Standard Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products and Lubricants[1]

This standard is issued under the fixed designation D 6300; 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.

INTRODUCTION

Both Research Report RR:D02–1007, *Manual on Determining Precision Data for ASTM Methods on Petroleum Products and Lubricants*[2] and the ISO 4259, benefitted greatly from more than 50 years of collaboration between ASTM and the Institute of Petroleum (IP) in the UK. The more recent work was documented by the IP and has become ISO 4259.

ISO 4259 encompasses both the determination of precision and the application of such precision data. In effect, it combines the type of information in RR:D02–1007[2] regarding the determination of the precision estimates and the type of information in Practice D 3244 for the utilization of test data. The following practice, intended to replace RR:D02–1007,[2] differs slightly from related portions of the ISO standard. This new practice is consistent with the computer software, ADJD6300 D2PP, Version 4.43, Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products.

1. Scope

1.1 This practice covers the necessary preparations and planning for the conduct of interlaboratory programs for the development of estimates of precision (determinability, repeatability, and reproducibility) and of bias (absolute and relative), and further presents the standard phraseology for incorporating such information into standard test methods.

1.2 This practice is generally limited to homogeneous products with which serious sampling problems do not normally arise.

1.3 This practice may not be suitable for solid or semisolid products such as petroleum coke, industrial pitches, paraffin waxes, greases, or solid lubricants when the heterogeneous properties of the substances create sampling problems. In such instances, use Practice E 691 or consult a trained statistician.

1.4 A software program (ADJD6300) performs the necessary computations prescribed by this practice.

2. Referenced Documents

2.1 *ASTM Standards:*

D 123 Terminology Relating to Textiles[3]

D 3244 Practice for Utilization of Test Data to Determine Conformance with Specifications[4]

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications[5]

E 456 Terminology Relating to Quality and Statistics[5]

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method[5]

2.2 *ISO Standards:*

ISO 4259 Petroleum Products-Determination and Application of Precision Data in Relation to Methods of Test[6]

2.3 *ASTM Adjuncts:*

ADJD6300 D2PP, Version 4.43, Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products[7]

3. Terminology

3.1 *Definitions:*

3.1.1 *analysis of variance (ANOVA), n*—a procedure for dividing the total variation of a set of data into two or more parts, one of which estimates the error due to selecting and testing specimens and the other part(s) possible sources of added variation. **D 123**

[1] This practice is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.94 on Quality Assurance and Statistics.

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[2] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02–1007.

[3] *Annual Book of ASTM Standards*, Vol 07.01.

[4] *Annual Book of ASTM Standards*, Vol 05.02.

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

[6] Available from International Organization for Standardization, 1 rue de Varembé, Case postale 56, CH-1211 Geneva 20, Switzerland.

[7] Available from ASTM International Headquarters. Order Adjunct No. ADJD6300.

3.1.2 *bias*, *n*—the difference between the population mean of the test results and an accepted reference value. **E 456**

3.1.3 *bias, relative*, *n*—the difference between the population mean of the test results and an accepted reference value, which is the agreed upon value obtained using an accepted reference method for measuring the same property.

3.1.4 *degrees of freedom*, *n*—the divisor used in the calculation of variance.

3.1.4.1 *Discussion*—This definition applies strictly only in the simplest cases. Complete definitions are beyond the scope of this practice. **ISO 4259**

3.1.5 *determinability*, *n*—a quantitative measure of the variability associated with the same operator in a given laboratory obtaining successive determined values using the same apparatus for a series of operations leading to a single result; it is defined as that difference between two such single determined values as would be exceeded in the long run in only one case in 20 in the normal and correct operation of the test method.

3.1.5.1 *Discussion*—This definition implies that two determined values, obtained under determinability conditions, which differ by more than the determinability value should be considered suspect. If an operator obtains more than two determinations, then it would usually be satisfactory to check the most discordant determination against the mean of the remainder, using determinability as the critical difference **(1)**.[8]

3.1.6 *mean square*, *n— in analysis of variance*, a contraction of the expression "mean of the squared deviations from the appropriate average(s)" where the divisor of each sum of squares is the appropriate degrees of freedom. **D 123**

3.1.7 *normal distribution*, *n*—the distribution that has the probability function:

$$f(x) = (1/\sigma)\,(2\pi)^{-1/2}\exp\left[-\,(x-\mu)^2/2\sigma^2\right] \tag{1}$$

where:

x = a random variate,
μ = the mean distribution, and
σ = the standard deviation of the distribution.

(*Syn.* Gaussian distribution, law of error) **D 123**

3.1.8 *outlier*, *n*—a result far enough in magnitude from other results to be considered not a part of the set. **RR:D02–1007**

3.1.9 *precision*, *n*—the degree of agreement between two or more results on the same property of identical test material. In this practice, precision statements are framed in terms of *repeatability* and *reproducibility* of the test method.

3.1.9.1 *Discussion*—The testing conditions represented by repeatability and reproducibility should reflect the normal extremes of variability under which the test is commonly used. Repeatability conditions are those showing the least variation; reproducibility, the usual maximum degree of variability. Refer to the definitions of each of these terms for greater detail. **RR:D02–1007**

3.1.10 *random error*, *n*—the chance variation encountered in all test work despite the closest control of variables. **RR:D02–1007**

3.1.11 *repeatability*, *n*—the quantitative expression of the random error associated with a single operator in a given laboratory obtaining repetitive results by applying the same test method with the same apparatus under constant operating conditions on identical test material within a short interval of time on the same day. It is defined as the difference between two such results at the 95 % confidence level. **RR:D02–1007**

3.1.11.1 *Discussion*—Interpret as the value equal to or below which the absolute difference between two single test results obtained in the above conditions may expect to lie with a probability of 95 %. **ISO 4259**

3.1.11.2 *Discussion*—The difference is related to the repeatability standard deviation but it is not the standard deviation or its estimate. **RR:D02–1007**

3.1.12 *reproducibility*, *n*—a quantitative expression of the random error associated with different operators from different laboratories using different apparatus, each obtaining a single result by applying the same test method on an identical test sample. It is defined as the 95 % confidence limit for the difference between two such single and independent results.

3.1.12.1 *Discussion*—Interpret as the value equal to or below which the absolute difference between two single test results on identical material obtained by operators in different laboratories, using the standardized test, may be expected to lie with a probability of 95 %. **ISO 4259**

3.1.12.2 *Discussion*—The difference is related to the reproducibility standard deviation but is not the standard deviation or its estimate. **RR:D02–1007**

3.1.12.3 *Discussion*—In those cases where the normal use of the test method does not involve sending a sample to a testing laboratory, either because it is an in-line test method or because of serious sample instabilities or similar reasons, the precision test for obtaining reproducibility may allow for the use of apparatus from the participating laboratories at a common site (several common sites, if feasible). The statistical analysis is not affected thereby. However, the interpretation of the reproducibility value will be affected, and therefore, the precision statement shall, in this case, state the conditions to which the reproducibility value applies.

3.1.13 *standard deviation*, *n*—the most usual measure of the dispersion of observed values or results expressed as the positive square root of the variance. **E 456**

3.1.14 *sum of squares*, *n—in analysis of variance*, a contraction of the expression "sum of the squared deviations from the appropriate average(s)" where the average(s) of interest may be the average(s) of specific subset(s) of data or of the entire set of data. **D 123**

3.1.15 *variance*, *n*—a measure of the dispersion of a series of accepted results about their average. It is equal to the sum of the squares of the deviation of each result from the average, divided by the number of degrees of freedom. **RR:D02–1007**

3.1.16 *variance, between-laboratory*, *n*—that component of the overall variance due to the difference in the mean values obtained by different laboratories. **ISO 4259**

3.1.16.1 *Discussion*—When results obtained by more than one laboratory are compared, the scatter is usually wider than when the same number of tests are carried out by a single

[8] The bold numbers in parentheses refer to a list of references at the end of this practice.

laboratory, and there is some variation between means obtained by different laboratories. Differences in operator technique, instrumentation, environment, and sample "as received" are among the factors that can affect the between laboratory variance. There is a corresponding definition for between-operator variance.

3.1.16.2 *Discussion*—The term "between-laboratory" is often shortened to "laboratory" when used to qualify representative parameters of the dispersion of the population of results, for example as "laboratory variance."

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *determination*, *n*—the process of carrying out a series of operations specified in the test method whereby a single value is obtained.

3.2.2 *operator*, *n*—a person who carries out a particular test.

3.2.3 *probability density function*, *n*—function which yields the probability that the random variable takes on any one of its admissible values; here, we are interested only in the normal probability.

3.2.4 *result*, *n*—the final value obtained by following the complete set of instructions in the test method.

3.2.4.1 *Discussion*—It may be obtained from a single determination or from several determinations, depending on the instructions in the method. When rounding off results, the procedures described in Practice E 29 shall be used.

4. Summary of Practice

4.1 A draft of the test method is prepared and a pilot program can be conducted to verify details of the procedure and to estimate roughly the precision of the test method.

4.2 A plan is developed for the interlaboratory study using the number of participating laboratories to determine the number of samples needed to provide the necessary degrees of freedom. Samples are acquired and distributed. The interlaboratory study is then conducted on an agreed draft of the test method.

4.3 The data are summarized and analyzed. Any dependence of precision on the level of test result is removed by transformation. The resulting data are inspected for uniformity and for outliers. Any missing and rejected data are estimated. The transformation is confirmed. Finally, an analysis of variance is performed, followed by calculation of repeatability, reproducibility, and bias. When it forms a necessary part of the test procedure, the determinability is also calculated.

5. Significance and Use

5.1 ASTM test methods are frequently intended for use in the manufacture, selling, and buying of materials in accordance with specifications and therefore should provide such precision that when the test is properly performed by a competent operator, the results will be found satisfactory for judging the compliance of the material with the specification. Statements addressing precision and bias are required in ASTM test methods. These then give the user an idea of the precision of the resulting data and its relationship to an accepted reference material or source (if available). Statements addressing determinability are sometimes required as part of the test method procedure in order to provide early warning of a significant degradation of testing quality while processing any series of samples.

5.2 Repeatability and reproducibility are defined in the precision section of every Committee D02 test method. Determinability is defined above in Section 3. The relationship among the three measures of precision can be tabulated in terms of their different sources of variation (see Table 1).

5.2.1 When used, determinability is a mandatory part of the Procedure section. It will allow operators to check their technique for the sequence of operations specified. It also ensures that a result based on the set of determined values is not subject to excessive variability from that source.

5.3 A bias statement furnishes guidelines on the relationship between a set of test results and a related set of accepted reference values. When the bias of a test method is known, a compensating adjustment can be incorporated in the test method.

5.4 This practice is intended for use by D02 subcommittees in determining precision estimates and bias statements to be used in D02 test methods. Its procedures correspond with ISO 4259 and are the basis for the Committee D02 computer software, *Calculation if Precision Data: Petroleum Test Methods*. The use of this practice replaces that of Research Report RR:D02–1007.[2]

5.5 Standard practices for the calculation of precision have been written by many committees with emphasis on their particular product area. One developed by Committee E11 on Statistics is Practice E 691. Practice E 691 and this practice differ as outlined in Table 2.

6. Stages in Planning of an Interlaboratory Test Program for the Determination of the Precision of a Test Method

6.1 The stages in planning an interlaboratory test program are: preparing a draft method of test (see 6.2), planning and executing a pilot program with at least two laboratories (optional but recommended for new test methods) (see 6.3), planning the interlaboratory program (see 6.4), and executing the interlaboratory program (see 6.5). The four stages are described in turn.

6.2 *Preparing a Draft Method of Test*—This shall contain all the necessary details for carrying out the test and reporting

TABLE 1 Sources of Variation

	Method	Apparatus	Operator	Laboratory	Time
Reproducibility	Complete (Result)	Different	Different	Different	Specified
Repeatability	Complete (Result)	Same	Same	Same	Almost same
Determinability	Incomplete (Part result)	Same	Same	Same	Almost same

TABLE 2 Differences in Calculation of Precision in Practices D 6300 and E 691

Element	This Practice	Practice E 691
Applicability	Limited in general to homogeneous samples for which serious sampling problems do not normally arise.	Permits heterogeneous samples.
Number of duplicates	Two	Any number
Precision is written for	Test method	Each sample
Outlier tests:	Sequential	Simultaneous
Within laboratories	Cochran test	*k*-value
Between laboratories	Hawkins test	*h*-value
Outliers	Rejected, subject to subcommittee approval.	Rejected if many laboratories or for cause such as blunder or not following method.
	Retesting not generally permitted.	Laboratory may retest sample having rejected data.
Rejection limit	20 %	5 %
Analysis of variance	Two-way, applied globally to all the remaining data at once.	One-way, applied to each sample separately.
Precision multiplier	$t\sqrt{2}$, where t is the two-tailed Student's t for 95 % probability.	$2.8=1.96\sqrt{2}$
	Increases with decreasing laboratories × samples particularly below 12.	Constant.
Variation of precision with level	Minimized by data transformation. Equations for repeatability and reproducibility are generated in the retransformation process.	User may assess from individual sample precisions.

the results. Any condition which could alter the results shall be specified. The section on precision will be included at this stage only as a heading.

6.3 *Planning and Executing a Pilot Program with at Least Two Laboratories*:

6.3.1 A pilot program is recommended to be used with new test methods for the following reasons: (*1*) to verify the details in the operation of the test; (*2*) to find out how well operators can follow the instructions of the test method; (*3*) to check the precautions regarding sample handling and storage; and (*4*) to estimate roughly the precision of the test.

6.3.2 At least two samples are required, covering the range of results to which the test is intended to apply; however, include at least 12 laboratory-sample combinations. Test each sample twice by each laboratory under repeatability conditions. If any omissions or inaccuracies in the draft method are revealed, they shall now be corrected. Analyze the results for precision, bias, and determinability (if applicable) using this practice. If any are considered to be too large for the technical application, then consider alterations to the test method.

6.4 *Planning the Interlaboratory Program*:

6.4.1 There shall be at least five participating laboratories, but it is preferable to exceed this number in order to reduce the number of samples required and to make the precision statement as representative as possible of the qualified user population.

6.4.2 The number of samples shall be sufficient to cover the range of the property measured, and to give reliability to the precision estimates. If any variation of precision with level was observed in the results of the pilot program, then at least five samples shall be used in the interlaboratory program. In any case, it is necessary to obtain at least 30 degrees of freedom in both repeatability and reproducibility. For repeatability, this means obtaining a total of at least 30 pairs of results in the program.

6.4.3 For reproducibility, Fig. 1 gives the minimum number of samples required in terms of L, P, and Q, where L is the number of participating laboratories, and P and Q are the ratios of variance component estimates (see 8.3.1) obtained from the pilot program. Specifically, P is the ratio of the interaction component to the repeats component, and Q is the ratio of the laboratories component to the repeats component.

NOTE 1—Appendix X1 gives the derivation of the equation used. If Q is much larger than P, then 30 degrees of freedom cannot be achieved; the blank entries in Fig. 1 correspond to this situation or the approach of it (that is, when more than 20 samples are required). For these cases, there is likely to be a significant bias between laboratories. The program organizer shall be informed; further standardization of the test method may be necessary.

6.5 *Executing the Interlaboratory Program*:

6.5.1 One person shall oversee the entire program, from the distribution of the texts and samples to the final appraisal of the results. He or she shall be familiar with the test method, but should not personally take part in the actual running of the tests.

6.5.2 The text of the test method shall be distributed to all the laboratories in time to raise any queries before the tests begin. If any laboratory wants to practice the test method in advance, this shall be done with samples other than those used in the program.

