Designation: E 876 – 89 (Reapproved 1994)ε1

Standard Practice for Use of Statistics in the Evaluation of Spectrometric Data[1]

This standard is issued under the fixed designation E 876; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

ε[1] NOTE—Section 7 was added editorially in January 1995.

1. Scope

1.1 This practice provides for the statistical evaluation of data obtained from spectrometrical methods of analysis. Included are definitions used in statistics, methods to determine variance and standard deviation of data, and calculations for (*1*) estimate of variance and pooling estimates of variance, (*2*) standard deviation and relative standard deviation, (*3*) testing for outliers, (*4*) testing for bias, (*5*) establishing limits of detection, and (*6*) testing for drift.

2. Referenced Documents

2.1 *ASTM Standards:*

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials[2]

E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods[3]

E 178 Practice for Dealing with Outlying Observations[3]

E 305 Practice for Establishing and Controlling Spectrochemical Analytical Curves[2]

E 456 Terminology Relating to Quality and Statistics[3]

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this practice, refer to Terminologies E 135 and E 456.

3.1.2 All quantities computed from limited data are defined as estimates of the parameters that are properties of the system (population) from which the data were obtained.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *average measurement ($\bar{x}$)*—the arithmetic mean obtained by dividing the sum of the measurements by the number of measurements. It is an estimate of μ, the value of the population that the average would become if the number of measurements were infinite. Either $\bar{x}$ or μ may include a systematic error if there is a bias in the measurement.

3.2.2 *bias*—a systematic displacement of all or most determinations from the assumed true value. An acceptable bias should be agreed upon prior to testing a method. *Accuracy*, often used to qualify a method, is a measurement which includes both imprecision and bias.

NOTE 1—*Precision* and *bias* are discussed in detail in Practice E 177. In analytical methods, *precision* refers to the distribution of repeat determinations about the average. All analyses are presumed to have been made under the same set of conditions. Standard deviation provides a measure of this distribution.

NOTE 2—An evaluation of a method will be sample-dependent. Multiple samples should be tested for homogeneity since even certified reference materials may exhibit significantly different degrees of inhomogeneity. A measure of both sample and method precision may be made by replicating determinations on specific portions of the sample specimens.

3.2.3 *confidence to be placed on the estimate of mu (μ)*—the average, $\bar{x}$, is expected to be close toμ and should be very close if the number of determinations is large, no significant bias exists and the standard deviation, *s*, is small. The degree of closeness is expressed as a probability (*confidence level*) that μ is in a specified interval (*confidence interval*) centered at $\bar{x}$. With a certain probability, limits are placed on the quantity $\bar{x}$ which may include the unknown quantity μ. A probability level, *p* %, can be selected so that μ will be within the limits placed about $\bar{x}$. See 3.2.1

3.2.4 *degrees of freedom (df)*—the number of contributors to the deviations of a measurement. Since a deviation can be implied only when there are at least two members of a group, the degrees of freedom of a set of measurements is generally one less than the number of measurements. It is the sample size less the number of parameters estimated. If the group is a listing of a series of differences of measurements or a series of determinations of variance, the degrees of freedom is the number of these differences or the total of the degrees of freedom of each series of determinations.

3.2.5 *detection limit*—paraphrasing the definition in Terminology E 135, it is the lowest estimated concentration that permits a confident decision that an element is present. The actual concentration being measured falls within a confidence interval that encompasses the estimated concentration. The lowest estimate has a confidence interval that reaches to zero concentration, but not below. It cannot be assumed that the estimated concentration is an actual concentration. Neither can it be assumed that an actual concentration that equals the

[1] This practice is under the jurisdiction of ASTM Committee E-1 on Analytical Chemistry for Metals, Ores and Related Materials and is the direct responsibility of Subcommittee E01.22 on Statistics and Quality Control.

Current edition approved Nov. 20, 1989. Published January 1990. Originally published as E 876 – 82. Last previous edition E 876 – 89.

[2] *Annual Book of ASTM Standards*, Vol 03.05.

[3] *Annual Book of ASTM Standards*, Vol 14.02.

detection limit will always give a positive detection. The definition in Terminology E 135 properly characterizes this detection as being a limiting value. See also *determination limit* which follows.

3.2.6 *determination limit*—the estimated low concentration where the range of the encompassing confidence interval bears some specified maximum ratio to that concentration. The ratio would depend upon what is acceptable in a specific application.

3.2.7 *drift*—a gradual, systematic change in measurements (either increasing or decreasing) from start to completion of a set of replicate determinations of the same material.

3.2.8 *estimate of standard deviation (s)*—the square root of the estimate of variance. It is a measure of the variability of a set of values representing the whole population. It is an estimate of σ, the actual standard deviation of an infinite number of measurements. With normal distribution, 68 % of the values in a population will fall within ±σ of the true value, μ; 95 % within ±2 σ of μ; and 99.7 % within ±3 σ of μ.

3.2.9 *estimate of variance (s^2)*—a measure of precision of a measurement based on summing the squares of the deviations of individual determinations from the average and dividing by the degrees of freedom.

3.2.10 *outlier*—a measurement that, for a specific degree of confidence, is not part of the population.

3.2.11 *pooled estimate of variance (s_p^2)*—the combined estimate of variance calculated from two or more estimates under the same or similar conditions. Pooling estimates increases the degrees of freedom and improves the quality of the estimate if the variance is approximately the same for each measurement.

NOTE 3—If the concentration level varies considerably within the pooled data, the pooled variance may be inaccurate. It may be possible in such cases, however, to determine a valid estimate by pooling relative standard deviations.

3.2.12 *precision*—the agreement among repeat measurements, usually expressed as either repeatability or reproducibility as defined in Terminology E 456 (see Note 1 and Note 2).

3.2.13 *range (w)*—the difference between the highest and lowest measurements for a series of values obtained under identical conditions. Range is useful for estimating standard deviation and for determining if certain values are outliers.

3.2.14 *relative standard deviation (RSD)*—the standard deviation as a percentage of the average analysis or reading. By providing a means of expressing the precision in relative rather than absolute terms, it may serve to show a more consistent measure of precision for widely different values of $\bar{x}$.

3.2.15 *standard error*—a term sometimes used synonymously with standard deviation but which will be used here to measure how consistently the accepted true concentrations of a series of reference materials compare to the apparent concentrations determined from a calibration. It is an estimate that is similar to standard deviation except for the degrees of freedom used. When the measurement is used to define the effectiveness of the calibration established by these reference materials, the degrees of freedom is the number of data points minus the number of constants in the calibration (the sample size less the number of parameters estimated). If correction is made for spectral interference, the number of constants used in the correction should be counted as being calibration constants. This would be true whether correction was made to readings or to final concentrations. When the measurement is made with new data and applied to a previously determined calibration, the degrees of freedom is the number of references used to make the test. In either case, the significance of the measurement is limited to the range of concentration in the reference materials and implies that concentrations will be fairly well spread within that range.

4. Significance and Use

4.1 The data obtained in spectrometrical analyses may be evaluated as statistical measurements. Use of the various determinations of precision which follow permits a consistent basis for comparing methods of analysis or for monitoring their performance.

4.2 Some explanations are included to clarify the function of the statistical calculations being made.

4.3 Examples of all calculations are given in the appendixes.

5. Calculation

5.1 *Average ($\bar{x}$)*:

$$\bar{x} = \Sigma x/n \tag{1}$$

where:
Σx = the sum of all measurements, and
n = the number of measurements.

NOTE 4—Where all items of a category are included in a summation, the simple summation symbol Σ will be used. However, the strict mathematical statement of Eq 1 is:

$$\bar{x} = \sum_{i=1}^{n} (x_i)/n$$

where $x_1, x_2, \ldots x_n$ is the population of all n determinations which were made. Since no other constrictions are being made on the summation, the simpler statement of Eq 1 clearly shows the required operation.

5.2 *Variance (s^2)*:

5.2.1 Following directly from the definition of 3.2.9 (see Note 4 and Note 5):

$$s^2 = \Sigma(x_i - \bar{x})^2/(n - 1) \tag{2}$$

where:
x_i = an individual determination, and
n = the number of determinations.

5.2.2 An alternative determination that can be readily handled with a calculator without first determining $\bar{x}$ is (see Note 4):

$$s^2 = [\Sigma(x^2) - (\Sigma x)^2/n]/(n - 1) \tag{3}$$

NOTE 5—To prevent significant errors in calculating s^2 do not round the sum of the squares of differences, $\Sigma(x_i - \bar{x})^2$ in Eq 2, nor the sum of the squares of the measurement, $\Sigma(x^2)$, and the square of the sum, $(\Sigma x)^2$, of Eq 3. Although these equations are algebraically identical, they may give slightly different results with large numbers or large summations on a computer because of greater round off errors from using Eq 3 instead of Eq 2.

NOTE 6—The numerators of Eq 2 and Eq 3 are often referred to as the "sum of squares," meaning the sum of the squares of deviation. Using Eq 3, its effectiveness in being a measure of the degree of deviation of a series of values from each other can be seen by considering some simple lists. For example, 2, 3, 4 totals up to 9 for an average of 3. Summing the squares of the three values yields 4 + 9 + 16 = 29. The square of the sum divided by the number of values is $9^2/3 = 81/3 = 27$. The sum of squares becomes 29 − 27 = 2. If the list were 1, 3, 5, the sum would still be 9 and the term $(\Sigma x)^2/n$ would remain as 27. The summing of the squares of the three values, however, would yield 1 + 9 + 25 = 35, and the sum of squares would now become 35 − 27 = 8, giving a quantitative statement as to how much more deviation there is in the second set than the first. The sum of squares is insensitive to the level of the readings. Thus, if the list were 3, 4, 5, the summing would yield $9 + 16 + 25 - 12^2/3 = 50 - 48 = 2$, resulting in the same difference as the first set as it should since the deviations are the same. If the list were 3, 3, 3, the $\Sigma(x^2)$ term would become 27 and the sum of squares would properly be zero since the $(\Sigma x)^2/n$ would also be 27 and the list shows no deviation.

