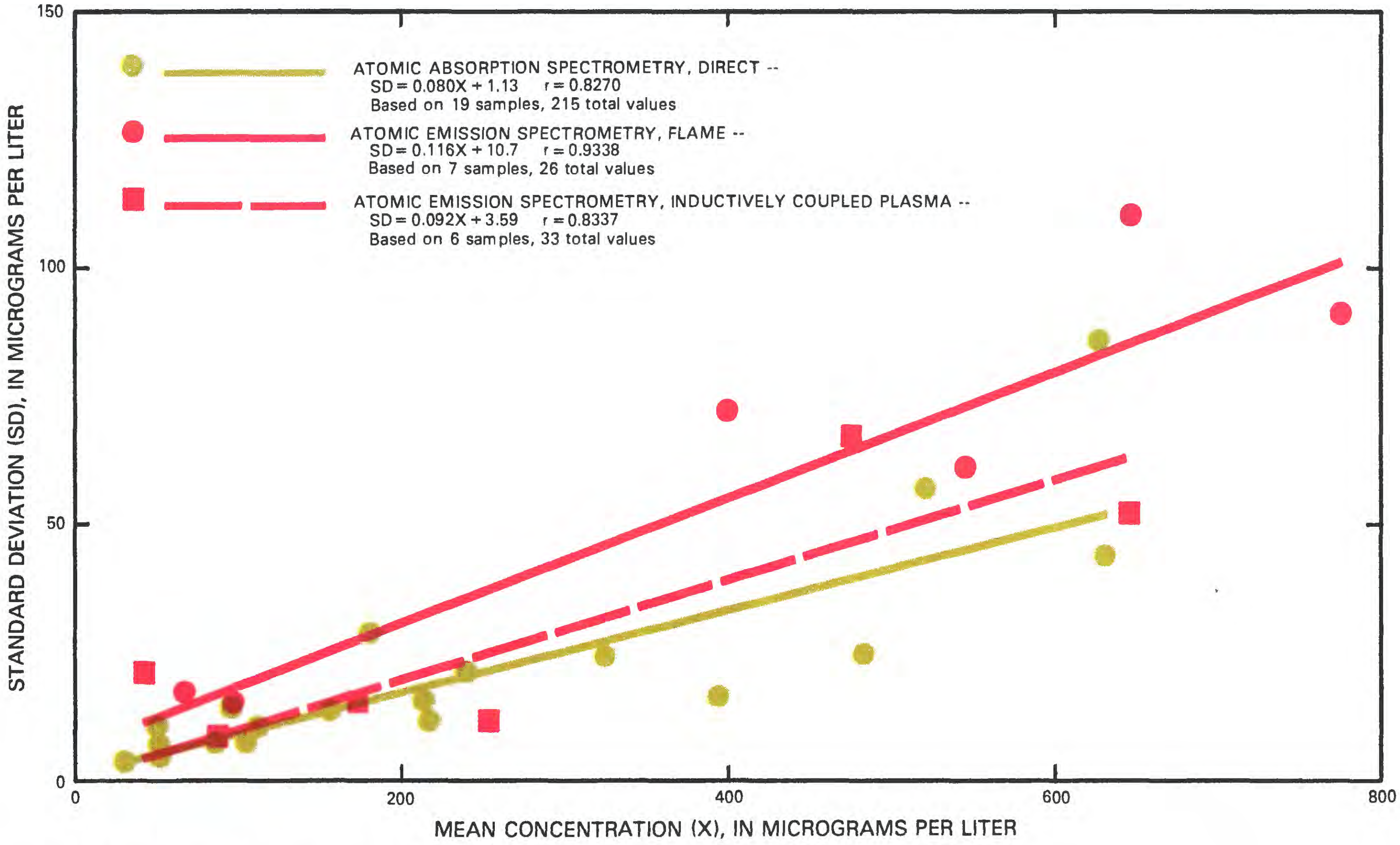

Figure 41. Interlaboratory precision of three methods used to determine lithium.

MAGNESIUM

Five methods were used to determine magnesium during the period of record. However, the majority of data were obtained from the AAS, direct and titration, calculation, hardness minus calcium methods (fig. 42).

No statistically significant difference is found in the concentrations reported by the different methods. However, the precision obtained by the titration, calculation method is significantly different than those obtained by the AAS, direct or the emission, ICP methods (fig. 43). Because the results obtained for magnesium by titration, calculation depend on the results obtained for calcium in addition to the results obtained in the titration for hardness, it is not surprising that results were more variable and that the precision appeared worse for the titration, calculation method than for the other two methods.

References to the methods are given below:

Method	*Reference*
Atomic absorption spectrometry, direct	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a
Atomic emission spectrometry, direct-current plasma	—
Atomic emission spectrometry, flame	—
Atomic emission spectrometry, inductively coupled plasma	Fishman and Bradford, 1982
Titration, calculation, hardness minus calcium	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Brown and others, 1970

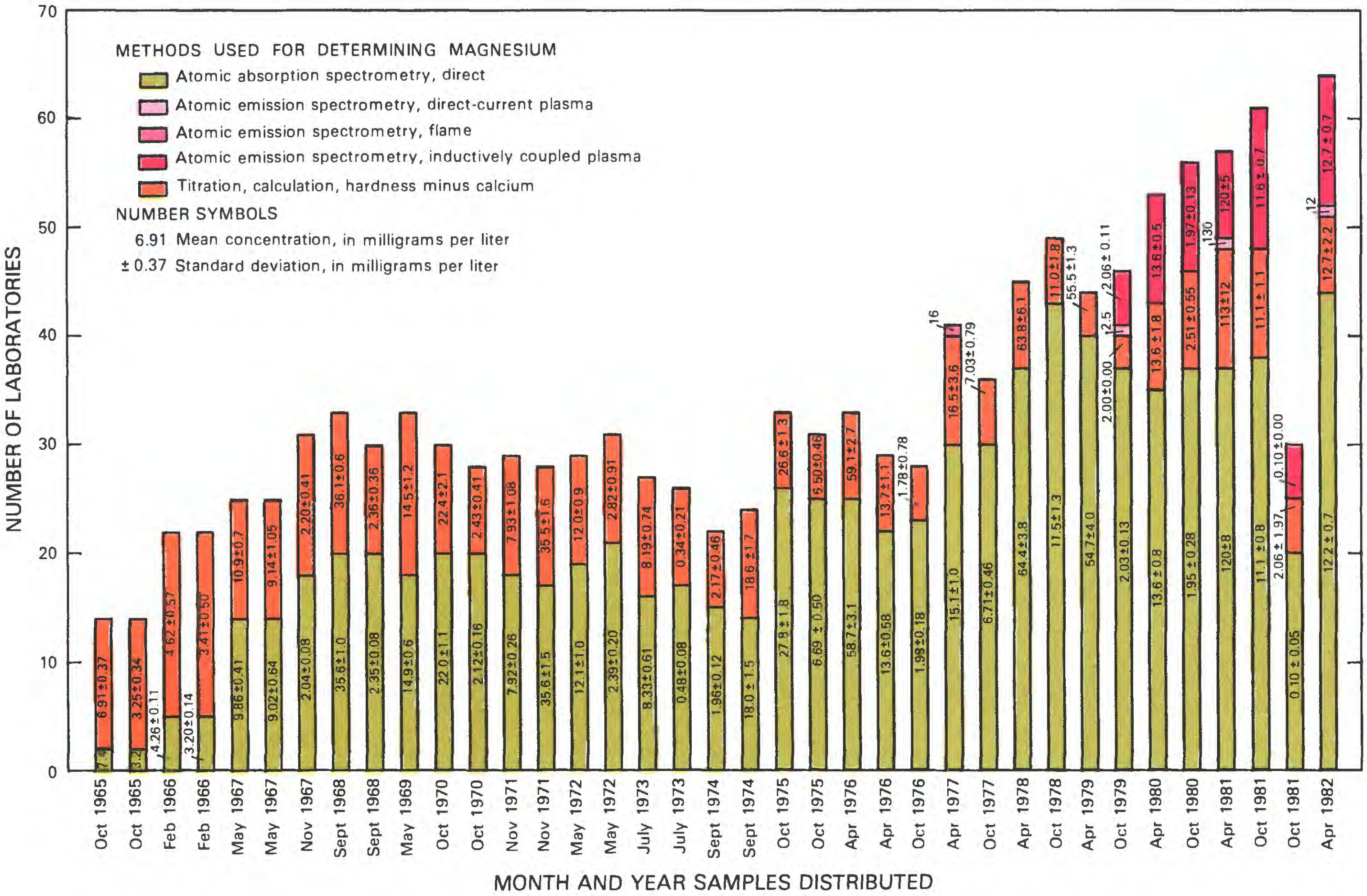

Figure 42. Mean concentrations and standard deviations for magnesium in 37 Standard Reference Water Samples.

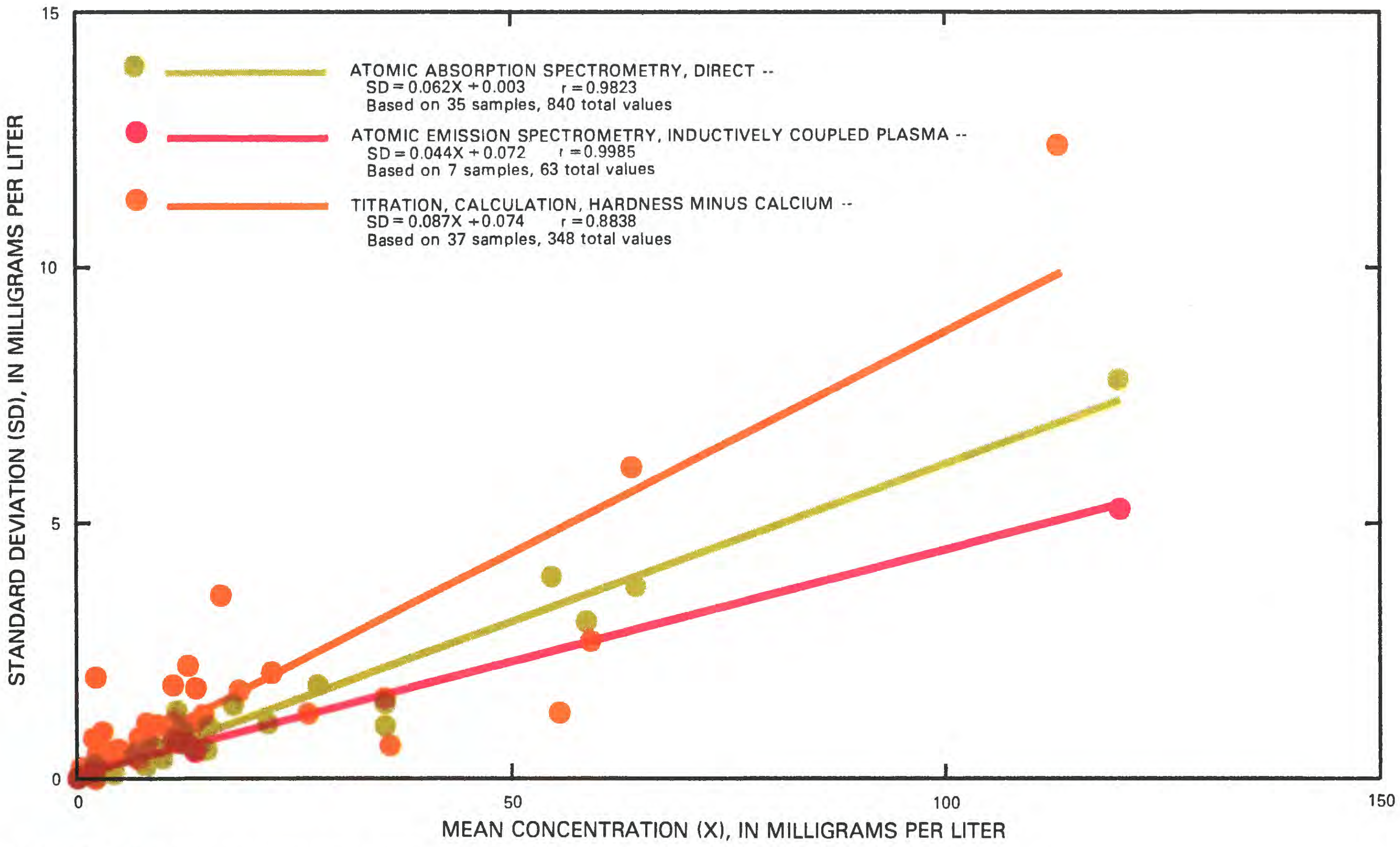

Figure 43. Interlaboratory precision of three methods used to determine magnesium.

MANGANESE

Ten methods were used to determine manganese (fig. 44). However, most of the data are for the AAS, direct method, with data from the AAS, graphite-furnace and emission, ICP methods more abundant in recent years.

No significant difference is found among the concentrations reported for the different methods. Even when examining more limited data sets such as those from the AAS, direct and AAS, graphite-furnace methods for SRWS distributed in or after October 1975, or those from the AAS, direct; AAS, graphite-furnace; and emission, ICP methods for SRWS distributed in or after October 1979, no significant difference exists among concentrations reported for the methods.

Although the concentrations do not show a significant difference, the AAS, direct; AAS, graphite-furnace; and emission, ICP methods do have significantly different precisions. In general, larger standard deviations are associated with the AAS, graphite-furnace method than with the other two methods (fig. 45). A less than 5-percent chance exists that the intercept of the precision model for the AAS, direct method is equal to zero.

The four standard deviation values from the colorimetric, tetrabase method do show a significant difference in precision compared to those for the emission, ICP method, but do not differ significantly from precisions of either the AAS, direct or AAS, graphite-furnace methods. However, four values are really too few to place much confidence in this data analysis.

References to the methods are given below:

Method	*Reference*
Atomic absorption spectrometry, chelation-extraction with ammonium pyrrolidine dithiocarbamate and methyl isobutyl ketone	American Public Health Association and others, 1980 Skougstad and others, 1979
Atomic absorption spectrometry, direct	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a
Atomic absorption spectrometry, graphite-furnace	U.S. Environmental Protection Agency, 1979a
Atomic emission spectrometry, arc-spark	Barnett and Mallory, 1971
Atomic emission spectrometry, direct-current plasma	American Society for Testing and Materials, 1983
Atomic emission spectrometry, inductively coupled plasma	Fishman and Bradford, 1982 U.S. Environmental Protection Agency, 1979b
Colorimetric, periodate	American Public Health Association and others, 1975 Rainwater and Thatcher, 1960
Colorimetric, persulfate	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983
Colorimetric, tetrabase	—
Neutron activation	—

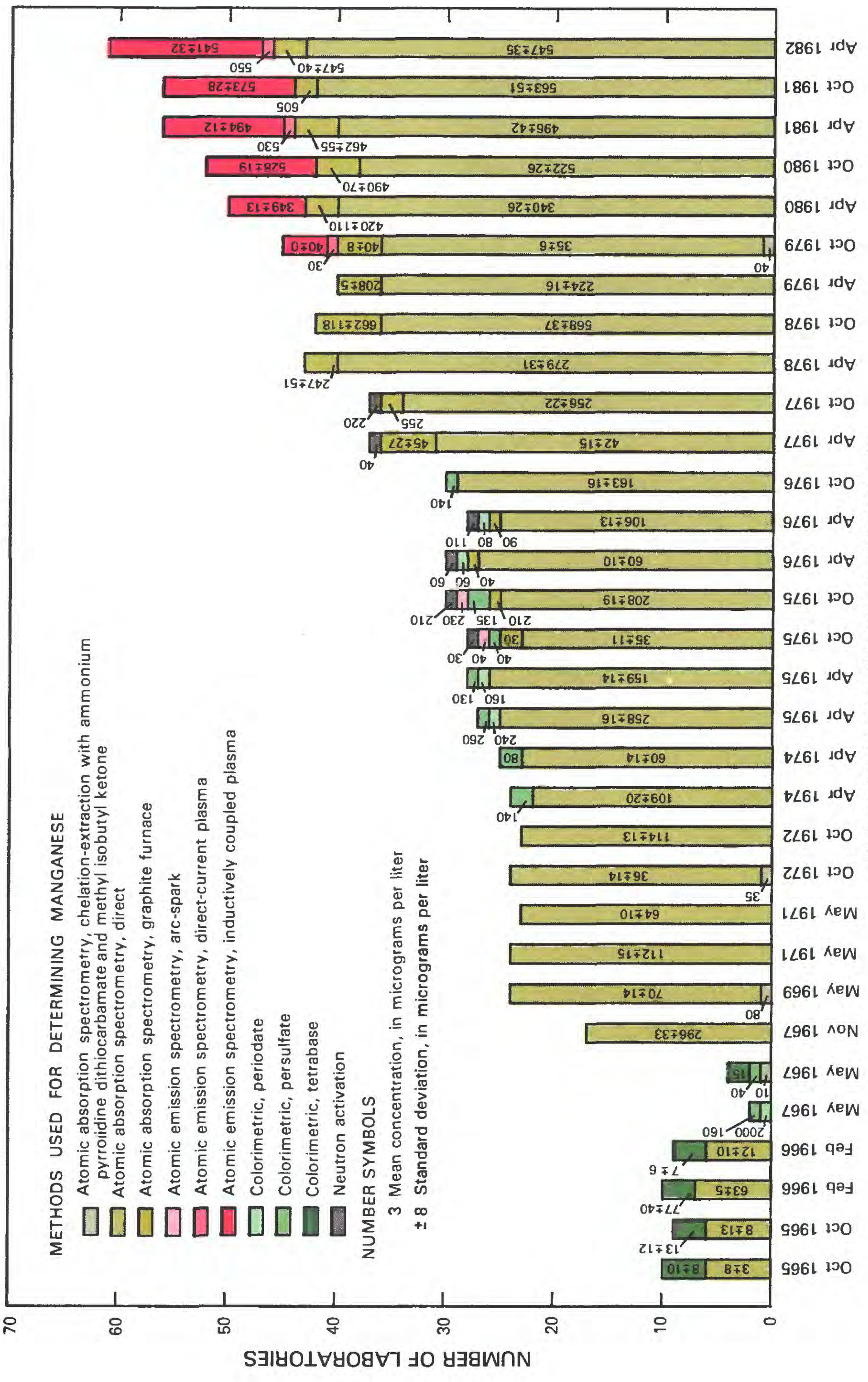

Figure 44. Mean concentrations and standard deviations for manganese in 32 Standard Reference Water Samples.

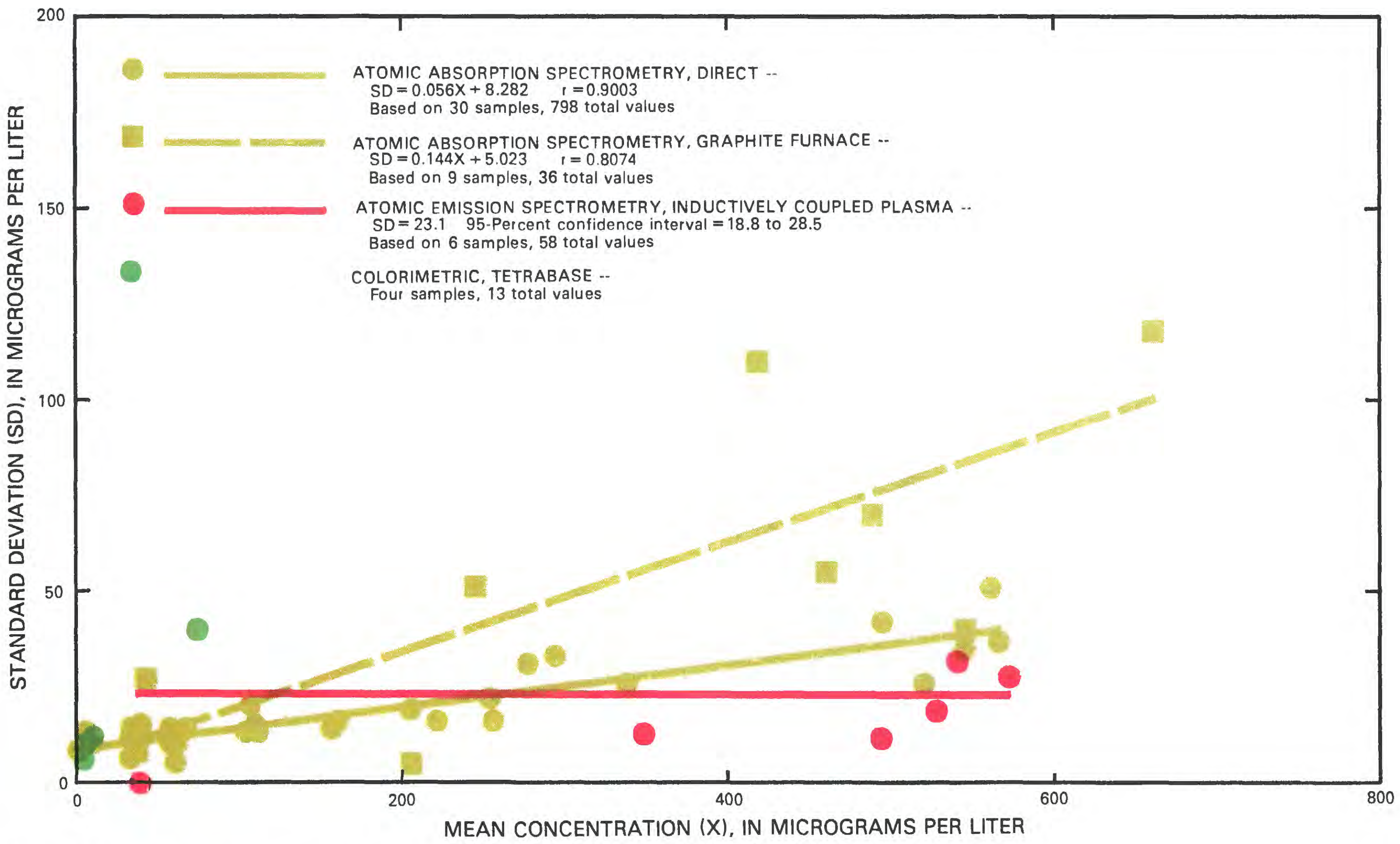

Figure 45. Interlaboratory precision of four methods used to determine manganese.

MERCURY

Automated and manual AAS, flameless procedures were used to determine mercury (figs. 46 and 47). However, it should be noted that there are many more data available for the manual procedure than for the automated procedure.

No significant differences exist between the two methods, either for precisions or for concentrations. A less than 5-percent chance exists that the intercept of the precision model for the manual procedure is zero.