6.5.3 The samples shall be accumulated, subdivided, and distributed by the organizer, who shall also keep a reserve of each sample for emergencies. It is most important that the individual laboratory portions be homogeneous. Instructions to each laboratory shall include the following:

6.5.3.1 The agreed draft method of test;

6.5.3.2 Material Safety Data Sheets, where applicable, and the handling and storage requirements for the samples;

6.5.3.3 The order in which the samples are to be tested (a different random order for each laboratory);

6.5.3.4 The statement that two test results are to be obtained in the shortest practical period of time on each sample by the same operator with the same apparatus. For statistical reasons it is imperative that the two results are obtained independently of each other, that is, that the second result is not biased by knowledge of the first. If this is regarded as impossible to achieve with the operator concerned, then the pairs of results shall be obtained in a blind fashion, but ensuring that they are

L = number of participating laboratories

P = interaction variance component/repeats variance component

Q = laboratories variance component/repeats variance component

L=5

P \ Q	0	1	2	3	4	5	6	7	8	9
0	4									
1	5									
2	6	11								
3	6	9								
4	7	8	16							
5	7	8	12							
6	7	8	11	19						
7	7	8	10	15						
8	7	8	9	13						
9	7	8	9	11	17					

L=6

P \ Q	0	1	2	3	4	5	6	7	8	9
0	3									
1	4	11								
2	5	7								
3	5	7	14							
4	5	6	10							
5	6	6	8	15						
6	6	6	8	11						
7	6	6	7	10	15					
8	6	6	7	9	12					
9	6	6	7	8	10	15				

L=7

P \ Q	0	1	2	3	4	5	6	7	8	9
0	4									
1	5									
2	6	11								
3	6	9								
4	7	8	16							
5	7	8	12							
6	7	8	11	19						
7	7	8	10	15						
8	7	8	9	13						
9	7	8	9	11	17					

L=8

P \ Q	0	1	2	3	4	5	6	7	8	9
0	3									
1	3	5								
2	4	5	9							
3	4	5	7	14						
4	4	4	6	9	20					
5	4	4	5	7	11					
6	4	4	5	6	8	13				
7	4	4	5	6	7	10	16			
8	4	5	5	6	6	8	11	18		
9	4	5	5	5	6	7	9	13		

L=9

P \ Q	0	1	2	3	4	5	6	7	8	9
0	2									
1	3	4								
2	3	4	7							
3	3	4	5	9						
4	4	4	5	6	11					
5	4	4	5	6	7	12				
6	4	4	4	5	6	9	14			
7	4	4	4	5	6	7	10	15		
8	4	4	4	5	5	6	8	10	16	
9	4	4	4	5	5	6	7	8	11	18

L=10

P \ Q	0	1	2	3	4	5	6	7	8	9
1	2	8								
1	3	4	11							
2	3	4	5	12						
3	3	3	4	6	13					
4	3	4	4	5	7	14				
5	3	4	4	5	6	8	14			
6	3	4	4	4	5	6	9	14		
7	3	4	4	4	5	6	7	9	14	
8	3	4	4	4	5	5	6	7	10	14
9	4	4	4	4	4	5	6	6	8	10

L=11

P \ Q	0	1	2	3	4	5	6	7	8	9
0	2	4								
1	2	3	5							
2	3	3	3	7						
3	3	3	4	5	8					
4	3	3	4	4	6	8	18			
5	3	3	4	4	5	6	9	15		
6	3	3	3	4	4	5	6	9	14	
7	3	3	3	4	4	5	5	7	9	13
8	3	3	3	4	4	4	5	6	7	9
9	3	3	3	4	4	4	5	5	6	7

L=12

P \ Q	0	1	2	3	4	5	6	7	8	9
0	2	4								
1	2	3	5							
2	2	3	4	6	14					
3	3	3	3	4	6	11				
4	3	3	3	4	5	6	9			
5	3	3	3	4	4	5	6	9	16	
6	3	3	3	3	4	4	5	6	9	13
7	3	3	3	3	4	4	5	5	6	8
8	3	3	3	3	4	4	4	5	5	6
9	3	3	3	3	3	4	4	4	5	6

L=13

P \ Q	0	1	2	3	4	5	6	7	8	9
0	2	3								
1	2	3	4	12						
2	2	3	3	4	8					
3	2	3	3	4	5	7	14			
4	3	3	3	3	4	5	7	10		
5	3	3	3	3	4	4	5	6	9	15
6	3	3	3	3	3	4	4	5	6	8
7	3	3	3	3	3	4	4	4	5	6
8	3	3	3	3	3	3	4	4	5	5
9	3	3	3	3	3	3	4	4	4	5

L=14

P \ Q	0	1	2	3	4	5	6	7	8	9
0	2	3								
1	2	2	3	7						
2	2	2	3	4	6	12				
3	2	2	3	3	4	5	8	18		
4	2	3	3	3	3	4	5	7	11	
5	2	3	3	3	3	4	4	5	6	8
6	3	3	3	3	3	3	4	4	5	6
7	3	3	3	3	3	3	3	4	4	5
8	3	3	3	3	3	3	3	4	4	4
9	3	3	3	3	3	3	3	3	4	4

L=15

P \ Q	0	1	2	3	4	5	6	7	8	9
0	2	2	13							
1	2	2	3	5	19					
2	2	2	2	3	3	4	7			
3	2	2	3	3	3	4	6	9		
4	2	2	3	3	4	4	5	7	10	
5	2	2	3	3	3	3	4	4	5	6
6	2	2	3	3	3	3	3	4	4	5
7	2	2	3	3	3	3	3	3	4	4
8	2	2	3	3	3	3	3	3	3	4
9	2	2	3	3	3	3	3	3	3	3

L=16

P \ Q	0	1	2	3	4	5	6	7	8	9
0	2	5								
1	2	2	3	4	8					
2	2	2	2	3	4	5	9			
3	2	2	2	3	3	4	4	6	9	
4	2	2	2	3	3	3	4	4	5	6
5	2	2	2	3	3	3	3	4	4	5
6	2	2	2	2	3	3	3	3	4	4
7	2	2	2	2	3	3	3	3	3	4
8	2	2	2	2	3	3	3	3	3	3
9	2	2	2	2	3	3	3	3	3	3

FIG. 1 Determination of Number of Samples Required (see 6.4.3)

carried out in a short period of time (preferably the same day). The term *blind fashion* means that the operator does not know that the sample is a duplicate of any previous run.

6.5.3.5 The period of time during which repeated results are to be obtained and the period of time during which all the samples are to be tested;

6.5.3.6 A blank form for reporting the results. For each sample, there shall be space for the date of testing, the two results, and any unusual occurrences. The unit of accuracy for reporting the results shall be specified. This should be, if possible, more digits reported than will be used in the final test method, in order to avoid having rounding unduly affect the estimated precision values.

6.5.3.7 When it is required to estimate the determinability, the report form must include space for each of the determined values as well as the test results.

6.5.3.8 A statement that the test shall be carried out under normal conditions, using operators with good experience but not exceptional knowledge; and that the duration of the test shall be the same as normal.

6.5.4 The pilot program operators may take part in the interlaboratory program. If their extra experience in testing a few more samples produces a noticeable effect, it will serve as a warning that the test method is not satisfactory. They shall be identified in the report of the results so that any such effect may be noted.

6.5.5 It can not be overemphasized that the statement of precision in the test method is to apply to test results obtained by running the agreed procedure exactly as written. Therefore, the test method must not be significantly altered after its precision statement is written.

7. Inspection of Interlaboratory Results for Uniformity and for Outliers

7.1 *Introduction*:

7.1.1 This section specifies procedures for examining the results reported in a statistically designed interlaboratory program (see Section 6) to establish:

7.1.1.1 The independence or dependence of precision and the level of results;

7.1.1.2 The uniformity of precision from laboratory to laboratory, and to detect the presence of outliers.

NOTE 2—The procedures are described in mathematical terms based on the notation of Annex A1 and illustrated with reference to the example data (calculation of bromine number) set out in Annex A2. Throughout this section (and Section 8), the procedures to be used are first specified and then illustrated by a worked example using data given in Annex A2.

NOTE 3—It is assumed throughout this section that all the deviations are either from a single normal distribution or capable of being transformed into such a distribution (see 7.2). Other cases (which are rare) would require different treatment that is beyond the scope of this practice. See **(2)** for a statistical test of normality.

NOTE 4—Although the procedures shown here are in a form suitable for hand calculation, it is strongly advised that an electronic computer be used to store and analyze interlaboratory test results, based on the procedures of this practice. ADJD6300 D2PP, Version 4.43, Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products, has been designed for this purpose.

7.2 *Transformation of Data*:

7.2.1 In many test methods the precision depends on the level of the test result, and thus the variability of the reported results is different from sample to sample. The method of analysis outlined in this practice requires that this shall not be so and the position is rectified, if necessary, by a transformation.

7.2.2 The laboratories' standard deviations D_j, and the repeats standard deviations d_j (see Annex A1) are calculated and plotted separately against the sample means m_j. If the points so plotted may be considered as lying about a pair of lines parallel to the m-axis, then no transformation is necessary. If, however, the plotted points describe non-horizontal straight lines or curves of the form $D = f_1(m)$ and $d = f_2(m)$, then a transformation will be necessary.

7.2.3 The relationships $D = f_1(m)$ and $d = f_2(m)$ will not in general be identical. The statistical procedures of this practice require, however, that the same transformation be applicable both for repeatability and for reproducibility. For this reason the two relationships are combined into a single dependency relationship $D = f(m)$ (where D now includes d) by including a dummy variable T. This will take account of the difference between the relationships, if one exists, and will provide a means of testing for this difference (see A4.1).

7.2.4 The single relationship D = f(m) is best estimated by weighted linear regression analysis. Strictly speaking, an iteratively weighted regression should be used, but in most cases even an unweighted regression will give a satisfactory approximation. The derivation of weights is described in A4.2, and the computational procedure for the regression analysis is described in A4.3. Typical forms of dependence D = f(m) are given in A3.1. These are all expressed in terms of at most two (2) transformation parameters, B and B_0.

7.2.5 The typical forms of dependence, the transformations they give rise to, and the regressions to be performed in order to estimate the transformation parameters B, are all summarized in A3.2. This includes statistical tests for the significance of the regression (that is, is the relationship $D = f(m)$ parallel to the m-axis), and for the difference between the repeatability and reproducibility relationships, based at the 5 % significance level. If such a difference is found to exist, or if no suitable transformation exists, then the alternative methods of Practice E 691 shall be used. In such an event it will not be possible to test for laboratory bias over all samples (see 7.6) or separately estimate the interaction component of variance (see 8.2).

7.2.6 If it has been shown at the 5 % significance level that there is a significant regression of the form $D = f(m)$, then the appropriate transformation $y = F(x)$, where x is the reported result, is given by the equation

$$F(x) = K \int \frac{dx}{f(x)} \tag{2}$$

where K = a constant. In that event, all results shall be transformed accordingly and the remainder of the analysis carried out in terms of the transformed results. Typical transformations are given in A3.1.

7.2.7 The choice of transformation is difficult to make the subject of formalized rules. Qualified statistical assistance may be required in particular cases. The presence of outliers may affect judgement as to the type of transformation required, if any (see 7.7).

7.2.8 *Worked Example*:

7.2.8.1 Table 3 lists the values of m, D, and d for the eight

TABLE 3 Computed from Bromine Example Showing Dependence of Precision on Level

Sample Number	3	8	1	4	5	6	2	7
m	0.756	1.22	2.15	3.64	10.9	48.2	65.4	114
D	0.0669 (14)	0.159 (9)	0.729 (8)	0.211 (11)	0.291 (9)	1.50 (9)	2.22 (9)	2.93 (9)
d	0.0500 (9)	0.0572 (9)	0.127 (9)	0.116 (9)	0.0943 (9)	0.527 (9)	0.818 (9)	0.935 (9)

samples in the example given in Annex A2, correct to three significant digits. Corresponding degrees of freedom are in parentheses. Inspection of the values in Table 3 shows that both *D* and *d* increase with *m*, the rate of increase diminishing as *m* increases. A plot of these figures on log-log paper (that is, a graph of log *D* and *log d* against *log m*) shows that the points may reasonably be considered as lying about two straight lines (see Fig. A4.1 in Annex A4). From the example calculations given in A4.4, the gradients of these lines are shown to be the same, with an estimated value of 0.638. Bearing in mind the errors in this estimated value, the gradient may for convenience be taken as 2/3.

$$\int x^{-\frac{2}{3}}\,dx = 3x^{\frac{1}{3}} \qquad (3)$$

7.2.8.2 Hence, the same transformation is appropriate both for repeatability and reproducibility, and is given by the equation. Since the constant multiplier may be ignored, the transformation thus reduces to that of taking the cube roots of the reported bromine numbers. This yields the transformed data shown in Table A1.3, in which the cube roots are quoted correct to three decimal places.

7.3 *Tests for Outliers*:

7.3.1 The reported data or, if it has been decided that a transformation is necessary, the transformed results shall be inspected for outliers. These are the values which are so different from the remainder that it can only be concluded that they have arisen from some fault in the application of the test method or from testing a wrong sample. Many possible tests may be used and the associated significance levels varied, but those that are specified in the following subsections have been found to be appropriate in this practice. These outlier tests all assume a normal distribution of errors.

7.3.2 *Uniformity of Repeatability*—The first outlier test is concerned with detecting a discordant result in a pair of repeat results. This test **(3)** involves calculating the e_{ij}^2 over all the laboratory/sample combinations. Cochran's criterion at the 1 % significance level is then used to test the ratio of the largest of these values over their sum (see A1.5). If its value exceeds the value given in Table A2.2, corresponding to one degree of freedom, *n* being the number of pairs available for comparison, then the member of the pair farthest from the sample mean shall be rejected and the process repeated, reducing *n* by 1, until no more rejections are called for. In certain cases, specifically when the number of digits used in reporting results leads to a large number of repeat ties, this test can lead to an unacceptably large proportion of rejections, for example, more than 10 %. If this is so, this rejection test shall be abandoned and some or all of the rejected results shall be retained. A decision based on judgement will be necessary in this case.

7.3.3 *Worked Example*— In the case of the example given in Annex A2, the absolute differences (ranges) between transformed repeat results, that is, of the pairs of numbers in Table A1.3, in units of the third decimal place, are shown in Table 4. The largest range is 0.078 for Laboratory G on Sample 3. The sum of squares of all the ranges is

$$0.042^2 + 0.021^2 + \ldots + 0.026^2 + 0^2 = 0.0439.$$

Thus, the ratio to be compared with Cochran's criterion is

TABLE 4 Absolute Differences Between Transformed Repeat Results: Bromine Example

Laboratory	Sample							
	1	2	3	4	5	6	7	8
A	42	21	7	13	7	10	8	0
B	23	12	12	0	7	9	3	0
C	0	6	0	0	7	8	4	0
D	14	6	0	13	0	8	9	32
E	65	4	0	0	14	5	7	28
F	23	20	34	29	20	30	43	0
G	62	4	78	0	0	16	18	56
H	44	20	29	44	0	27	4	32
J	0	59	0	40	0	30	26	0

$$\frac{0.078^2}{0.0439} = 0.138 \qquad (4)$$

where 0.138 is the result obtained by electronic calculation of unrounded factors in the expression. There are 72 ranges and as, from Table A2.2, the criterion for 80 ranges is 0.1709, this ratio is not significant.

7.3.4 *Uniformity of Reproducibility*:

7.3.4.1 The following outlier tests are concerned with establishing uniformity in the reproducibility estimate, and are designed to detect either a discordant pair of results from a laboratory on a particular sample or a discordant set of results from a laboratory on all samples. For both purposes, the Hawkins' test **(4)** is appropriate.

7.3.4.2 This involves forming for each sample, and finally for the overall laboratory averages (see 7.6), the ratio of the largest absolute deviation of laboratory mean from sample (or overall) mean to the square root of certain sums of squares (A1.6).

7.3.4.3 The ratio corresponding to the largest absolute deviation shall be compared with the critical 1 % values given in Table A1.5, where *n* is the number of laboratory/sample cells in the sample (or the number of overall laboratory means) concerned and where *v* is the degrees of freedom for the sum of squares which is additional to that corresponding to the sample in question. In the test for laboratory/sample cells *v* will refer to other samples, but will be zero in the test for overall laboratory averages.

7.3.4.4 If a significant value is encountered for individual samples the corresponding extreme values shall be omitted and the process repeated. If any extreme values are found in the laboratory totals, then all the results from that laboratory shall be rejected.