5.2.3 *Estimate from Duplicate Determinations*—The difference between duplicate determinations can be used to estimate variance from $s^2 = \Delta^2/2$ where Δ is the difference. It is a special case of Eq 3, for then, if the two measurements are x_1 and x_2:

$$s^2 = [x_1^2 + x_2^2 - (x_1 + x_2)^2/2]/(2 - 1) \quad (4)$$

$$= [2(x_1^2 + x_2^2) - (x_1^2 + 2x_1x_2 + x_2^2)]/2$$

$$= \tfrac{1}{2}(x_1^2 - 2x_1x_2 + x_2^2) = \tfrac{1}{2}(x_1 - x_2)^2.$$

When there are K duplicates, the pooling of the individual estimates, as in 5.2.4, becomes (see Note 4):

$$s^2 = \Sigma\Delta^2/2K \quad (5)$$

If many duplicates are used, the degrees of freedom increases and the quality of the estimate of s^2 improves.

NOTE 7—The estimate from duplicates is particularly useful in production laboratories where routinely analyzed samples can be analyzed a second time to obtain a measure of precision under practical conditions.

5.2.4 *Pooled Estimate of Variance*—Where there is more than one set of similar repeat determinations, an improved overall estimate of variance may be made by pooling the individual estimates. Weight each individual variance, s_i^2, by its degrees of freedom, sum the weighted variances, and divide by the total degrees of freedom:

$$s_p^2 = [(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2 + \ldots + (n_k - 1)s_k^2]/[(n_1 - 1) + (n_2 - 1) + \ldots + (n_k - 1)] \quad (6)$$

where:

n_i = the number of measurements in each set, and therefore
$(n_i - 1)$ = each degrees of freedom, and
k = the number of sets.

5.2.4.1 In the special case of Eq 4, all of the $(n_i - 1)$ values are one, allowing for the summation of the $\Delta^2/2$ values with no weighting. If individual variances were not determined previously, the pooled estimate of variance can take the following form (see Note 4):

$$s_p^2 = \{\Sigma(x_i^2) - [(\Sigma x_1)^2/n_1 + (\Sigma x_2)^2/n_2 + \ldots + (\Sigma x_k)^2/n_k]\}/(N - k) \quad (7)$$

where:

x_i represents all readings, and
N = the total number of readings.

NOTE 8—Pooling two or more estimates of variance is valid only if each set of analyses was obtained under similar or identical conditions with samples of similar composition and history. The pooling is valid only if variabilities are statistically the same.

5.3 *Standard Deviation* (*s*)—The estimate of standard deviation follows directly from variance as:

$$s = \sqrt{s^2} \quad (8)$$

5.3.1 A close estimate of s can be determined from the value of range, w, as defined in 3.2.13:

$$s_r = w/\sqrt{n'} = (x_h - x_l)/\sqrt{n'} \quad (9)$$

where:

x_h = the highest measurement in a set,
x_l = the lowest measurement in a set, and
n' = number of measurements, limited from 4 through 12.

Reliable estimates from range by Eq 8 can be made only for sets of measurements from four through twelve. If extended beyond twelve measurements, the estimate will be low.

5.3.2 Repeat measurements, even when made on different days, might be biased because the second and subsequent values are expected to agree with the initial value. In cooperative analyses, a laboratory might make extra determinations and report only those that show good agreement. To overcome the possibility of such prejudiced results, an estimate of standard deviation may be calculated from single determinations made on pairs of samples having similar composition in a number of different laboratories or by a number of different analysts. For a single pair, determine the differences in measurement and pool as a special set (see Note 4):

$$s_d = \sqrt{[\Sigma(D^2) - (\Sigma D)^2/T]/2(T - 1)} \quad (10)$$

where:

D = difference between values reported, and
T = number of laboratories or analysts.

5.4 *Relative Standard Deviation* (RSD):

$$RSD = 100s/\bar{x} \quad (11)$$

where:

s = standard deviation estimate, and
$\bar{x}$ = average.

5.4.1 A pooling of relative standard deviation can be done in the manner of Eq 5 after squaring the RSD values. The precaution of Note 8 applies with the exception that the concentration of the element being measured may vary, but only to the extent that there is no pattern of RSD varying with concentration. For example, low concentrations might show higher RSD values than high concentrations, making it inappropriate to pool RSD values over such a wide range of concentration. Using ν to represent RSD, the pooled estimate would be:

$$\nu = \sqrt{\frac{(n_1 - 1)\nu_1^2 + (n_2 - 1)\nu_2^2 + \ldots + (n_k - 1)\nu_k^2}{(n_1 - 1) + (n_2 - 1) + \ldots + (n_k - 1)}} \quad (12)$$

5.5 *Standard Error*—Determine from the differences between the assumed true concentrations of reference materials and the concentrations calculated from a calibration using (see Note 4):

$$SE = \sqrt{\Sigma(c_d - c_t)^2/f} \quad (13)$$

where:

c_d = a concentration determined from a calibration,
c_t = an accepted true concentration of the same material, and
f = the degrees of freedom in the observations.

If SE is calculated to determine how well the reference materials fit the curve they have defined, f is the number of observations minus the number of constants in the calibration curve. If SE is calculated with an independent set of reference materials, f equals the number of observations.

5.6 *Confidence Interval*—As discussed in 3.2.3, limits may be set by adding and subtracting from $\bar{x}$ the quantity $k\sigma\sqrt{n}$ for $\bar{x} - k\sigma/\sqrt{n} \leq \mu \leq \bar{x} + k\sigma/\sqrt{n}$ where the value of k depends upon the confidence level desired. Specifically, for a 95 % confidence level, $k = 1.960$; for 99 %, $k = 2.576$; and for 90 %, $k = 1.645$. These are the "*t*" values which appear in Table 1 for infinite degrees of freedom which is used when the variability is not estimated but known.

5.6.1 In practice, the estimate, s, is known rather than σ. To reflect the uncertainty of substituting s for σ, a larger factor is used to determine the likely interval straddling μ. The practical limit is then calculated by using $ts/\sqrt{n}$ for $k\sigma/\sqrt{n}$ permitting the statement of confidence interval as:

$$\bar{x} - ts/\sqrt{n} \leq \mu \leq \bar{x} + ts/\sqrt{n} \quad (14)$$

TABLE 1 Student's *t*-Table[A]

Degrees of Freedom	Probability Level[B]		
	0.10	0.05	0.01
1	6.314	12.706	63.657
2	2.920	4.303	9.925
3	2.353	3.182	5.841
4	2.132	2.776	4.604
5	2.015	2.571	4.032
6	1.943	2.447	3.707
7	1.895	2.365	3.499
8	1.860	2.306	3.355
9	1.833	2.262	3.250
10	1.812	2.228	3.169
12	1.782	2.179	3.055
14	1.761	2.145	2.977
16	1.746	2.120	2.921
18	1.734	2.101	2.878
20	1.725	2.086	2.845
25	1.708	2.060	2.787
30	1.696	2.042	2.750
∞	1.6448	1.9600	2.5758

[A] Table available in any standard publication of statistical tables, usually entitled the *t*-Test for Significance or Distribution of *t* (Two-Tailed Test). Credit usually given to Fisher, R. A., *Statistical Methods for Research Workers*, published by Oliver and Boyd, Edinburgh, Scotland, 1925–1950.

[B] Probability, p, stated decimally, that values will exceed a mean by the stated "t" factor times the standard deviation which was estimated at the listed degrees of freedom. For the probability, or confidence level, that a measurement will not exceed this quantity, use $(1 - p)$ 100. Thus, for a value for p of 0.05, the confidence level is (1 − 0.05) 100 = 95 %. The table can be converted to a One-tail Test by dividing the probability level by 2, such as is required for determining detection as described in 6.2.2.

where the multiplier, t, is taken from a Student's *t*-table, an extract of which is shown in Table 1. The square root of n takes into account that the limits apply to the average of n determinations. The "*t*" values have been computed on the assumption that the errors follow the normal error distribution curve and that the measurements are independent.

5.6.2 Eq 13 can be restated as $\bar{x} - \mu \leq ts/\sqrt{n}$ and $\mu - \bar{x} \leq ts/\sqrt{n}$. When the "*t*" values become critical these expressions become equalities, $\bar{x} - \mu = ts/\sqrt{n}$ and $\mu - \bar{x} = ts/\sqrt{n}$, making the critical "*t*" value become:

$$t = |\bar{x} - \mu|\sqrt{n}/s \quad (15)$$

NOTE 9—The t and F tables show the probability, decimally, for measurements not to exceed certain values (see Tables 1-3). These translate directly to the confidence level by subtracting the probability from 1 and multiplying by 100. Thus, if the probability for a measurement not to exceed a certain value is 0.05, the confidence level that the measurement will fall within the range indicated by the critical value is (1 − 0.05)100 = 95 %.

5.7 *Tests for Outliers*—A detailed test for outliers is described in Practice E 178. Some commonly used procedures are given below:

NOTE 10—An apparent outlying value may be merely an extreme example of random variability, in which case it should be retained with other data, or it may be the result of gross deviation from the prescribed analytical procedure, or an error in calculating or recording the analysis. The reason for aberrant values may warrant investigation.

5.7.1 For four or more determinations, estimate the standard deviation and then repeat the calculation with the suspect value eliminated. If the second estimate is smaller by a factor of two or more, the suspect value may be excluded. For this test, it may be particularly useful to use the estimate of s_r by range of Eq 8.

5.7.2 For triplicate determinations, list the values in increasing or decreasing order as R_1, R_2, and R_3, with R_1 being the suspect value. Calculate as follows:

$$\text{Test ratio} = (R_1 - R_2)/(R_1 - R_3), \text{ provided } R_2 \neq R_3 \quad (16)$$

If the test ratio is larger than 0.941, the suspect value may be rejected with a 95 % confidence that it is an outlier. When the readings are not precise enough to show a difference between R_2 and R_3, the test may still be done by making one reading higher by 5 in the next decimal place and the other lower by that amount. For example, if the two readings are 1.23, one can be made 1.235, and the other 1.225.