References to the methods are given below:

Method	*Reference*
Atomic absorption spectrometry, flameless	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a
Atomic absorption spectrometry, flameless, automated	Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a

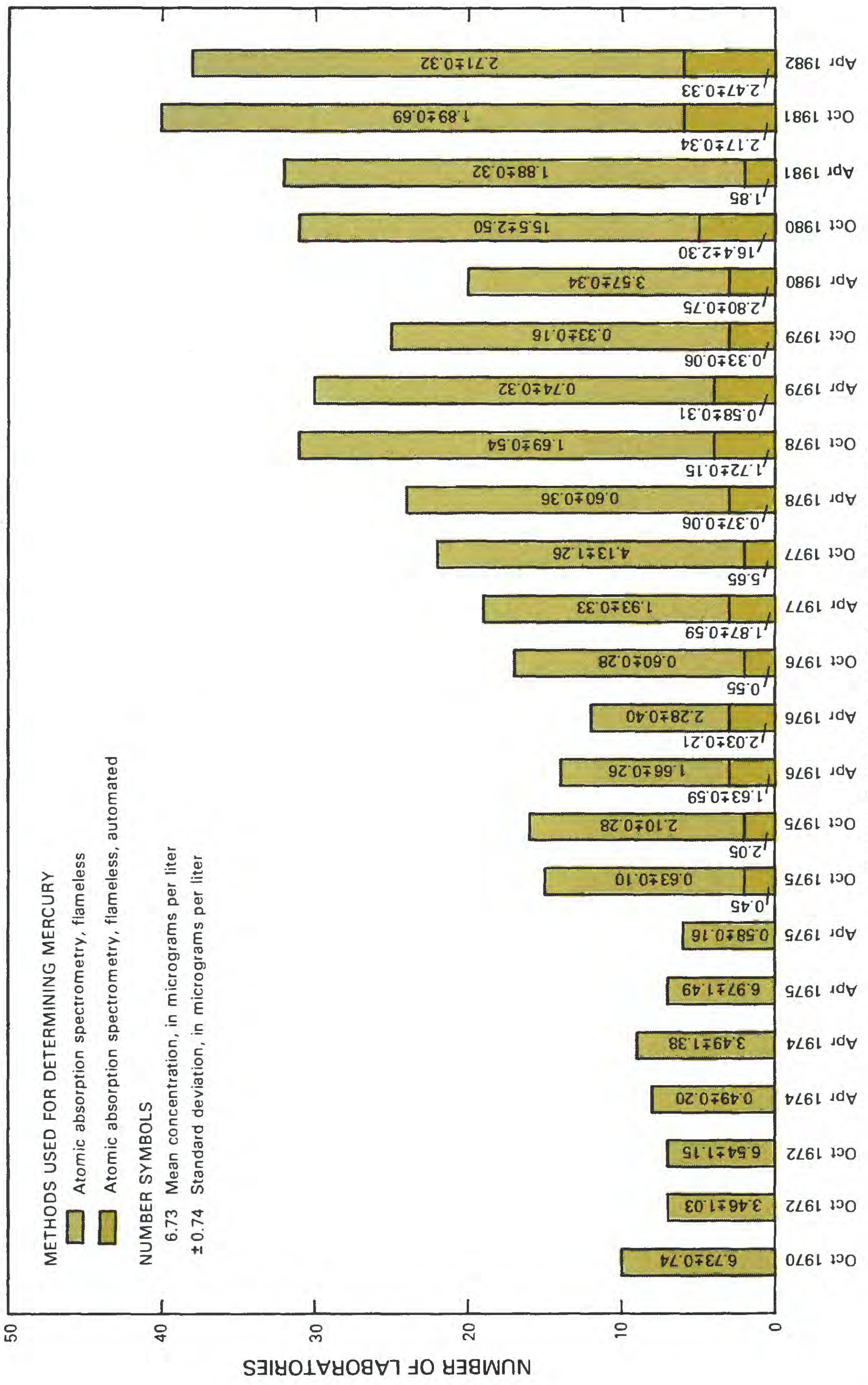

Figure 46. Mean concentrations and standard deviations for mercury in 23 Standard Reference Water Samples.

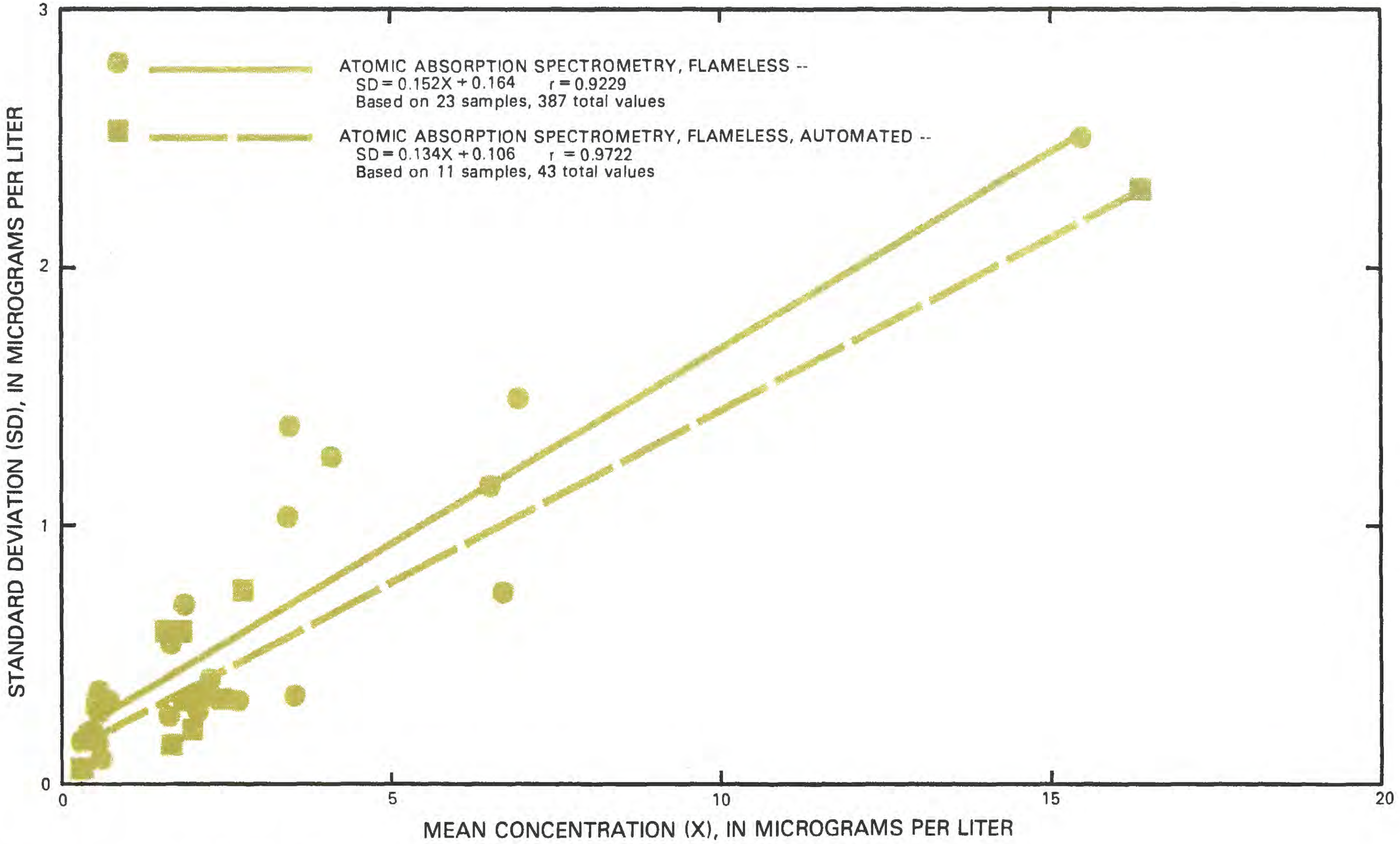

Figure 47. Interlaboratory precision of two methods used to determine mercury.

MOLYBDENUM

Six methods were being used to determine molybdenum, although very few data are available for the emission, arc-spark and neutron activation methods (fig. 48). No significant difference between concentrations are reported for methods, whether all data are considered together or whether data are limited to what may be a more meaningful (for comparing methods) set of data from SRWS distributed in or after October 1979.

Because relatively few concentrations are associated with the *n*'s greater than 2, there were relatively few data to use in developing the analytical precision models and it is likely that the models will change when additional data become available. Meanwhile, although the models developed appear quite different (fig. 49), no significant difference exists among precisions of the different methods. A less than a 5-percent chance exists that the intercept of the precision model for the AAS, 8-hydroxyquinoline-MIBK method is equal to zero.

References to the methods are given below:

Method	*Reference*
Atomic absorption spectrometry, chelation-extraction with 8-hydroxyquinoline and methyl isobutyl ketone	American Society for Testing and Materials, 1983 Skougstad and others, 1979
Atomic absorption spectrometry, direct	American Pubic Health Association and others, 1980 American Society for Testing and Materials, 1983 U.S. Environmental Protection Agency, 1979a
Atomic absorption spectrometry, graphite-furnace	U.S. Environmental Protection Agency, 1979a
Atomic emission spectrometry, arc-spark	Barnett and Mallory, 1971
Atomic emission spectrometry, inductively coupled plasma	Fishman and Bradford, 1982
Neutron activation	—

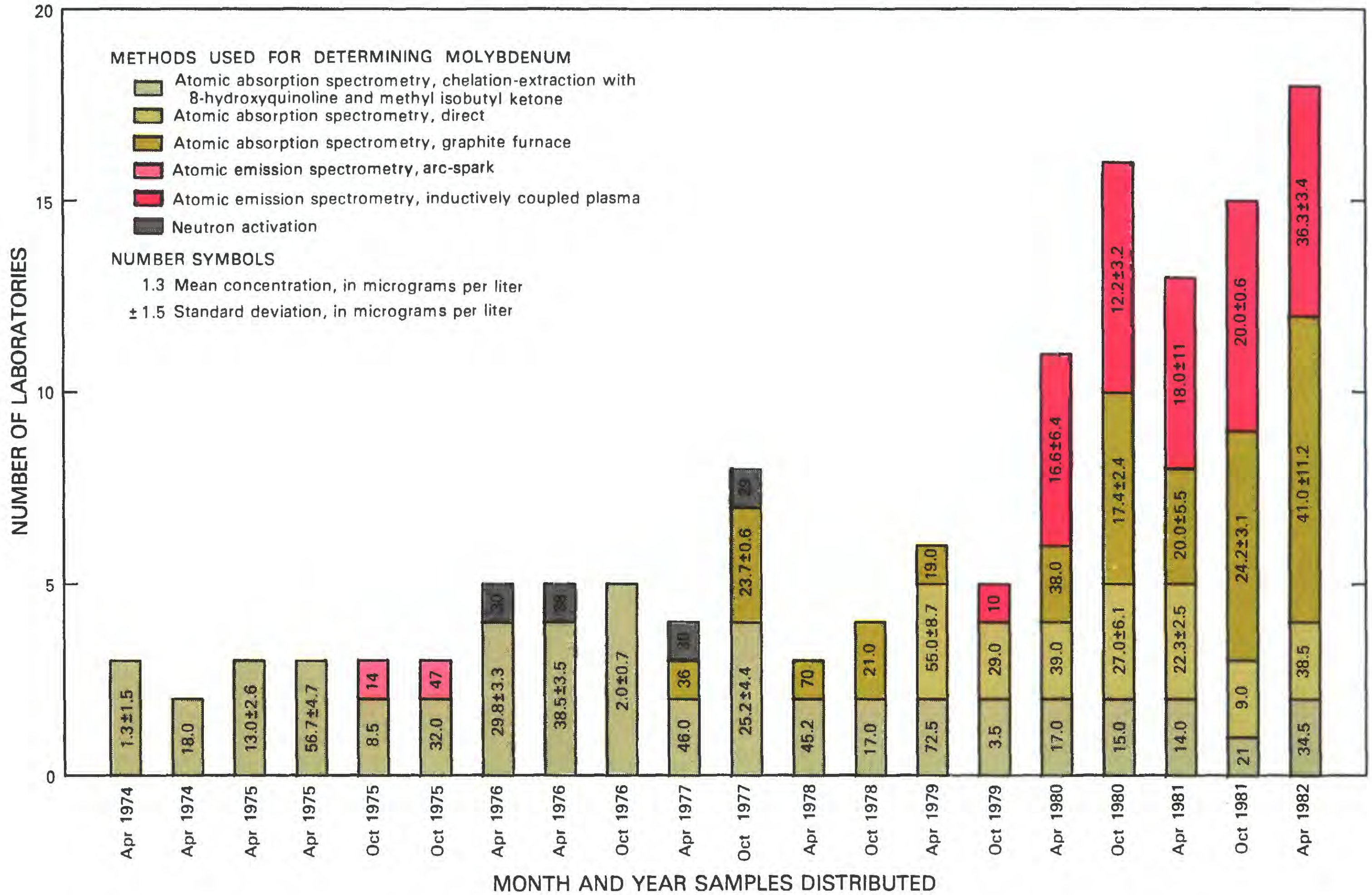

Figure 48. Mean concentrations and standard deviations for molybdenum in 20 Standard Reference Water Samples.

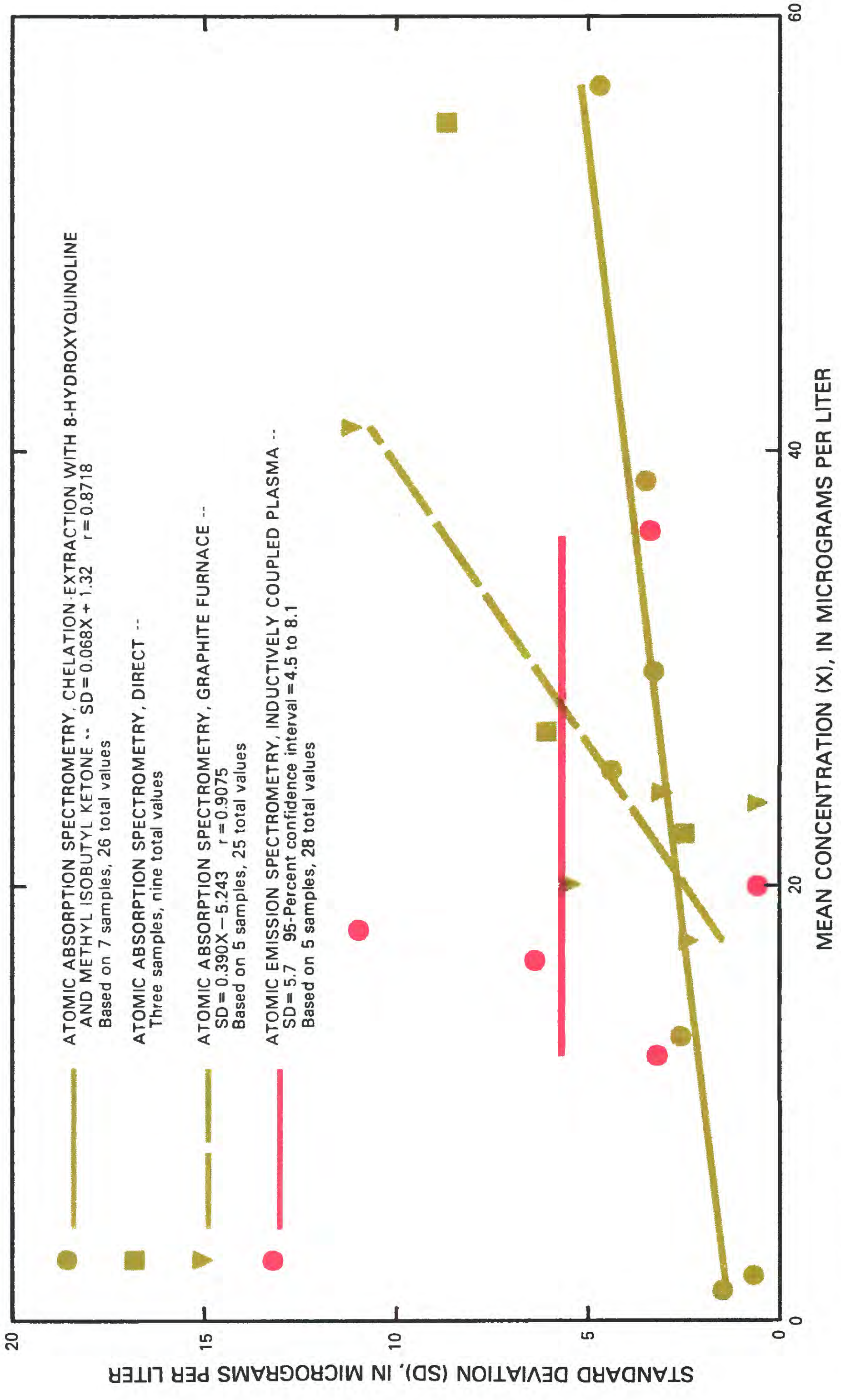

Figure 49. Interlaboratory precision of four methods used to determine molybdenum.

NICKEL

Seven methods were used to determine nickel (fig. 50), with most of the data being obtained from the AAS, APDC-MIBK; AAS, direct; and AAS, graphite-furnace methods. Examining data from all SRWS or data from SRWS distributed in or after October 1975 (when more than just the AAS, direct method were reported) indicates that no significant differences exist in concentrations determined by the different methods. However, a significant difference is found between concentrations reported for the AAS, direct and AAS, graphite-furnace methods when data are limited to SRWS distributed in or after October 1979 (when data for the emission, ICP method are first recorded).

Like the concentration comparisons, a comparison of the standard deviations for the methods indicates that the precision of the AAS, direct method is significantly different from those for the AAS, APDC-MIBK and AAS, graphite-furnace methods (fig. 51). Although standard deviations were computed for only four SRWS for the emission, ICP method, these limited data indicate that the precision of the AAS, direct method is not significantly different from that for the emission, ICP method. In addition, no significant difference exists in the precisions of the AAS, APDC-MIBK; AAS, graphite-furnace; and emission, ICP methods.

References to the methods are given below:

Method	*Reference*
Atomic absorption spectrometry, chelation-extraction with ammonium pyrrolidine dithiocarbamate and methyl isobutyl ketone	American Public Health Association and others, 1980 Skougstad and others, 1979
Atomic absorption spectrometry, chelation-extraction with pyrrolidine dithiocarbamic acid in chloroform	American Society for Testing and Materials, 1983 U.S. Environmental Protection Agency, 1979a
Atomic absorption spectrometry, direct	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a
Atomic absorption spectrometry, graphite-furnace	U.S. Environmental Protection Agency, 1979a
Atomic emission spectrometry, arc-spark	Barnett and Mallory, 1971
Atomic emission spectrometry, direct-current plasma	American Society for Testing and Materials, 1983
Atomic emission spectrometry, inductively coupled plasma	U.S. Environmental Protection Agency, 1979b

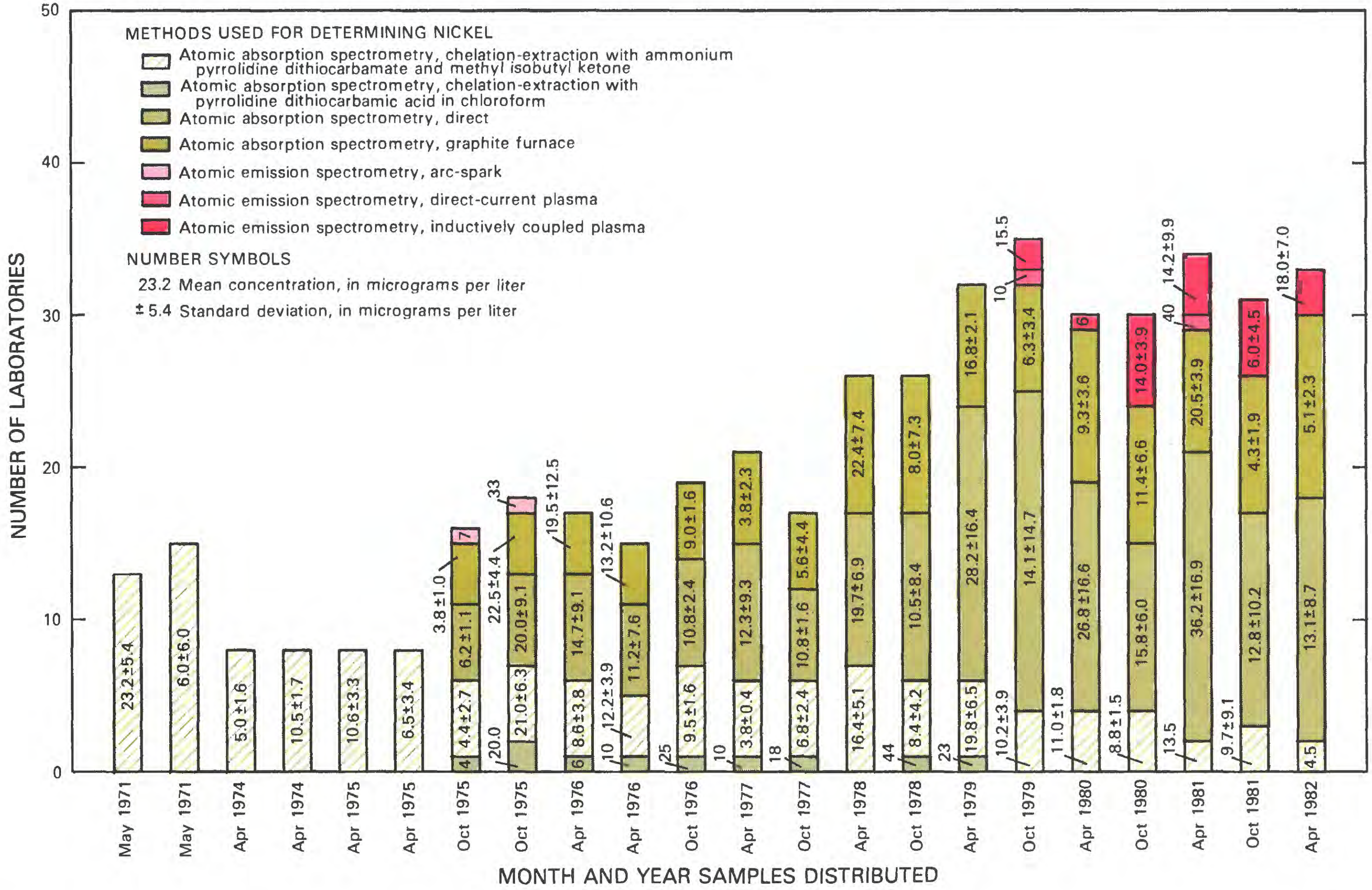

Figure 50. Mean concentrations and standard deviations for nickel in 22 Standard Reference Water Samples.

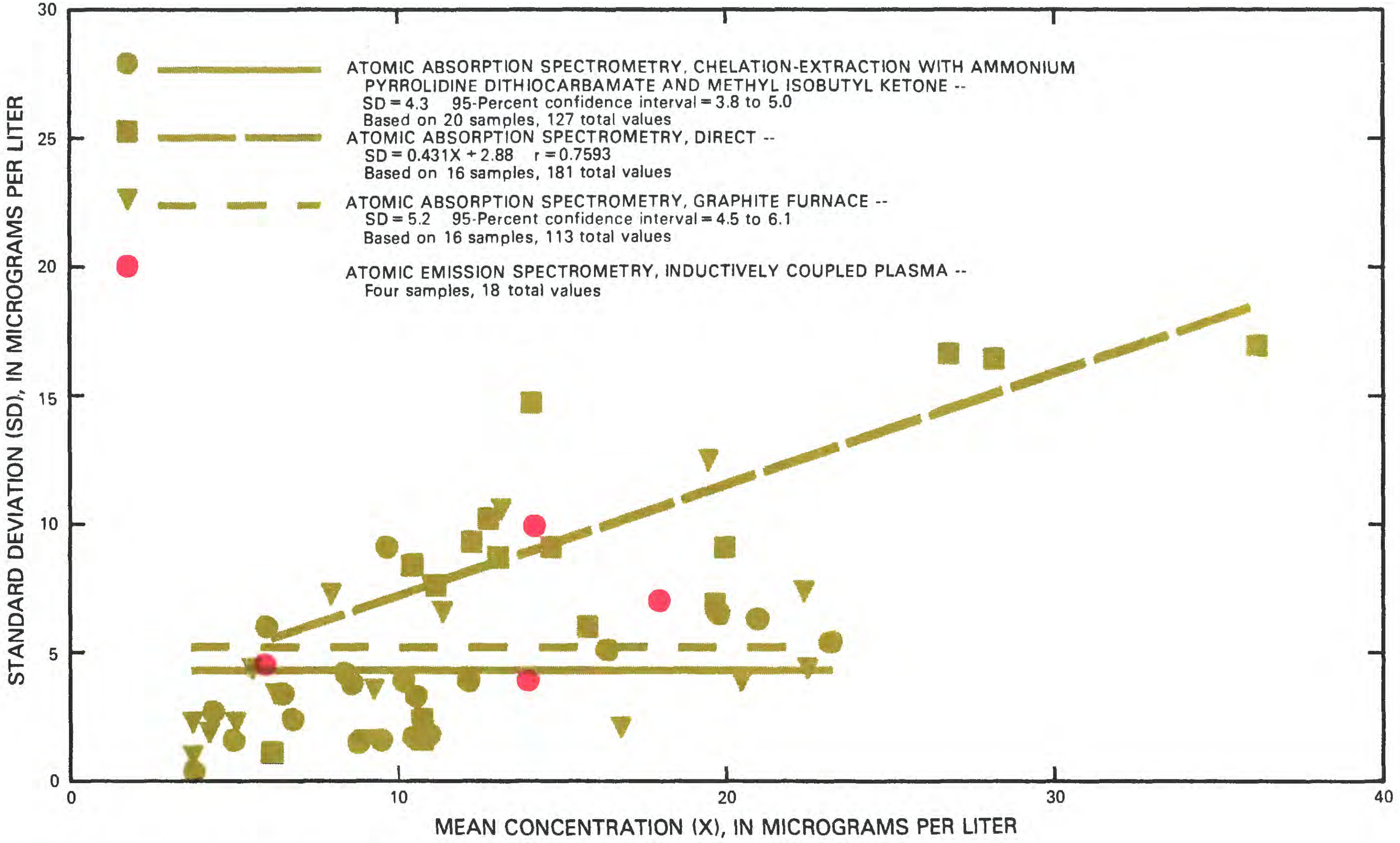

Figure 51. Interlaboratory precision of four methods used to determine nickel.