7.3.4.5 If the test leads to an unacceptably large proportion of rejections, for example, more than 10 %, then this rejection test shall be abandoned and some or all of the rejected results shall be retained. A decision based on judgement will be necessary in this case.

7.3.5 *Worked Example*:

7.3.5.1 The application of Hawkins' test to cell means within samples is shown below.

7.3.5.2 The first step is to calculate the deviations of cell means from respective sample means over the whole array. These are shown in Table 5, in units of the third decimal place.

TABLE 5 Deviations of Cell Means from Respective Sample Means: Transformed Bromine Example

Laboratory	Sample 1	2	3	4	5	6	7	8
A	20	8	14	15	10	48	6	3
B	75	7	20	9	10	47	6	3
C	64	35	3	20	30	4	22	25
D	314	33	18	42	7	39	80	50
E	32	32	30	9	7	18	18	39
F	75	97	31	20	30	8	74	53
G	10	34	32	20	20	61	9	62
H	42	13	4	42	13	21	8	50
J	1	28	22	29	14	8	10	53
Sum of Squares	117	15	4	6	3	11	13	17

The sum of squares of the deviations are then calculated for each sample. These are also shown in Table 5 in units of the third decimal place.

7.3.5.3 The cell to be tested is the one with the most extreme deviation. This was obtained by Laboratory D from Sample 1. The appropriate Hawkins' test ratio is therefore:

$$B^* = \frac{0.314}{\sqrt{0.117 + 0.015 + \ldots + 0.017}} = 0.7281 \quad (5)$$

7.3.5.4 The critical value, corresponding to n = 9 cells in sample 1 and v = 56 extra degrees of freedom from the other samples is interpolated from Table A1.5 as 0.3729. The test value is greater than the critical value, and so the results from Laboratory D on Sample 1 are rejected.

7.3.5.5 As there has been a rejection, the mean value, deviations, and sum of squares are recalculated for Sample 1, and the procedure is repeated. The next cell to be tested will be that obtained by Laboratory F from Sample 2. The Hawkins' test ratio for this cell is:

$$B^* = \frac{0.097}{\sqrt{0.006 + 0.015 + \ldots + 0.017}} = 0.3542 \quad (6)$$

7.3.5.6 The critical value corresponding to n = 9 cells in Sample 2 and v = 55 extra degrees of freedom is interpolated from Table A1.5 as 0.3756. As the test ratio is less than the critical value there will be no further rejections.

7.4 *Rejection of Complete Data from a Sample*:

7.4.1 The laboratories standard deviation and repeats standard deviation shall be examined for any outlying samples. If a transformation has been carried out or any rejection made, new standard deviations shall be calculated.

7.4.2 If the standard deviation for any sample is excessively large, it shall be examined with a view to rejecting the results from that sample.

7.4.3 Cochran's criterion at the 1 % level can be used when the standard deviations are based on the same number of degrees of freedom. This involves calculating the ratio of the largest of the corresponding sums of squares (laboratories or repeats, as appropriate) to their total (see A1.5). If the ratio exceeds the critical value given in Table A2.2, with n as the number of samples and v the degrees of freedom, then all the results from the sample in question shall be rejected. In such an event care should be taken that the extreme standard deviation is not due to the application of an inappropriate transformation (see 7.1), or undetected outliers.

7.4.4 There is no optimal test when standard deviations are based on different degrees of freedom. However, the ratio of the largest variance to that pooled from the remaining samples follows an F-distribution with v_1 and v_2 degrees of freedom (see A1.7). Here v_1 is the degrees of freedom of the variance in question and v_2 is the degrees of freedom from the remaining samples. If the ratio is greater than the critical value given in A2.6, corresponding to a significance level of 0.01/S where S is the number of samples, then results from the sample in question shall be rejected.

7.4.5 *Worked Example*:

7.4.5.1 The standard deviations of the transformed results, after the rejection of the pair of results by Laboratory D on Sample 1, are given in Table 6 in ascending order of sample mean, correct to three significant digits. Corresponding degrees of freedom are in parentheses.

7.4.5.2 Inspection shows that there is no outlying sample among these. It will be noted that the standard deviations are now independent of the sample means, which was the purpose of transforming the results.

7.4.5.3 The values in Table 7, taken from a test program on bromine numbers over 100, will illustrate the case of a sample rejection.

7.4.5.4 It is clear, by inspection, that the laboratories standard deviation of Sample 93 at 15.76 is far greater than the others. It is noted that the repeats standard deviation in this sample is correspondingly large.

7.4.5.5 Since laboratory degrees of freedom are not the same over all samples, the variance ratio test is used. The variance pooled from all samples, excluding Sample 93, is the sum of the sums of squares divided by the total degrees of freedom, that is

$$\frac{(8 \times 5.10^2 + 9 \times 4.20^2 + ... + 8 \times 3.85^2)}{(8 + 9 + ... + 8)} = 19.96 \quad (7)$$

7.4.5.6 The variance ratio is then calculated as

$$\frac{15.26^2}{19.96} = 11.66 \quad (8)$$

where 11.66 is the result obtained by electronic calculation without rounding the factors in the expression.

7.4.5.7 From Table A1.8 the critical value corresponding to a significance level of 0.01/8 = 0.00125, on 8 and 63 degrees

TABLE 6 Standard Deviations of Transformed Results: Bromine Example

Sample number	3	8	1	4	5	6	2	7
m	0.9100	1.066	1.240	1.538	2.217	3.639	4.028	4.851
D	0.0278	0.0473	0.0354	0.0297	0.0197	0.0378	0.0450	0.0416
	(14)	(9)	(13)	(11)	(9)	(9)	(9)	(9)
d	0.0214	0.0182	0.028	0.0164	0.0063	0.0132	0.0166	0.0130
	(9)	(9)	(8)	(9)	(9)	(9)	(9)	(9)

TABLE 7 Example Statistics Indicating Need to Reject an Entire Sample

Sample number	90	89	93	92	91	94	95	96
m	96.1	99.8	119.3	125.4	126.0	139.9	139.4	159.5
D	5.10	4.20	15.26	4.40	4.09	4.87	4.74	3.85
	(8)	(9)	(8)	(11)	(10)	(8)	(9)	(8)
d	1.13	0.99	2.97	0.91	0.73	1.32	1.12	1.36
	(8)	(8)	(8)	(8)	(8)	(8)	(8)	(8)

of freedom, is approximately 4. The test ratio greatly exceeds this and results from Sample 93 shall therefore be rejected.

7.4.5.8 Turning to repeats standard deviations, it is noted that degrees of freedom are identical for each sample and that Cochran's test can therefore be applied. Cochran's criterion will be the ratio of the largest sum of squares (Sample 93) to the sum of all the sums of squares, that is

$$2.97^2/(1.13^2+0.99^2+...+1.36^2) = 0.510 \tag{9}$$

This is greater than the critical value of 0.352 corresponding to $n = 8$ and $v = 8$ (see Table A2.2), and confirms that results from Sample 93 shall be rejected.

7.5 *Estimating Missing or Rejected Values*:

7.5.1 *One of the Two Repeat Values Missing or Rejected*—If one of a pair of repeats (Y_{ij1} or Y_{ij2}) is missing or rejected, this shall be considered to have the same value as the other repeat in accordance with the least squares method.

7.5.2 *Both Repeat Values Missing or Rejected*:

7.5.2.1 If both the repeat values are missing, estimates of a_{ij} ($= Y_{ij1}+Y_{ij2}$) shall be made by forming the laboratories × samples interaction sum of squares (see Eq 17), including the missing values of the totals of the laboratories/samples pairs of results as unknown variables. Any laboratory or sample from which all the results were rejected shall be ignored and new values of L and S used. The estimates of the missing or rejected values shall be those that minimize the interaction sum of squares.

7.5.2.2 If the value of single pair sum a_{ij} has to be estimated, the estimate is given by the equation:

$$a_{ij} = \frac{1}{(L-1)(S'-1)}(LL_1 + S'S_1 - T_1) \tag{10}$$

where:

L_1 = total of remaining pairs in the ith laboratory,
S_1 = total of remaining pairs in the jth sample,
S' = S – number of samples rejected in 7.4, and
T_1 = total of all pairs except a_{ij}.

7.5.2.3 If more estimates are to be made, the technique of successive approximation can be used. In this, each pair sum is estimated in turn from Eq 10, using L_1, S_1, and T_1, values, which contain the latest estimates of the other missing pairs. Initial values for estimates can be based on the appropriate sample mean, and the process usually converges to the required level of accuracy within three complete iterations **(5)**.

7.5.3 *Worked Example*:

7.5.3.1 The two results from Laboratory D on Sample 1 were rejected (see 7.3.4) and thus a_{41} has to be estimated.

Total of remaining results in Laboratory 4 = 36.354
Total of remaining results in Sample 1 = 19.845
Total of all the results except a_{41}= 348.358
Also S' = 8 and L = 9.

Hence, the estimate of a_{41} is given by

$$a_{ij} = \frac{1}{(9-1)(8-1)}[(9 \times 36.354) + (8 \times 19.845) - 348.358] \tag{11}$$

Therefore,

$$a_{ij} = \frac{137.588}{56} = 2.457 \tag{12}$$

7.6 *Rejection Test for Outlying Laboratories*:

7.6.1 At this stage, one further rejection test remains to be carried out. This determines whether it is necessary to reject the complete set of results from any particular laboratory. It could not be carried out at an earlier stage, except in the case where no individual results or pairs are missing or rejected. The procedure again consists of Hawkins' test (see 7.3.4), applied to the laboratory averages over all samples, with any estimated results included. If any laboratories are rejected on all samples, new estimates shall be calculated for any remaining missing values (see 7.5).

7.6.2 *Worked Example*:

7.6.2.1 The procedure on the laboratory averages shown in Table 8 follows exactly that specified in 7.3.4. The deviations of laboratory averages from the overall mean are given in Table 9 in units of the third decimal place, together with the sum of squares. Hawkins' test ratio is therefore:

$$B^* = 0.026/\sqrt{0.00222} = 0.5518 \tag{13}$$

Comparison with the value tabulated in Table A1.5, for $n = 9$ and $v = 0$, shows that this ratio is not significant and therefore no complete laboratory rejections are necessary.

7.7 *Confirmation of Selected Transformation*:

7.7.1 At this stage it is necessary to check that the rejections carried out have not invalidated the transformation used. If necessary, the procedure from 7.2 shall be repeated with the outliers replaced, and if a new transformation is selected, outlier tests shall be reapplied with the replacement values reestimated, based on the new transformation.

7.7.2 *Worked Example*:

7.7.2.1 It was not considered necessary in this case to repeat the calculations from 7.2 with the outlying pair deleted.

TABLE 8 Averages of All Transformed Results from Each Laboratory

Laboratory	A	B	C	D	E	F	G	H	J	Grand Average
Average	2.437	2.439	2.424	2.426[A]	2.444	2.458	2.410	2.428	2.462	2.436

[A] Including estimated value.

TABLE 9 Absolute Deviations of Laboratory Averages from Grand Average × 1000

Laboratory	A	B	C	D	E	F	G	H	J	Sum of Squares
Deviation	1	3	12	10	8	22	26	8	26	2.22

8. Analysis of Variance and Calculation of Precision Estimates

8.1 After the data have been inspected for uniformity, a transformation has been performed, if necessary, and any outliers have been rejected (see Section 7), an analysis of variance shall be carried out. First an analysis of variance table shall be constructed, and finally the precision estimates derived.

8.2 *Analysis of Variance*:

8.2.1 *Forming the Sums of Squares for the Laboratories × Samples Interaction Sum of Squares*—The estimated values, if any, shall be put in the array and an approximate analysis of variance performed.

$$\mathrm{M} = \text{mean correction} = T^2/2L'S' \tag{14}$$

where:

L' = L – number of laboratories rejected in 7.6 – number of laboratories with no remaining results after rejections in 7.3.4,
S' = total of remaining pairs in the jth sample, and
T = the total of all duplicate test results.

$$\text{Samples sum of squares} = [\sum_{j=1}^{S'} (g_j^2/2L')] - M \tag{15}$$

where g_j is the sum of sample j test results.

$$\text{Laboratories sum of squares} = [\sum_{i=1}^{L'} (h_i^2/2S')] - M \tag{16}$$

where h_i is the sum of laboratory i test results.

$$\text{Pairs sum of squares} = (1/2)\,[\sum_{i=1}^{L'} \sum_{j=1}^{S'} a_{ij}^2] - M \tag{17}$$

I = Laboratories × samples interaction sum of squares
= (pairs sum of squares) – (laboratories sum of squares) – (sample sum of squares)

Ignoring any pairs in which there are estimated values, repeats sum of squares,

$$E = (1/2) \sum_{i=1}^{L'} \sum_{j=1}^{S'} e_{ij}^2 \tag{18}$$

The purpose of performing this approximate analysis of variance is to obtain the minimized laboratories × samples interaction sum of squares, I. This is then used as indicated in 8.2.2, to obtain the laboratories sum of squares. If there were no estimated values, the above analysis of variance is exact and paragraph 8.2.2 shall be disregarded.

8.2.1.1 *Worked Example*:

$$\text{Mean correction} = \frac{350.815^2}{144} \tag{19}$$

$$= 854.6605$$

where 854.6605 is the result obtained by electronic calculation without rounding the factors in the expression.

Samples sum of squares

$$= \frac{22.302^2 + 72.512^2 + ... + 19.192^2}{18} - 854.6605 \tag{20}$$

$$= 293.5409$$

Laboratories sum of squares

$$= \frac{38.992^2 + 39.020^2 + ... + 39.387^2}{16} - 854.6605 \tag{21}$$

$$= 0.0356$$

$$\text{Pairs sum of squares} = (1/2)\,(2.520^2 + 8.041^2 + ... + 2.238^2) - 854.6605 \tag{22}$$

$$= 293.6908$$

$$\text{Repeats sum of squares} = (1/2)\,(0.042^2 + 0.021^2 + ... + 0^2) \tag{23}$$

$$= 0.0219$$

Table 10 can then be derived.

8.2.2 *Forming the Sum of Squares for the Exact Analysis of Variance*:

8.2.2.1 In this subsection, all the estimated pairs are disregarded and new values of g_j are calculated. The following sums of squares for the exact analysis of variance **(6)** are formed.

$$\text{Uncorrected sample sum of squares} = \sum_{j=1}^{S'} \frac{g_j^2}{S_j} \tag{24}$$

where:

S_j = 2(L' – number of missing pairs in that sample).

$$\text{Uncorrected pairs sum of squares} = (1/2) \sum_{i=1}^{L'} \sum_{j=1}^{S'} a_{ij}^2 \tag{25}$$

The laboratories sum of squares is equal to (pairs sum of squares) – (samples sum of squares) – (the minimized laboratories × samples interaction sum of squares)

$$= (1/2)\,[\sum_{i=1}^{L'} \sum_{j=1}^{S'} a_{ij}^2] - \left[\sum_{j=1}^{S'} \frac{g_j^2}{S_j}\right] - I \tag{26}$$

8.2.2.2 *Worked Example*:

Uncorrected samples sum of squares

TABLE 10 Sums of Squares: Bromine Example

Sources of Variation	Sum of Squares
Samples	293.5409
Laboratories	0.0356
Laboratories × samples interaction	0.1143
Pairs	293.6908
Repeats	0.0219

$$= \frac{19.845^2}{16} + \frac{72.512^2}{18} + ... + \frac{19.192^2}{18} \quad (27)$$

$$= 1145.1834$$

$$\text{Uncorrected pairs sum of squares} = \frac{2.520^2}{2} + \frac{8.041^2}{2} + ... + \frac{2.238^2}{2} \quad (28)$$

$$= 1145.3329$$

Therefore, laboratories sum of squares

$$= 1145.3329 - 1145.1834 + 0.1143 \quad (29)$$

$$= 0.0352$$

8.2.3 *Degrees of Freedom*:

8.2.3.1 The degrees of freedom for the laboratories are (L'–1). The degrees of freedom for laboratories × samples interaction are (L'–1)(S'–1) for a complete array and are reduced by one for each pair which is estimated. The degrees of freedom for repeats are ($L'S'$) and are reduced by one for each pair in which one or both values are estimated.