NOTE 11—The test in 5.7.2 is a special case of the Dixon Criteria. Practice E 178 shows how the Dixon test can be applied to up to 30 observations and lists significant test values for 90 %, 95 %, and 99 % confidence levels.

5.7.3 A more reliable test can be made if there is a good record of the standard deviation or relative standard deviation expected for the level of readings or determinations being made. If pooling was used to make the estimate of s or RSD it should represent an estimation based on a relatively high degrees of freedom, permitting a favorable use of a Student's *t*-Table (see Table 1). Calculate the average reading and use Eq 13 to determine a confidence interval that encompasses that average. If a suspect value does not fit within these limits, exclude it.

TABLE 2 *F* Test for Equality of Variances, 0.05 Probability[A]

Degrees of Freedom Denominator	Degrees of Freedom of Numerator, the Greater Mean Square												
	1	2	3	4	5	6	7	8	10	12	16	20	30
3	10.13	9.55	9.28	9.12	9.01	8.94	8.88	8.84	8.78	8.74	8.69	8.66	8.62
4	7.71	6.94	6.59	6.39	6.26	6.16	6.09	6.04	5.96	5.91	5.84	5.80	5.74
5	6.61	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.74	4.68	4.60	4.56	4.50
6	5.99	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.06	4.00	3.92	3.87	3.81
7	5.59	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.63	3.57	3.49	3.44	3.38
8	5.32	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.34	3.28	3.20	3.15	3.08
10	4.96	4.10	3.71	3.48	3.33	3.22	3.14	3.07	2.97	2.91	2.82	2.77	2.70
12	4.75	3.88	3.49	3.26	3.11	3.00	2.92	2.85	2.76	2.69	2.60	2.54	2.46
14	4.60	3.74	3.34	3.11	2.96	2.85	2.77	2.70	2.60	2.53	2.44	2.39	2.31
16	4.49	3.63	3.24	3.01	2.85	2.74	2.66	2.59	2.49	2.42	2.33	2.28	2.20
20	4.35	3.49	3.10	2.87	2.71	2.60	2.52	2.45	2.35	2.28	2.18	2.12	2.04
25	4.24	3.38	2.99	2.76	2.60	2.49	2.41	2.34	2.24	2.16	2.06	2.00	1.92
30	4.17	3.32	2.92	2.69	2.53	2.42	2.34	2.27	2.16	2.09	1.99	1.93	1.84

[A] Extract of tables for the *F* test which are available in any standard publication of statistical tables. This specific extract is from Snedecor, G. W., and Cochran, W. G., *Statistical Methods*, The Iowa State University Press, Ames, IA, Sixth Edition, 1967. The first column shows the degrees of freedom of the denominator, which would be the lesser of the mean squares being compared.

TABLE 3 *F* Test for Equality of Variances, 0.01 Probability[A]

Degrees of Freedom Denominator	Degrees of Freedom of Numerator, the Greater Mean Square												
	1	2	3	4	5	6	7	8	10	12	16	20	30
3	34.12	30.82	29.46	28.71	28.24	27.91	27.67	27.49	27.23	27.05	26.83	26.69	26.50
4	21.20	18.00	16.69	15.98	15.52	15.21	14.98	14.80	14.54	14.37	14.15	14.02	13.83
5	16.26	13.27	12.06	11.39	10.97	10.67	10.45	10.29	10.05	9.89	9.68	9.55	9.38
6	13.74	10.92	9.78	9.15	8.75	8.47	8.26	8.10	7.87	7.72	7.52	7.39	7.23
7	12.25	9.55	8.45	7.85	7.46	7.19	7.00	6.84	6.62	6.47	6.27	6.15	5.98
8	11.26	8.65	7.59	7.01	6.63	6.37	6.19	6.03	5.82	5.67	5.48	5.36	5.20
10	10.04	7.56	6.55	5.99	5.64	5.39	5.21	5.06	4.85	4.71	4.52	4.41	4.25
12	9.33	6.93	5.95	5.41	5.06	4.82	4.65	4.50	4.30	4.16	3.98	3.86	3.70
14	8.86	6.51	5.56	5.03	4.69	4.46	4.28	4.14	3.94	3.80	3.62	3.51	3.34
16	8.53	6.23	5.29	4.77	4.44	4.20	4.03	3.89	3.69	3.55	3.37	3.25	3.10
20	8.10	5.85	4.94	4.43	4.10	3.87	3.71	3.56	3.37	3.23	3.05	2.94	2.77
25	7.77	5.57	4.68	4.18	3.86	3.63	3.46	3.32	3.13	2.99	2.81	2.70	2.54
30	7.56	5.39	4.51	4.02	3.70	3.47	3.30	3.17	2.98	2.84	2.66	2.55	2.38

[A] Extract of tables for the *F* test which are available in any standard publication of statistical tables. This specific extract is from Snedecor, G. W., and Cochran, W. G., *Statistical Methods*, The Iowa State University Press, Ames, IA, Sixth Edition, 1967. The first column shows the degrees of freedom of the denominator, which would be the lesser of the mean squares being compared.

5.7.4 For duplicate determinations, if the values seem to be far apart and an estimate of standard deviation has already been established, a third value should be obtained if the difference between the two readings is greater than 2.8*s*. Subsequent testing, as in 5.7.2 or 5.7.3, would be appropriate to determine if one reading should be rejected.

6. Applications

6.1 *Testing for Bias*—Bias can be detected in various ways.

6.1.1 *Analysis of Variance*—A series of single measurements on a suite of samples can be subjected to an analysis of variance to determine the precision of the method and to detect bias in different sets of the running of the suite of samples. The sets may be the results determined by different methods, different laboratories, or different analysts. It is required that any one grouping of samples be close in composition. Details on the analysis of variance appear in Snedecor and Cochran.[4]

6.1.1.1 Obtain the differences between actual measurements and the assumed correct values in order to put the values into a common population. Call the differences remainders or "*r*" values. Prepare a table of "*r*" values with samples in lines and sets in columns. Table 4 contains a general example of a tabulation of "*r*" values for *n* samples and *m* sets with summations under each column for Σr, $(\Sigma r)^2$ and $\Sigma(r^2)$ and with the grand totals of these.

6.1.1.2 Set up a table of comparisons of variance as shown in Table 5.

NOTE 12—The sum of squares for within samples could also be obtained by pooling the variances of the individual sets. The $B/n - G^2/mn$ used for the sum of squares between sets is equivalent to using the averages of each set, $\Sigma(\bar{x})^2 - (\Sigma \bar{x})^2/m$, when that sum is multiplied by the number of samples, *n*, to reflect that this measure of deviation is for an average of *n* readings instead of for single readings.

6.1.1.3 Use a table of critical values of *F*, extracts of which appear in Tables 2 and 3, to test the significance of the comparison of s_b^2 and s_w^2 by obtaining the ratio:

$$F = s_b^2/s_w^2 \quad (17)$$

If the calculation for *F* is larger than the value listed for the combination of degrees of freedom values involved, as shown in Table 2 or Table 3, there is evidence that a bias exists between laboratories, methods, or analysts at the confidence level of that table.

[4] Snedecor, G. W., and Cochran, W. G., *Statistical Methods*, The Iowa State University Press, Ames, IA, Sixth Edition, 1967, pp. 258–298.

TABLE 4 General Example of Tabulation of "*r*" Values

Sample	Set	A	B	...	M	Totals	
1		r_{1a}	r_{1b}	...	r_{1m}	...	
2		r_{2a}	r_{2b}	...	r_{2m}	...	
...		...	...	...	...	...	
n		r_{na}	r_{nb}	...	r_{nm}	...	
Σr_{ij}		$\sum_{i=1}^{n} r_{ia}$	$\sum_{i=1}^{n} r_{ib}$	...	$\sum_{i=1}^{n} r_{im}$	$\sum_{j=a}^{m}\sum_{i=1}^{n} r_{ij}$	$= G$ [A]
$(\Sigma r_{ij})^2$		$(\sum_{i=1}^{n} r_{ia})^2$	$(\sum_{i=1}^{n} r_{ib})^2$	...	$(\sum_{i=1}^{n} r_{im})^2$	$\sum_{j=a}^{m}(\sum_{i=1}^{n}) r_{ij}$	$= B$ [A]
$\Sigma(r_{ij})^2$		$\sum_{i=1}^{n}(r_{ia})^2$	$\sum_{i=1}^{n}(r_{ib})^2$	...	$\sum_{i=1}^{n}(r_{im})^2$	$\sum_{j=a}^{m}\sum_{i=1}^{n} r_{ij}$	$= W$ [A]

[A] G = grand total,
B = deviations between sets, and
W = deviations within one laboratory.

TABLE 5 Comparisons of Variance

Source of Variation	Degrees of Freedom	Sum of Squares	Variance	
Total	$mn - 1$	$W - G^2/mn$	s_t^2	
Between sets	$m - 1$	$B/n - G^2/mn$	s_b^2	} = sum of squares/degrees of freedom
Within samples	$m\ (n - 1)$	$W - B/n$	s_w^2	

Note—$W - B/n$ may be obtained by difference of the other two sums of squares.

NOTE 13—In looking at the two *F* tables, it may be noted that a calculated *F* ratio might fail in the 0.05 probability table, equivalent to the 95 % confidence level, and yet pass in the 0.01 probability table, 99 % confidence level (see Note 9). This should not be interpreted that there is a 99 % confidence that there is no bias even though there appears to be a 95 % confidence that bias does exist. The broader acceptance of the 0.01 probability of Table 3 merely means that the range of acceptable values of a normal distribution excludes values greater than about ± 2.6 σ, whereas, the acceptance level of 0.05 excludes greater than only about ±2.0 σ.