NITRATE NITROGEN

Six methods were used to determine nitrate nitrogen (fig. 52). Although the colorimetric, phenoldisulfonic acid method was preferred in the first few years of the study, the colorimetric, cadmium reduction, automated method appears to have been the preferred method in later years of the study. It is assumed that the cadmium and hydrazine methods actually were used to determine "nitrite plus nitrate nitrogen" and that nitrate was reported after the nitrite value was subtracted; therefore, also see the summary under nitrite plus nitrate nitrogen.

Concentrations produced by the colorimetric, cadmium reduction method are significantly different from those for the colorimetric, brucine and colorimetric, cadmium reduction, automated methods. No other significant difference is found in concentrations reported for the different methods.

The precisions for the colorimetric, brucine method and for the colorimetric, phenoldisulfonic acid method are not significantly different from those for the colorimetric, cadmium reduction, automated and colorimetric, hydrazine reduction, automated methods, even though the models appear to be quite different (fig. 53). A significant difference exists between the precision for the colorimetric, cadmium reduction method and the precisions for all other methods; however, note that the concentration range for the colorimetric, cadmium reduction method is very limited.

References to the methods are given below:

Method	*Reference*
Colorimetric, brucine	American Public Health Association and others, 1975 American Society for Testing and Materials, 1983 Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a
Colorimetric, cadmium reduction	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 U.S. Environmental Protection Agency, 1979a
Colorimetric, cadmium reduction, automated	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a
Colorimetric, hydrazine reduction, automated	U.S. Environmental Protection Agency, 1979a
Colorimetric, phenoldisulfonic acid	American Public Health Association and others, 1971 Rainwater and Thatcher, 1960
Titration, reduction to ammonium ion	American Public Health Association and others, 1980 Rainwater and Thatcher, 1960

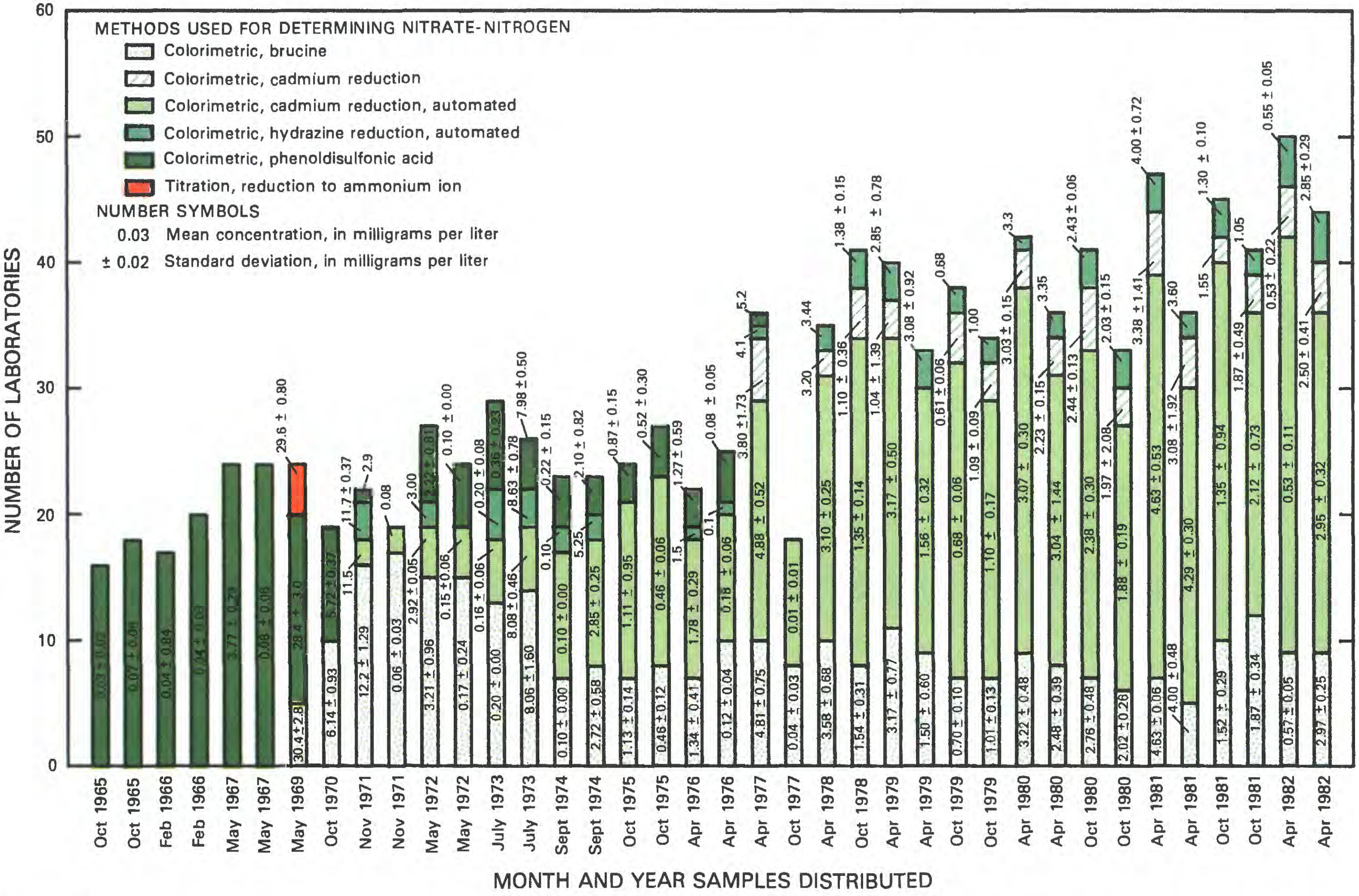

Figure 52. Mean concentrations and standard deviations for nitrate nitrogen in 38 Standard Reference Water Samples.

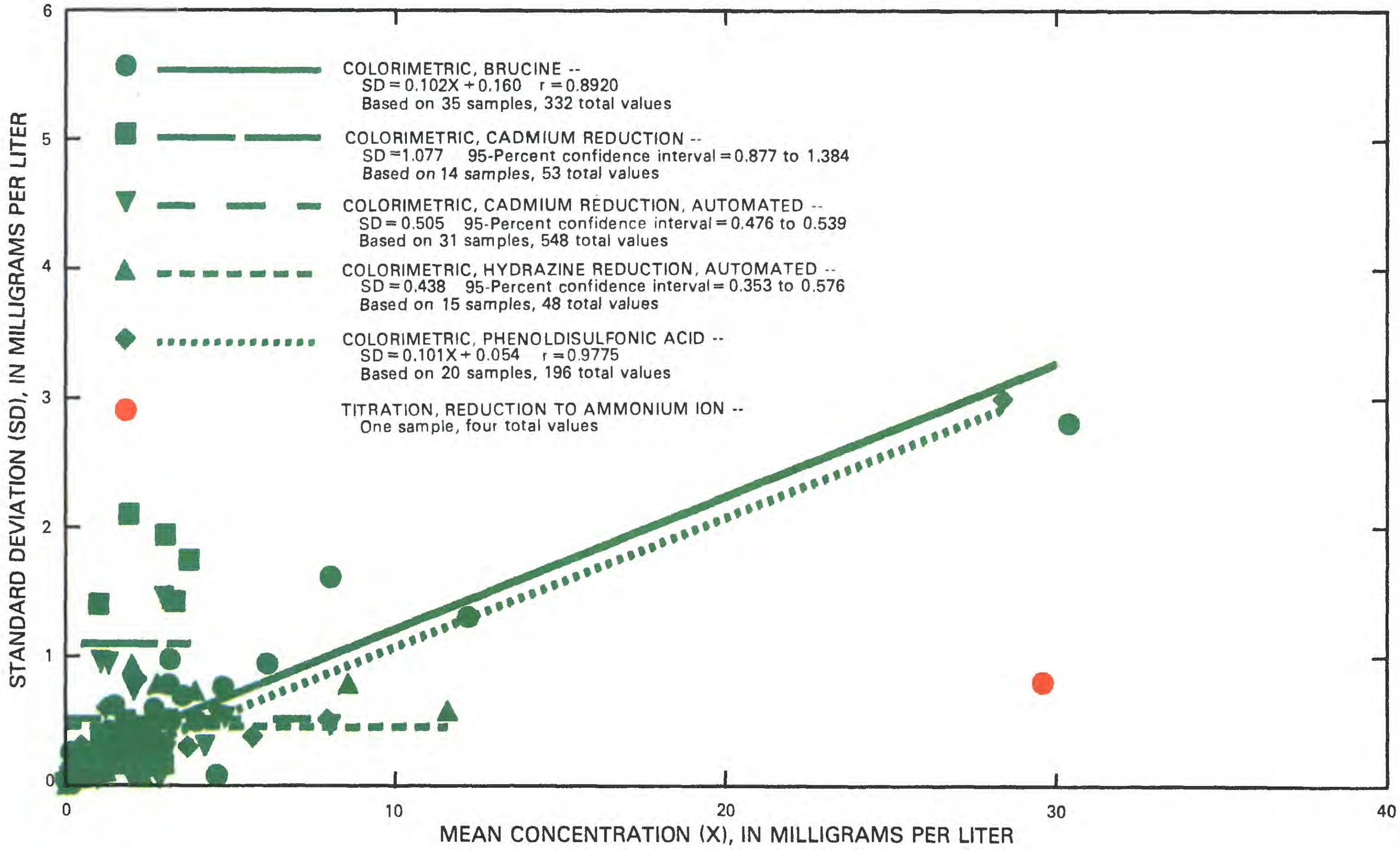

Figure 53. Interlaboratory precision of six methods used to determine nitrate nitrogen.

NITRITE NITROGEN

Two methods were used to determine nitrite nitrogen (fig. 54). No significant difference exists between the two methods, either in reported concentrations or analytical precision (fig. 55).

References to the methods are given below:

Method	*Reference*
Colorimetric, diazotization	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a
Colorimetric, diazotization, automated	American Society for Testing and Materials, 1983 Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a

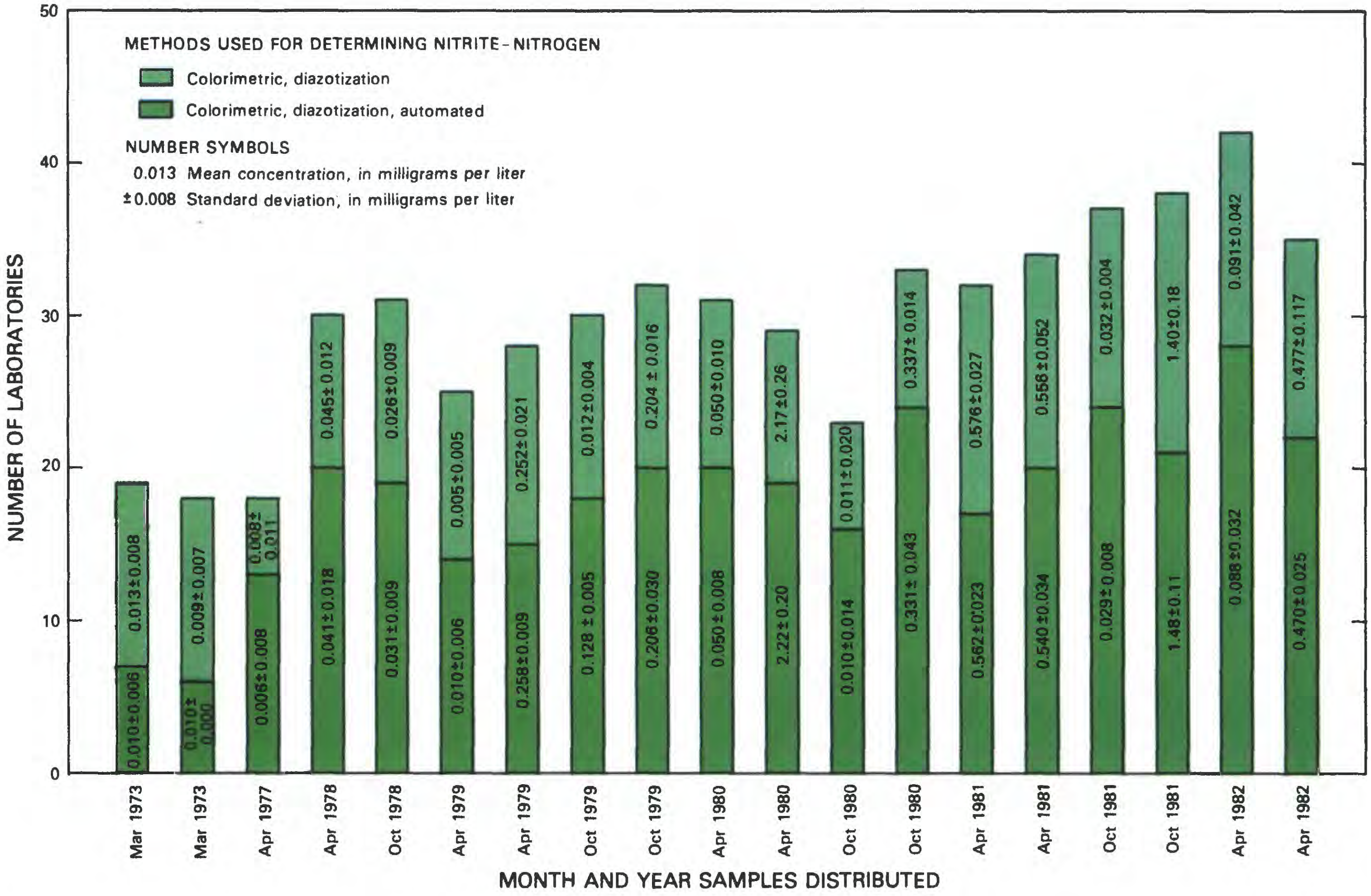

Figure 54. Mean concentrations and standard deviations for nitrite nitrogen in 19 Standard Reference Water Samples.

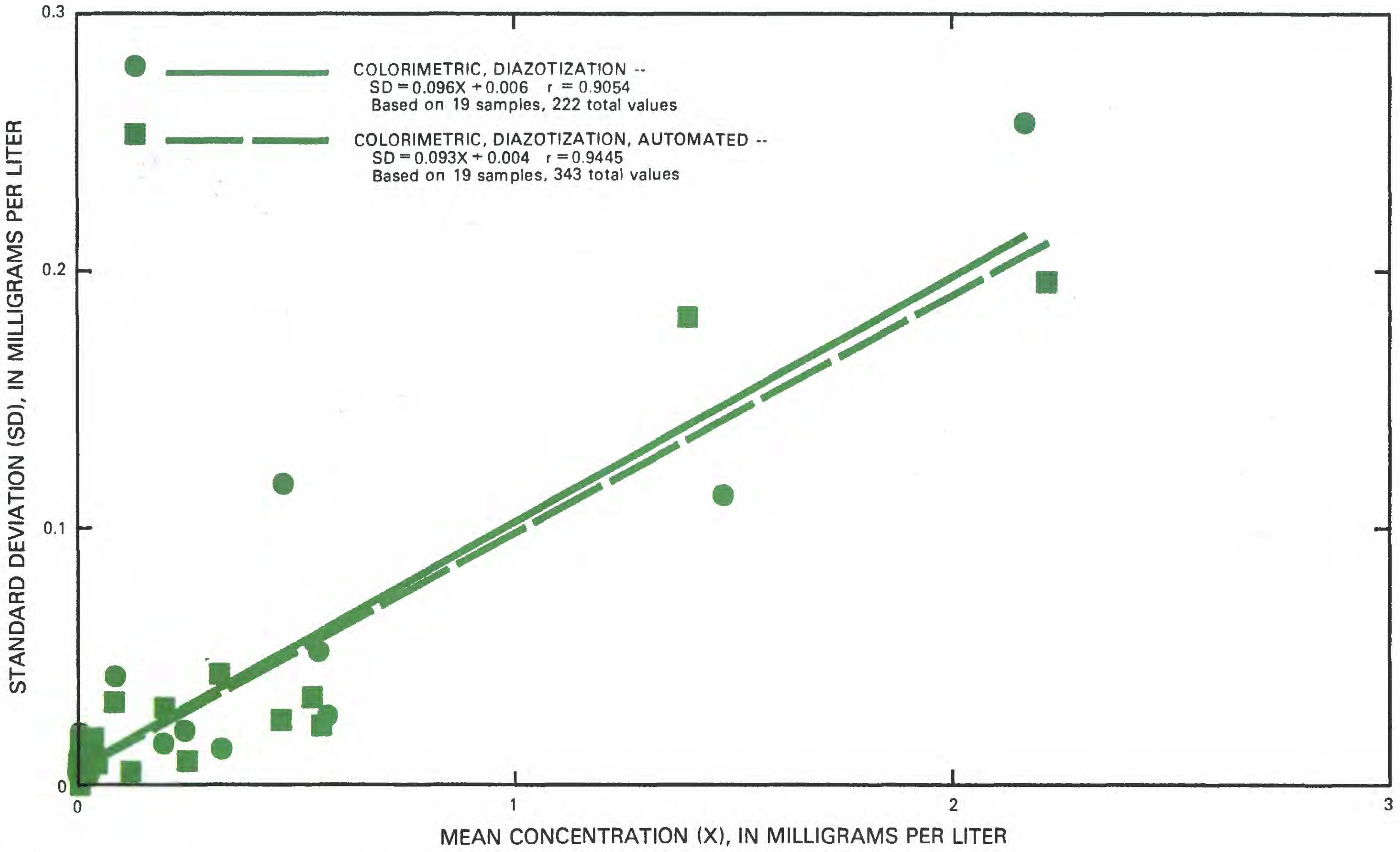

Figure 55. Interlaboratory precision of two methods used to determine nitrite nitrogen.

NITRITE PLUS NITRATE NITROGEN

Laboratories participating in the analyses of the SRWS were requested to report "nitrite" plus "nitrate". Because it is recognized that laboratories using the two automated procedures shown on figure 56 would have determined "nitrate plus nitrite" and then subtracted the nitrite value to obtain nitrate, the values for the two individual constituents were added together for any laboratory reporting both values. Although both methods were used for all SRWS, most of the laboratories used the colorimetric, cadmium reduction, automated method.

No significant difference is found in either the concentrations or precisions reported for the two methods, despite the fact that the statistical models for the precisions of the two methods appear to vary considerably (fig. 57). Some of the variance in the precision may be due to rounding in reporting the individual constituents, prior to recombining them for this data analysis.

References to the methods are given below:

Method	*Reference*
Colorimetric, cadmium reduction, automated	American Public Health Association and others, 1980
	American Society for Testing and Materials, 1983
	Skougstad and others, 1979
	U.S. Environmental Protection Agency, 1979a
Colorimetric, hydrazine reduction, automated	U.S. Enviromental Protection Agency, 1979a

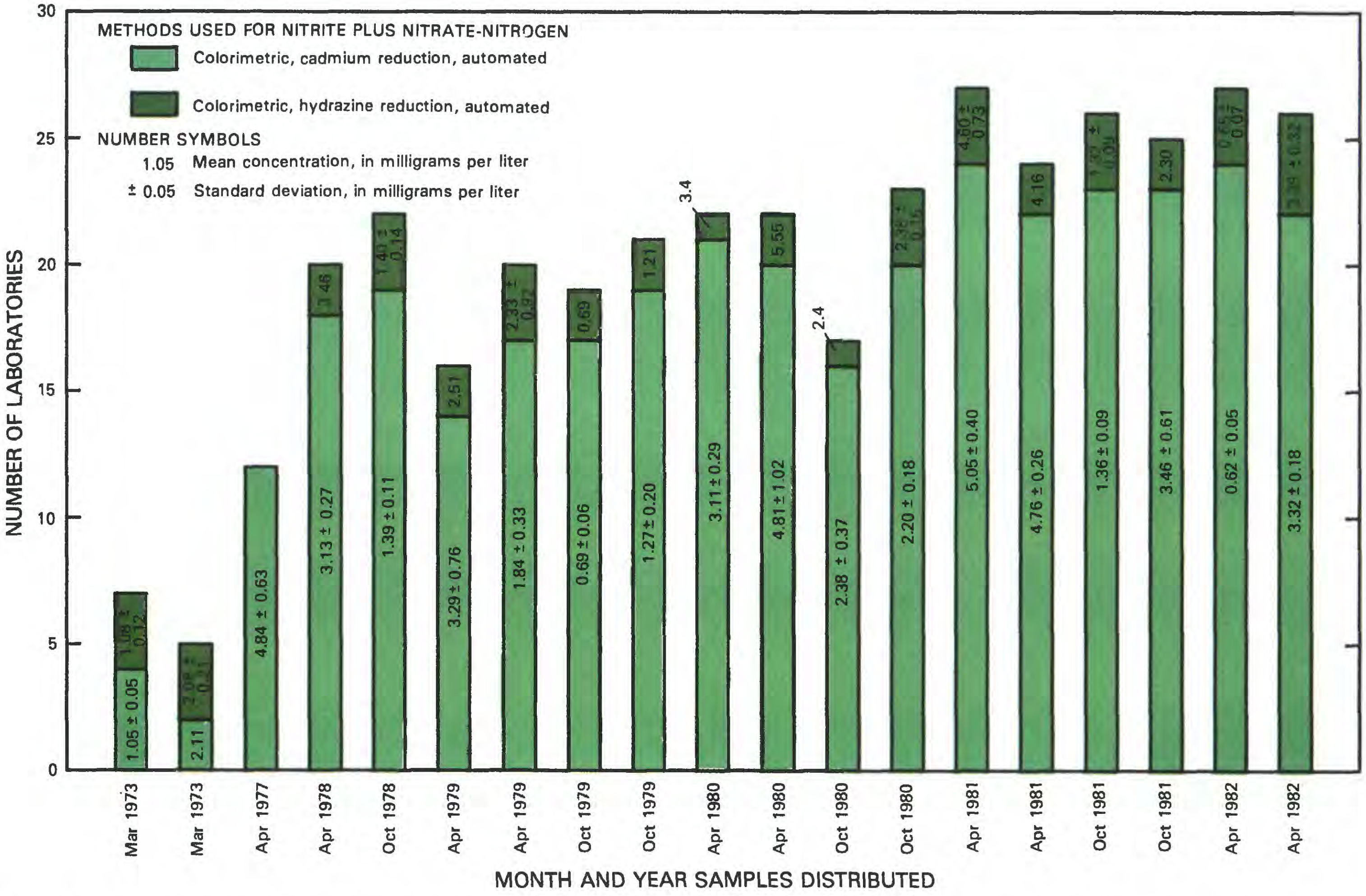

Figure 56. Mean concentrations and standard deviations for nitrite plus nitrate nitrogen in 19 Standard Reference Water Samples.