8.2.3.2 *Worked Example*—There are eight samples and nine laboratories in this example. As no complete laboratories or samples were rejected, then S' = 8 and L' = 9.

Laboratories degrees of freedom = L–1 = 8.

Laboratories × samples interaction degrees of freedom if there had been no estimates, would have been (9–1)(8–1) = 56. But one pair was estimated, hence laboratories × samples interaction degrees of freedom = 55. Repeats degrees of freedom would have been 72 if there had been no estimates. In this case one pair was estimated, hence repeats degrees of freedom = 71.

8.2.4 *Mean Squares and Analysis of Variance*:

8.2.4.1 The mean square in each case is the sum of squares divided by the corresponding degrees of freedom. This leads to the analysis of variance shown in Table 11. The ratio M_L/M_{LS} is distributed as F with the corresponding laboratories and interaction degrees of freedom (see A1.7). If this ratio exceeds the 5 % critical value given in Table A1.6, then serious bias between the laboratories is implied and the program organizer shall be informed (see 6.5); further standardization of the test method may be necessary, for example, by using a certified reference material.

8.2.4.2 *Worked Example*— The analysis of variance is shown in Table 12. The ratio M_L/M_{LS} = 0.0044/0.002078 has a value 2.117. This is greater than the 5 % critical value obtained from Table A1.6, indicating bias between laboratories.

TABLE 11 Analysis of Variance Table

Sources of Variation	Degrees of Freedom	Sum of Squares	Mean Square
Laboratories	L' − 1	Laboratories sum of squares	M_L
Laboratories × samples	(L' − 1) (S' − 1) − number of estimated pairs	I	M_{LS}
Repeats	$L'S'$ − number of pairs in which one or both values are estimated	E	M_r

TABLE 12 Analysis of Variance Table: Transformed Benzene Example

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F
Laboratories	0.0352	8	0.004400	2.117
Laboratories × samples	0.1143	55	0.002078	
Repeats	0.0219	71	0.000308	...

8.3 *Expectation of Mean Squares and Calculation of Precision Estimates*:

8.3.1 *Expectation of Mean Squares with No Estimated Values*—For a complete array with no estimated values, the expectations of mean squares are

Laboratories: $\sigma_o^2 + 2\sigma_1^2 + 2S'\ \sigma_2^2$
Laboratories × samples: $\sigma_o^2 + 2\sigma_1^2$
Repeats: σ_o^2

where:

σ_1^2 = the component of variance due to interaction between laboratories and samples, and

σ_2^2 = the component of variance due to differences between laboratories.

8.3.2 *Expectation of Mean Squares with Estimated Values*:

8.3.2.1 The coefficients of σ_1^2 and σ_2^2 in the expectation of mean squares are altered in the cases where there are estimated values. The expectations of mean squares then become

Laboratories: $\alpha\sigma_o^2 + 2\sigma_1^2 + \beta\ \sigma_2^2$
Laboratories × samples: $\gamma\sigma_o^2 + 2\sigma_1^2$
Repeats: σ_o^2

where:

$$\beta = 2\,\frac{K - S'}{L' - 1'} \quad (30)$$

where:

K = the number of laboratory × sample cells containing at least one result, and α and γ are computed as in 8.3.2.5

8.3.2.2 If there are no cells with only a single estimated result, then α = γ = 1.

8.3.2.3 If there are no empty cells (that is, every lab has tested every sample at least once, and $K = L' \times S'$), then α and γ are both one plus the proportion of cells with only a single result.

8.3.2.4 If there are both empty cells and cells with only one result, then, for each lab, compute the proportion of samples tested for which there is only one result, p_i, and the sum of these proportions over all labs, P. For each sample, compute the proportion of labs that have tested the sample for which there is only one result on it, q_j, and the sum of these proportions over samples, Q. Compute the total number of cells with only one result, W, and the proportion of these among all nonempty cells, W/K. Then

$$\alpha = 1 + \frac{P - W/K}{L'-1} \quad (31)$$

and

$$\gamma = 1 + \frac{W - P - Q + W/K}{K - L' - S' + 1} \quad (32)$$

NOTE 5—These subsections are based upon the assumptions that both samples and laboratories are random effects.

8.3.2.5 *Worked Example*—For the example, which has eight samples and nine laboratories, one cell is empty (Laboratory D on Sample 1), so K = 71 and

$$\beta = 2\,\frac{71 - 8}{(9 - 1)} = 15.75 \tag{33}$$

None of the nonempty cells has only one result, so $\alpha = \gamma = 1$. To make the example more interesting, assume that only one result remains from Laboratory A on Sample 1. Then $W = 1$, $p_1 = 1/8$, $p_2 = p_3 = ... = p_9 = 0$, and $P = 0.125$. We compute $q_1 = 1/8$ (we don't count Laboratory D in the denominator), $q_2 = q_3 = ... = q_8 = 0$, and $Q = 0.125$. Consequently,

$$\alpha = 1 + \frac{0.125 - 1/71}{9 - 1} = 1.014 \tag{34}$$

and

$$\gamma = 1 + \frac{1 - 0.125 - 0.125 + 1/71}{55} = 1.014 \tag{35}$$

8.3.3 *Calculation of Precision Estimates*:

8.3.3.1 *Repeatability*—The repeatability variance is twice the mean square for repeats. The repeatability estimate is the product of the repeatability standard deviation and the "*t*-value" with appropriate degrees of freedom (see Table A2.3) corresponding to a two-sided probability of 95 %. Round calculated estimates of repeatability in accordance with Practice E 29, specifically paragraph 7.6 of that practice. Note that if a transformation $y = f(x)$ has been used, then

$$r(x) \approx \left|\frac{dx}{dy}\right| r(y) \tag{36}$$

where $r(x)$, $r(y)$ are the corresponding repeatability functions (see). A similar relationship applies to the reproducibility functions $R(x)$, $R(y)$.

8.3.3.2 *Worked Example*:

$$\text{Repeatability variance} = 2\sigma_o^2 \tag{37}$$
$$= 0.000616$$
$$\text{Repeatability of } y = t_{71}\sqrt{0.000616}$$
$$= 1.994\ x\ 0.0428$$
$$= 0.0495$$
$$\text{Repeatability of } x = 3x^{2/3} \times 0.0495$$
$$= 0.148x^{2/3}$$

8.3.3.3 *Reproducibility*—Reproducibility variance = 2 $(\sigma_o^2 + \sigma_1^2 + \sigma_2^2)$ and can be calculated using Eq 38.

$$\text{Reproducibility variance} \tag{38}$$
$$= \frac{2}{\beta} M_L + \left(1 - \frac{2}{\beta}\right) M_{LS} + \left(2 - \gamma + \frac{2}{\beta}(\gamma - \alpha)\right) M_r$$

where the symbols are as set out in 8.2.4 and 8.3.2. The reproducibility estimate is the product of the reproducibility standard deviation and the "*t*-value" with appropriate degrees of freedom (see Table A2.3), corresponding to a two-sided probability of 95 %. An approximation **(7)** to the degrees of freedom of the reproducibility variance is given by Eq 39.

$$v = \frac{(Reproducibility\ variance)^2}{\frac{r_1^2}{L' - 1} + \frac{r_2^2}{v_{LS}} + \frac{r_3^2}{v_r}} \tag{39}$$

where:

r_1, r_2, and r_3 = the three successive terms in Eq 38,
v_{LS} = the degrees of freedom for laboratories × samples, and
v_r = the degrees of freedom for repeats.

(1) Round calculated estimates of reproducibility in accordance with Practice E 29, specifically paragraph 7.6 of that practice.

(2) Substantial bias between laboratories will result in a loss of degrees of freedom estimated by Eq 39. If reproducibility degrees of freedom are less than 30, then the program organizer shall be informed (see 6.5); further standardization of the test method may be necessary.

8.3.3.4 *Worked Example*—Recalling that $\alpha = \gamma = 1$ (not 1.014, as shown in Eq 34 and 35):

$$\text{Reproducibility variance} \tag{40}$$
$$= \left(\frac{2}{15.75} \times 0.00440\right) + \left(\frac{13.75}{15.75} \times 0.002078\right) + 0.000308$$
$$= 0.000559 + 0.001814 + 0.000308$$
$$= 0.002681$$

$$v = \frac{0.002681^2}{\frac{0.000559^2}{8} + \frac{0.001814^2}{55} + \frac{0.000308^2}{71}} \tag{41}$$
$$= 72$$

$$\text{Reproducibility of } y = t_{72}\sqrt{0.002681} \tag{42}$$
$$= 0.1034$$
$$\text{Reproducibility of } x = 0.310x^{2/3}$$

8.3.3.5 *Determinability*—When determinability is relevant, it shall be calculated by the same procedure as is used to calculate repeatability except that pairs of determined values replace test results. This will as much as double the number of "laboratories" for the purposes of this calculation.

8.3.4 *Bias*:

8.3.4.1 Bias equals average sample test result minus its accepted reference value. In the ideal case, average 30 or more test results, measured independently by processes in a state of statistical control, for each of several relatively uniform materials, the reference values for which have been established by one of the following alternatives, and subtract the reference values. In practice, the bias of the test method, for a specific material, may be calculated by comparing the sample average with the accepted reference value.

8.3.4.2 Accepted reference values may be one of the following: an assigned value for a Standard Reference Material, a consensus value based on collaborative experimental work under the guidance of a scientific or engineering organization, an agreed upon value obtained using an accepted reference method, or a theoretical value.

8.3.4.3 Where possible, one or more materials with accepted reference values shall be included in the interlaboratory program. In this way sample averages free of outliers will become available for use in determining bias.

8.3.4.4 Because there will always be at least some bias because of the inherent variability of test results, it is recommended to test the bias value by applying Student's *t* test using the number of laboratories degrees of freedom for the sample made available during the calculation of precision. When the calculated *t* is less than the critical value at the 5 % confidence level, the bias should be reported as not significant.

8.4 *Precision and Bias Section for a Test Method*—When the precision of a test method has been determined, in accordance with the procedures set out in this practice, it shall be included in the test method as illustrated in these examples:

8.4.1 *Precision*—The precision of this test method, which was determined by statistical examination of interlaboratory results using Practice D 6300, is as follows.

8.4.1.1 *Repeatability*—The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would in the long run, in the normal and correct operation of the test method exceed the following values only in one case in 20.

$$Repeatability = 0.148\, x^{2/3} \quad (43)$$

where x is the average of two results.

8.4.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would in the long run exceed the following values only in one case in 20.

$$Reproducibility = 0.310\, x^{2/3} \quad (44)$$

where x is the average of two results.

8.4.1.3 If determinability is relevant, it shall precede repeatability in the statement above. The unit of measurement shall be specified when it differs from that of the test result:

8.4.1.4 *Determinability*—The difference between the pair of determined values averaged to obtain a test result would, in the long run, in the normal and correct operation of the test method, exceed the following value in only one case in 20. When this occurs, the operator must take corrective action:

$$Determinability = 0.59\sqrt{m} \quad (45)$$

where m is the mean of the two determined values in mL.

8.4.2 A graph or table may be used instead of, or in addition to, the equation format shown above. In any event, it is helpful to include a table of typical values like Table 13.

8.4.3 The wording to be used for test methods where the statistical treatment applied is unknown is: "The precision of this test is not known to have been obtained in accordance with currently accepted guidelines (for example, in Committee D02, Practice D 6300)." The existing statement of precision would then follow.

8.5 *Data Storage*:

8.5.1 The interlaboratory program data should be preserved for general reference. Prepare a research report containing details of the test program, including description of the samples, the raw data, and the calculations described herein. Send the file to ASTM Headquarters and request a File Reference Number.

8.5.2 Use the following footnote style in the precision section of the test method. "The results of the cooperative test program, from which these values have been derived, are filed at ASTM Headquarters as RR:D02–XXXX."

9. Keywords

9.1 interlaboratory; precision; repeatability; reproducibility; round robin

TABLE 13 Typical Precision Values: Bromine Example

Average Value Bromine Numbers	Repeatability Bromine Numbers	Reproducibility Bromine Numbers
1.0	0.15	0.31
2.0	0.23	0.49
10.0	0.69	1.44
20.0	1.09	2.28
100.0	3.19	6.68

ANNEXES

(Mandatory Information)

A1. NOTATION AND TESTS

A1.1 The Following Notation Is Used Throughout This Practice:

a	=	the sum of duplicate test results,
e	=	the difference between duplicate test results,
g	=	the sum of sample test results,
h	=	the sum of laboratory test results,
i	=	the suffix denoting laboratory number,
j	=	the suffix denoting sample number,
S	=	the number of samples,
T	=	the total of all duplicate test results,
L	=	the number of laboratories,
m	=	the mean of sample test results,
x	=	the mean of a pair of test results in repeatability and reproducibility statements,
x...	=	an individual test result,
y...	=	a transformed value of x..., and
v	=	the degrees of freedom.

A1.2 Array of Duplicate Results from Each of L Laboratories on S Samples and Corresponding Means m_j

A1.2.1 See Table A1.1.

NOTE A1.1—If a transformation $y = F(x)$ of the reported data is

TABLE A1.1 Typical Layout of Data from Round Robin

	Sample			
Laboratory	1	2	j	S
1	x_{111} x_{112}	x_{121} x_{122}	x_{1j1} x_{1j2}	x_{1S1} x_{1S2}
2	x_{211} x_{212}	x_{221} x_{222}	x_{2j1} x_{2j2}	x_{2S1} x_{2S2}
i	x_{i11} x_{i12}	x_{i21} x_{i22}	x_{ij1} x_{ij2}	x_{iS1} x_{iS2}
L	x_{L11} x_{L12}	x_{L21} x_{L22}	x_{Lj1} x_{Lj2}	x_{LS1} x_{LS2}
Total	g_1	g_2	g_j	g_s
Mean	m_1	m_2	m_j	m_s

necessary (see 7.2), then corresponding symbols y_{ij1} and y_{ij2} are used in place of x_{ij1} and x_{ij2}.

A1.3 Array of Sums of Duplicate Results, of Laboratory Totals h_i and Sample Totals g_j

A1.3.1 See Table A1.2.

A1.3.2 If any results are missing from the complete array, then the divisor in the expression for m_j will be correspondingly reduced.

A1.4 Sums of Squares and Variances (7.2)

A1.4.1 *Repeats Variance for Sample j*:

$$d_j^2 = \frac{\sum_{i=1}^{L} e_{ij}^2}{2L} \tag{A1.1}$$

where:

L = the repeats degrees of freedom for Sample j, one degree of freedom for each laboratory pair. If either or both of a laboratory/sample pair of results is missing, the corresponding term in the numerator is omitted and the factor L is reduced by one.

A1.4.2 *Between Cells Variance for Sample j*:

$$C_j^2 = \left[\sum_{i=1}^{L} \frac{a_{ij}^2}{n_{ij}} - \frac{g_j^2}{S_j}\right] / (L-1) \tag{A1.2}$$

A1.4.3 *Laboratories Variance for Sample j*:

TABLE A1.2 Typical Layout of Sums of Duplicate Results[A]

	Sample				
Laboratory	1	2	j	S	Total
1	a_{11}	a_{12}	a_{1j}	a_{iS}	h_1
2	a_{21}	a_{22}	a_{2j}	a_{2S}	h_2
i	a_{i1}	a_{i2}	a_{ij}	a_{i1}	h_i
L	a_{L1}	a_{L2}	a_{Lj}	a_{LS}	h_L
Total	g_1	g_2	g_j	g_S	T

[A] $a_{ij} = x_{ij1} + x_{ij2}$ (or $a_{ij} = y_{ij1} + y_{ij2}$, if a transformation has been used)
$e_{ij} = x_{ij1} - x_{ij2}$ (or $a_{ij} = y_{ij1} - y_{ij2}$, if a transformation has been used)

$$g_j = \sum_{i=1}^{L} a_{ij} \qquad h_i = \sum_{j=1}^{S} a_{ij}$$

$$m_j = g_j / 2L \qquad T = \sum_{i=1}^{L} h_i = \sum_{j=1}^{S} g_j$$

$$D_j^2 = \frac{1}{K_j}[C_j^2 + (K_j - 1)\, d_j^2] \tag{A1.3}$$

where:

$$K_j = (S_j^2 - \sum_{i=1}^{L} n_{ij}^2) / [S_j \, (L-1)] \tag{A1.4}$$

n_{ij} = number of results obtained by Laboratory i from Sample j,
S_j = total number of results obtained from Sample j, and
L = number of cells in Sample j containing at least one result.