6.1.2 *Bias Between Paired Observations*—A series of measurements on a suite of samples can be subjected to a *t*-test to determine if these measurements differ significantly from assumed correct values. Observing sign, obtain the differences between the measured and the assumed values. Calculate the average difference and standard deviation of these differences. Calculate *t* using Eq 14 and compare with a *t* value in Table 1 where the degrees of freedom are the same as those used to determine standard deviation. If the calculated value exceeds the tabulated value, a significant difference exists. This is a two-tailed test. The test will be improved if the standard deviation is pooled from several similar suites of samples.

6.1.3 *Using Standard Error*—Bias can be tested by determining the standard error (see 3.2.15) for the calibration fit and comparing to another standard error obtained with additional reference materials or with some or all of the original reference materials run at a later date. Bias will be detected if the latter error is appreciably larger than the former.

6.1.4 *Using Plotting*—A plotting of determined concentrations against assumed correct concentrations will show a fixed bias if the data points form a 45° line that does not go through the origin of the plot. If the data points form a straight line which is not at 45°, it will show a bias that changes as the concentration changes.

6.2 *Detection Limit*—Determination that an element is present requires observing a spectral response that is significantly greater than spectral background. Multiple analyses of several specimens containing residual amounts of the elements and only insignificant amounts of any interfering elements are needed to establish this limit. These elements should be homogeneously distributed in each specimen. If possible, primary reference materials and high-purity materials, such as zone-refined metals, shall be used. Analyzed samples that appear to be consistent may be used. If the elements are not homogeneously distributed, the determined detection limit will be higher than for homogeneous specimens. This higher detection limit, however, will have to be accepted if practical samples are not expected to be any more homogeneous.

6.2.1 Calculate the averages of the readings of spectral response for each specimen and obtain an overall estimate of standard deviation from a pooling of estimates of variance.

NOTE 14—Use of the precision measurement of background should generally be avoided since the measurement of an actual element signal may show a greater random scatter than the background itself. On the other hand, in photographic photometry, the relative intensity of background may not be able to be measured as precisely as a discrete spectral line image. Background may be used only if it appears to have a standard deviation that is consistent with that shown by low concentrations.

6.2.2 The confidence interval discussed in 5.6 considers the probability that μ falls within a range of measurements centered about the average, $\bar{x}$. For detection, concern is that, at a certain confidence level, zero concentration is not in this range of measurement. The probability that μ may be higher than $\bar{x}$ does not deny that an element has been detected. Only the probability that μ may be lower than $\bar{x}$ is significant in establishing detection. Therefore, use Table 1 to determine the multiplier, *t*, applicable for an acceptable probability and the overall degrees of freedom used for obtaining the estimate of standard deviation, but divide the table probability levels by 2. For example, to calculate detection with a 95 % confidence, use the column headed with the probability of 0.10.

NOTE 15—The detections which are defined here are in terms of the apparent concentrations of a calibration assuming no error in the calibration nor in the standardization procedure used to maintain it. Practice

E 305 discusses the confidence limits of the slope and intercept of a calibration.

6.2.2.1 If the data are plotted as a straight line of concentration on the ordinate and relative readings or intensity ratios on the abscissa of the graph, the slope of the line will directly relate to detection from:

$$c = mts/\sqrt{n} \quad (18)$$

where:
- m = slope of curve in terms of concentration (percent or parts per million) division per reading division,
- t = the multiplier determined in 6.2.2,
- s = the overall estimate of standard deviation, and
- n = the number of replicates.

NOTE 16—Readings from samples having much more than detectable concentrations can be included in the establishment of the curve only if they are consistent with the linear relationship. Practice E 305 deals with establishing linear analytical curves.

6.2.2.2 If readings are on a logarithmic basis, and a curve has been established for low concentrations that is linear in terms of log concentration and log readings, a detection limit can be determined from how much a concentration changes for a significant change in reading. To realize whatever detection is achievable, limited only by the precision of reading, background correction would likely be necessary. A general statement of such a concentration curve, for common base logs, might be:

$$c = a(10^{kR} - B) \quad (19)$$

where:
- a = calibration constant,
- k = constant which would be other than 1.0 if the function of log reading did not make an ideal 45° calibration line with log concentration,
- R = log reading, and
- B = correction for background. (Background correction is discussed in Practice E 305.)

Determine the concentration for the lowest reading observed in the system and repeat the calculation after adding the product "$ts/\sqrt{n}$" to this reading. The detection will be the difference in concentration calculations, stating it generally as (see Note 15):

$$\Delta c = a[10^{k(R + ts/\sqrt{n})} - 10^{kR}] \quad (20)$$

NOTE 17—Nonlinear relationships may be used if the curvature is not severe. An acceptable estimate of detection will be made, however, only if the low reading is close to the limit of detection. As was done for Eq 19, the detection will be the difference between the calculation of the concentration for the low reading and the calculation when the low reading is increased by the product $ts/\sqrt{n}$.

6.3 *Determination Limit*—Practical spectrometric calibration equations are usually stated with the observed measurement as the independent variable, $\bar{x}$, and the concentration as the dependent variable, $\hat{y}$. The confidence interval shown in Eq 13 can be restated in terms of concentration as:

$$\hat{y} - ts_c/\sqrt{n} \leq c \leq \hat{y} + ts_c/\sqrt{n} \quad (21)$$

where:
- $\hat{y}$ = the calculated, apparent concentration,
- t = a multiplier from a Student's t-table,
- s_c = the standard deviation in terms of concentration,
- n = the number of replicates burned, and
- c = the average population concentration.

6.3.1 A standard deviation determined for observations (readings) may be converted to concentration terms by $s_c = ms$, where m is the slope of the calibration curve in the area of interest. When the left hand inequality of Eq 20 is subtracted from the right hand inequality, the difference, $2ts_c/\sqrt{n}$, is the range of the interval. The ratio of this range to the apparent concentration is:

$$\rho = 2ts_c/\sqrt{n}\hat{y} \quad (22)$$

Therefore the limit of determination is (see Note 15):

$$\hat{y} = 2ts_c/\sqrt{n}\rho \quad (23)$$

If the analyst wishes to work at a level where the ratio of range to apparent concentration is less than 1 (one), the determination limit becomes higher. Thus if the specified ratio, ρ, is set at 0.5, the determination limit becomes $4ts_c/\sqrt{n}$.

6.4 *Test for Drift*—The test for drift is designed to determine statistically if analyses from an instrument or procedure are changing systematically in relation to time in either an increasing or decreasing manner. The concern is that repeat determinations may not be distributed normally about the mean value. One of the following three approaches can be taken.

6.4.1 In calibrating a spectrometric method it is advisable to bracket a series of excitations by running a particular specimen or group of specimens before and after running the series. The same precaution might be taken with a set of critical analyses. Assuming that an estimate of standard deviation has been made for the method or can be made by pooling the precision of the measurements just run, there would be evidence of drift at somewhat less than a 95 % confidence level if the change in average readings was:

$$\Delta = |\bar{x}_1 - \bar{x}_2| > 2s\sqrt{(n_1 + n_2)/n_1 n_2}, \text{ or } (a) \quad (24)$$

$$|\Delta| > 2s\sqrt{2/n} \quad \text{if} \quad n_1 = n_2 \quad (b)$$

where:
- s = established or pooled estimate of standard deviation,
- n_1 = number of multiplets in first average, and
- n_2 = number of multiplets in second average.

NOTE 18—In multiplet excitations on a single specimen, the effective standard deviation of the average is $\sigma_n = \sigma/\sqrt{n}$ where n is the number of multiplets. When two sets of readings are taken on the same specimen, it is expected that their averages will not deviate by more than the root mean square of their standard deviations: $\Delta = |x_1 - x_2| \leq \sqrt{\sigma_1^2 + \sigma_2^2}$. If the two σ values are the same, as would be true if the same number of multiplets was run for each average, then $|\Delta| \leq \sigma\sqrt{2}$. For different levels of multiplets in the two averages, $|\Delta| \leq \sqrt{\sigma^2/n_1 + \sigma^2/n_2}$ or $\sigma\sqrt{(n_1 + n_2)/n_1 n_2}$. These are stated at the 68 % confidence level. A more practical criterion would be at the 95 % confidence level with 2σ replacing σ. Furthermore, at some reduction in the 95 % confidence level, the σ should be replaced by s leading to Eq 24(a) and Eq 24(b).

6.4.2 Drift can be detected by making many runs on the same specimen in a short sequence of time. The greater the number of runs, the smaller will be the detectable level of drift.

Frequent excitation, however, may cause overheating. Unless drift from heating is being studied, it would be appropriate to run at least two specimens in an alternate sequence or allow a reasonable cooling period between excitations. To analyze for drift, list each reading in the order taken along with its sequence position, 1, 2, 3,⋯ . Call the readings *y* and the sequence positions *x*, and determine the apparent shift in *y* for changes in *x* by calculating a slope, *m*, from:

$$m = [n\Sigma(xy) - \Sigma x\Sigma y]/[n\Sigma(x^2) - (\Sigma x)^2] \quad (25)$$

which is the formula for slope in a linear regression of *n* pairs of *x* and *y* values. There will be approximately a 95 % confidence level that drift occurred if the slope is:

$$|m| > 2s\sqrt{2}/(n-1) \quad (26)$$

where *n* is the number of readings used to define the slope. If a sequence of twenty readings is taken, drift per time interval as small as 0.2 of the standard deviation can be detected; for ten readings, drifts of 0.5 *s*; and for six readings, drifts of 1.0 *s* can be detected.