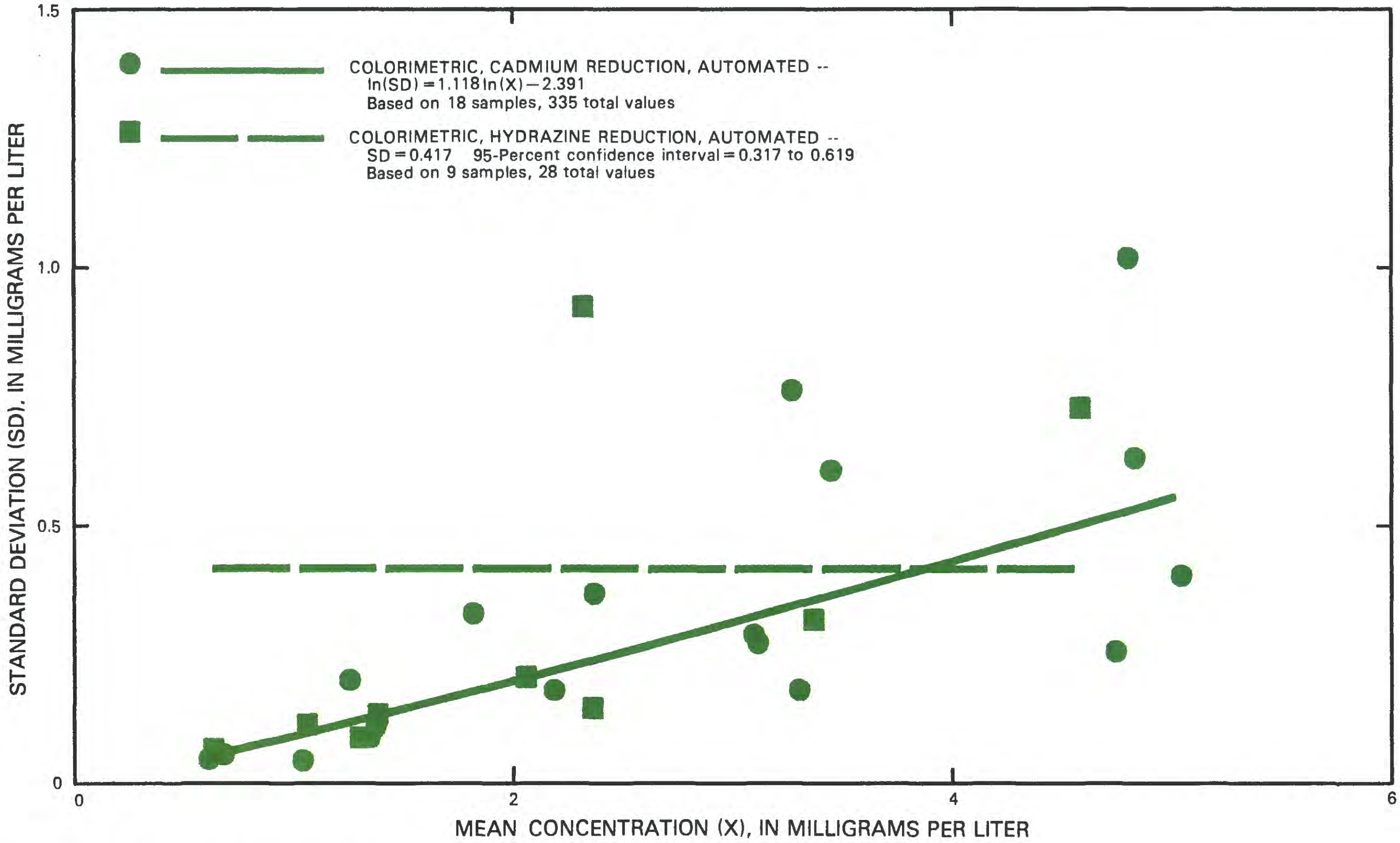

Figure 57. Interlaboratory precision of two methods used to determine nitrite plus nitrate nitrogen.

ORGANIC NITROGEN

Four methods, all relying on a Kjeldahl digestion, were used to determine organic nitrogen (fig. 58). Many laboratories may have chosen to determine "ammonia plus organic nitrogen" and subtracted the ammonia to obtain the organic nitrogen value. A significant difference is found between the concentrations reported for the nesslerization or titration method and those reported for the continuous digestion plus colorimetric, indophenol method. No other significant difference exists among the concentrations reported for the four methods.

Unlike the data reported for "ammonia plus organic nitrogen" (see fig. 9), a significant difference exists between the precisions reported for the Kjeldahl digestion, nesslerization or titration and the Kjeldahl digestion, continuous plus colorimetric, indophenol, automated methods (fig. 59). The precisions of the methods do not seem to vary with concentration.

References to the methods are given below:

Method	*Reference*
Kjeldahl digestion plus nesslerization or titration	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a
Kjeldahl digestion plus colorimetric, indophenol, automated	Skougstad and others, 1979
Kjeldahl digestion plus colorimetric, salicylate, automated	Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a
Kjeldahl digestion, continuous plus colorimetric, indophenol, automated	U.S. Environmental Protection Agency, 1979a

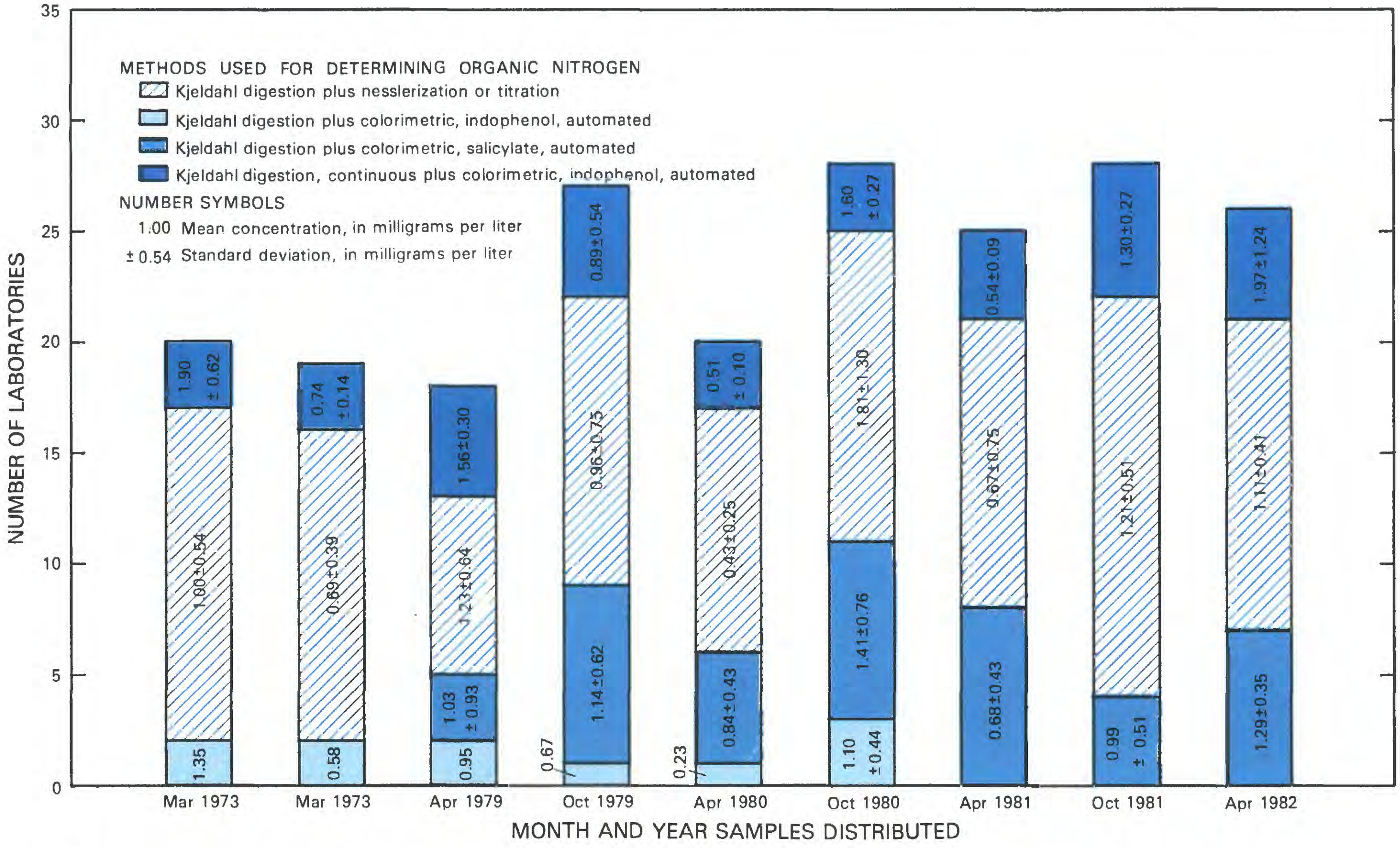

Figure 58. Mean concentrations and standard deviations for organic nitrogen in nine Standard Reference Water Samples.

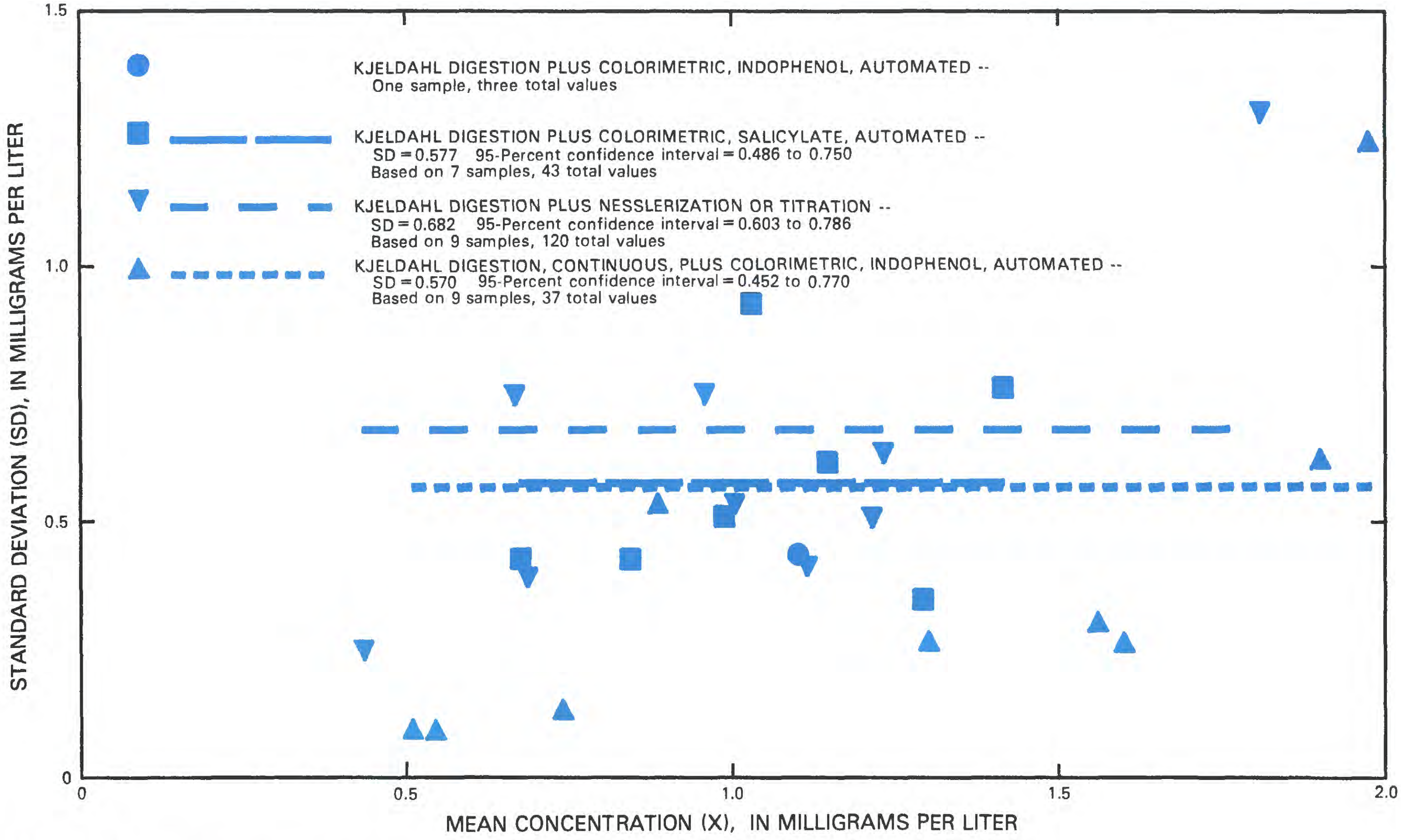

Figure 59. Interlaboratory precision of four methods used to determine organic nitrogen.

ORTHOPHOSPHATE PHOSPHORUS

Four methods were used to determine orthophosphate in the nine SRWS distributed for analyses (fig. 60). However, most of the data were from the manual or automated colorimetric, phosphomolybdate, ascorbic acid methods. No significant difference exists in the concentrations reported. Similarly, no significant difference is found among the precisions reported for the three methods shown on figure 61.

References to the methods are given below:

Method	*Reference*
Colorimetric, phosphomolybdate, ascorbic acid	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a
Colorimetric, phosphomolybdate, ascorbic acid, automated	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a
Colorimetric, phosphomolybdate, stannous chloride	American Public Health Association and others, 1980 American Society for Testing and Materials, 1971 Rainwater and Thatcher, 1960
Colorimetric, phosphomolybdate, stannous chloride, automated	U.S. Environmental Protection Agency, 1971

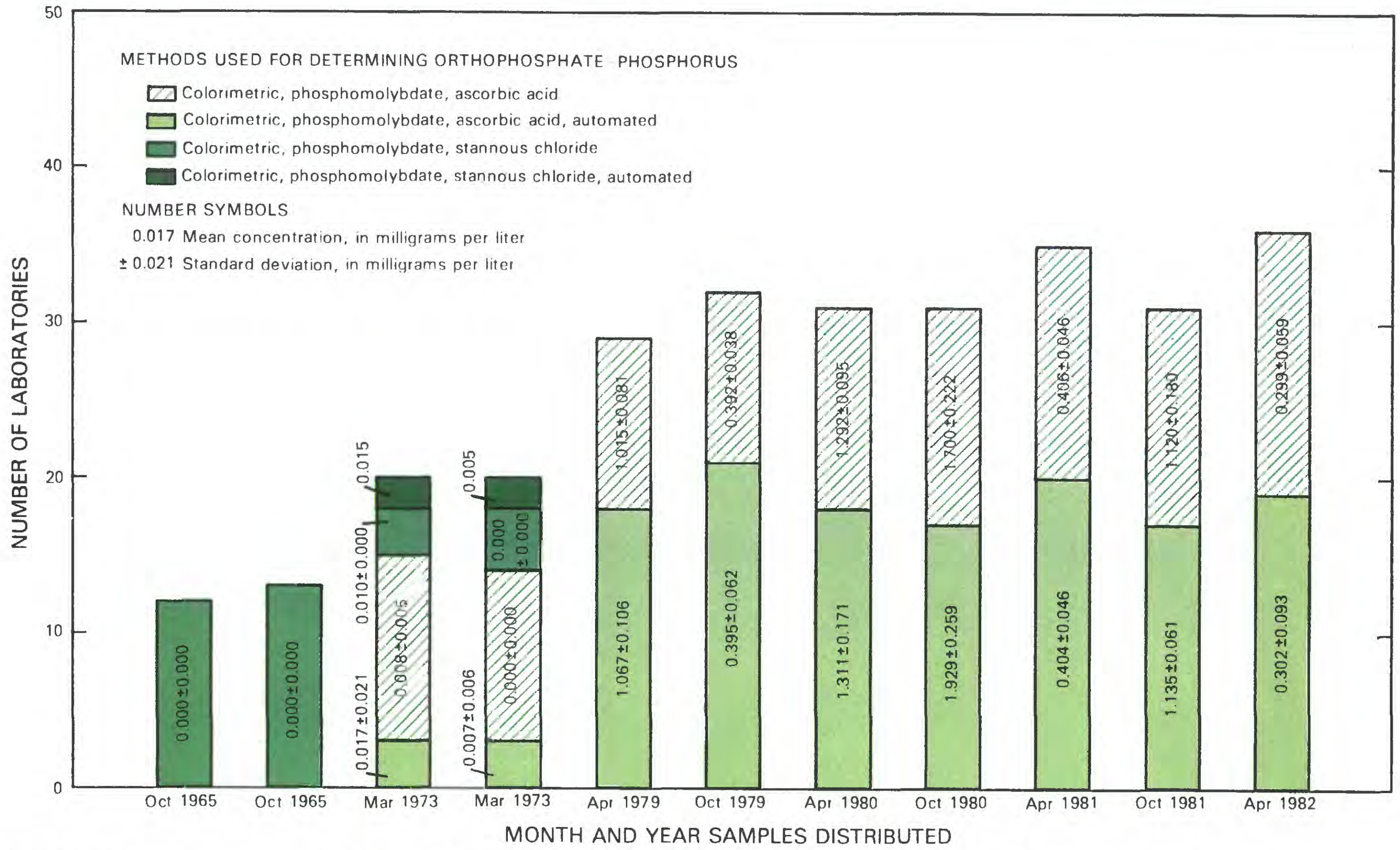

Figure 60. Mean concentrations and standard deviations for orthophosphate phosphorus in 11 Standard Reference Water Samples.

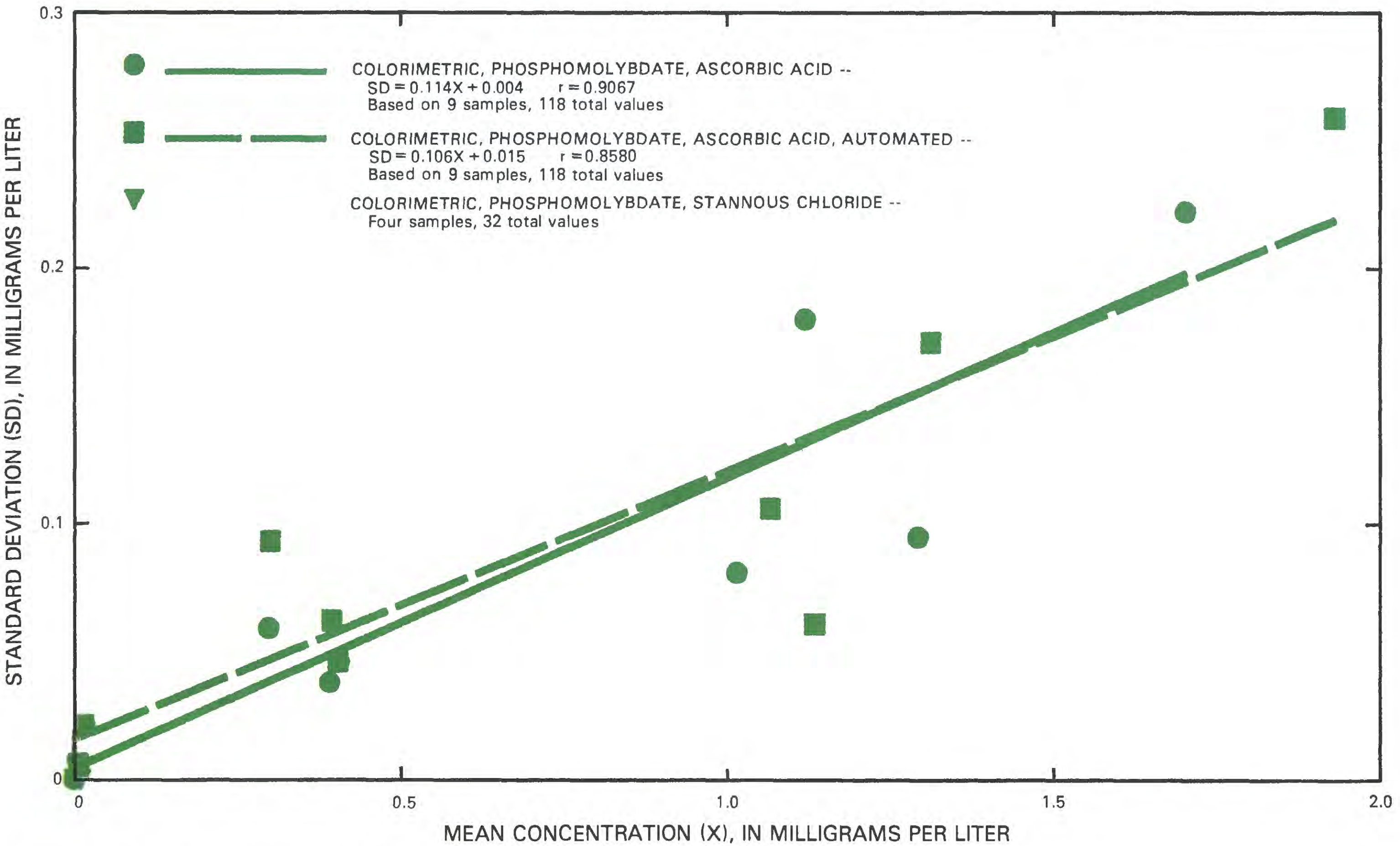

Figure 61. Interlaboratory precision of three methods used to determine orthophosphate phosphorus.

PHOSPHORUS

Four methods were used to determine phosphorus (fig. 62). However, almost all data were from either the automated or manual colorimetric, phosphomolybdate, ascorbic acid methods. No significant difference exists among the concentrations reported for the four methods.

Similarly, no significant difference exists among the precisions reported for the three methods shown on figure 63, even though the precision for the automated ascorbic acid method appears to vary with concentration and the precision for the manual ascorbic acid procedure does not. A less than 5-percent chance exists that the intercept of the model for the colorimetric, ascorbic acid, automated method is equal to zero.

References to the methods are given below:

Method	*Reference*
Colorimetric, phosphomolybdate, ascorbic acid	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a
Colorimetric, phosphomolybdate, ascorbic acid, automated	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a
Colorimetric, phosphomolybdate, stannous chloride	American Public Health Association and others, 1980 American Society for Testing and Materials, 1971 Rainwater and Thatcher, 1960
Colorimetric, phosphomolybdate, stannous chloride, automated	U.S. Environmental Protection Agency, 1971

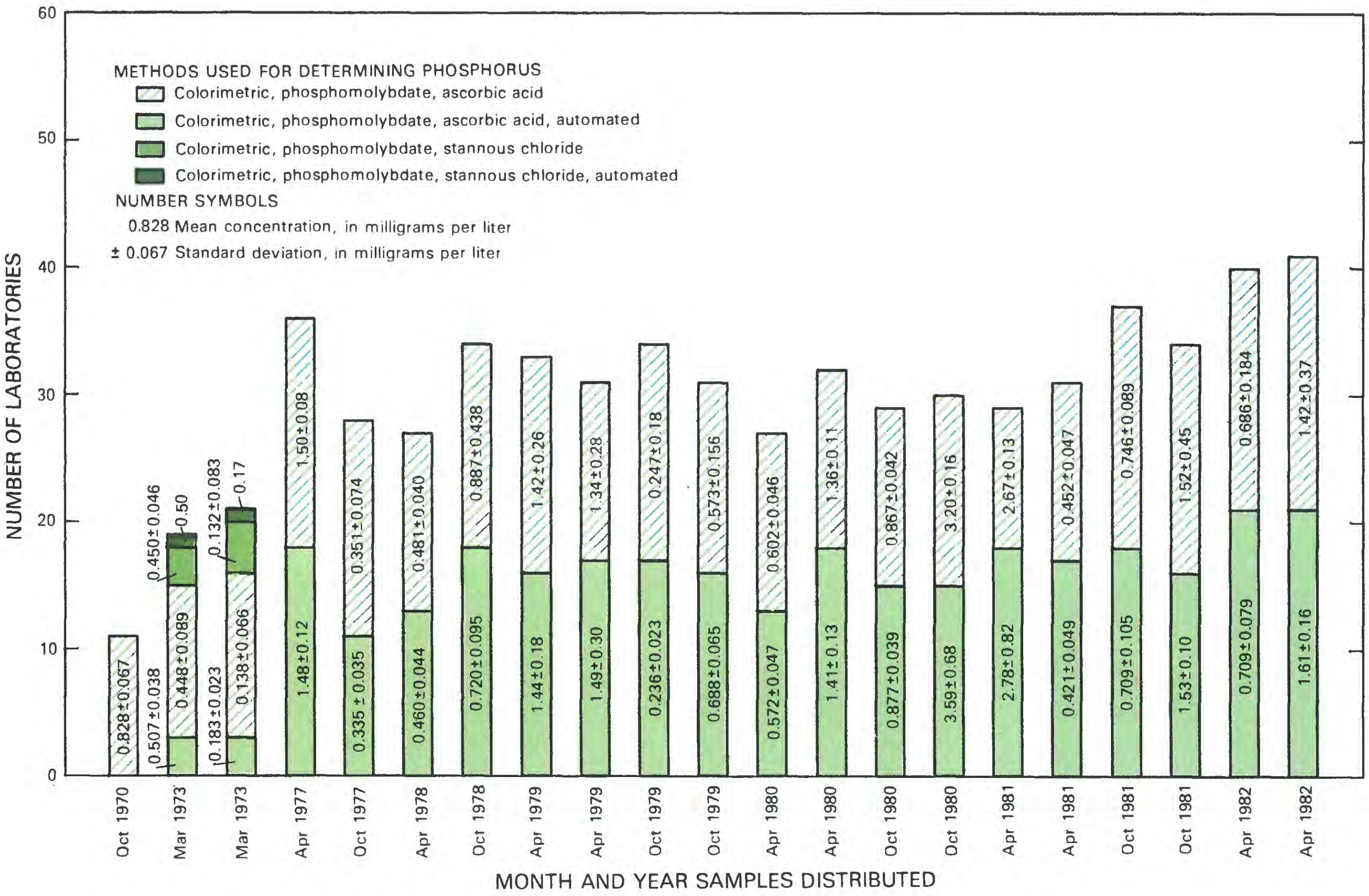

Figure 62. Mean concentrations and standard deviations for phosphorus in 21 Standard Reference Water Samples.