A1.4.4 Laboratories degrees of freedom for Sample j is given approximately **(6)** by:

$$v_j = \frac{(K_j D_j^2)^2}{\frac{(C_j^2)^2}{L-1} + \frac{[(K_j-1)d_j^2]^2}{L}} \tag{A1.5}$$

(rounded to the nearest integer)

A1.4.5 If either or both of a laboratory/sample pair of results is missing, the factor L is reduced by one.

A1.4.6 If both of a laboratory/sample pair of results is missing, the factor (L – 1) is reduced by one.

A1.5 Cochran's Test

A1.5.1 The largest sum of squares, SS_k, out of a set of n mutually independent sums of squares each based on v degrees of freedom, can be tested for conformity in accordance with:

$$\textit{Cochran's criterion} = \frac{SS_k}{\sum_{i=1}^{n} SS_i} \tag{A1.6}$$

A1.5.2 The test ratio is identical if sum of squares values are replaced by mean squares (variance estimates). If the calculated ratio exceeds the critical value given in Table A1.3, then the sum of squares in question, SS_k, is significantly greater than the others with a probability of 99 %. Examples of SS_i include $e_{ij}{}^2$ and $d_j{}^2$(Eq A1.1).

A1.6 Hawkins' Test

A1.6.1 An extreme value in a data set can be tested as an outlier by comparing its deviation from the mean value of the data set to the square root of the sum of squares of all such deviations. This is done in the form of a ratio. Extra information on variability can be provided by including independent sums of squares into the calculations. These will be based on v degrees of freedom and will have the same population variance as the data set in question. Table A1.4 shows the values that are required to apply Hawkins' test to individual samples. The test procedure is as follows:

A1.6.1.1 Identify the sample k and cell mean a_{ik}/n_{ik}, which has the most extreme absolute deviation $|a_{ik}/n_{ik} - m_k|$. The cell identified will be the candidate for the outlier test, be it high or low.

A1.6.1.2 Calculate the total sum of squares of deviations

$$SS = \sum_{i=1}^{S} SS_j \tag{A1.7}$$

A1.6.1.3 Calculate the test ratio

TABLE A1.3 Cube Root of Bromine Number for Low Boiling Samples

	Sample							
Laboratory	1	2	3	4	5	6	7	8
A	1.239	4.010	0.928	1.547	2.224	3.586	4.860	1.063
	1.281	4.031	0.921	1.560	2.231	3.596	4.852	1.063
B	1.193	4.029	0.884	1.547	2.231	3.691	4.856	1.063
	1.216	4.041	0.896	1.547	2.224	3.682	4.853	1.063
C	1.216	3.990	0.913	1.518	2.183	3.647	4.826	1.091
	1.216	3.996	0.913	1.518	2.190	3.639	4.830	1.091
D	1.601	3.992	0.928	1.587	2.210	3.674	4.774	1.000
	1.578	3.998	0.928	1.574	2.210	3.682	4.765	1.032
E	1.281	3.998	0.940	1.547	2.217	3.619	4.871	1.091
	1.216	3.994	0.940	1.547	2.231	3.624	4.864	1.119
F	1.216	4.135	0.896	1.504	2.257	3.662	4.946	1.119
	1.193	4.115	0.862	1.533	2.237	3.632	4.903	1.119
G	1.239	3.996	0.917	1.518	2.197	3.586	4.850	1.032
	1.301	3.992	0.839	1.518	2.197	3.570	4.832	0.976
H	1.260	4.051	0.921	1.474	2.204	3.674	4.860	1.032
	1.216	4.031	0.892	1.518	2.204	3.647	4.856	1.000
J	1.281	4.086	0.932	1.587	2.231	3.662	4.873	1.119
	1.281	4.027	0.932	1.547	2.231	3.632	4.847	1.119

TABLE A1.4 Calculations for Hawkins' Test for Outliers[A]

	Sample			
	1	2	j	S
No. of cells	n_1	n_2	n_j	n_s
Sample mean	m_1	m_2	m_j	m_s
Sum of squares	SS_1	SS_2	SS_j	SS_s

[A] n_j = the number of cells in Sample j which contains at least one result,
m_j = the mean of Sample j, and
SS_j = the sum of squares of deviations of cell means a_{ij}/n_{ij} from sample mean m_j, and is given by

$$SS_j = (L-1)\,C_j^2$$

(L–1) is the between cells (laboratories) degrees of freedom, and shall be reduced by 1 for every cell in Sample j which does not contain a result.

$$B^* = \frac{|a_{ik}/n_{ik} - m_k|}{\sqrt{SS}} \tag{A1.8}$$

A1.6.1.4 Compare the test ratio with the critical value from Table A1.5, for $n = n_k$ and extra degrees of freedom v where

$$v = \sum_{j=1}^{S} (n_j - 1),\, j \neq k. \tag{A1.9}$$

A1.6.1.5 If B^* exceeds the critical value, reject results from the cell in question (Sample k, Laboratory i), modify n_k, m_k and SS_k values accordingly, and repeat from A1.6.1.1.

NOTE A1.2—Hawkins' test applies theoretically to the detection of only a single outlier laboratory in a sample. The technique of repeated tests for a single outlier, in the order of maximum deviation from sample mean, implies that the critical values in Table A1.5 will not refer exactly to the 1 % significance level. It has been shown by Hawkins, however, that if $n \geq 5$ and the total degrees of freedom ($n + v$) are greater than 20, then this effect is negligible, as are the effects of masking (one outlier hiding another) and swamping (the rejection of one outlier leading to the rejection of others).

A1.6.1.6 When the test is applied to laboratories averaged over all samples, Table A1.4 will reduce to a single column containing:
n = number of laboratories = L,
m = overall mean = T/N, where N is the total number of results in the array, and
SS = sum of squares of deviations of laboratory means from the overall mean, and is given by

$$SS = \sum_{i=1}^{L} \left(\frac{h_i}{n_i} - m\right)^2 \tag{A1.10}$$

where:
n_i = the number of results in Laboratory i.

In the test procedure, therefore, identify the laboratory mean h_i/n_i which differs most from the overall mean, m. The corresponding test ratio then becomes:

$$B^* = \frac{|\,h_i/n_i - m|}{\sqrt{SS}} \tag{A1.11}$$

A1.6.1.7 This shall be compared with the critical value from Table A1.5 as before, but now with extra degrees of freedom v = 0. If a laboratory is rejected, adjust the values of n, m, and SS accordingly and repeat the calculations.

A1.7 Variance Ratio Test (*F*-Test)

A1.7.1 A variance estimate V_1, based on v_1 degrees of freedom, can be compared with a second estimate V_2, based on v_2 degrees of freedom, by calculating the ratio

$$F = \frac{V_1}{V_2} \tag{A1.12}$$

A1.7.2 If the ratio exceeds the appropriate critical value given in Tables A1.6-A1.9, where v_1 corresponds to the numerator and v_2 corresponds to the denominator, then V_1 is greater than V_2 at the chosen level of significance.

TABLE A1.5 Critical Values of Hawkins' 1 % Outlier Test for *n* = 3 to 50 and υ = 0 to 200

	Degrees of Freedom υ											
n	0	5	10	15	20	30	40	50	70	100	150	200
3	0.8165	0.7240	0.6100	0.5328	0.4781	0.4049	0.3574	0.3233	0.2769	0.2340	0.1926	0.1674
4	0.8639	0.7505	0.6405	0.5644	0.5094	0.4345	0.3850	0.3492	0.3000	0.2541	0.2096	0.1824
5	0.8818	0.7573	0.6530	0.5796	0.5258	0.4510	0.4012	0.3647	0.3142	0.2668	0.2204	0.1920
6	0.8823	0.7554	0.6571	0.5869	0.5347	0.4612	0.4115	0.3749	0.3238	0.2755	0.2280	0.1988
7	0.8733	0.7493	0.6567	0.5898	0.5394	0.4676	0.4184	0.3819	0.3307	0.2819	0.2337	0.2039
8	0.8596	0.7409	0.6538	0.5901	0.5415	0.4715	0.4231	0.3869	0.3358	0.2868	0.2381	0.2079
9	0.8439	0.7314	0.6493	0.5886	0.5418	0.4738	0.4262	0.3905	0.3396	0.2906	0.2416	0.2112
10	0.8274	0.7213	0.6439	0.5861	0.5411	0.4750	0.4283	0.3930	0.3426	0.2936	0.2445	0.2139
11	0.8108	0.7111	0.6380	0.5828	0.5394	0.4753	0.4295	0.3948	0.3448	0.2961	0.2469	0.2162
12	0.7947	0.7010	0.6318	0.5790	0.5373	0.4750	0.4302	0.3960	0.3466	0.2981	0.2489	0.2181
13	0.7791	0.6910	0.6254	0.5749	0.5347	0.4742	0.4304	0.3968	0.3479	0.2997	0.2507	0.2198
14	0.7642	0.6812	0.6189	0.5706	0.5319	0.4731	0.4302	0.3972	0.3489	0.3011	0.2521	0.2212
15	0.7500	0.6717	0.6125	0.5662	0.5288	0.4717	0.4298	0.3973	0.3496	0.3021	0.2534	0.2225
16	0.7364	0.6625	0.6061	0.5617	0.5256	0.4701	0.4291	0.3972	0.3501	0.3030	0.2544	0.2236
17	0.7235	0.6535	0.5998	0.5571	0.5223	0.4683	0.4282	0.3968	0.3504	0.3037	0.2554	0.2246
18	0.7112	0.6449	0.5936	0.5526	0.5189	0.4665	0.4272	0.3964	0.3505	0.3043	0.2562	0.2254
19	0.6996	0.6365	0.5876	0.5480	0.5155	0.4645	0.4260	0.3958	0.3506	0.3047	0.2569	0.2262
20	0.6884	0.6286	0.5816	0.5436	0.5120	0.4624	0.4248	0.3951	0.3505	0.3051	0.2575	0.2269
21	0.6778	0.6209	0.5758	0.5392	0.5086	0.4603	0.4235	0.3942	0.3503	0.3053	0.2580	0.2275
22	0.6677	0.6134	0.5702	0.5348	0.5052	0.4581	0.4221	0.3934	0.3500	0.3055	0.2584	0.2280
23	0.6581	0.6062	0.5647	0.5305	0.5018	0.4559	0.4206	0.3924	0.3496	0.3056	0.2588	0.2285
24	0.6488	0.5993	0.5593	0.5263	0.4984	0.4537	0.4191	0.3914	0.3492	0.3056	0.2591	0.2289
25	0.6400	0.5925	0.5540	0.5221	0.4951	0.4515	0.4176	0.3904	0.3488	0.3056	0.2594	0.2293
26	0.6315	0.5861	0.5490	0.5180	0.4918	0.4492	0.4160	0.3893	0.3482	0.3054	0.2596	0.2296
27	0.6234	0.5798	0.5440	0.5140	0.4885	0.4470	0.4145	0.3881	0.3477	0.3053	0.2597	0.2299
28	0.6156	0.5737	0.5392	0.5101	0.4853	0.4447	0.4129	0.3870	0.3471	0.3051	0.2599	0.2302
29	0.6081	0.5678	0.5345	0.5063	0.4821	0.4425	0.4113	0.3858	0.3464	0.3049	0.2600	0.2304
30	0.6009	0.5621	0.5299	0.5025	0.4790	0.4403	0.4097	0.3846	0.3458	0.3047	0.2600	0.2306
35	0.5686	0.5361	0.5086	0.4848	0.4641	0.4294	0.4016	0.3785	0.3421	0.3031	0.2600	0.2312
40	0.5413	0.5136	0.4897	0.4688	0.4504	0.4191	0.3936	0.3722	0.3382	0.3010	0.2594	0.2314
45	0.5179	0.4939	0.4728	0.4542	0.4377	0.4094	0.3859	0.3660	0.3340	0.2987	0.2586	0.2312
50	0.4975	0.4764	0.4577	0.4410	0.4260	0.4002	0.3785	0.3600	0.3299	0.2962	0.2575	0.2308

TABLE A1.6 Critical 5 % Values of F

		υ_1															
		3	4	5	6	7	8	9	10	15	20	30	50	100	200	500	∞
υ_2	3	9.28	9.12	9.01	8.94	8.89	8.85	8.81	8.79	8.70	8.66	8.62	8.58	8.55	8.54	8.53	8.53
	4	6.59	6.39	6.26	6.16	6.09	6.04	6.00	5.96	5.86	5.80	5.75	5.70	5.66	5.65	5.64	5.63
	5	5.41	5.19	5.05	4.95	4.88	4.82	4.77	4.74	4.62	4.56	4.50	4.44	4.41	4.39	4.37	4.37
	6	4.76	4.53	4.39	4.28	4.21	4.15	4.10	4.06	3.94	3.87	3.81	3.75	3.71	3.69	3.68	3.67
	7	4.35	4.12	3.97	3.87	3.79	3.73	3.68	3.64	3.51	3.44	3.38	3.32	3.27	3.25	3.24	3.23
	8	4.07	3.84	3.69	3.58	3.50	3.44	3.39	3.35	3.22	3.15	3.08	3.02	2.97	2.95	2.94	2.93
	9	3.86	3.63	3.48	3.37	3.29	3.23	3.18	3.14	3.01	2.94	2.86	2.80	2.76	2.73	2.72	2.71
	10	3.71	3.48	3.33	3.22	3.14	3.07	3.02	2.98	2.85	2.77	2.70	2.64	2.59	2.56	2.55	2.54
	15	3.29	3.06	2.90	2.79	2.71	2.64	2.59	2.54	2.40	2.33	2.25	2.18	2.12	2.10	2.08	2.07
	20	3.10	2.87	2.71	2.60	2.51	2.45	2.39	2.35	2.20	2.12	2.04	1.97	1.91	1.88	1.86	1.84
	30	2.92	2.69	2.53	2.42	2.33	2.27	2.21	2.16	2.01	1.93	1.84	1.76	1.70	1.66	1.64	1.62
	50	2.79	2.56	2.40	2.29	2.20	2.13	2.07	2.03	1.87	1.78	1.69	1.60	1.52	1.48	1.46	1.44
	100	2.70	2.46	2.31	2.19	2.10	2.03	1.97	1.93	1.77	1.68	1.57	1.48	1.39	1.34	1.31	1.28
	200	2.65	2.42	2.26	2.14	2.06	1.98	1.93	1.88	1.72	1.62	1.52	1.41	1.32	1.26	1.22	1.19
	500	2.62	2.39	2.23	2.12	2.03	1.96	1.90	1.85	1.69	1.59	1.48	1.38	1.28	1.21	1.16	1.11
	∞	2.60	2.37	2.21	2.10	2.01	1.94	1.88	1.83	1.67	1.57	1.46	1.35	1.24	1.17	1.11	1.00