TABLE 6 Critical Values of η for Drift Indication

Sample Size	Confidence Level	
	95 %	99 %
4	0.78	0.63
5	0.82	0.54
6	0.89	0.56
7	0.94	0.61
8	0.98	0.66
9	1.02	0.71
10	1.06	0.75
11	1.10	0.79
12	1.13	0.83
15	1.21	0.92
20	1.30	1.04
25	1.37	1.13

6.4.2.1 If a value for *s* was not previously established, it could be estimated from the data at hand. Use of Eq 2 or Eq 3 would be inappropriate since these would be affected by drift. The general approach of Eq 4 is better. Eq 4 can be used with a larger degree of freedom by using each successive difference in the sequence of readings rather than just working with isolated pairs of readings. With readings arranged in chronological order, $x_1, x_2, x_3, \cdots x_n$, a sum of the squares of successive differences can be defined as:

$$\Sigma\Delta_s^2 = \sum_{i=1}^{n-1} (x_{i+1} - x_i)^2 \quad (27)$$

Use of $\Sigma\Delta_s^2$ imposes a small distortion on the degree of freedom because all but the first and last readings are used twice. As compensation, to keep the estimate unbiased, the standard deviation from a sequence can be stated as:

$$s_s = \sqrt{\Sigma\Delta_s^2/2(P - 1/2)} \quad (28)$$

where *P* is the number of pairs.

6.4.3 A method for detecting drift that is insensitive to the apparent standard deviation involves a comparison of a mean successive difference with the standard variance.[5] Using the designation of the squares of successive differences which was used in Eq 25, a variance, δ^2, is defined as:

$$\delta^2 = \Sigma\Delta_s^2/(n-1) \quad (29)$$

where *n* is the number of measurements, and therefore, $(n - 1)$ is the number of differences used in the calculation. For the same set of data, s^2 is calculated as prescribed by Eq 2 or Eq 3 and a ratio, η, determined from:

$$\eta = \delta^2/s^2 \quad (30)$$

Refer to Table 6 which lists critical values for η for both a 95 % probability and a 99 % probability. In either case, if the calculated η is less than the value listed in the table for the number of measurements made, there is evidence of drift at the probability level stated.

7. Keywords

7.1 data; evaluation; laboratory; spectrometric; statistics

[5] Bennett, C. A., "Application of Tests for Randomness," *Industrial and Engineering Chemistry*, Vol 43, No. 9, September 1951, pp. 2063–2067.

APPENDIXES

(Nonmandatory Information)

X1. MEASUREMENT DATA

X1.1 A consistent set of measurements is used to give examples of how to apply the various equations of statistical evaluation. The set which appears in Table X1.1 is a random sampling of measurements fitting a population having $\mu = 50$ and $\sigma = 2$.

TABLE X1.1 Measurement Data

	A	B	C	D
1	49.7	49.5	50.3	47.4
2	51.2	50.9	49.5	47.4
3	52.1	46.0	51.1	52.2
4	51.4	49.8	46.7	52.4
5	53.0	47.2	48.9	48.6

X2. AVERAGE AND VARIANCE

X2.1 Calculations from a Series of Readings

X2.1.1 *Average Measurement*—Arrange the measurement data from Table X1.1 as in Column 1 of Table X2.1. Add the first column to obtain the sum of 995.3. The total number of measurements, *n*, is 20. Calculate average, $\bar{x}$, from Eq 1:

$$\bar{x} = 995.3/20 = 49.76 \quad \text{(X2.1)}$$

Note that the average was taken to one decimal point more than the original data to avoid rounding errors in further calculations. Election was made to round to an even digit since the calculation to three decimal points came to 49.765.

X2.1.2 *Estimate of Variance, First Method*—Using the $\bar{x}$ obtained in X2.1.1, subtract $\bar{x}$ from each reading as done in Column 2 of Table X2.1. Square each difference and list as done in Column 3. Note that the number of decimal points in Column 3 has been increased to four decimal places to fully reflect the two decimal points in the unsquared differences of Column 2. Add Columns 2 and 3 obtaining the sums 0.10 and 80.4660 respectively. If no errors had been made in the differences in Column 2, the sum would be zero or close to zero. The discrepancy in Table X2.1 is due to the fact that 49.76 was used for $\bar{x}$ instead of 49.765. The degrees of freedom are one less than the number of measurements or 20 − 1 = 19. Calculate variance, s^2, from Eq 2:

$$s^2 = 80.4660/19 = 4.2351 \quad \text{(X2.2)}$$

X2.1.3 *Estimate of Variance, Second Method*—Obtain the sum of the readings of Column 1, 995.3 as shown in Table X2.1. Calculate the square of each reading as shown in Column 4 and the sum of these squares, 49611.57. Since the total number of measurements was 20, calculate the variance, s^2, from Eq 3:

$$s^2 = \frac{49611.57 - (995.3)^2/20}{20 - 1} \quad \text{(X2.3)}$$

TABLE X2.1 Summations for Average and Variance

	x_i	$x_i - \bar{X}$	$(x_i - \bar{X})^2$	$(x_i)^2$
	49.7	−0.06	0.0036	2470.09
	51.2	1.44	2.0736	2621.44
	52.1	2.34	5.4756	2714.41
	51.4	1.64	2.6896	2641.96
	53.0	3.24	10.4976	2809.00
	49.5	−0.26	0.0676	2450.25
	50.9	1.14	1.2996	2590.81
	46.0	−3.76	14.1376	2116.00
	49.8	0.04	0.0016	2480.04
	47.2	−2.56	6.5536	2227.84
	50.3	0.54	0.2916	2530.09
	49.5	−0.26	0.0676	2450.25
	51.1	1.34	1.7956	2611.21
	46.7	−3.06	9.3636	2180.89
	48.9	−0.86	0.7396	2391.21
	47.4	−2.36	5.5696	2246.76
	47.4	−2.36	5.5696	2246.76
	52.2	2.44	5.9536	2724.84
	52.4	2.64	6.9696	2745.76
	48.6	−1.16	1.3456	2361.96
Sums	995.3	0.10	80.4660	49611.57

$$= \frac{49611.57 - 990622.09/20}{19}$$

$$= (49611.57 - 49531.1045)/19$$

$$= 80.4655/19 = 4.2350$$

X2.1.4 *Estimate of Variance from Duplicate Determinations*—Take the measurement data of Columns A and B in Table X1.1 as duplicate readings and do the same with Columns C and D to form a series of duplicate readings as shown in Table X2.2. Obtain the differences in the duplicate readings as shown in Column 3 and the squares of these differences as shown in Column 4. Obtain the sum of the squares, 120.15, as shown in Column 4. Calculate the variance, s^2, from Eq 4 using $K = 10$ for the ten pairs of readings:

$$s^2 = 120.15/2(10) = 6.0075 \text{ or } 6.008 \quad \text{(X2.4)}$$

X2.1.5 *Pooled Estimate of Variance*—Rearrange the measurement data from Table X1.1 in an arbitrary way to represent five sets of repeat determinations done with varied multiplicities, as shown in Table X2.3. Treat the data in two different ways: first, as if individual variances had been determined on each set, and then, as if these variances had not been previously determined.

X2.1.5.1 The column headed s_i^2 shows individual calculations of variance as determined by either Eq 2 or Eq 3, followed by the degrees of freedom of $n_i - 1$. Weight each variance by multiplying by the degrees of freedom as shown in the column headed $(n_i - 1)s_i^2$. Obtain the sum of this column, 53.715, and also obtain the sum of the preceding degrees of freedom values, 15. Calculate the pooled estimate of variance, s_p^2, from Eq 5, noting the sums obtained in Table X2.3 are the numerator and denominator, respectively, of Eq 5:

$$s_p^2 = 53.715/15 = 3.581 \quad \text{(X2.5)}$$

X2.1.5.2 If individual variances were not determined previously, obtain the sums of readings as shown in the column headed Σx_i in Table X2.3. Square these sums in the next column headed $(\Sigma x_i)^2$ and show total number of readings in the column headed *n*. Obtain the sum of the *n* column, 20, which is *N*, the total of individual measurements. Divide each $(\Sigma x_i)^2$ value by *n* to obtain the next column and obtain its sum, 49557.854 as shown. Make a final column of the sums of the

TABLE X2.2 Calculations from Duplicates

x_1	x_2	Δx	$(\Delta x)^2$	$\bar{x}$
49.7	49.5	0.2	0.04	49.6
51.2	50.9	0.3	0.09	51.05
52.1	46.0	6.1	37.21	49.05
51.4	49.8	1.6	2.56	50.6
53.0	47.2	5.8	33.64	50.1
50.3	47.4	2.9	8.41	48.85
49.5	47.4	2.1	4.41	48.45
51.1	52.2	−1.1	1.21	51.65
46.7	52.4	−5.7	32.49	49.55
48.9	48.6	0.3	0.09	48.75
		Sum	120.15	

TABLE X2.3 Calculations with Different Multiplicates of Measurement

Measurements	s_i^2	$n_i - 1$	$(n_i - 1)\ s_i^2$	Σx_i	$(\Sigma x_i)^2$	n	$(\Sigma x_i)^2/n$	$\Sigma(x_i)^2$
49.7 51.2 52.1 51.4	1.020	3	3.060	204.4	41779.36	4	10444.840	10447.90
53.0 49.5 50.9	3.103	2	6.206	153.4	23531.56	3	7843.853	7850.06
46.0 49.8 47.2 50.3 49.5	3.463	4	13.852	242.8	58951.84	5	11790.368	11804.22
51.1 46.7 48.9 47.4	3.789	3	11.367	194.1	37674.81	4	9418.703	9430.07
47.4 52.2 52.4 48.6	6.410	3	19.230	200.6	40240.36	4	10060.090	10079.32
Sums		15	53.715			20	49557.854	49611.57

squares of each reading as shown under the heading $\Sigma(x_i^2)$ and obtain the sum of this column, 49611.57. Noting that $k = 5$ for the number of sets of measurements, obtain s_p^2 from Eq 6:

$$s_p^2 = (49611.57 - 49557.854)/(20 - 5) \quad \text{(X2.6)}$$
$$= 53.716/15 = 3.581$$

X3. STANDARD DEVIATION AND RELATIVE STANDARD DEVIATION

X3.1 *Estimation from Variance*—Summarize the calculations of variance obtained in Appendix X2 in Table X3.1. The estimate of standard deviation, *s*, follows directly from the square root operation of Eq 7. Obtain the values shown under ν from Eq 10 using $\bar{x} = 49.76$ as it was determined in X2.1.1. Show the degrees of freedom for each method in the final column. From the known population of the measurement data of Table X1.1, the relative standard deviation is $\nu = 100\sigma/\mu = 100(2)/50 = 4$.