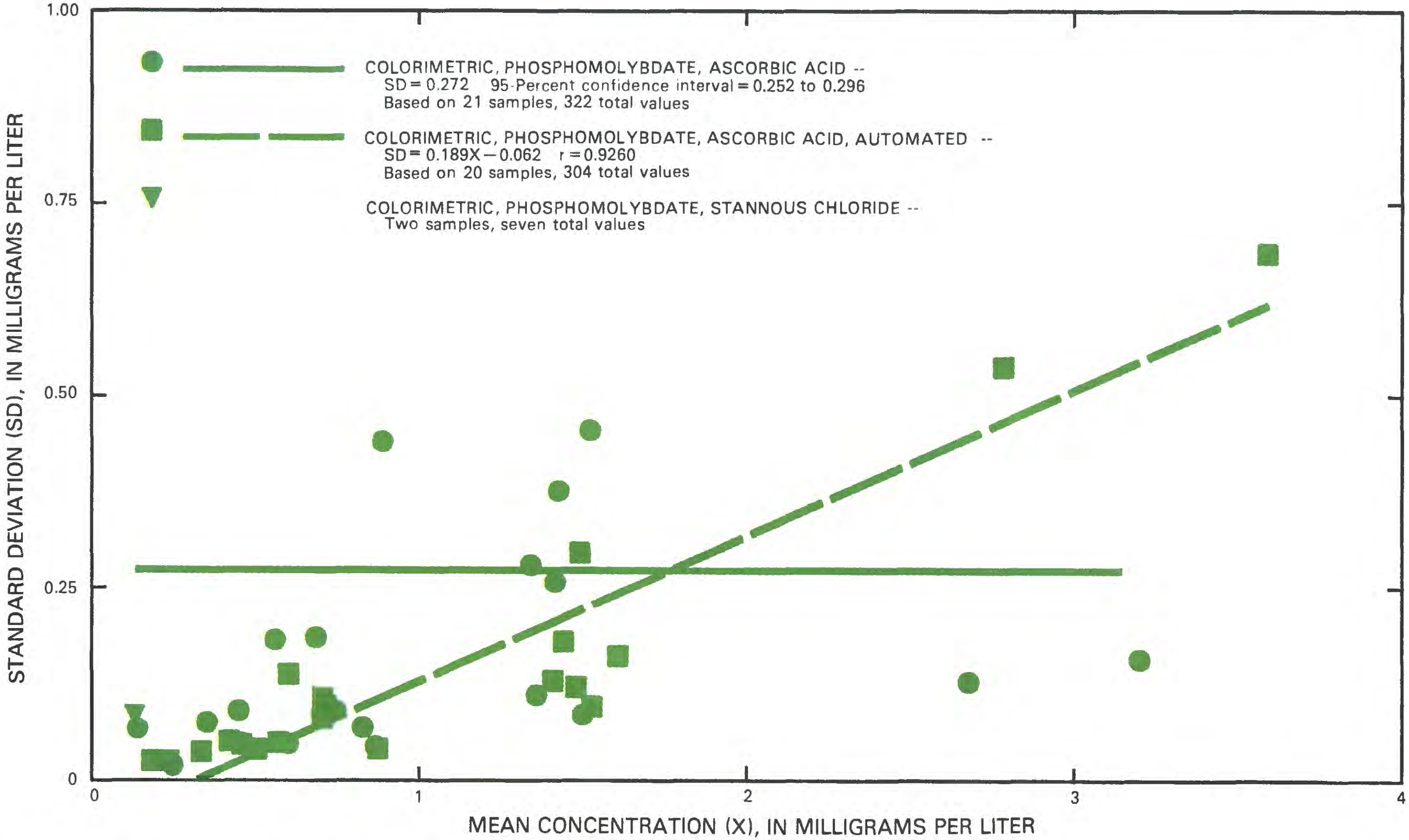

Figure 63. Interlaboratory precision of three methods used to determine phosphorus.

POTASSIUM

Five methods were used to determine potassium (fig. 64). Almost all data were obtained by AAS, direct or by emission, flame or, in the last few years, by emission, ICP.

No significant difference is found among the concentrations reported by the different methods. The precision of the emission, flame method is significantly different (generally larger) than that of the AAS, direct method (fig. 65). However, if only the SRWS for which emission, ICP results are available are considered, no significant difference is observed between the precisions obtained by the emission, flame; AAS, direct; and emission, ICP methods.

References to the methods are given below:

Method	*Reference*
Atomic absorption spectrometry, direct	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a
Atomic emission spectrometry, arc-spark	—
Atomic emission spectrometry, direct-current plasma	—
Atomic emission spectrometry, flame	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Rainwater and Thatcher, 1960
Atomic emission spectrometry, inductively coupled plasma	—

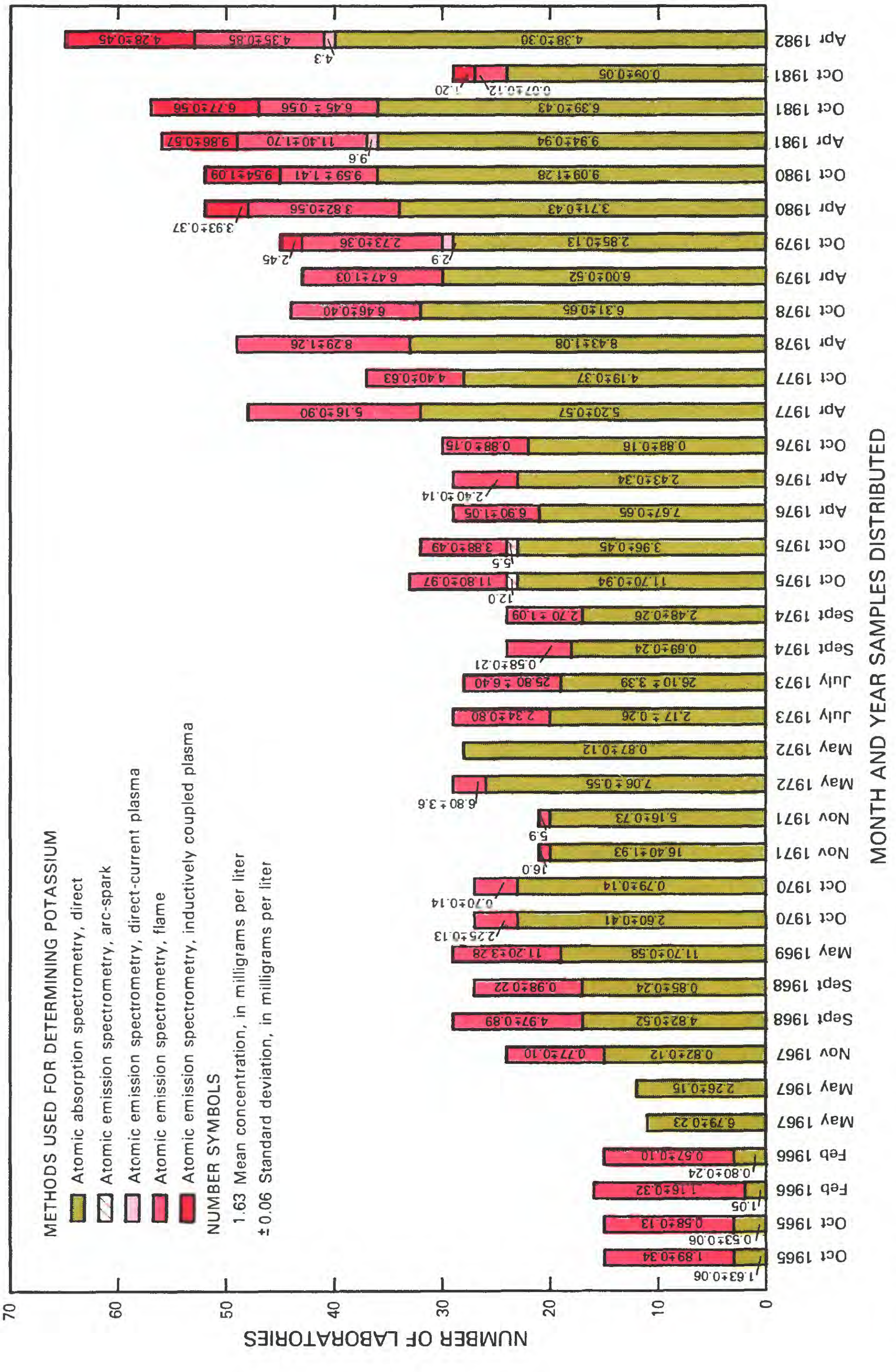

Figure 64. Mean concentrations and standard deviations for potassium in 37 Standard Reference Water Samples.

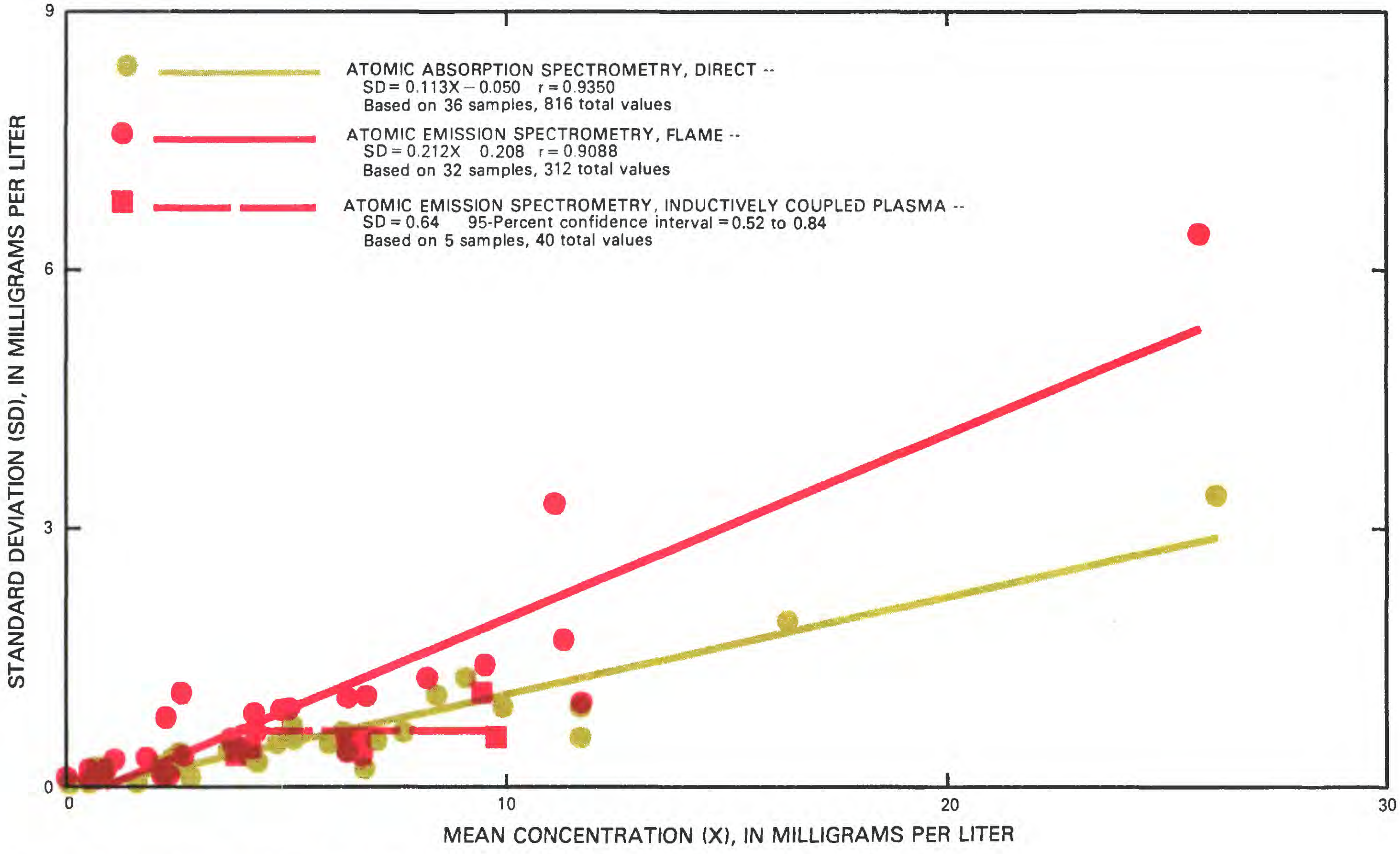

Figure 65. Interlaboratory precision of three methods used to determine potassium.

SELENIUM

Four methods were used to determine selenium (fig. 66). If all data are examined, or if the data are limited to SRWS distributed in or after April 1976 (when methods other than the AAS, hydride ($SnCl_2$) method were first reported), or if the data are limited to SRWS distributed in or after April 1979 (when the automated procedure was first reported), the concentrations determined by the AAS, hydride ($NaBH_4$) method are significantly different from those for the other three methods. If data from just the AAS, hydride ($NaBH_4$) and AAS, hydride ($SnCl_2$) for SRWS distributed in or after April 1976 are examined, a significant difference is found in concentrations; if just the manual and automated AAS, hydride ($NaBH_4$) methods are compared for SRWS distributed in or after April 1980 (when data from the two methods were first reported), a significant difference is observed in concentrations.

The precision of the manual AAS, hydride ($NaBH_4$) method is different from those for the AAS, hydride ($SnCl_2$) and AAS, graphite-furnace methods. As can be seen in figure 67, the precision of the AAS, hydride ($NaBH_4$) method appears to be generally worse than those for the other two methods.

References to the methods are given below:

Method	*Reference*
Atomic absorption spectrometry, graphite-furnace	U.S. Environmental Protection Agency, 1979a
Atomic absorption spectrometry, hydride (sodium borohydride)	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983
Atomic absorption spectrometry, hydride (sodium borohydride), automated	Fishman and Bradford, 1982
Atomic absorption spectrometry, hydride (stannous chloride)	Skougstad and others, 1979

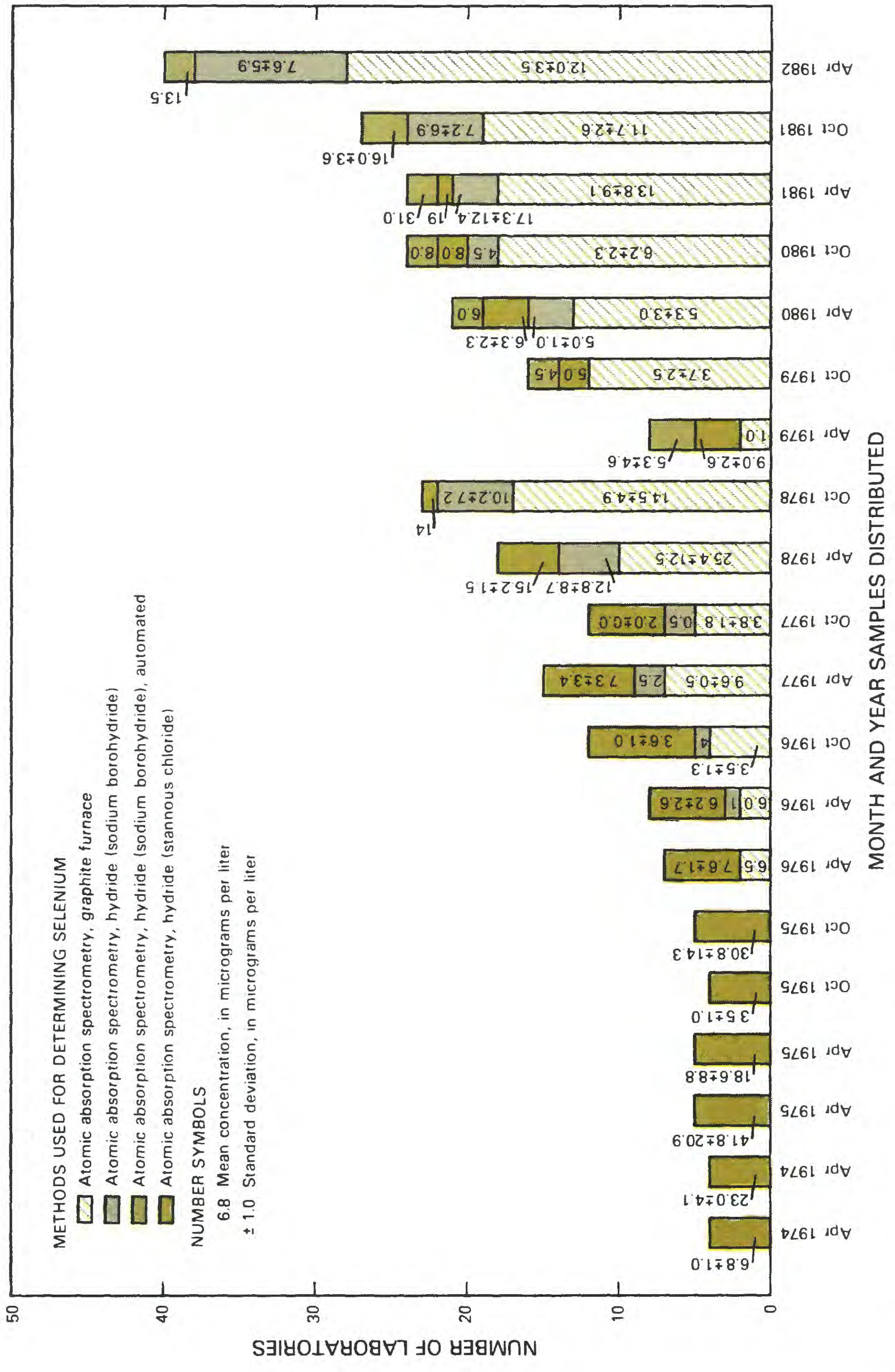

Figure 66. Mean concentrations and standard deviations for selenium in 20 Standard Reference Water Samples.

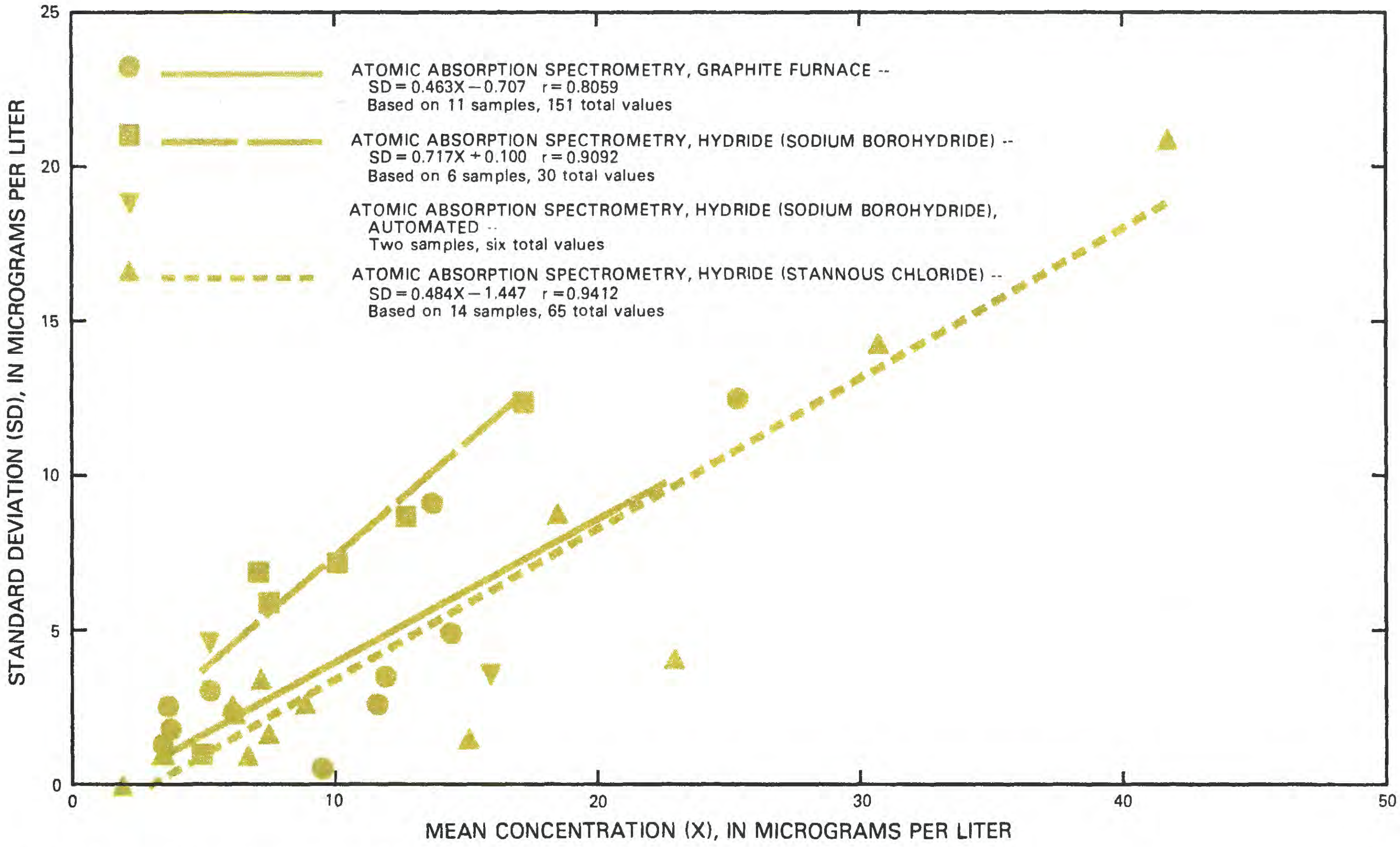

Figure 67. Interlaboratory precision of four methods used to determine selenium.

SILICA

Seven methods were used to determine silica (fig. 68); however, it should be noted that the various colorimetric methods are all rather similar chemically. Concentrations reported for the atomic absorption method were significantly different than concentrations reported for the colorimetric, molydosilicate; colorimetric, molybdate blue; and colorimetric, molybdate blue, automated methods. However, if data are limited to SRWS distributed in or after October 1979, when the only other non-colorimetric method (emission, ICP) was used, no significant difference is found between the concentrations. In any case, no other significant difference is observed in the concentrations obtained by the methods.

Precision models were determined for six of the methods (fig. 69). The standard deviation changed with concentration only for the colorimetric, molybdate blue, manual procedure. The model indicated on figure 69 was based on the analyses of 35 SRWS (a total of 430 values); it excludes the concentration of 36.5 mg/L that was reported for the SRWS distribution in November 1971 (the only concentration that was over 25 mg/L). If the value for this SRWS is included, the model changes to $SD=0.039x+0.30$ with $r=0.6596$ (compared to $SD=0.065x+0.10$ with $r=0.8053$).