TABLE A1.7 Critical 1 % Values of F

	υ_1															
υ_2	3	4	5	6	7	8	9	10	15	20	30	50	100	200	500	∞
3	29.5	28.7	28.2	27.9	27.7	27.5	27.3	27.2	26.9	26.7	26.5	26.4	26.2	26.2	26.1	26.1
4	16.7	16.0	15.5	15.2	15.0	14.8	14.7	14.5	14.2	14.0	13.8	13.7	13.6	13.5	13.5	13.5
5	12.1	11.4	11.0	10.7	10.5	10.3	10.2	10.1	9.72	9.55	9.38	9.24	9.13	9.08	9.04	9.02
6	9.78	9.15	8.75	8.47	8.26	8.10	7.98	7.87	7.56	7.40	7.23	7.09	6.99	6.93	6.90	6.88
7	8.45	7.85	7.46	7.19	6.99	6.84	6.72	6.62	6.31	6.16	5.99	5.86	5.75	5.70	5.67	5.65
8	7.59	7.01	6.63	6.37	6.18	6.03	5.91	5.81	5.52	5.36	5.20	5.07	4.96	4.91	4.88	4.86
9	6.99	6.42	6.06	5.80	5.61	5.47	5.35	5.26	4.96	4.81	4.65	4.52	4.42	4.36	4.33	4.31
10	6.55	5.99	5.64	5.39	5.20	5.06	4.94	4.85	4.56	4.41	4.25	4.12	4.01	3.96	3.93	3.91
15	5.42	4.89	4.56	4.32	4.14	4.00	3.89	3.80	3.52	3.37	3.21	3.08	2.98	2.92	2.89	2.87
20	4.94	4.43	4.10	3.87	3.70	3.56	3.46	3.37	3.09	2.94	2.78	2.64	2.54	2.48	2.44	2.42
30	4.51	4.02	3.70	3.47	3.30	3.17	3.07	2.98	2.70	2.55	2.39	2.25	2.13	2.07	2.03	2.01
50	4.20	3.72	3.41	3.19	3.02	2.89	2.79	2.70	2.42	2.27	2.10	1.95	1.82	1.76	1.71	1.68
100	3.98	3.51	3.21	2.99	2.82	2.69	2.59	2.50	2.22	2.07	1.89	1.73	1.60	1.52	1.47	1.43
200	3.88	3.41	3.11	2.89	2.73	2.60	2.50	2.41	2.13	1.97	1.79	1.63	1.48	1.39	1.33	1.28
500	3.82	3.36	3.05	2.84	2.68	2.55	2.44	2.36	2.07	1.92	1.74	1.56	1.41	1.31	1.23	1.16
∞	3.78	3.32	3.02	2.80	2.64	2.51	2.41	2.32	2.04	1.88	1.70	1.52	1.36	1.25	1.15	1.00

TABLE A1.8 Critical 0.1 % Values of F

	υ_1															
υ_2	3	4	5	6	7	8	9	10	15	20	30	50	100	200	500	∞
3	141	137	135	133	132	131	130	129	127	126	125	125	124	124	124	124
4	56.2	53.4	51.7	50.5	49.7	49.0	48.5	48.0	46.8	46.1	45.4	44.9	44.5	44.3	44.1	44.0
5	33.2	31.1	29.8	28.8	28.2	27.6	27.2	26.9	25.9	25.4	24.9	24.4	24.1	23.9	23.8	23.8
6	23.7	21.9	20.8	20.0	19.5	19.0	18.7	18.4	17.6	17.1	16.7	16.3	16.0	15.9	15.8	15.8
7	18.8	17.2	16.2	15.5	15.0	14.6	14.3	14.1	13.3	12.9	12.5	12.2	11.9	11.8	11.7	11.7
8	15.8	14.4	13.5	12.9	12.4	12.0	11.8	11.5	10.8	10.5	10.1	9.80	9.57	9.46	9.39	9.34
9	13.9	12.6	11.7	11.1	10.7	10.4	10.1	9.89	9.24	8.90	8.55	8.26	8.04	7.93	7.86	7.81
10	12.6	11.3	10.5	9.92	9.52	9.20	8.96	8.75	8.13	7.80	7.47	7.19	6.98	6.87	6.81	6.76
15	9.34	8.25	7.57	7.09	6.74	6.47	6.26	6.08	5.53	5.25	4.95	4.70	4.51	4.41	4.35	4.31
20	8.10	7.10	6.46	6.02	5.69	5.44	5.24	5.08	4.56	4.29	4.01	3.77	3.58	3.48	3.42	3.38
30	7.05	6.12	5.53	5.12	4.82	4.58	4.39	4.24	3.75	3.49	3.22	2.98	2.79	2.69	2.63	2.59
50	6.34	5.46	4.90	4.51	4.22	4.00	3.82	3.67	3.20	2.95	2.68	2.44	2.24	2.14	2.07	2.03
100	5.85	5.01	4.48	4.11	3.83	3.61	3.44	3.30	2.84	2.59	2.32	2.07	1.87	1.75	1.68	1.62
200	5.64	4.81	4.29	3.92	3.65	3.43	3.26	3.12	2.67	2.42	2.15	1.90	1.68	1.55	1.46	1.39
500	5.51	4.69	4.18	3.82	3.54	3.33	3.16	3.02	2.58	2.33	2.05	1.80	1.57	1.43	1.32	1.23
∞	5.42	4.62	4.10	3.74	3.47	3.27	3.10	2.96	2.51	2.27	1.99	1.73	1.49	1.34	1.21	1.00

TABLE A1.9 Critical 0.05 % Values of F

	υ_1															
υ_2	3	4	5	6	7	8	9	10	15	20	30	50	100	200	500	∞
3	225	218	214	211	209	208	207	206	203	201	199	198	197	197	196	196
4	80.1	76.1	73.6	71.9	70.6	69.7	68.9	68.3	66.5	65.5	64.6	63.8	63.2	62.9	62.7	62.6
5	44.4	41.5	39.7	38.5	37.6	36.9	36.4	35.9	34.6	33.9	33.1	32.5	32.1	31.8	31.7	31.6
6	30.4	28.1	26.6	25.6	24.9	24.3	23.9	23.5	22.4	21.9	21.4	20.9	20.5	20.3	20.2	20.1
7	23.5	21.4	20.2	19.3	18.7	18.2	17.8	17.5	16.5	16.0	15.5	15.1	14.7	14.6	14.5	14.4
8	19.4	17.6	16.4	15.7	15.1	14.6	14.3	14.0	13.1	12.7	12.2	11.8	11.6	11.4	11.4	11.3
9	16.8	15.1	14.1	13.3	12.8	12.4	12.1	11.8	11.0	10.6	10.2	9.80	9.53	9.40	9.32	9.26
10	15.0	13.4	12.4	11.8	11.3	10.9	10.6	10.3	9.56	9.16	8.75	8.42	8.16	8.04	7.96	7.90
15	10.8	9.48	8.66	8.10	7.68	7.36	7.11	6.91	6.27	5.93	5.58	5.29	5.06	4.94	4.87	4.83
20	9.20	8.02	7.28	6.76	6.38	6.08	5.85	5.66	5.07	4.75	4.42	4.15	3.93	3.82	3.75	3.70
30	7.90	6.82	6.14	5.66	5.31	5.04	4.82	4.65	4.10	3.80	3.48	3.22	3.00	2.89	2.82	2.78
50	7.01	6.01	5.37	4.93	4.60	4.34	4.14	3.98	3.45	3.16	2.86	2.59	2.37	2.25	2.17	2.13
100	6.43	5.47	4.87	4.44	4.13	3.89	3.70	3.54	3.03	2.75	2.44	2.18	1.95	1.82	1.74	1.67
200	6.16	5.23	4.64	4.23	3.92	3.68	3.49	3.34	2.83	2.56	2.25	1.98	1.74	1.60	1.50	1.42
500	6.01	5.09	4.51	4.10	3.80	3.56	3.36	3.21	2.72	2.45	2.14	1.87	1.61	1.46	1.34	1.24
∞	5.91	5.00	4.42	4.02	3.72	3.48	3.30	3.14	2.65	2.37	2.07	1.79	1.53	1.36	1.22	1.00

A2. EXAMPLE RESULTS OF TEST FOR DETERMINATION OF BROMINE NUMBER AND STATISTICAL TABLES

A2.1 Bromine Number for Low Boiling Samples

A2.1.1 See Table A2.1.

A2.2 Cube Root of Bromine Number for Low Boiling Samples

A2.2.1 See Table A1.3.

A2.3 Critical 1 % Values of Cochran's Criterion for *n* Variance Estimates and *v* Degrees of Freedom

A2.3.1 See Table A2.2.

A2.4 Critical Values of Hawkins' 1 % Outlier Test for *n* = 3 to 50 and *v* = 0 to 200

A2.4.1 See Table A1.5.

A2.4.2 The critical values in the table are correct to the fourth decimal place in the range $n = 3$ to 30 and $v = 0$, 5, 15, and 30 **(3)**. Other values were derived from the Bonferroni inequality as

$$B^* = t\left[\frac{(n-1)}{n\,(n+v-2+t^2)}\right]^{\frac{1}{2}} \quad \text{(A2.1)}$$

where t is the upper 0.005/ n fractile of a t-variate with $n + v - 2$ degrees of freedom. The values so computed are only slightly conservative, and have a maximum error of approximately 0.0002 above the true value. If critical values are required for intermediate values of n and v, they may be estimated by second order interpolation using the square of the reciprocals of the tabulated values. Similarly, second order extrapolation can be used to estimate values beyond $n = 50$ and $v = 200$.

A2.5 Critical Values of *t*

A2.5.1 See Table A2.3.

A2.6 Critical Values of *F*[9]

A2.6.1 *Critical 5 % Values of F*—See Table A1.6.

A2.6.2 *Critical 1 % Values of F*—See Table A1.7.

A2.6.3 *Critical 0.1 % Values of F*—See Table A1.8.

A2.6.4 *Critical 0.05 % Values of F*—See Table A1.9.

A2.6.5 *Approximate Formula for Critical Values of F*—Critical values of F for untabulated values of v_1, and v_2 may be approximated by second order interpolation from the tables. Critical values of F corresponding to v_1 >30 and v_2 >30 degrees of freedom and significance level 100 (1–P) %, where P is the probability, can also be approximated from the formula

$$log_{10}\ (F) = \frac{A(P)}{\sqrt{b - B(P)}} - C(P)\left(\frac{1}{v_1} + \frac{1}{v_2}\right) \quad \text{(A2.2)}$$

where:

$$b = 2/\left(\frac{1}{v_1} + \frac{1}{v_2}\right) \quad \text{(A2.3)}$$

A2.6.5.1 Values of $A\,(P)$, $B\,(P)$, and $C(P)$ are given in Table A2.4 for typical values of significance level 100 (1–P) %.

A2.7 *Critical Values of the Normal Distribution (see Table A2.5)*:

[9] See **(8)** for the source of these tables.

TABLE A2.1 Bromine Number for Low Boiling Samples

	Sample							
Laboratory	1	2	3	4	5	6	7	8
A	1.9	64.5	0.80	3.7	11.0	46.1	114.8	1.2
	2.1	65.5	0.78	3.8	11.1	46.5	114.2	1.2
B	1.7	65.4	0.69	3.7	11.1	50.3	114.5	1.2
	1.8	66.0	0.72	3.7	11.0	49.9	114.3	1.2
C	1.8	63.5	0.76	3.5	10.4	48.5	112.4	1.3
	1.8	63.8	0.76	3.5	10.5	48.2	112.7	1.3
D	4.1	63.6	0.80	4.0	10.8	49.6	108.8	1.0
	4.0	63.9	0.80	3.9	10.8	49.9	108.2	1.1
E	2.1	63.9	0.83	3.7	10.9	47.4	115.6	1.3
	1.8	63.7	0.83	3.7	11.1	47.6	115.1	1.4
F	1.8	70.7	0.72	3.4	11.5	49.1	121.0	1.4
	1.7	69.7	0.64	3.6	11.2	47.9	117.9	1.4
G	1.9	63.8	0.77	3.5	10.6	46.1	114.1	1.1
	2.2	63.6	0.59	3.5	10.6	45.5	112.8	0.93
H	2.0	66.5	0.78	3.2	10.7	49.6	114.8	1.1
	1.8	65.5	0.71	3.5	10.7	48.5	114.5	1.0
J	2.1	68.2	0.81	4.0	11.1	49.1	115.7	1.4
	2.1	65.3	0.81	3.7	11.1	47.9	113.9	1.4

TABLE A2.2 Critical 1 % Values of Cochran's Criterion for *n* Variance Estimates and υ Degrees of Freedom[A]

	Degrees of Freedom υ								
n	1	2	3	4	5	10	15	20	30	50
3	0.9933	0.9423	0.8831	0.8335	0.7933	0.6743	0.6145	0.5775	0.5327	0.4872
4	0.9676	0.8643	0.7814	0.7212	0.6761	0.5536	0.4964	0.4620	0.4213	0.3808
5	0.9279	0.7885	0.6957	0.6329	0.5875	0.4697	0.4168	0.3855	0.3489	0.3131
6	0.8828	0.7218	0.6258	0.5635	0.5195	0.4084	0.3597	0.3312	0.2982	0.2661
7	0.8376	0.6644	0.5685	0.5080	0.4659	0.3616	0.3167	0.2907	0.2606	0.2316
8	0.7945	0.6152	0.5209	0.4627	0.4227	0.3248	0.2832	0.2592	0.2316	0.2052
9	0.7544	0.5727	0.4810	0.4251	0.3870	0.2950	0.2563	0.2340	0.2086	0.1842
10	0.7175	0.5358	0.4469	0.3934	0.3572	0.2704	0.2342	0.2135	0.1898	0.1673
11	0.6837	0.5036	0.4175	0.3663	0.3318	0.2497	0.2157	0.1963	0.1742	0.1532
12	0.6528	0.4751	0.3919	0.3428	0.3099	0.2321	0.2000	0.1818	0.1611	0.1414
13	0.6245	0.4498	0.3695	0.3223	0.2909	0.2169	0.1865	0.1693	0.1498	0.1313
14	0.5985	0.4272	0.3495	0.3043	0.2741	0.2036	0.1748	0.1585	0.1400	0.1226
15	0.5747	0.4069	0.3318	0.2882	0.2593	0.1919	0.1645	0.1490	0.1315	0.1150
20	0.4799	0.3297	0.2654	0.2288	0.2048	0.1496	0.1274	0.1150	0.1010	0.0879
25	0.4130	0.2782	0.2220	0.1904	0.1699	0.1230	0.1043	0.0939	0.0822	0.0713
30	0.3632	0.2412	0.1914	0.1635	0.1455	0.1046	0.0885	0.0794	0.0694	0.0600
35	0.3247	0.2134	0.1685	0.1435	0.1274	0.0912	0.0769	0.0690	0.0601	0.0519
40	0.2940	0.1916	0.1507	0.1281	0.1136	0.0809	0.0681	0.0610	0.0531	0.0457
45	0.2690	0.1740	0.1364	0.1158	0.1025	0.0727	0.0611	0.0547	0.0475	0.0409
50	0.2481	0.1596	0.1248	0.1057	0.0935	0.0661	0.0555	0.0496	0.0431	0.0370
60	0.2151	0.1371	0.1068	0.0902	0.0796	0.0561	0.0469	0.0419	0.0363	0.0311
70	0.1903	0.1204	0.0935	0.0788	0.0695	0.0487	0.0407	0.0363	0.0314	0.0269
80	0.1709	0.1075	0.0832	0.0701	0.0617	0.0431	0.0360	0.0320	0.0277	0.0236
90	0.1553	0.0972	0.0751	0.0631	0.0555	0.0387	0.0322	0.0287	0.0248	0.0211
100	0.1424	0.0888	0.0685	0.0575	0.0505	0.0351	0.0292	0.0260	0.0224	0.0191

[A] These values are slightly conservative approximations calculated via Bonferroni's inequality **(3)** as the upper 0.01/*n* fractile of the beta distribution. If intermediate values are required along the *n*-axis, they may be obtained by linear interpolation of the reciprocals of the tabulated values. If intermediate values are required along the *v*-axis, they may be obtained by second order interpolation of the reciprocals of the tabulated values.

A2.7.1 Critical values *Z* corresponding to a single-sided probability *P*, or to a double-sided significance level 2 (1–*P*) are given below in terms of the "standard normal deviate," where

$$Z = \frac{x - \mu}{\sigma} \qquad \text{(A2.4)}$$

and where μ and σ are the mean and standard deviation respectively of the normal distribution.