X3.1.1 *Pooling Relative Standard Deviation*—Use the values under Columns ν and degrees of freedom in Table X3.1 to calculate ν_p in Eq 11:

$$\nu_p = \sqrt{[19(4.14)^2 + 10(4.92)^2 + 15(3.80)^2]/(19 + 10 + 15)} \quad \text{(X3.1)}$$
$$= \sqrt{(325.6524 + 242.0640 + 216.6000)/44}$$
$$= \sqrt{17.8254} = 4.22\ \%$$

X3.2 *Estimation of Standard Deviation from Range*—Look at the measurement data in Table X1.1 in various ways to apply the estimation of *s* from range using Eq 8. In the first set, consider five cases of four runs A, B, C, and D. In the second set, consider four cases of five runs 1, 2, 3, 4, and 5. In the third set, let A and B be a case of ten runs, and C and D be another case of ten runs. Finally, look at the whole set of twenty readings as one overall case. Summarize as in Table X3.2. Include a pooling of variance in order to determine an overall estimate of *s* in each set. Note that the last case exceeded the number of twelve measurements in an overextension of the estimate and that a low estimate of *s* resulted as predicted in 5.3.1.

TABLE X3.1 Calculation from Variance

Method	s^2	s	ν	Degrees of Freedom
Eq 2 or Eq 3	4.235	2.06	4.14	19
Eq 4	6.008	2.45	4.92	10
Eq 5 or Eq 6	3.581	1.89	3.80	15

X3.3 *Estimation of Standard Deviation Using Single Determinations of Similar Specimens*—Use the measurement data in Columns A and B of Table X1.1 as if they were two different specimens run on five different days or in five different laboratories. Furthermore, in order that Specimen B be somewhat different than Specimen A, let the values under Column B be reduced by 2 to represent a μ of 48. Show these as specimen readings in Table X3.3. Show the difference between readings in the column under *d* and the square of these values under the column d^2. Obtain the sum of the values for *d* and d^2 which are 24.0 and 149.54 respectively. Estimate *s* from Eq 9:

$$s = \sqrt{[149.54 - (24.0)^2/5]/2(5 - 1)} \quad \text{(X3.2)}$$
$$= \sqrt{(149.54 - 115.20)/2(4)}$$
$$= \sqrt{34.34/8} = \sqrt{4.29} = 2.07$$

TABLE X3.2 Estimation Standard Deviation from Range

Set	Case	Range, w	s_r	s_r^2	s_p
First Set:	1	50.3–47.4 = 2.9	1.45	2.1025	$\frac{31.8550}{5} = 6.3710$
$n = 4$	2	51.2–47.4 = 3.8	1.90	3.6100	$s_p = \sqrt{6.3710} = 2.52$
$\sqrt{n} = 2.000$	3	52.2–46.0 = 6.2	3.10	9.6100	
	4	52.4–46.7 = 5.7	2.85	8.1225	
	5	53.0–47.2 = 5.8	2.90	8.4100	
			Sum	31.8550	
Second Set:	A	53.0–49.7 = 3.3	1.48	2.1904	$\frac{15.8850}{4} = 3.9713$
$n = 5$	B	50.9–46.0 = 4.9	2.19	4.7961	$s_p = \sqrt{3.9713} = 1.99$
$\sqrt{n} = 2.236$	C	51.1–46.7 = 4.4	1.97	3.8809	
	D	52.4–47.4 = 5.0	2.24	5.0176	
			Sum	15.8850	
Third Set:	A, B	53.0–46.0 = 7.0	2.21	4.8841	$\frac{8.1341}{2} = 4.0621$
$n = 10$	C, D	52.4–46.7 = 5.7	1.80	3.2400	
$\sqrt{n} = 3.162$			Sum	8.1241	$s_p = \sqrt{4.0621} = 2.02$
Fourth Set:					
$n = 20$		53.0–46.0 = 7.0	1.57		
$\sqrt{n} = 4.472$					

TABLE X3.3 Estimation of Standard Deviation from Pairs of Similar Specimens

Case	Specimen A	Specimen B	d	d^2
1	49.7	47.5	2.2	4.84
2	51.2	48.9	2.3	5.29
3	52.1	44.0	8.1	65.61
4	51.4	47.8	3.6	12.96
5	53.0	45.2	7.8	60.84
		Sums	24.0	149.54

X4. CONFIDENCE FOR ESTIMATION OF MU

X4.1 *Interval Around $\bar{x}$ Including μ*—The estimate of s from the determination of duplicate determinations in X2.1.4 was 2.45 at a degrees of freedom of 10. To determine, at the 95 % confidence level, what range of values around the duplicate average will encompass μ, refer to Table 1 and note that the t multiplier for the 95 % confidence level and a degree of freedom of 10 is 2.228. Use Eq 13 to determine that μ will be included in the range:

$$\bar{x} \pm 2.228(2.45)/\sqrt{2} = \bar{x} \pm 3.86 \quad \text{(X4.1)}$$

When applied to the first duplicate reading of Table X2.2, the confidence interval that will include the μ of the population is 49.6± 3.86. In other words, there is a confidence level of 95 % that μ will fall within the interval of 45.74 to 53.46.

X4.2 *Determination of Minimum Number of Measurements to Achieve Some Limited Confidence Interval*—Use Eq 14 to determine the minimum number of readings needed to have μ fall within some acceptable limits of $\bar{x}$. For example, consider that a value of $\bar{x}$ must be found which is within 2 divisions of μ with a 95 % confidence level. If the measurement of precision of the method, as determined in the case of duplicate readings of X2.1.4, is $s = 2.45$ based on a degrees of freedom of 10, and the t multiplier found in Table 1, as discussed in X4.1, is 2.228,Eq 14 states:

$$2.228 = 2\sqrt{n}/2.45 \text{ or } \sqrt{n} = 1/2\,(2.228)(2.45) = 2.73 \quad \text{(X4.2)}$$

Now $n = (2.73)^2 = 7.45$ which indicates that a minimim of 8 readings should be taken. If only a 90 % confidence level is needed for μ to fall within ±2 divisions of $\bar{x}$ under the same conditions, the t multiplier from Table 1 is now found to be only 1.812 and, from Eq 14:

$$1.812 = 2\sqrt{n}/2.45 \text{ or } \sqrt{n} = 1/2\,(1812)(2.45) = 2.22 \quad \text{(X4.3)}$$

Now $n = (2.22)^2 = 4.93$, indicating that only 5 readings would be needed.

X5. TESTING FOR BIAS

X5.1 Let the measurement data in Table X1.1 represent five samples (1–5) analyzed in four different laboratories (A–D). Furthermore, in order that the readings might represent different samples, let the readings for Sample 2 be two divisions higher than shown in the list of basic values. Similarly, let Sample 3 read two divisions lower, let Sample 4 read four divisions higher, and let Sample 5 read four divisions lower. The revised series of readings appears in Table X5.1 which also shows the assumed correct values.

X5.2 Revise the data as described in 6.1.1.1 to be a display of "*r*" values, remainders, which are differences to the assumed values (see Table X5.2 and Note X5.1). Following the directions of the equations designated in Table 4, add the columns for the Σx values and show their total as $-4.70 = G$. Square the Σx values and show their total as $114.57 = B$. For each column, square each "*r*" value and show the sum of these squares as $\Sigma(x^2)$, followed by the total of these as $81.57 = W$.

NOTE X5.1—The same list of "*r*" values would have been obtained if the original measurement data had not been changed and all samples assumed to have correct readings of 50.0.

X5.3 Set up a comparison of variances as described in 6.1.1.2 after making the calculations labeled in Table 5. Note that for the four laboratories, $m = 4$, and with each running five samples, $n = 5$.

X5.3.1 The calculations for degrees of freedom values will be:

$$mn - 1 = 4(5) - 1 = 19 \quad \text{(X5.1)}$$

$$m - 1 = 4 - 1 = 3$$

$$m(n - 1) = 4(5 - 1) = 16$$

X5.3.2 The calculations for the sums of squares will be:

$$W - G^2/mn = 81.57 - (-4.7)^2/4(5) \quad \text{(X5.2)}$$

$$= 81.57 - 1.10 = 80.47$$

$$B/n - G^2/mn = 114.57/5 - 1.10 = 21.81$$

$$\text{By difference, } W - B/n = 58.66$$

X5.3.3 The final values for variance will be each sum of squares divided by its respective degrees of freedom. See Table X5.3.

X5.4 Test the significance of the comparison of s_b^2 and s_w^2 by calculating the *F* ratio of Eq 16:

$$F = 7.27/3.67 = 1.98 \quad \text{(X5.3)}$$

TABLE X5.1 Single Readings of a Suite of Samples

Sample	Laboratory A	B	C	D	Assumed Correct Value
1	49.7	49.5	50.3	47.4	50.0
2	53.2	52.9	51.5	49.4	52.0
3	50.1	44.0	49.1	50.2	48.0
4	55.4	53.8	50.7	56.4	54.0
5	49.0	43.2	44.9	44.6	46.0

TABLE X5.2 Summations for Comparison of Variance

Sample	Differences, *r* A	B	C	D	Totals
1	−0.3	−0.5	−0.3	−2.6	
2	1.2	0.9	−0.5	−2.6	
3	2.1	−4.0	1.1	2.2	
4	1.4	−0.2	−3.3	2.4	
5	3.0	−2.8	−1.1	−1.4	
Σx	7.4	−6.6	−3.5	−2.0	$-4.7 = G$
$(\Sigma x)^2$	54.76	43.56	12.25	4.00	$114.57 = B$
$\Sigma(x^2)$	16.90	24.94	13.65	26.08	$81.57 = W$

TABLE X5.3 Final Values for Variance

Source of Variation	Degrees of Freedom	Sum of Squares	Variance
Total	19	80.47	$4.24 = s_t^2$
Between sets	3	21.81	$7.27 = s_b^2$
Within samples	16	58.66	$3.67 = s_w^2$

where the degrees of freedom of the numerator are 3 and the degrees of freedom of the denominator are 16. For these degrees of freedom, the *F* ratio for 0.05 probability from Table 2 is 3.24. Since the *F* ratio that was calculated is well below 3.24, there is a 95 % confidence level that there was no significant bias among laboratories. It may also be noted that the variance for the total system, 4.24, agrees well with $\sigma^2 = 4.0$ for the random numbers used.