The precision for the colorimetric, heteropoly blue procedure is significantly different from the precision for the other five procedures; as can be seen in figure 69, the standard deviation is larger than those for the other procedures. The precision for the colorimetric, molybdate blue, manual procedure is significantly different from the precisions for the AAS, direct and colorimetric, molybdosilicate methods as well as from that for the colorimetric, hetropoly blue method; this is true whether or not the 36.5 mg/L point is included. If only data for SRWS distributed in or after October 1979 are examined and the precisions for the AAS, direct; colorimetric, molybdate blue; colorimetric, molybdate blue, automated; colorimetric, molybdosilicate; and emission, ICP methods are compared, the precision of the AAS, direct method shows a significant difference compared to that reported for the colorimetric, molybdate blue method.

References to the methods are given below:

Method	*Reference*
Atomic absorption spectrometry, direct	American Public Health Association and others, 1980 Skougstad and others, 1979
Atomic emission spectrometry, inductively coupled plasma	Fishman and Bradford, 1982
Colorimetric, heteropoly blue	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 U.S. Environmental Protection Agency, 1979a
Colorimetric, heteropoly blue, automated	American Public Health Association and others, 1980
Colorimetric, molybdate blue	American Society for Testing and Materials, 1983 Skougstad and others, 1979
Colorimetric, molybdate blue, automated	Skougstad and others, 1979
Colorimetric, molybdosilicate	American Public Health Association and others, 1980

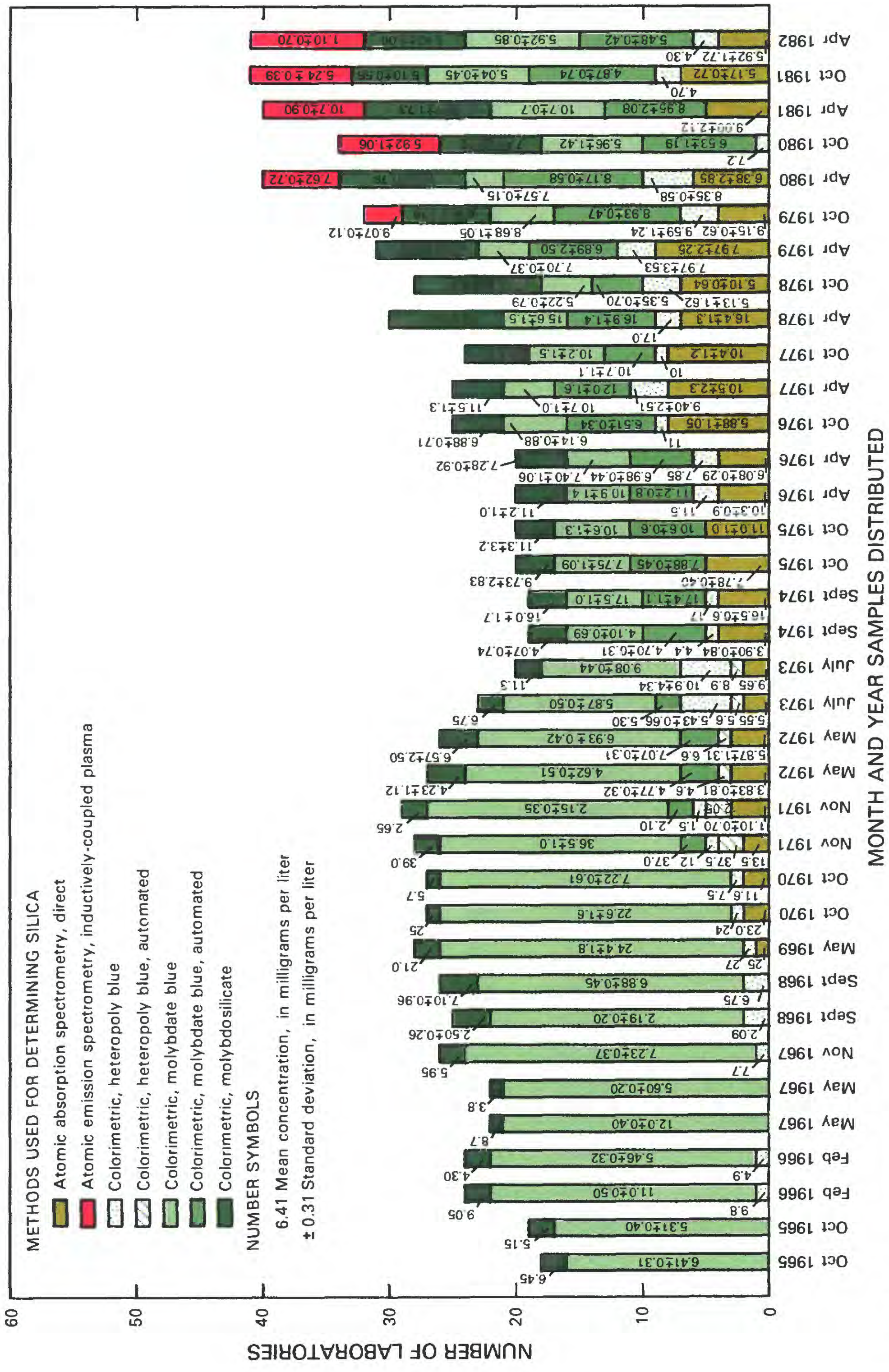

Figure 68. Mean concentrations and standard deviations for silica in 36 Standard Reference Water Samples.

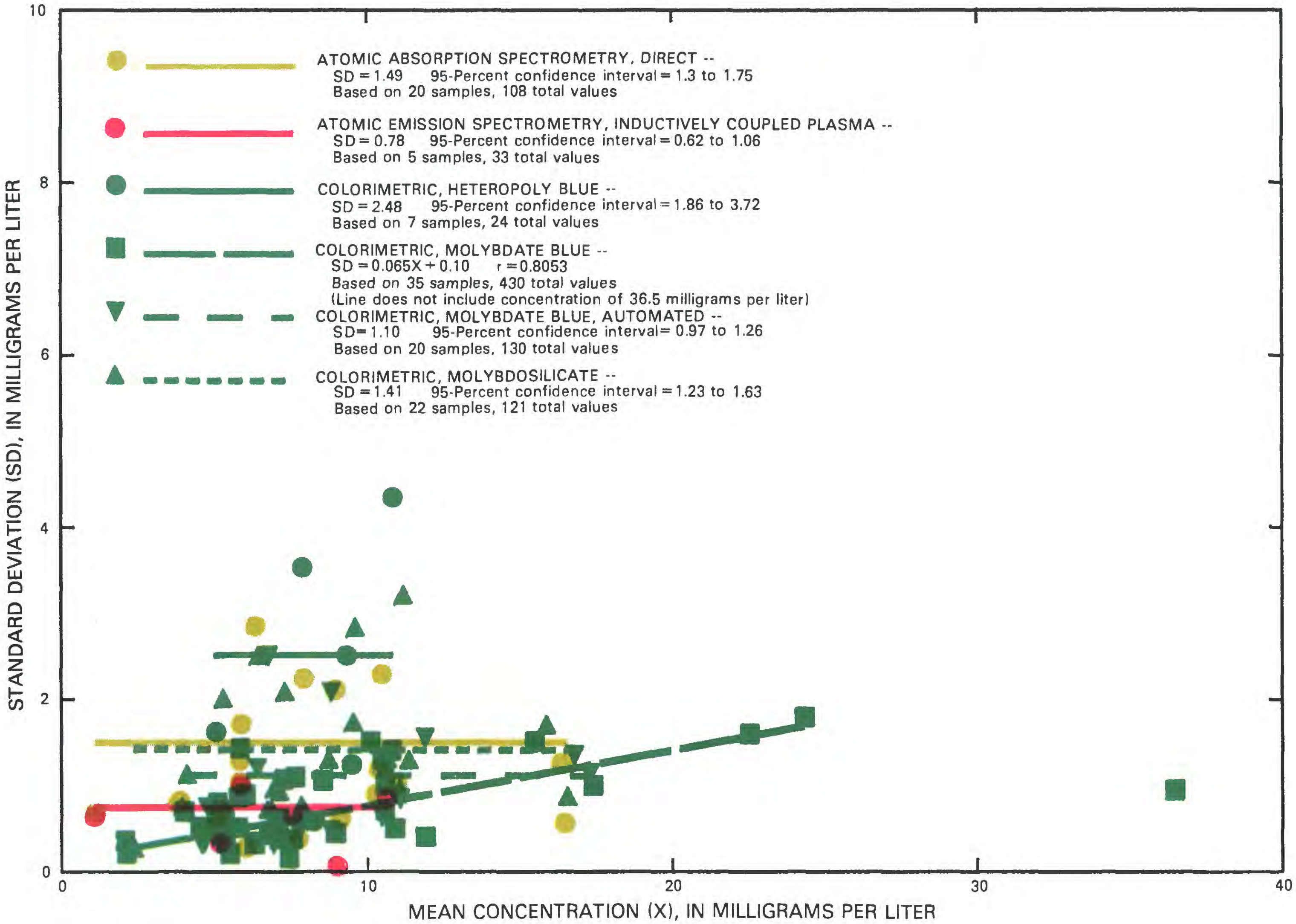

Figure 69. Interlaboratory precision of six methods used to determine silica.

SILVER

Six methods were used to determine silver, although most of the data were from the AAS, APDC-MIBK; AAS, direct; and AAS, graphite-furnace procedures (fig. 70). Data for the emission, arc-spark; emission, ICP; and neutron-activation methods are too limited to reach valid conclusions. No significant difference exists among concentrations reported for the methods.

The precision of the AAS, direct method is significantly different from the precision of the other methods. The concentration of 17.8 μg/L has been omitted from the precision model for the AAS, direct method shown in fig. 71; a less than 5-percent chance exists that the intercept of this model is equal to zero. If the point representing the 17.8 μg/L concentration is included, the model for the AAS, direct method would change from $SD=0.331x+1.43$ to $SD=-0.544x+0.105x^2-0.004x^3+3.64$.

References to the methods are given below:

Method	*Reference*
Atomic absorption spectrometry, chelation-extraction with ammonium pyrrolidine dithiocarbamate and methyl isobutyl ketone	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979
Atomic absorption spectrometry, direct	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 U.S. Environmental Protection Agency, 1979a
Atomic absorption spectrometry, graphite-furnace	American Society for Testing and Materials, 1983 U.S. Environmental Protection Agency, 1979a
Atomic emission spectrometry, arc-spark	Barnett and Mallory, 1971
Atomic emission spectrometry, inductively coupled plasma	—
Neutron activation	—

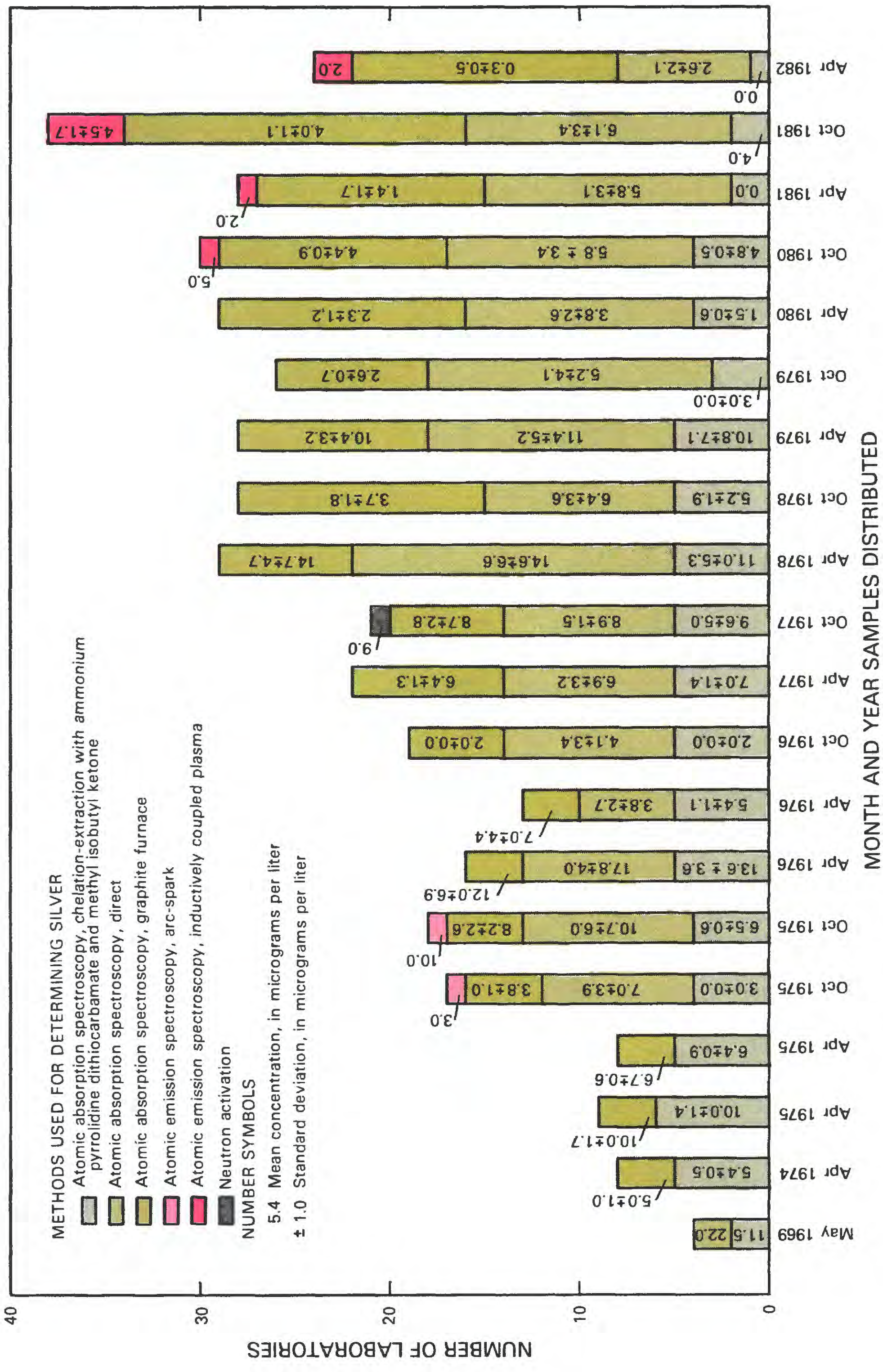

Figure 70. Mean concentrations and standard deviations for silver in 20 Standard Reference Water Samples.

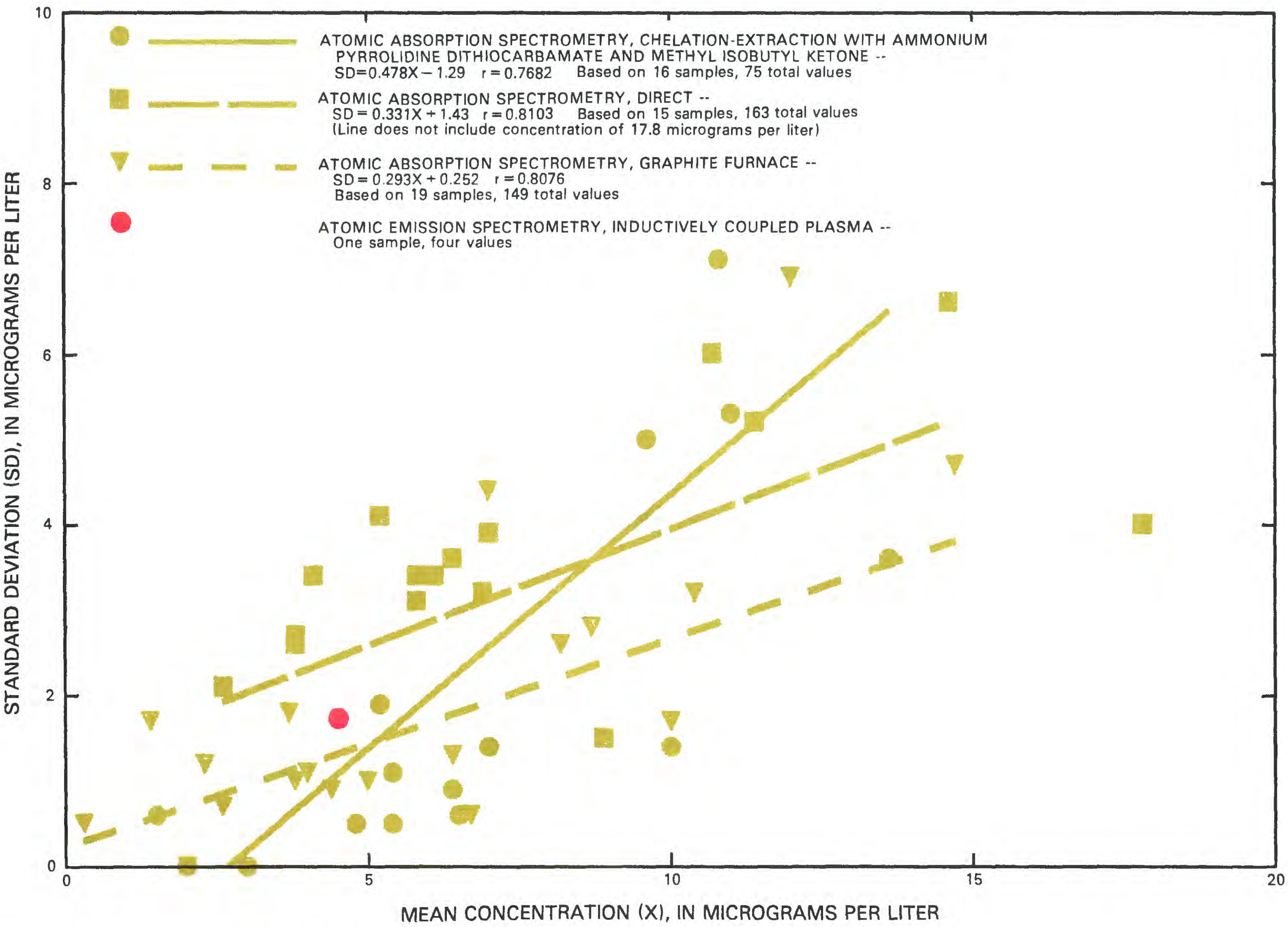

Figure 71. Interlaboratory precision of four methods used to determine silver.

SODIUM

Seven methods were used to determine sodium, although primarily data were from the AAS, direct or emission, flame methods or, in the last few years, from the emission, ICP method (fig. 72). When all of the data are considered, no significant difference is observed in the concentrations.

When the two methods with data for the entire period of record, the AAS, direct and emission, flame methods are compared to each other, neither the concentrations or precisions (figs. 72 and 73) are significantly different. However, when the data for SRWS distributed in or after October 1979 are compared for AAS, direct; emission, flame; and emission, ICP methods, the precision (but not the concentration) for the emission, flame method is signficantly different than those for the other two methods. A less than 5-percent chance exists that the intercept for the precision model of the emission, flame method is equal to zero.

References to the methods are given below:

Method	*Reference*
Atomic absorption spectrometry, direct	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a
Atomic emission spectrometry, arc-spark	—
Atomic emission spectrometry, direct-current plasma	—
Atomic emission spectrometry, flame	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Rainwater and Thatcher, 1960
Atomic emission spectrometry, inductively coupled plasma	Fishman and Bradford, 1982
Gravimetric	American Public Health Association and others, 1975
Neutron activation	—

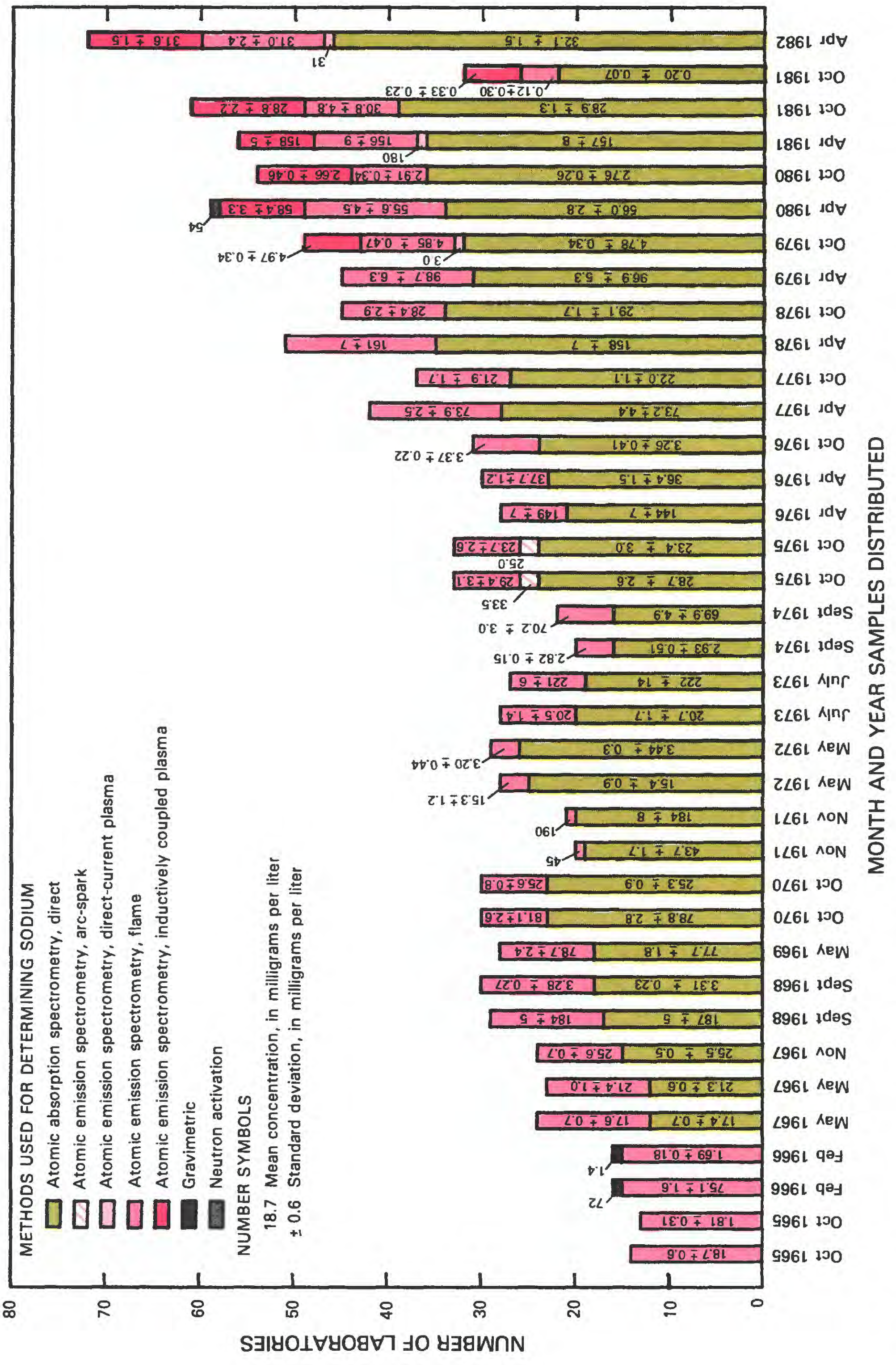

Figure 72. Mean concentrations and standard deviations for sodium in 37 Standard Reference Water Samples.