TABLE A2.3 Critical Values of *t*

Degrees of Freedom	Double-Sided % Significance Level						
	50	40	30	20	10	5	1
1	1.000	1.376	1.963	3.078	6.314	12.706	63.657
2	0.816	1.061	1.386	1.886	2.920	4.303	9.925
3	0.765	0.978	1.250	1.638	2.353	3.182	5.841
4	0.741	0.941	1.190	1.533	2.132	2.776	4.604
5	0.727	0.920	1.156	1.476	2.015	2.571	4.032
6	0.718	0.906	1.134	1.440	1.943	2.447	3.707
7	0.711	0.896	1.119	1.415	1.895	2.365	3.499
8	0.706	0.889	1.108	1.397	1.860	2.306	3.355
9	0.703	0.883	1.100	1.383	1.833	2.262	3.250
10	0.700	0.879	1.093	1.372	1.812	2.228	3.165
11	0.697	0.876	1.088	1.363	1.796	2.201	3.106
12	0.695	0.873	1.083	1.356	1.782	2.179	3.055
13	0.694	0.870	1.079	1.350	1.771	2.160	3.012
14	0.692	0.868	1.076	1.345	1.761	2.145	2.977
15	0.691	0.866	1.074	1.341	1.753	2.131	2.947
16	0.690	0.865	1.071	1.337	1.746	2.120	2.921
17	0.689	0.863	1.069	1.333	1.740	2.110	2.898
18	0.688	0.862	1.067	1.330	1.734	2.101	2.878
19	0.688	0.861	1.066	1.328	1.729	2.093	2.861
20	0.687	0.860	1.064	1.325	1.725	2.086	2.845
21	0.686	0.859	1.063	1.323	1.721	2.080	2.831
22	0.686	0.858	1.061	1.321	1.717	2.074	2.819
23	0.685	0.858	1.060	1.319	1.714	2.069	2.807
24	0.685	0.857	1.059	1.318	1.711	2.064	2.797
25	0.684	0.856	1.058	1.316	1.708	2.060	2.787
26	0.684	0.856	1.058	1.315	1.706	2.056	2.779
27	0.684	0.855	1.057	1.314	1.703	2.052	2.771
28	0.683	0.855	1.056	1.313	1.701	2.048	2.763
29	0.683	0.854	1.055	1.311	1.699	2.045	2.756
30	0.683	0.854	1.055	1.310	1.697	2.042	2.750
40	0.681	0.851	1.050	1.303	1.684	2.021	2.704
50	0.680	0.849	1.048	1.299	1.676	2.008	2.678
60	0.679	0.848	1.046	1.296	1.671	2.000	2.660
120	0.677	0.845	1.041	1.289	1.658	1.980	2.617
∞	0.674	0.842	1.036	1.282	1.645	1.960	2.576

TABLE A2.4 Constants for Approximating Critical Values of F[A]

100 (1–P) %	$A(P)$	$B(P)$	$C(P)$
10.0 %	1.1131	0.77	0.527
5.0 %	1.4287	0.95	0.681
2.5 %	1.7023	1.14	0.846
1.0 %	2.0206	1.40	1.073
0.5 %	2.2373	1.61	1.250
0.1 %	2.6841	2.09	1.672
0.05 %	2.8580	2.30	1.857

[A] For values of P not given above, critical values of F may be obtained by second order interpolation/extrapolation of log (F) (either tabulated or estimated from the formula) against log (1–P).

TABLE A2.5 Critical Values of the Normal Distribution[A]

P	0.70	0.80	0.90	0.95	0.975	0.99	0.995
Z	0.524	0.842	1.282	1.645	1.960	2.326	2.576
2(1–P)	0.60	0.40	0.20	0.10	0.05	0.02	0.01

[A] When P is less than 0.5 the appropriate critical value is the negative of the value corresponding to a probability (1–P).

A3. TYPES OF DEPENDENCE AND CORRESPONDING TRANSFORMATIONS (7.2)

A3.1 Types of Dependence

A3.1.1 See Table A3.1.

A3.2 Transformation Procedure

A3.2.1 The following steps shall be taken in identifying the correct type of transformation and its parameters, B or B_0, or both.

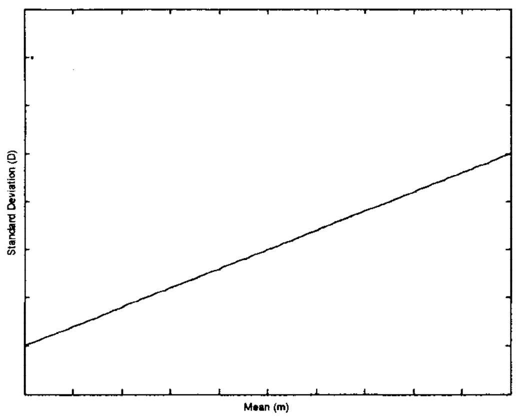
A3.2.1.1 Plot laboratories standard deviations, D, and repeats standard deviations, d, against sample means in the form of scatter diagrams. Refer to Figs. A3.1-A3.6 and identify the type of transformation to be applied (if any).

A3.2.1.2 With the exception of the power transformation (Type 2 in Table A3.1), the transformation parameter is either known in advance or estimated from the scatter diagrams. For the arcsin (Type 3) and logistic (Type 4) transformations, B will be the upper limit of the rating scale or "score" that defines results. For the log (Type 1) transformation, calculate B_0 from the intercept and slope (B_0 = intercept/slope), estimated from

TABLE A3.1 Types of Dependence[A]

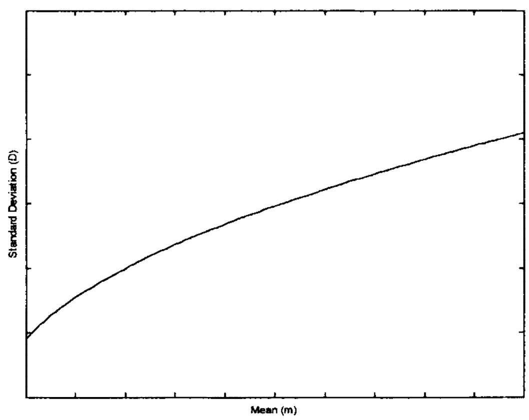
Form of Dependence	Transformations	Form of Line to be Fitted	dx/dy	Remarks
$D = K(m + B_0)$ $m + B_0 > 0$	$y = \log(x + B_0)$ Type 1 – "log"	$\log(D) = b_o +$ $+ b_1\log(m + B_0) + b_2T + b_3T\log(m + B_0)$ Test: $b_1 = 1$, $b_3 = 0$	$(x + B_0)$	Care must be taken if $(x + B_0)$ is small, as rounding becomes critical
$D = K(m+B_0)^B$ $m + B_0 > 0$, $B \neq 1$	$y = (x+B_0)^{1-B}$ Type 2 – "power"	$\log(D) = b_o + B\log(m + B_0) + b_2T +$ $b_3T\log(m+B_0)$ Test: $B \neq 1$, $b_3 = 0$	$(x + B_0)^B/(1 - B)$	B = ½ or 2 are common cases. If B is not different from 1, use log transform 1 above. The fitted line may pass through the origin.
$D=K[(m/B)\ (1-m/B)]^{1/2}$ $0 \leq m \leq B$	$y=\arcsin(x/B)^{1/2}$ Type 3 – "arcsin"	$\log(D) = b_o + b_1\log[m\ (B-m)] + b_2T +$ $b_3T\log[m\ (B - m)]$ Test: $b_1 = 1/2$, $b_3 = 0$	$2[x\ (B-x)]^{1/2}$	This case often arises when results are reported as percentages or qualitatively as "scores." If x is always small compared to B, the transformation reduces to $y=(x)^{1/2}$, a special case of 2 above.
$D=K[\ (m/B)(1-m/B)]$ $0 \leq m \leq B$	$y=\log[x/(B-x)]$ Type 4 – "logistic"	$\log(D) = b_o + b_1\log[m\ (B-m)] + b_2T +$ $b_3T\log[m\ (B - m)]$ Test: $b_1 = 1$, $b_3 = 0$	$x\ (B-x)/B$	This case arises when results are reported on a scale of 0 to B. If x is always small compared to B, then the transformation reduces to $y = \log(x)$ a special case of 1 above.
$D=K[(m^2+B^2)/B]$ $B > 0$	$y = \arctan(x/B)$ Type 5 – "arctan"	$\log(D) = b_o + b_1\log(m^2+B^2) + b_2T +$ $b_3T\log(m^2+B^2)$ Test: $b_1 = 1$, $b_3 = 0$	$(x^2 + B^2)/B$	The fitted line does not pass through the origin. If B is small, the transformation reduces to $y = 1/x$, a special case of 2 above.

[A] The forms of dependence above are shown graphically in the corresponding Figs. A3.1-A3.6. In all cases, K can be any positive constant, and "log" refers to natural logarithms. The form of line to be fitted includes a dummy variable T (see A4.1) by which it is possible to test for a difference in the transformation as applied to repeatability and reproducibility.



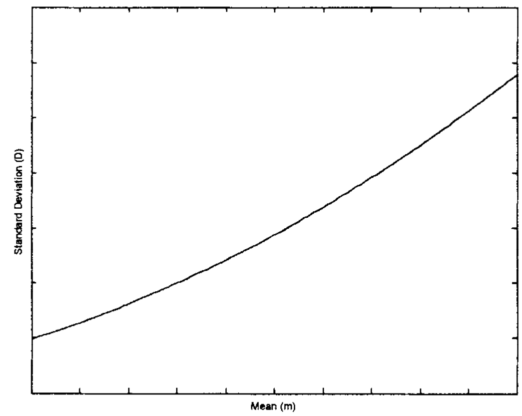
$D = K(m + B_0),\ m + B_0 > 0$

FIG. A3.1 Type 1, log



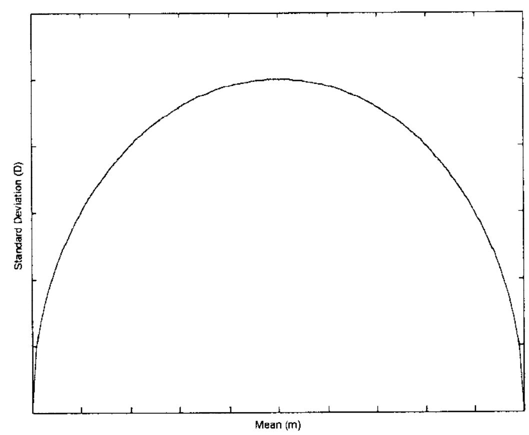
$D = K(m+B_0)^B,\ m + B_0 > 0,\ 0 < B < 1$

FIG. A3.2 Type 2, power



$D = K(m+B_0)^B,\ m + B_0 > 0,\ B > 1$

FIG. A3.3 Type 2, power



$D=K[(m/B)\ (1-m/B)]^{1/2},\ 0 \leq m \leq B$

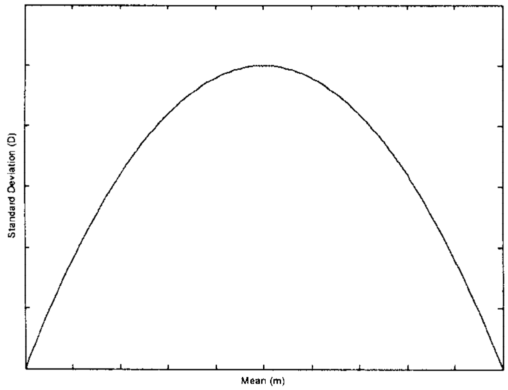
FIG. A3.4 Type 3, arcsin

the scatter diagrams. Similarly, estimate *B* from the intercept in the case of the arctan (Type 5) transformation. In every case, *B* or B_0, or both, shall be rounded to give a meaningful value that satisfies the plots for both the laboratories and repeats standard deviations.

A3.2.1.3 In the case of the power transform, *B* and $B_0 = 0$ will be estimated as part of the line fitting procedure described in the next section (A3.2.1.4). A non-zero B_0 may be estimated by minimizing the sum of squared residuals from the fitted line. Function minimization using a simplex procedure due to Nelder and Meade **(9,10)** has been found satisfactory. This is applied to the functional form of the line shown in Table A3.1 using the calculated sample means and standard deviations. The values and significances of all the constants are determined simultaneously as part of the simplex minimization. For detailed discussion of simplex minimization consult a trained statistician.

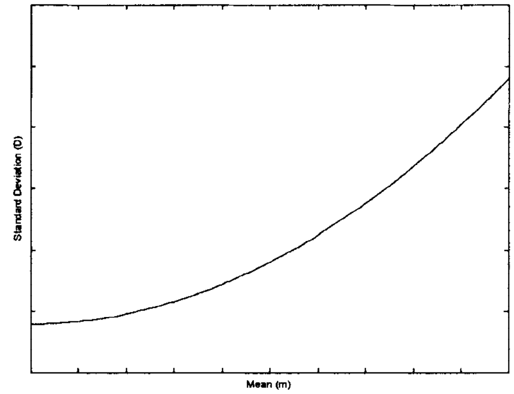
A3.2.1.4 In order to confirm the selected transformation type, and to estimate the parameter *B* in the case of the power transformation, fit the line specified in Table A3.1, corresponding to the transformation in question, in accordance with the computational procedure in A4.3. For the power transformation, coefficient *B*, shall differ significantly from zero and shall be rounded to a meaningful value. For the arcsin transformation, b_1 shall have a value not significantly different from 0.5. Similarly, b_1 shall not significantly differ from a value of one for the logistic, log, and arctan transformations. In every case the test specified in Table A3.1 shall be applied at the 5 % significance level. Failure of this test implies either that the type of transformation or its parameter *B* is incorrect. Similarly, coefficient b_3 shall in every case be tested as zero. Failure in this case implies that the transformation is different for repeatability and reproducibility. In some cases the presence of outliers (see 7.3) can give rise to this difference.

A3.2.1.5 If the tests applied above were satisfactory, transform all the results accordingly, recalculate means and standard deviations using transformed results, and create new scatter diagrams as in A3.2.1. These will now show a uniform level for



$D = K[(m/B)\ (1 - m/B)],\ 0 \leq m \leq B$

FIG. A3.5 Type 4, logistic



$D = K[(m^2 + B^2)/B],\ B > 0$

FIG. A3.6 Type 5, arctan

laboratories standard deviation, and a uniform (but not necessarily the same) level for repeats standard deviation. A statistical test for uniformity is given in 7.4.

A4. WEIGHTED LINEAR REGRESSION ANALYSIS (7.2)

A4.1 Explanation for Use of a Dummy Variable

A4.1.1 Two different variables Y_1 and Y_2, when plotted against the same independent variable X, will in general give different linear relationships of the form

$$Y_1 = b_{10} + b_{11}X \qquad (A4.1)$$
$$Y_2 = b_{20} + b_{21}X$$

where the coefficients b_{ij} are estimated by regression analysis. In order to compare the two relationships, a dummy variable T can be defined such that

$T = T_1$, a constant value for every observation of Y_1,
$T = T_2$, a constant value for every observation of Y_2, and
$T_1 \neq T_2$

A4.1.2 Letting Y represent the combination of Y_1 and Y_2, plot a single relationship

$$Y = b_0 + b_1X + b_2T + b_3TX \qquad (A4.2)$$

where, as before, the coefficients b_i are estimated by regression analysis. By comparing Eq A4.1 and Eq A4.2), it is evident that

$$b_{10} = b_0 + b_2T_1 \qquad (A4.3)$$
$$b_{20} = b_0 + b_2T_2$$

and that therefore

$$b_{10} - b_{20} = b_2\ (T_1 - T_2) \qquad (A4.4)$$

A4.1.3 Similarly,

$$b_{11} - b_{21} = b_3\ (T_1 - T_2) \qquad (A4.5)$$

A4.1.4 In order to test for a difference between b_{10} and b_{20} therefore, it is only necessary to test for a non-zero coefficient b_2. Similarly, to test for a difference between b_{11} and b_{21}, test for a non-zero coefficient b_3.