X5.5 Retest for bias after altering the data to have Laboratory D read 2 divisions low:

X5.5.1 The column marked D in Table X5.4 would then appear as:

Sample	*r*
1	−4.6
2	−4.6
3	0.2
4	0.4
5	−3.4

X5.5.2 The sums from Column D and the totals calculated as shown in Table X5.2 would now appear as:

	D	Totals
Σx	−12.0	$-14.7 = G$
$(\Sigma x)^2$	144.0	$254.57 = B$
$\Sigma(x^2)$	54.08	$109.57 = W$

X5.5.3 The calculations for the sums of squares then become:

$$W - G^2/mn = 109.57 - (-14.7)^2/20 \quad \text{(X5.4)}$$

TABLE X5.4 Comparison of Variances

Source of Variation	Degrees of Freedom	Sum of Squares	Variance
Total	19	98.77	$5.20 = s_t^2$
Between sets	3	40.11	$13.37 = s_b^2$
Within samples	16	58.66	$3.67 = s_w^2$

$$= 109.57 - 10.80 = 98.77$$

$$B/n - G^2/mn = 254.57/5 - 10.80 = 40.11$$

$$W - B/n = 58.66$$

X5.5.4 The comparison of variances is shown in Table X5.4.

X5.5.5 The calculation of the *F* ratio then becomes:

$$F = 13.37/3.67 = 3.64 \quad \text{(X5.5)}$$

This exceeds the 0.05 probability for *F* which, as previously determined, is 3.24, indicating, at the 95 % confidence level, that there is a bias among laboratories.

X5.6 Using data from Table X5.1, test for bias between readings for Laboratory A and the assumed values by applying the procedure described in 6.1.2. Differences are listed in Table X5.2. For Laboratory A, the average difference is 1.48 and Eq 3 can be used with the sums shown to determine the standard deviation at 4 df as being 1.219. The calculation of *t* from Eq 14 is:

$$t = 1.48(\sqrt{5})/1.219 = 2.714 \quad \text{(X5.6)}$$

Since this is less than the 2.776 value for *t* in Table 1 for 4 df and the probability level of 0.05, there is a 95 % confidence that there is no bias. The calculations for other laboratories show even lower calculations for *t*, namely 1.465, 0.935, and 0.356 respectively for B, C, and D, supporting the test of X5.4 which showed no significant bias among laboratories.

X5.6.1 If the previous test is applied to the case of X5.5.1 in which the readings of Laboratory D were given a − 2.0 bias, the average difference becomes −2.4 while the standard deviation remains high at 2.514, and the calculation of *t* is as follows:

$$t = |-2.4|(\sqrt{5})/2.514 = 2.315 \quad \text{(X5.7)}$$

This does not indicate any bias at the 95 % confidence level. Although its readings were biased, the critical *t* value calculated for Laboratory D is lower than the *t* value calculated for the unbiased readings of Laboratory A. A misleading conclusion is made because the test used a standard deviation based on only 4 df. See the following section.

X5.6.2 The test for bias between paired observations is improved if a pooling is made with the standard deviations of differences calculated for all four laboratories involved. The individual values for *s* are 1.219, 2.014, 1.673, and 2.514. The pooled estimate of standard deviation at 16 df becomes $s_p = 1.915$. When this is used for the biased readings of Laboratory D,

$$t = |-2.4|\,(\sqrt{5})/1.915 = 2.802 \quad \text{(X5.8)}$$

This now does not indicate a significant bias when compared to the *t* value of 2.120 from Table 1 for 16 df. Using the pooled estimate of standard deviation, Laboratory A still does not show a bias since its *t* value now calculates as being only 1.728.

X5.7 Table X5.5 shows a series of average readings of reference materials employed for the calibration of copper in aluminum alloys. Since matrix dilution was used, the values for the copper content are in terms of relative percent copper. The calibration equation appears at the bottom of the table as a function of a second degree equation, with *x* representing readings.

X5.7.1 From the original data, calculations of apparent relative concentrations are compared to assumed correct values. Differences and the squares of differences are shown. The square of the standard error of the fit to the calibration curve is obtained by summing the squares of the differences and dividing, in this case, by 12, the degrees of freedom of 15 data points reduced by 3 for the number of coefficients in the calibration equation. Using Eq 12, as shown in Table X5.5, the resulting standard error of the fit is 0.0679 relative percent copper.

X5.7.2 At a later date, the same suite of reference materials was analyzed as if they were unknown specimens. The resulting readings are shown in the column headed "New

TABLE X5.5 Calibration of Copper in Aluminum

Original Reading	Relative % Cu	Calculation Value	Difference	Difference Squared	New Reading	Calculation Value	Difference	Difference Squared
4459	7.81	7.797	−0.013	0.000171	4448	7.775	−0.035	0.001250
2815	4.59	4.573	−0.017	0.000283	2839	4.619	0.029	0.000826
2692	4.34	4.340	0.000	0.000000	2763	4.475	0.135	0.018124
2722	4.34	4.397	0.057	0.003257	2717	4.388	0.048	0.002268
2678	4.42	4.314	−0.106	0.011240	2713	4.380	−0.040	0.001595
2655	4.22	4.271	0.051	0.002561	2681	4.320	0.100	0.009928
2635	4.13	4.233	0.103	0.010593	2645	4.252	0.122	0.014826
2495	4.01	3.970	−0.040	0.001599	2504	3.987	−0.023	0.000535
2566	4.00	4.103	0.103	0.010641	2457	3.899	−0.101	0.010219
2410	3.91	3.811	−0.099	0.009775	2394	3.781	−0.129	0.016568
2305	3.61	3.616	0.006	0.000032	2318	3.640	0.030	0.000887
2321	3.70	3.645	−0.055	0.002985	2295	3.597	−0.103	0.010597
2344	3.66	3.688	0.028	0.000792	2294	3.595	−0.065	0.004199
1617	2.39	2.356	−0.034	0.001171	1657	2.428	0.038	0.001446
282	0.00	0.016	0.016	0.000245	273	0.000	0.000	0.000000
			sum	0.055347			sum	0.093267
			SE = $\sqrt{0.055347/(15-3)}$ = 0.0679				SE = $\sqrt{0.093267/15}$ = 0.0789	

where:
Relative % Cu = $-0.461 + 0.0016794x + 0.0000000387x^2$

Reading" in Table X5.5. As in X5.7.1, comparisons are made between apparent and assumed concentrations. In this case, although the sum of the squares of differences is higher, the degrees of freedom, the full number of 15 data points, is also higher and leads to a standard error of 0.0789. Since there is little difference between this standard error and the one calculated in X5.7.1, the existing calibration remains valid.

X6. ESTABLISHING DETECTION LIMIT

X6.1 *Using a Linear Plot*—Revise the measurement data in Table X1.1 to have it represent readings for four different samples (A–D) having concentrations of 0.010, 0.020, 0.030, and 0.040. For each successive sample, have the readings increase 5.0 for each increase in concentration of 0.010. This will make the display shown in Table X6.1.

X6.1.1 From the summations in Table X6.1, calculate a pooled estimate of standard deviation by first estimating variance, using Eq 6:

$$s_p^2 = \{66165.57 - [(257.4)^2 + (268.4)^2 + (296.5)^2 + (323.0)^2]/5\}/(20 - 4) \quad \text{(X6.1)}$$
$$= 3.666$$

Now:

$$s_p = 1.91 \quad \text{(X6.2)}$$

X6.1.2 If the four analyzed samples are used to define the analytical curve for the low-level concentrations, a linear regression to determine the curve would yield:

$$\%c = 0.002161(\text{reading}) - 0.0988 \quad \text{(X6.3)}$$

X6.1.3 Refer to Table 1. The pooled estimate of standard deviation, 1.91, was made with a total degrees of freedom of 16. To make a determination of detection limit at the 95 % confidence level, refer to the column under the probability of 0.100 and read a *t* value of 1.746 for 16 df. Since the slope of the analytical curve is 0.002161 % per division, the detection limit is determined from Eq 17:

TABLE X6.1 Suite of Samples in Linear Readout

Concentration	0.010	0.020	0.030	0.040
Readings:	49.7	54.5	60.3	62.4
	51.2	55.9	59.5	62.4
	52.1	51.0	61.1	67.2
	51.4	54.8	56.7	67.4
	53.0	52.2	58.9	63.6
Sums	257.4	268.4	296.5	323.0
Average	51.5	53.7	59.3	64.6
Σ (Reading)^2	13256.90	14423.94	17593.65	20891.08
Overall Σ (Reading)^2		66165.57		

$$c = 0.002161(1.746)(1.91) = 0.007\ \% \quad \text{(X6.4)}$$

This is the detection limit of a single excitation of a sample. The detection limit would be lower for replicate analyses. For a replication of five, *c* is divided by $\sqrt{5}$, yielding a detection limit of 0.003 %.

X6.2 *Using a Logarithmic Plot*—Relist the values from Table X6.1 by showing their logarithmic values in Table X6.2. To make the reading values realistic, divide them by 100 before taking logarithms.

X6.2.1 Using Eq 6:

$$s_p^2 = \{1.22323548 - [(-1.4422)^2 + (-1.3521)^2 + (-1.1355)^2 + (-0.9500)^2]/5\}/(20 - 4) \quad \text{(X6.5)}$$
$$= 0.00020252$$

Now:

$$s_p = 0.0142 \quad \text{(X6.6)}$$

X6.2.2 A straight line working curve can be made for this data by making a background correction in the form of Eq 18:

$$c = 0.2125(10^R - 0.457) \quad \text{(X6.7)}$$

where *R* is the log reading.