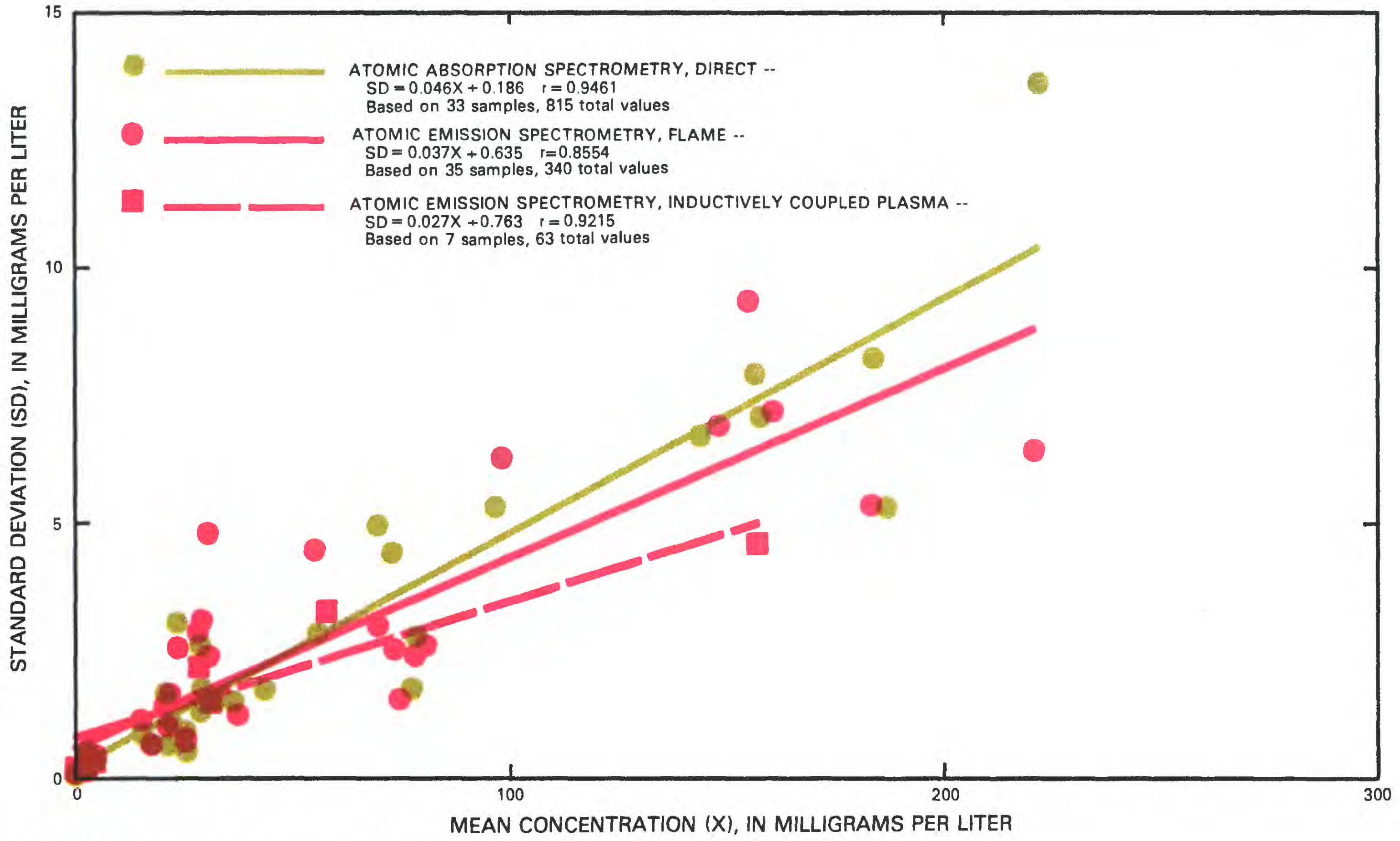

Figure 73. Interlaboratory precision of three methods used to determine sodium.

SPECIFIC CONDUCTANCE

Specific conductance in µS/cm at 25 °C was determined in 36 SRWS (with a total of 1,303 values). Because it is generally impossible in the reports to differentiate between the types of instruments used or even to determine if conductance or resistance was read, all reported data were combined (American Public Health Association and others, 1980; American Society for Testing and Materials, 1983; Skougstad and others, 1979; U.S. Environmental Protection Agency, 1979a). The model for estimating the precision that can be obtained in measuring specific conductance between 9.0 and 2,082 µS/cm at 25 °C is given in figure 74.

STRONTIUM

Four methods were used to determine strontium (fig. 75), although most of the data are from the AAS, direct method. The emission, flame method gave concentrations that are significantly different from those obtained by the AAS, direct and emission, ICP methods. No other signficant difference is found in concentrations reported for the methods.

A comparison between the data used to determine the precision models for the AAS, direct and emission, ICP methods indicates that the analytical precisions of the two methods are significantly different (fig. 76). However, if only data for the eleven SRWS issued in or after October 1979 are considered (that is, if the AAS, direct data are limited to SRWS for which emisison, ICP data are also available), no significant difference exists between methods. The model for the AAS, direct method would be $(\ln(SD)=0.804\ln(x)-0.833$ if only the eleven SRWS are considered instead of $\ln(SD)=0.680\ln(x)-0.007$ if all 39 SRWS for which Sr data are available are considered.)

References to the methods are given below:

Method	*Reference*
Atomic absorption spectrometry, direct	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979
Atomic emission spectrometry, direct-current plasma	American Society for Testing and Materials, 1983
Atomic emission spectrometry, flame	American Public Health Association and others, 1980
Atomic emission spectrometry, inductively coupled plasma	Fishman and Bradford, 1982

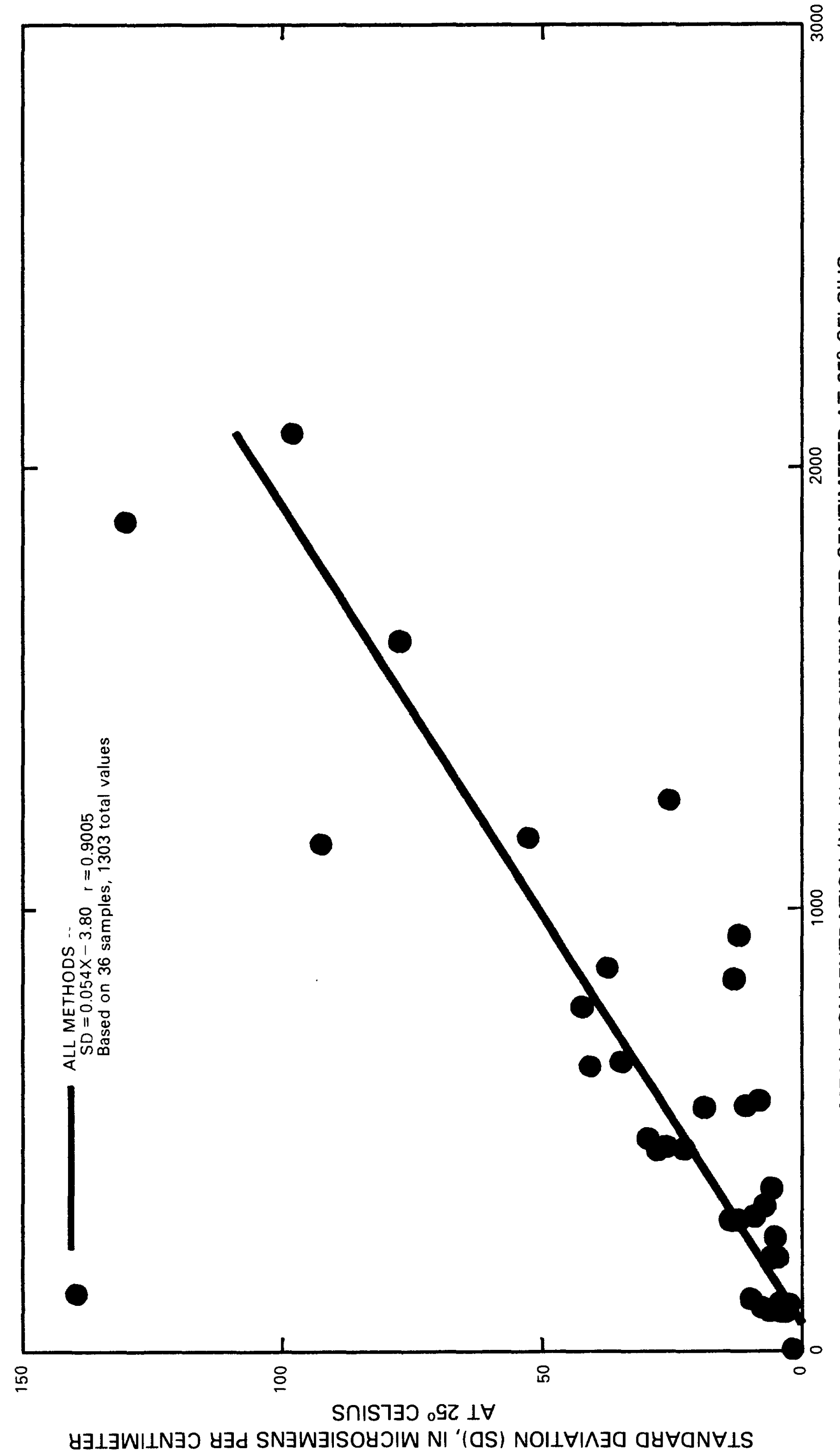

Figure 74. Interlaboratory precision for specific conductance.

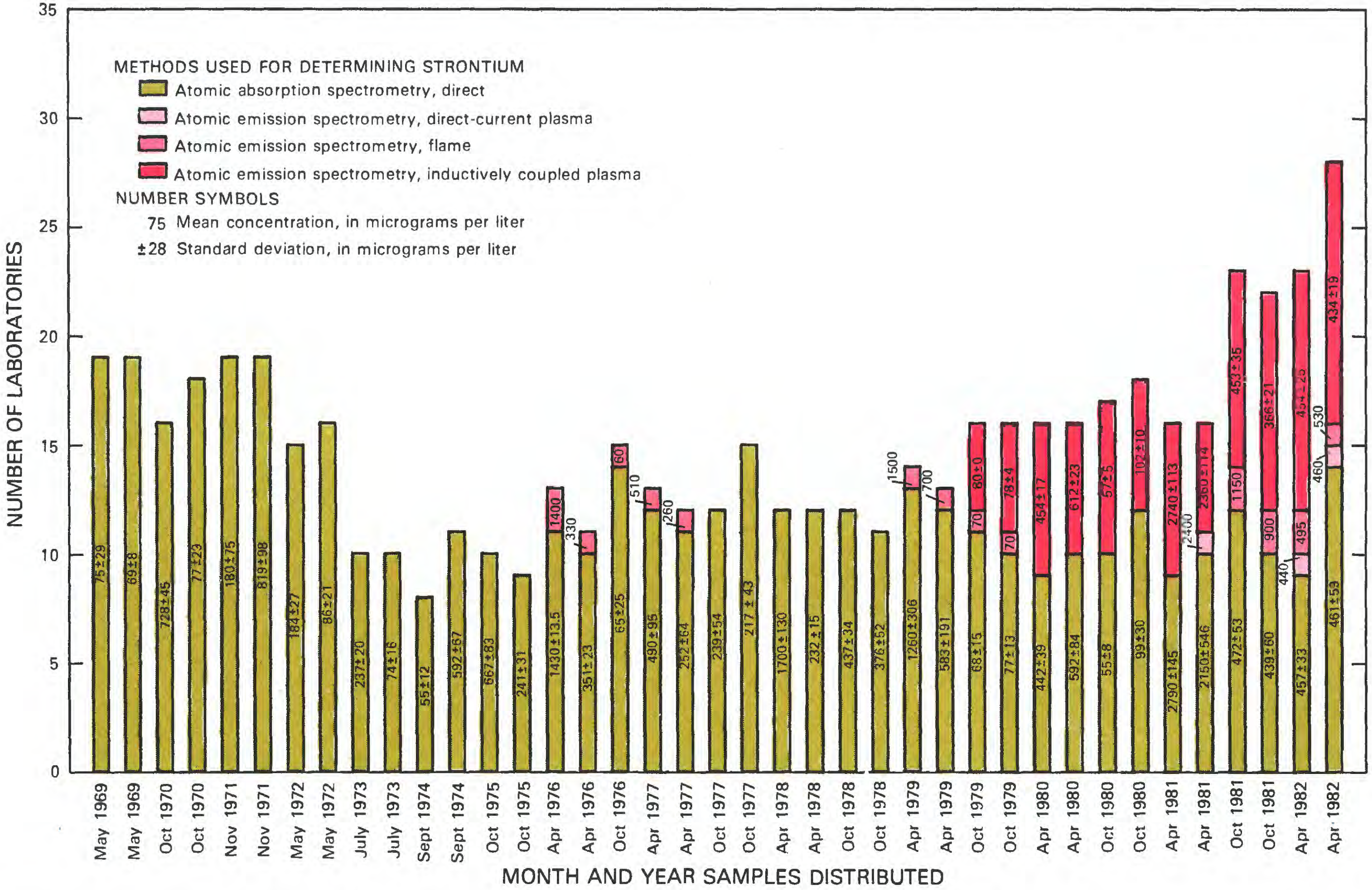

Figure 75. Mean concentrations and standard deviations for strontium in 39 Standard Reference Water Samples.

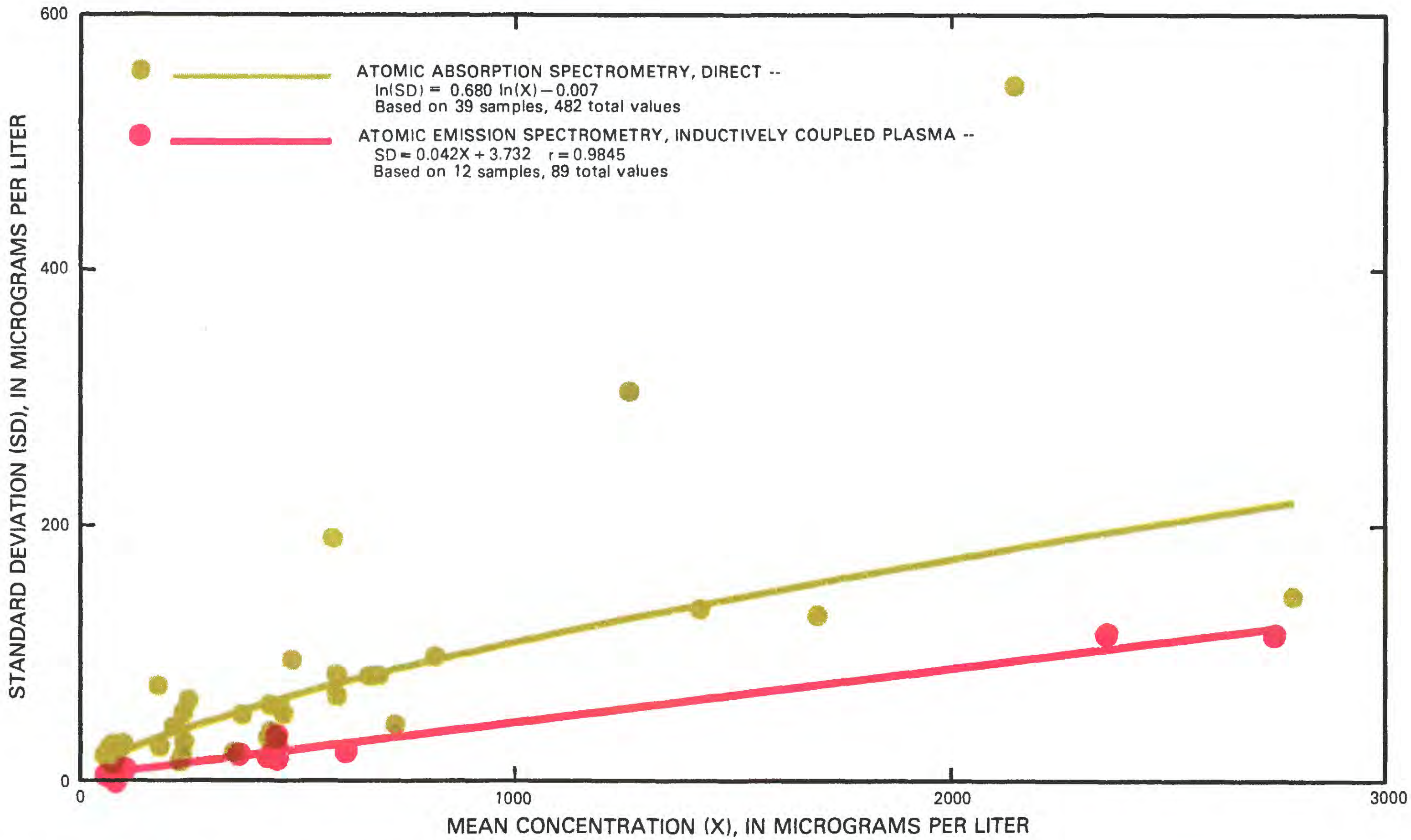

Figure 76. Interlaboratory precision of two methods used to determine strontium.

SULFATE

Five methods were used to determine sulfate with a noticeable shift from use of the titration, thorin method to the titration, turbidmetric and colorimetric, methylthymol blue, automated methods (fig. 77). No significant difference exists betweem the concentrations determined by the different methods.

Sufficient data were available to calculate precision models for four methods (fig. 78). A significant difference exists between the precision for the titration, turbidimetric method and the precisions for the other methods. Standard deviations for the turbidimetric procedure were generally higher than the standard deviations for the colorimetric, methylthymol blue, automated; gravimetric, barium sulfate; and titration, thorin (with visible or spectrophotometric detection) methods. A less than 5-percent chance exists that the intercept of the precision model for colorimetric, methylthymol blue procedure is equal to zero.

References to the methods are given below:

Method	*Reference*
Colorimetric, methylthymol blue, automated	American Public Health Association and others, 1980 Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a
Gravimetric, barium sulfate	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Rainwater and Thatcher, 1960 U.S. Environmental Protection Agency, 1979a
Titration, thorin	American Society for Testing and Materials, 1983 Skougstad and others, 1979
Titration, turbidimetric	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Rainwater and Thatcher, 1960 U.S. Environmental Protection Agency, 1979a
Titration, turbidimetric, automated	—

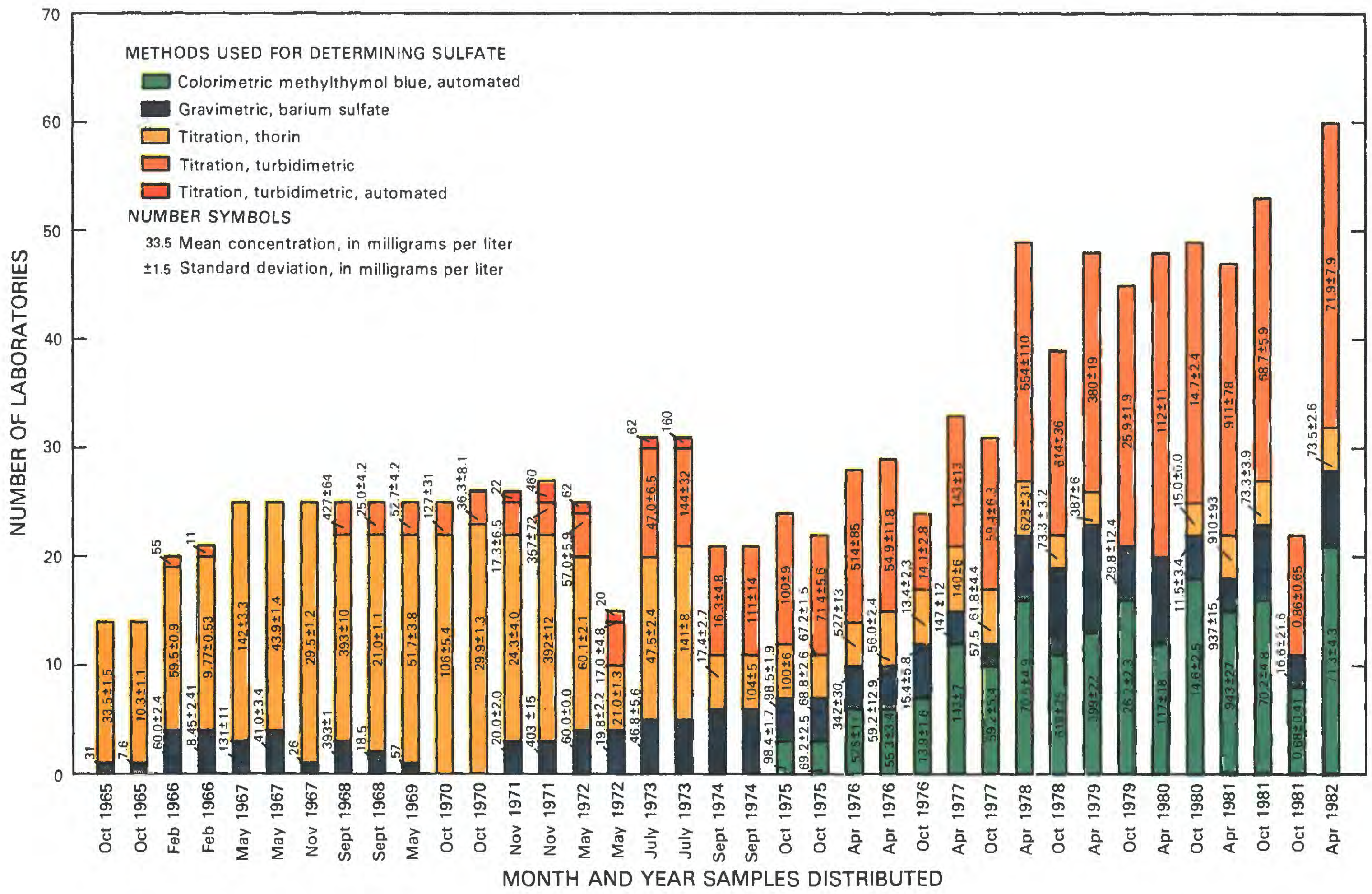

Figure 77. Mean concentrations and standard deviations for sulfate in 37 Standard Reference Water Samples.

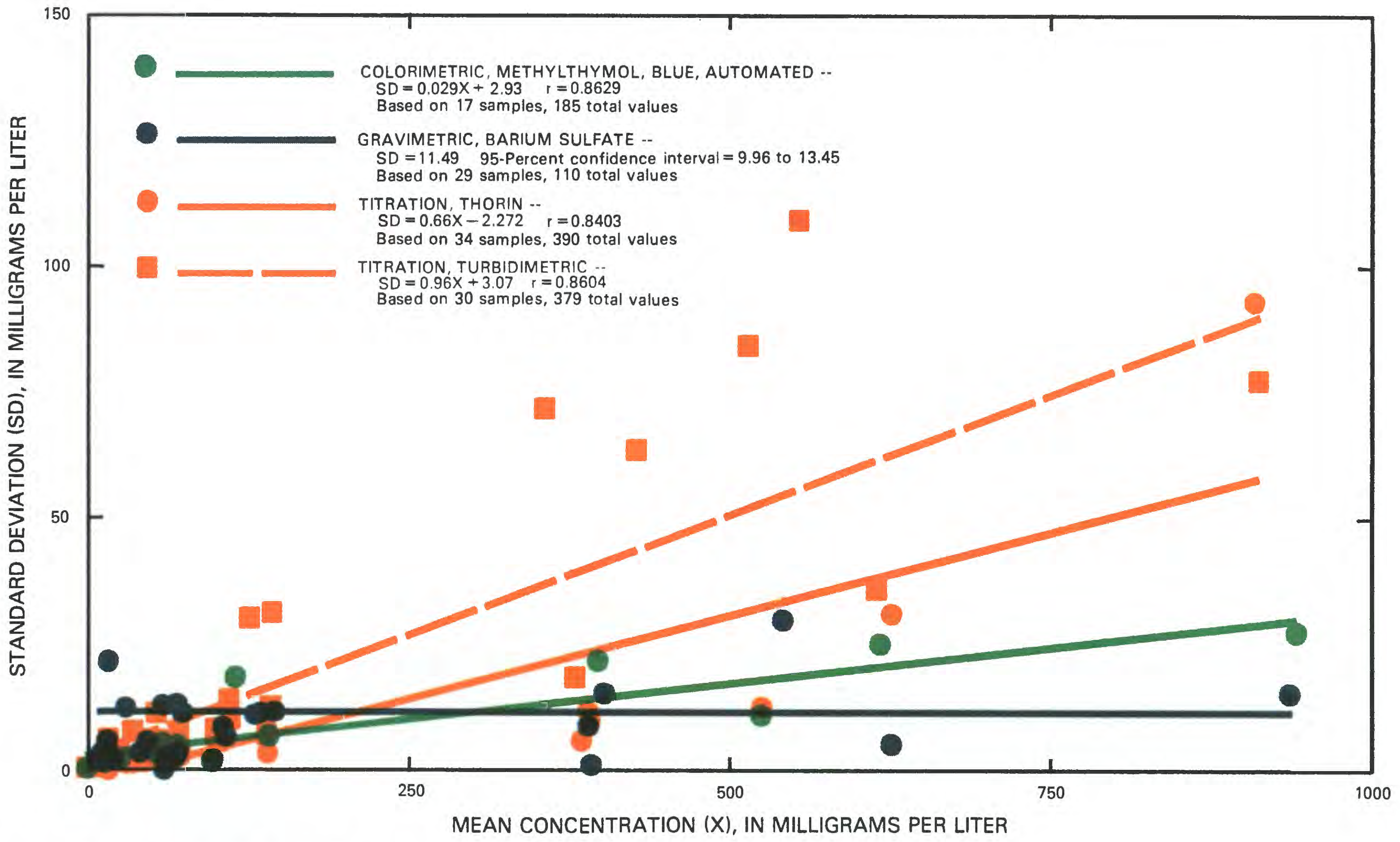

Figure 78. Interlaboratory precision of five methods used to determine sulfate.