A4.1.5 Any non-zero values can be chosen for T_1 and T_2. However, since reproducibility is the basis of tests for quality control against specifications, weighting shall reflect this in the estimation of precision relationships. An "importance ratio" of 2:1 in the favor of reproducibility shall be applied by setting $T_1 = 1$ and $T_2 = -2$, where T_1 refers to the plot of laboratories standard deviation and T_2 refers to the repeats standard deviation.

A4.2 Derivation of Weights Used in Regression Analysis

A4.2.1 In order to account for the relative precision of fitted variables in a regression analysis, weights shall be used that are inversely proportional to the variances of the fitted variables.

A4.2.1.1 For a variable D, which is an estimate of population standard deviation σ, based on $v\ (D)$ degrees of freedom, the variance of D is given by

$$Var\ (D) = \sigma^2/2v\ (D) \qquad (A4.6)$$

A4.2.1.2 Replacing σ^2 by its estimate D^2, the weight for this variable will be approximated by

$$w(D) = 2v\ (D)\ /\ D^2 \qquad (A4.7)$$

A4.2.1.3 It is clear that as standard deviation D increases, so will the weight decrease. For this reason the fitted variable in the weighted regression shall instead be a function of standard deviation, which yields weights independent of the fitted variable.

A4.2.1.4 In cases where a function *g(D)* is fitted, rather than D itself, the variance formula becomes

$$Var\ [\ \log\ (D)] = \frac{1}{D^2}\ Var\ (D) = \frac{1}{D^2}\ \frac{\sigma^2}{2v\ (D)} \qquad (A4.8)$$

A4.2.1.5 Once again replacing σ^2 by its estimate D^2, the weight for *log(D)* will be approximated by

$$w[\log\ (D)] = 2v\ (D) \qquad (A4.9)$$

A4.2.1.6 In relation to laboratories standard deviation D and repeats standard deviation d, therefore, it is necessary to perform regression analysis in terms of *log(D)* and *log(d)*, since weighting will then take account only of the amount of data on which the standard deviation was based. A relationship estimated in this way will be less dependent on samples which have a high proportion of missing results.

A4.2.1.7 Denoting degrees of freedom as *v(D)* for laboratory standard deviations *D* and *v(d)* for repeats standard deviations *d*, formulae for calculating weights then become

$$w[\log(D)] = 2v(D) \tag{A4.10}$$

$$w[\log(d)] = 2v(d) \tag{A4.11}$$

NOTE A4.1—Unweighted regression corresponds to weighted regression in which all the weights have a constant value 1.

A4.3 Computational Procedure for Regression Analysis

A4.3.1 The following technique gives the best fitting straight line of the form of Eq A4.2.

A4.3.1.1 First draw up a table (see Table A4.1) giving values of the variables to be plotted in the regression, together with corresponding weights. Functions g_1 and g_2 will always be natural logarithms corresponding to the transformation in question, as specified in A3.2.

A4.3.1.2 Using the symbols defined in Table A4.1, the line to be fitted (Eq A4.2) becomes

$$y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 \tag{A4.12}$$

A4.3.1.3 The intercept b_0 can be eliminated by rewriting this as

$$(y - \bar{y}) = b_1(x_1 - \bar{x}_1) + b_2(x_2 - \bar{x}_2) + b_3(x_3 - \bar{x}_3) \tag{A4.13}$$

where y, x_1, x_2, and x_3 are weighted mean values, for example

$$\overline{x_2} = \frac{\sum_{i-1}^{n} w_i x_{2i}}{\sum_{i=1}^{n} w_i} \tag{A4.14}$$

and where n is the number of points (twice the number of samples) to be plotted.

A4.3.1.4 The least squares solution of Eq A4.14 requires the solution of the set of simultaneous equations of the form

TABLE A4.1 Arrangement of Variables for Regression Analysis

Sample	Standard Deviation Function g_1	Sample Mean Function g_2	Dummy T	Tg_2	Weight
1	$g_1(D_1)$	$g_2(m_1)$	1	$g_2(m_1)$	$2v(D_1)$
2	$g_1(D_2)$	$g_2(m_2)$	1	$g_2(m_2)$	$2v(D_2)$
3	$g_1(D_3)$	$g_2(m_3)$	1	$g_2(m_3)$	$2v(D_3)$
.	.	.	.	.	.
.	.	.	.	.	.
.	.	.	.	.	.
S	$g_1(D_s)$	$g_2(m_s)$	1	$g_2(m_s)$	$2v(D_s)$
1	$g_1(d_1)$	$g_2(m_1)$	–2	$-2g_2(m_1)$	$2v(d_1)$
2	$g_1(d_2)$	$g_2(m_2)$	–2	$-2g_2(m_2)$	$2v(d_2)$
3	$g_1(d_3)$	$g_2(m_3)$	–2	$-2g_2(m_3)$	$2v(d_3)$
.	.	.	.	.	.
.	.	.	.	.	.
.	.	.	.	.	.
S	$g_1(d_s)$	$g_2(m_s)$	–2	$-2g_2(m_s)$	$2v(d_s)$
Symbol	y_i	x_{1j}	x_{2i}	x_{3i}	w_i

$$\begin{aligned} a_{y1} &= a_{11}b_1 + a_{12}b_2 + a_{13}b_3 \\ a_{y2} &= a_{21}b_1 + a_{22}b_2 + a_{23}b_3 \\ a_{y3} &= a_{31}b_1 + a_{32}b_2 + a_{33}b_3 \end{aligned} \tag{A4.15}$$

A4.3.1.5 Examples of a_{ij} and a_{yi} elements, in terms of weighted means $\bar{x}_i$, are as follows

$$a_{22} = \Sigma w_i (x_{2i} - \bar{x}_2)^2 \qquad a_{23} = \Sigma w_i (x_{2i} - \bar{x}_2)(x_{3i} - \bar{x}_3) \tag{A4.16}$$

$$a_{y2} = \Sigma w_i (y_i - \bar{y})(x_{2i} - \bar{x}_2) \qquad a_{yy} = \Sigma w_i (y_i - \bar{y})^2$$

A4.3.1.6 Having solved the equations for b_1, b_2, and b_3, calculate the intercept from the weighted means of the variables as

$$b_0 = \bar{y} - b_1\bar{x}_1 - b_2\bar{x}_2 - b_3\bar{x}_3 \tag{A4.17}$$

A4.3.1.7 Coefficient estimates b_i can be summarized in tabular form, together with test statistics, as in Table A4.2.

A4.3.1.8 In order to complete the table, it is necessary to calculate the standard deviation of the observed y values about the estimated line. This is called the residual standard deviation, and is given by

$$s = \sqrt{\frac{1}{n-4}(a_{yy} - b_1a_{y1} - b_2a_{y2} - b_3a_{y3})} \tag{A4.18}$$

A4.3.1.9 Standard errors of the estimates then become

$$e_i = s\sqrt{c_{ii}}, \text{ for } i = 1 \text{ to } 3 \tag{A4.19}$$

and

$$e_0 = s\sqrt{\frac{1}{n} + c_{11}\bar{x}_1^2 + c_{22}\bar{x}_2^2 + c_{33}\bar{x}_3^2 + 2c_{12}\bar{x}_1\bar{x}_2 + 2c_{13}\bar{x}_1\bar{x}_3 + 2c_{23}\bar{x}_2\bar{x}_3} \tag{A4.20}$$

where the elements c_{jj} correspond to the inverse of the matrix containing elements a_{jj}.

A4.3.1.10 The *t*-ratios are the ratios $(b_i–K)/\, e_j$, where K is a constant, and by comparing these to the critical values of t in Table A2.3, it is possible to test if coefficient b_i differs from K. If t_i is greater than the critical value corresponding to 5 % significance and (n–4) degrees of freedom, then the coefficient can be regarded as differing from K. In particular, t_1 will identify an inappropriate slope b_1 and t_3 will indicate whether the slope is different for laboratories and repeats standard deviations. Since laboratories standard deviation will generally be larger than repeats standard deviation at the same level of sample mean, t_2 will in general indicate a non-zero coefficient b_2.

A4.4 Worked Example

A4.4.1 This section describes the fitting of a power function (Type 2 of Table A3.1) using weighted linear regression according to the procedure of A3.2. Rounded sample means

TABLE A4.2 Presentation of Estimates from Regression Analysis

Fitted Variable	Coefficient Estimate	Standard Error of Estimate	*t*-Ratio
Intercept	b_0	e_0	t_0
Sample Mean	b_1	e_1	t_1
Dummy	b_2	e_2	t_2
Dummy × mean	b_3	e_3	t_3

and standard deviations are given in Table 3, 7.2, based on the bromine number data in A2.1.

A4.4.1.1 Scatter diagrams identified the power transformation as appropriate, as indicated by the log-log plot shown in Fig. A4.1.

A4.4.1.2 Transformation parameter *B* need not be estimated from Fig. A4.1, since it will be given in the regression analysis that follows.

A4.4.1.3 The form of the line to be fitted (Table A3.1) is

$$log(D) = b_0 + b_1 \log(m) + b_2 T + b_3 T \log(m) \quad \text{(A4.21)}$$

A4.4.1.4 The table of values to be fitted (see Table A4.1) is shown in Table A4.3.

A4.4.1.5 Least squares regression requires the solution of the simultaneous equations

$$614.671 = 999.894b_1 - 35.8524b_2 - 493.045b_3 \quad \text{(A4.22)}$$
$$188.526 = 35.8524b_1 + 673.920b_2 + 1409.58b_3$$
$$195.477 = -493.045b_1 + 1409.58b_2 + 5362.27b_3$$

A4.4.1.6 Also required are

$$a_{yy} = 505.668 \quad \text{(A4.23)}$$
$$s = 2.23868$$

A4.4.1.7 The solution is summarized in Table A4.4 (see Table A4.2):

A4.4.1.8 Comparing the *t*-ratios with the critical 5 % values for 12 degrees of freedom (namely 2.179) given in Table A2.3, it can be seen that the slope is significantly non-zero (b_1 = 0.638), confirming that a transformation was required. Furthermore, since coefficient b_3 does not significantly differ from zero, the slope (and resulting transformation) is the same for both laboratories and repeats standard deviations.

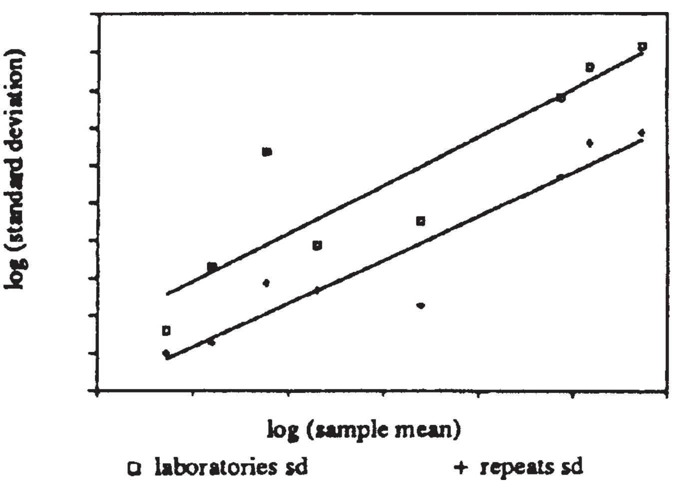


FIG. A4.1 Precisions Vary with Level

TABLE A4.3 Arrangement of Variables for Sample Data

Sample	Logarithm of Standard Deviation	Logarithm of Sample Mean	Dummy T	Dummy × log (mean)	Weight
1	–0.3158	0.7655	1	0.7655	16
2	0.7969	4.1804	1	4.1804	18
3	–2.7046	–0.2802	1	–0.2802	28
4	–1.5568	1.2932	1	1.2932	22
5	–1.2358	2.3888	1	2.3888	18
6	0.4029	3.8755	1	3.8755	18
7	1.0762	4.7378	1	4.7378	18
8	–1.8401	0.1975	1	0.1975	18
1	–2.0644	0.7655	–2	–1.5309	18
2	–0.2015	4.1804	–2	–8.3609	18
3	–2.9957	–0.2802	–2	0.5605	18
4	–2.1585	1.2932	–2	–2.5864	18
5	–2.3613	2.3888	–2	–4.7775	18
6	–0.6415	3.8755	–2	–7.7510	18
7	–0.0674	4.7378	–2	–9.4756	18
8	–2.8612	0.1975	–2	–0.3949	18
Symbol	y_i	x_{1i}	x_{2i}	x_{3i}	w_i

TABLE A4.4 Presentation of Estimates from Sample Data

Fitted Variable	Coefficient Estimate b_i	Standard Error of Estimate	*t*-Ratio
Intercept	–2.4064		
Log (mean)	0.63773	0.07359	8.67
Dummy	0.25496	0.13052	1.95
Dummy × log (mean)	0.02808	0.04731	0.59

A4.4.1.9 As the slope b_1 = 0.638 has a standard error of 0.074, the approximate 66 % confidence region of 0.638 ± 0.074 will contain the value 2/3. Rounding to this value is therefore reasonable, and leads to the convenient transformation

$$y = x^{1/3} \quad \text{(A4.24)}$$

A4.4.1.10 Having applied this transformation and recalculated sample means and standard deviations, corresponding scatter diagrams are shown in Fig. A4.2. These show uniform levels for both laboratories and repeats standard deviations for all samples except Sample 1. In the case of the latter sample, the extreme point is due to outliers.

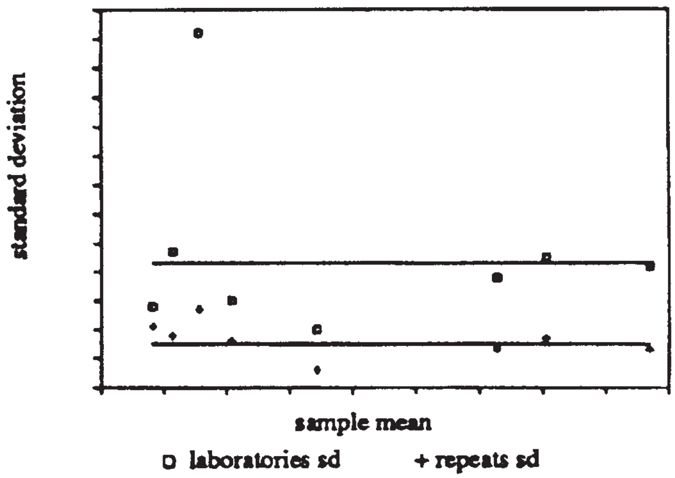


FIG. A4.2 After Transforming, Precisions Do Not Vary with Level

APPENDIX

(Nonmandatory Information)

X1. DERIVATION OF FORMULA FOR CALCULATING THE NUMBER OF SAMPLES REQUIRED (see 6.4.3)

X1.1 An analysis of variance is carried out on the results of the pilot program. Setting the three expressions in 8.3.1 equal to the corresponding mean squares and solving yields rough estimates of the three components of variance, namely:
σ_0^2 for repeats,
σ_1^2 for laboratories × samples interaction, and
σ_2^2 for laboratories.

X1.2 Substituting the above in Eq 39 (8.3.3.3) for calculating the reproducibility degrees of freedom, this becomes

$$\frac{(1 + P + Q)^2}{v} = \frac{[(1/2 + P) / S + Q]^2}{(L - 1)} + \frac{(S - 1)\,(1/2 + P)^2}{S^2(L - 1)} + \frac{1}{4LS} \tag{X1.1}$$

where:
P = σ_1^2/σ_0^2,
Q = σ_2^2/σ_0^2,
v = reproducibility degrees of freedom,
L = number of laboratories, and
S = number of samples.

X1.3 The formula rearranges into the form

$$aS + b = 0 \tag{X1.2}$$

where:
a = $vQ^2 - (1 + P + Q)^2(L - 1)$, and
b = $v[(2Q + 1/2 + P)\,(1/2 + P) + 0.25\,(L- 1) / L]$.

X1.3.1 Therefore $S = -b/a$ gives the values of S for given values of L, P, Q, and v.

X1.4 Fig. 1 is based on v = 30 degrees of freedom. For non-integral values of P and Q, S can be estimated by second order interpolation from the table.

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