X6.2.3 As was done in X6.1.3, use a *t* value of 1.746. Since $s = s_p = 0.0142$, the product $ts = 0.0248$. Use this in Eq 19 with the average lowest reading, $R = -0.2884$. The detection limit is calculated as a change in concentration:

$$\Delta c = 0.2125[10^{(-0.2884 + 0.0248)} - 10^{-0.2884}] \quad \text{(X6.8)}$$
$$= 0.2125(0.54500 - 0.51475) = 0.006\ \%$$

This is the detection limit of a single excitation when the procedure includes a background correction. For replicate analyses, such as the replication of five used in X6.1.3, the product, *ts*, in the exponent of Eq 19 is divided by $\sqrt{5}$, yielding:

$$\Delta c = 0.2125[10^{(-0.2884 + 0.0111)} - 10^{-0.2884}] \quad \text{(X6.9)}$$
$$= 0.2125(0.52808 - 0.51475) = 0.003\ \%$$

TABLE X6.2 Suite of Samples in Logarithm Readout

Log concentration	−2.0000	−1.6990	−1.5229	−1.3979
Log Readings:	−0.3036	−0.2636	−0.2197	−0.2048
	−0.2907	−0.2526	−0.2255	−0.2048
	−0.2832	−0.2924	−0.2140	−0.1726
	−0.2890	−0.2612	−0.2464	−0.1713
	−0.2757	−0.2823	−0.2299	−0.1965
Sums	−1.4422	−1.3521	−1.1355	−0.9500
Average	−0.2884	−0.2704	−0.2271	−0.1900
Σ (Reading)^2	0.41641318	0.36670821	0.25848131	0.18163278
Overall Σ (Reading)^2		1.22323548		

X7. ESTABLISHING DETERMINATION LIMIT

X7.1 *Determination Limit*—If a determination has significance only if the confidence interval containing the apparent concentration is half of that concentration, Eq 21 can be used whereρ is equal to 0.5. The standard deviation of measurement in X6.1 converts to a standard deviation of concentration by multiplying by the slope of the calibration line in X6.1.2, or s_c = 1.91(0.00216) = 0.00413. A different value for *t* than that used in X6.1.3 will be needed since the concern is now for deviations on either side of the apparent concentration. At a 95 % confidence level for 16 df , Table 1 shows that the factor 2.120 should be used. The determination limit for a replication of five burns then becomes:

$$\hat{y} = 2(2.120)(0.00413)/0.5\sqrt{5} = 0.016\ \% \qquad \text{(X7.1)}$$

X8. TESTING FOR DRIFT

X8.1 *Detection After a Time Lapse*—Consider that the measurements in Table X2.3 represent reanalyses of the same specimen at some time intervals to detect drift. Obtain the average of each set of measurements and relist in Table X8.1, including a second column to list the number of measurements in each average. Show the differences between averages in the third column, labeled Obs |Δ|. In the final column, labeled Critical |Δ|, show the calculation for the critical difference as designated in Eq 22a and Eq 22b. In none of the cases shown does the observed difference exceed the critical difference, and therefore, infers that there was no significant drift. For the calculation of critical |Δ|, the value for *s* was taken as 2.0.

X8.2 *Detection of Drift in a Sequence, First Method*—List the series of measurement data from Table X1.1, including the number of the sequence position as *x* and showing the reading as *y*, as shown in Table X8.2. Follow with columns labeled x^2 and *xy* and determine the sums of all four columns for use in Eq 23. In this case, *n* is 20. Calculate the slope as follows:

$$m = [20(10390.8) - 210(995.3)]/[20(2870) - (210)^2]$$

TABLE X8.1 Detection of Drift After a Time Lapse

Average Measurement	*n*	Obs |Δ|	Critical |Δ|
51.1	4		
		0.0	$2(2.0)\sqrt{\frac{4+3}{4(3)}} = 4.0\sqrt{7/12} = 3.06$
51.1	3		
		2.5	$2\ (2.0)\sqrt{\frac{3+5}{3(5)}} = 4.0\sqrt{8/15} = 2.92$
48.6	5		
		0.1	$2\ (2.0)\sqrt{\frac{5+4}{(5(4)}} = 4.0\sqrt{9/20} = 2.68$
48.5	4		
		1.65	$2\ (2.0)\sqrt{2/4} = 4.0\sqrt{0.5} = 2.83$
50.15	4		

TABLE X8.2 Detection of Drift in a Sequence, First Data

Sequence, *x*	Reading, *y*	x^2	*xy*	Δ	Δ^2
1	49.7	1	49.7	−1.5	2.25
2	51.2	4	102.4	−0.9	0.81
3	52.1	9	156.3	0.7	0.49
4	51.4	16	205.6	−1.6	2.56
5	53.0	25	265.0	3.5	12.25
6	49.5	36	297.0	−1.4	1.96
7	50.9	49	356.3	4.9	24.01
8	46.0	64	368.0	−3.8	14.44
9	49.8	81	448.2	2.6	6.76
10	47.2	100	472.0	−3.1	9.61
11	50.3	121	553.3	0.8	0.64
12	49.5	144	594.0	−1.6	2.56
13	51.1	169	664.3	4.4	19.36
14	46.7	196	653.8	−2.2	4.84
15	48.9	225	733.5	1.5	2.25
16	47.4	256	758.4	0.0	0.00
17	47.4	289	805.8	−4.8	23.04
18	52.2	324	939.6	−0.2	0.04
19	52.4	361	995.6	3.8	14.44
20	48.6	400	972.0		
Sums 210	995.3	2870	10390.8		142.31

$$= (207816.0 - 209013.0)/(57400 - 44100) \qquad \text{(X8.1)}$$

$$= -1197.0/13300 = -0.0900 \qquad \text{(X8.1)}$$

Determine the critical value for the slope from Eq 24, using *s* as 2.0:

$$|m| = 2(2.0)\sqrt{2}/(20 - 1) = 0.30 \qquad \text{(X8.2)}$$

Since the actual slope is less than the critical slope, there is no significant drift indicated.

X8.2.1 As discussed in 6.4.2.1, an estimate for *s* could have been made from the sequence that would not be affected by drift by observing the differences between successive readings. Expand Table X8.2 by adding a column to show the differences

between readings, Δ, and another for the square of these differences, Δ^2. Obtain the sum of Column Δ^2, and apply Eq 26 where P is 19 for the number of pairs used:

$$s_s = \sqrt{142.31/2(19 - 1/2)} = \sqrt{142.31/37} = 1.96 \quad \text{(X8.3)}$$

X8.2.2 The test can be repeated for a case in which drift is known to be present by having each successive reading in Table X8.2 reduced 0.2 divisions progressively, that is, no change in reading 1, − 0.2 in reading 2, − 0.4 in reading 3, etc. This list appears in Table X8.3. Proceed with the listing of x^2, xy, Δ, and Δ^2 as was done for Table X8.2. Calculate the slope from Eq 23 as follows:

TABLE X8.3 Detection of Drift in a Sequence, Second Data

Sequence, x	Reading, y	x^2	xy	Δ	Δ^2
1	49.7	1	49.7	−1.3	1.69
2	51.0	4	102.0	−0.7	0.49
3	51.7	9	155.1	0.9	0.81
4	50.8	16	203.2	−1.4	1.96
5	52.2	25	261.0	3.7	13.69
6	48.5	36	291.0	−1.2	1.44
7	49.7	49	347.9	5.1	26.01
8	44.6	64	356.8	−3.6	12.96
9	48.2	81	433.8	2.8	7.84
10	45.4	100	454.0	−2.9	8.41
11	48.3	121	531.3	1.0	1.00
12	47.3	144	567.6	−1.4	1.96
13	48.7	169	633.1	4.6	21.16
14	44.1	196	617.4	−2.0	4.00
15	46.1	225	691.5	1.7	2.89
16	44.4	256	710.4	0.2	0.04
17	44.2	289	751.4	−4.6	21.16
18	48.8	324	878.4	0.0	0.00
19	48.8	361	927.2	4.0	16.00
20	44.8	400	896.0		
Sums 210	957.3	2870	9858.8		143.51

$$\begin{aligned} m &= [20(9858.8) - 210(957.3)]/[20(2870) - (210)^2] \\ &= (197176.0 - 201033.0)/(57400 - 44100) \\ &= -3857.0/13300 = -0.2900 \end{aligned} \quad \text{(X8.4)}$$

This barely meets the no drift criterion, calculated previously for Eq 24, that the critical $|m| = 0.30$.

X8.3 *Detection of Drift in a Sequence, Second Method*— The data in Table X8.2 and Table X8.3 can be used to determine the average square of successive differences, δ^2, of Eq 27:

$$\delta^2 = 142.31/(20 - 1) = 7.490 \text{ from Table } X8.2, \text{ and} \quad \text{(X8.5)}$$

$$\delta^2 = 143.51/19 = 7.553 \text{ from Table } X8.3$$

Comparison must also be made with an estimate of standard deviation done by using either Eq 2 or Eq 3. This was demonstrated in X2.1.2 and X2.1.3 on the same data used for Table X8.2 with the calculation that $s^2 = 4.235$. For the case in Table X8.2, calculate the ratio η, from Eq 28:

$$\eta = 7.490/4.235 = 1.77 \quad \text{(X8.6)}$$

Observe that the critical value in Table 6 for a sample size of 20 and a probability of 95 % is 1.30. Since the calculation of η is greater than the critical value, there is no evidence of drift. In the case in Table X8.3, calculate the s^2 by either Eq 2 or Eq 3 as 6.895. Now:

$$\eta = 7.553/6.895 = 1.095 \quad \text{(X8.7)}$$

Since this is less than the critical value of 1.30, there is evidence at the 95 % probability level that there was drift. Note that Table 6 shows the critical value of 1.04 for a sample size of 20 at the 99 % probability level, therefore, the test does not quite show evidence of drift at that confidence level.