THALLIUM

Thallium was not requested to be determined on SRWS until 1978; thus, data are extremely limited. Two methods have been reported (fig. 79), and no significant difference exists between values reported for them.

Precision data are available only for the atomic absorption, graphite-furnace method. They are as follows: ±75 percent for a mean of 3.2 μg/L (4 laboratories), ±38 percent for a mean of 3.4 μg/L (5 laboratories), ±39 percent for a mean of 3.8 μg/L (6 laboratories), and ±20 percent for a mean of 5.0 μg/L (3 laboratories).

References to the methods are given below:

Method	*Reference*
Atomac absorption spectrometry, graphite-furnace	U.S. Environmental Protection Agency, 1979a
Voltammetry, anodic stripping	—

VANADIUM

Five methods were used to determine vanadium (fig. 80). No significant difference exists between the concentrations reported by the methods. This is also true when data are limited to just the AAS, graphite-furnace; colorimetric, catalytic oxidation; and emission, ICP methods, and even when the data are further limited by comparing just these three methods for SRWS distributed in 1980, 1981, and 1982 when the majority of data were obtained.

Precision data are quite limited (fig. 81), but no significant difference is indicated between the precisions of the methods.

References to the methods are given below:

Method	*Reference*
Atomic absorption spectrometry, graphite-furnace	U.S. Environmental Protection Agency, 1979a
Atomic emission spectrometry, inductively coupled plasma	Fishman and Bradford, 1982
Colorimetric, catalytic oxidation	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979
Colorimetric, catalytic oxidation, automated	Skougstad and others, 1979
Neutron activation	—

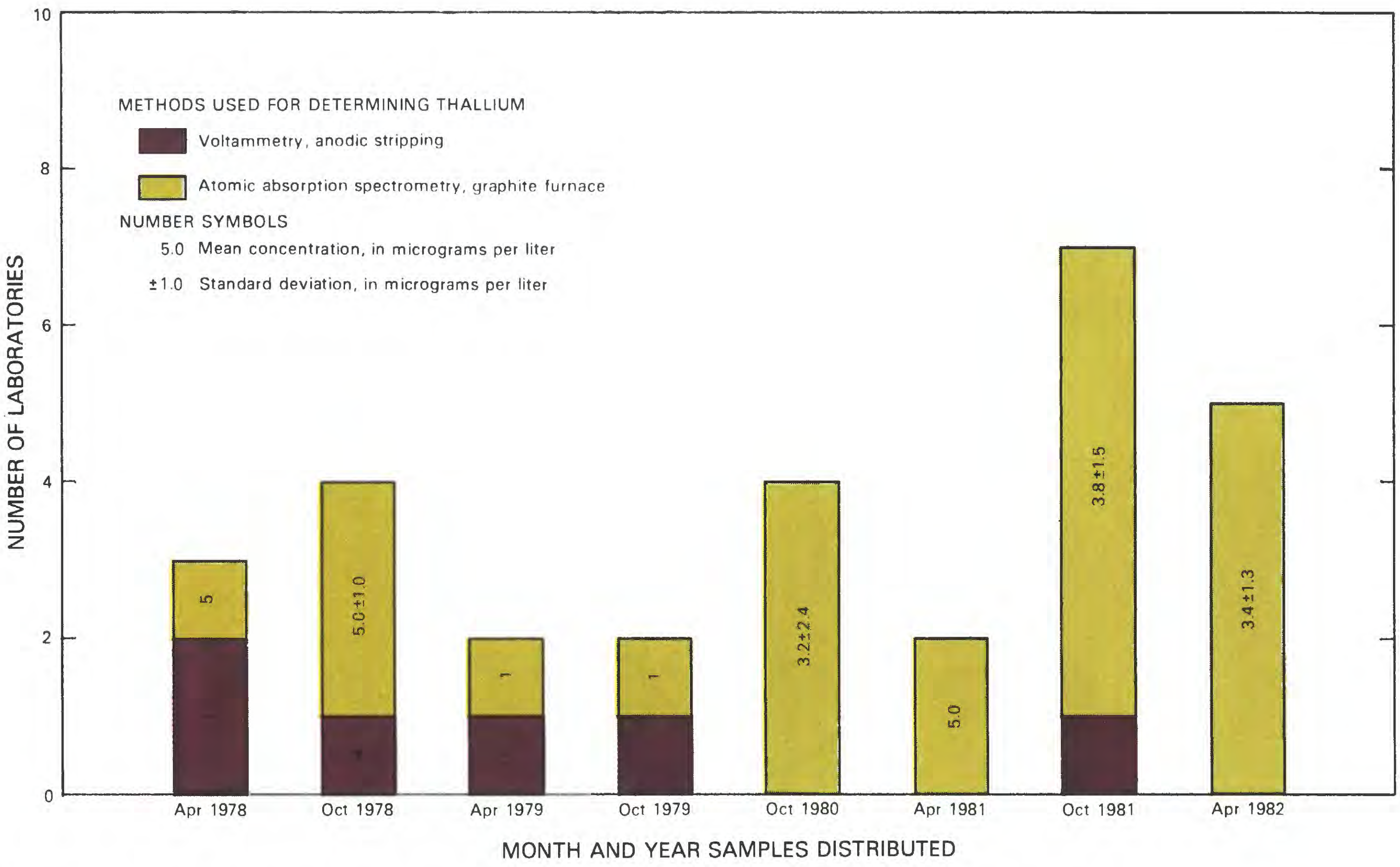

Figure 79. Mean concentrations and standard deviations for thallium in eight Standard Reference Water Samples.

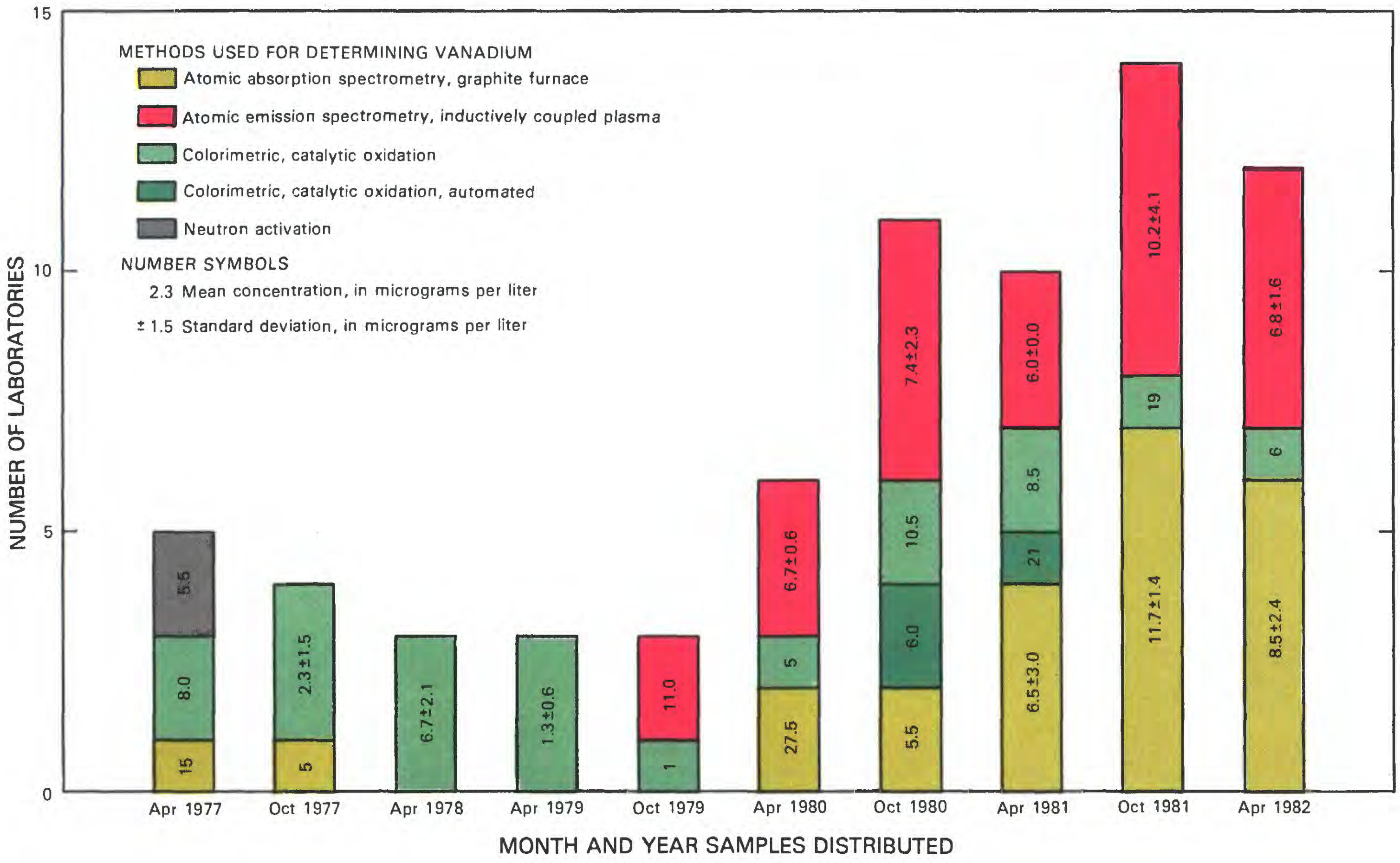

Figure 80. Mean concentrations and standard deviations for vanadium in 10 Standard Reference Water Samples.

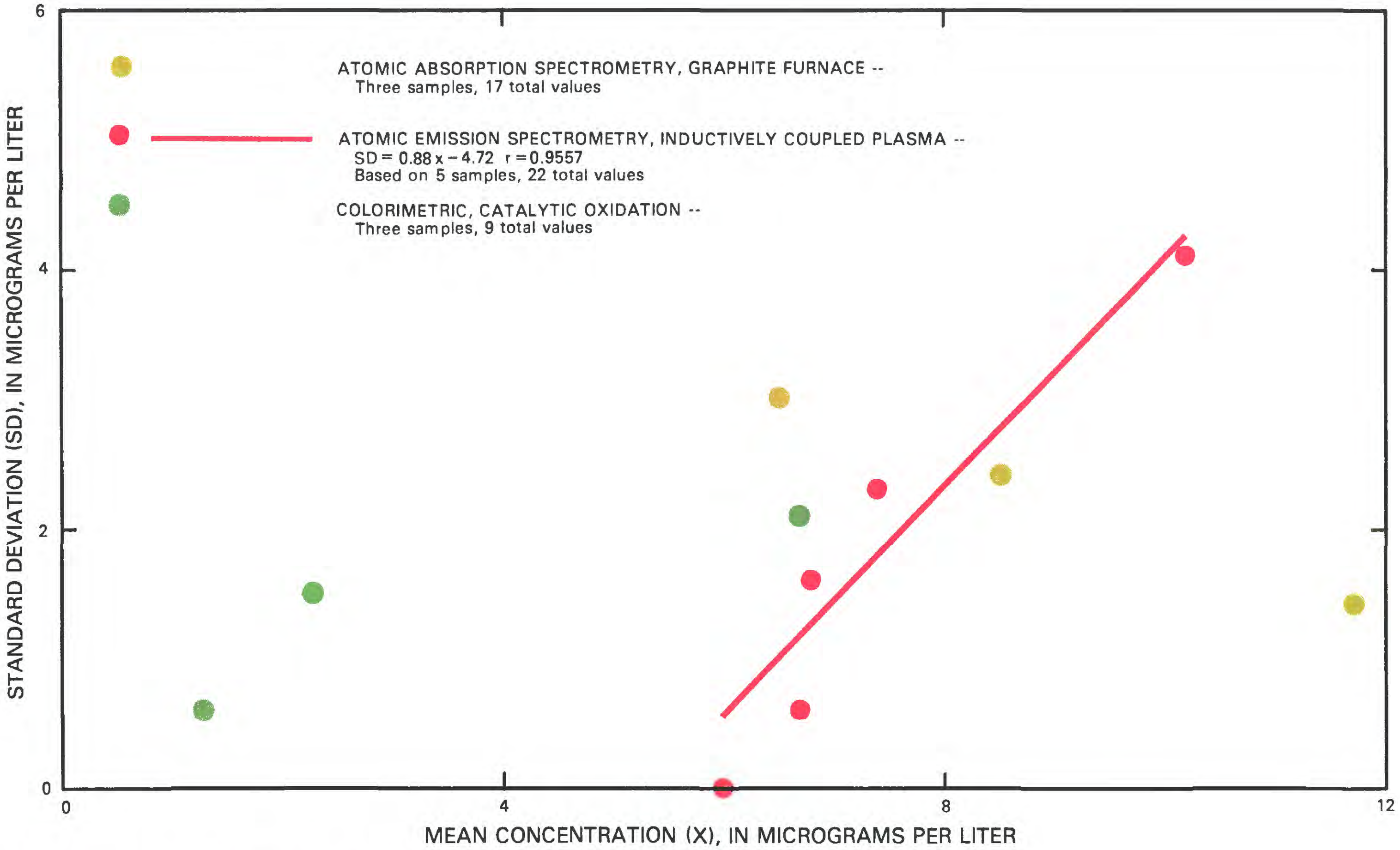

Figure 81. Interlaboratory precision of three methods used to determine vanadium.

ZINC

Almost all data are from the AAS, direct method; however, seven methods were used to determine zinc (fig. 82). Although no significant difference exists between the concentrations reported by the different methods, this conclusion could change if additional data from the methods other than AAS, direct were available. A comparison between the concentrations reported for AAS, direct; emission, ICP; and emission, DCP methods for SRWS distributed in or after October 1979, indicates no significant difference. Similarly, a comparison between the concentrations reported for just the AAS, direct and emission, ICP methods for SRWS distributed in or after October 1979, indicates no significant difference.

The precision model for the AAS, direct method was strongly influenced by data from analysis of a single SRWS in which the calculated mean concentration of 231 μg/L had a relative standard deviation of 109 percent (compared to a mean concentration of 236 μg/L and relative standard deviation of 7 percent for a different SRWS). Eliminating the influence of this single value changes the model from the 48.1 μg/L reported on figure 83 to a regression model $SD=0.070x+6.51$, $r=0.7967$.

In any case, no significant difference is found between the precisions for the AAS, direct and emission, ICP methods. The single standard deviation figure reported for the colorimetric, dithizone method also is not significantly different from the other two methods.

References to the methods are given below:

Method	*Reference*
Atomic absorption spectrometry, direct	American Public Health Association and others, 1980 American Society for Testing and Materials, 1983 Skougstad and others, 1979 U.S. Environmental Protection Agency, 1979a
Atomic emission spectrometry, arc-spark	Barnett and Mallory, 1971
Atomic emission spectrometry, direct-current plasma	American Society for Testing and Materials, 1983
Atomic emission spectrometry, inductively coupled plasma	Fishman and Bradford, 1982 U.S. Environmental Protection Agency, 1979b
Colorimetric, dithizone	American Public Health Association and others, 1980 Rainwater and Thatcher, 1960
Neutron activation	—
Voltammetry anodic stripping	—

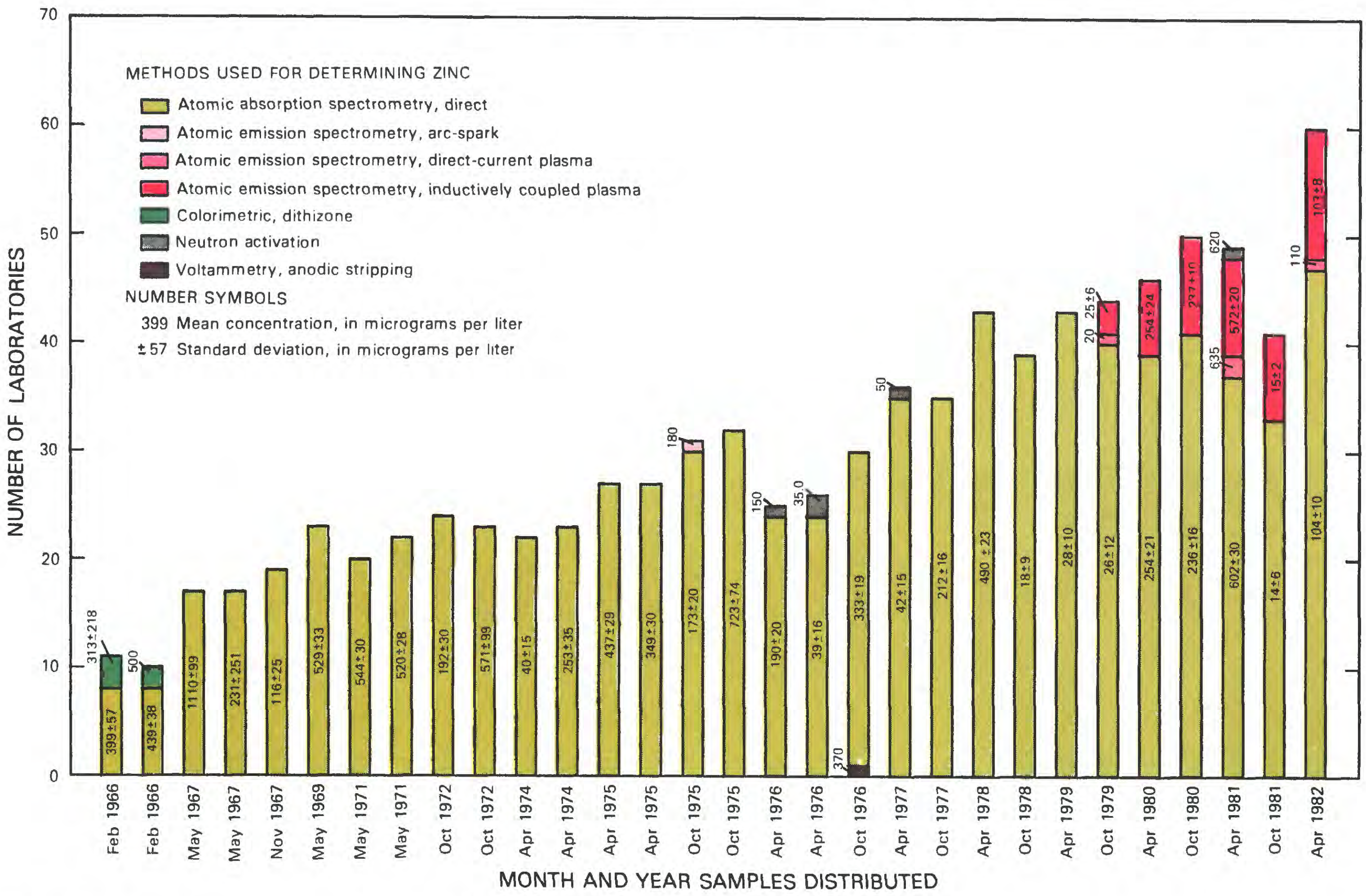

Figure 82. Mean concentrations and standard deviations for zinc in 30 Standard Reference Water Samples.

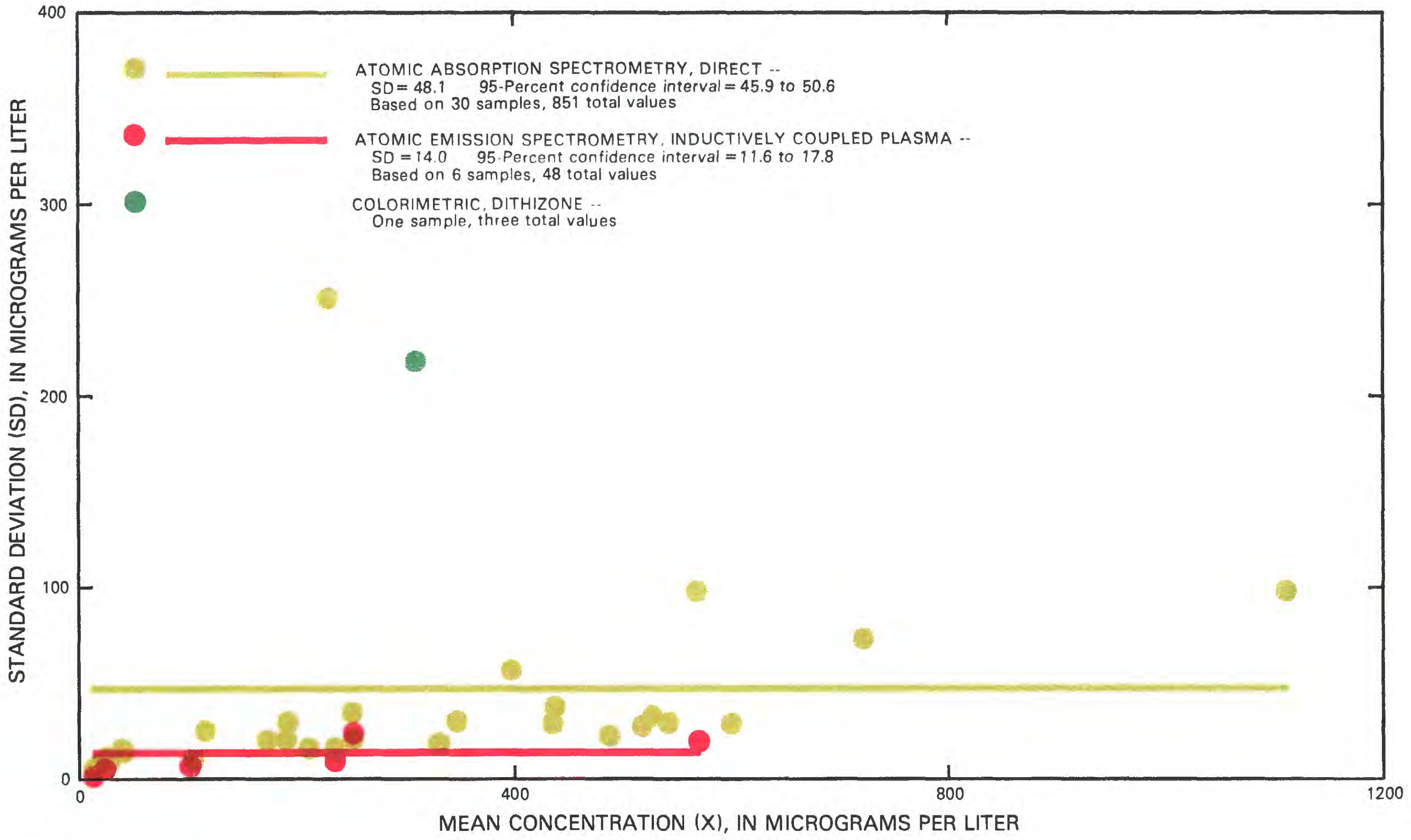

Figure 83. Interlaboratory precision of three methods used to determine zinc.

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