Designation: D 6259 – 98

An American National Standard

AMERICAN SOCIETY FOR TESTING AND MATERIALS
100 Barr Harbor Dr., West Conshohocken, PA 19428
Reprinted from the Annual Book of ASTM Standards. Copyright ASTM

Standard Practice for Determination of a Pooled Limit of Quantitation[1]

This standard is issued under the fixed designation D 6259; 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.

1. Scope

1.1 This practice covers the determination of a lower quantitative limit for a test method for an analyte. The determined lower limit is herinafter referred to as the *pooled limit of quantitation*.

1.2 Applicable test methods will produce test results greater than zero. Examples are those test methods that measure sample composition.

2. Referenced Documents

2.1 *ASTM Standards:*

E 456 Terminology Relating to Quality and Statistics[2]

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method[2]

3. Terminology

3.1 *Definitions:*

3.1.1 *pooled limit of quantitation*, *n*—level of property or concentration of analyte above which quantitative test results can be obtained with a specified degree of confidence. See 3.2.1 for acronym.

3.1.2 *repeatability conditions*, *n*—conditions under which test results are obtained with the same test method in the same laboratory by the same operator with the same equipment in the shortest practical period of time using test units or test specimens taken at random from a single quantity of material that is as nearly homogeneous as possible (see 10.3 of Practice E 691.)

NOTE 1—The *same operator, same equipment* requirement means that for a particular step in the measurement process the same combination of operator and equipment is used for every test result. Thus, one operator may prepare the test specimens, a second measure the dimensions, and a third measure the mass in a test method for measuring density.

NOTE 2—By *in the shortest practical period of time* is meant that the test results, at least for one material, are obtained in a time period not less than in normal testing and not so long as to permit significant change in test material, equipment, or environment. See Terminology E 456.

3.2 *Acronym*:

3.2.1 *PLOQ*, *n*—pooled limit of quantitation.

4. Summary of Practice

4.1 Determine the standard deviation of a test result, under repeatability conditions, at progressively higher levels of the analyte until the ratio of measured level to standard deviation becomes greater than ten and remains so.

5. Significance and Use

5.1 In a single laboratory, the limit of quantitation, LOQ, equal to ten standard deviations has been recommended.[3] A test result at this LOQ has an uncertainty of ±30 % at the 99 % confidence level. Similarly here, as a general estimate, the PLOQ, equal to ten repeatability standard deviations is recommended. A test result at this PLOQ has an uncertainty of ±30 % at the 99 % confidence level.

5.2 Values below the PLOQ are deemed to be too uncertain for meaningful use in commerce, or in regulatory activities.

5.3 Many test methods never find application outside their PLOQ. However, in the quest for ever more sensitive procedures, it can become difficult to distinguish an analytical response from background noise with the technology at hand. Test methods defective in design or poorly executed may also function outside their PLOQ.

6. Procedure

6.1 Make the preparations outlined in 6.2, then carry out one of the procedures described in 6.3.

6.2 *Preparations*:

6.2.1 *Select Test Levels*—Decide the objective of the test method, the range of typical samples it is expected to cover. Name a set of test levels covering this range and spaced to bracket the PLOQ. In some cases, the PLOQ will be well below the useful range. Then, it is only necessary to determine a *less than* value.

NOTE 3—Mean and standard deviation data from experienced laboratories, archived research reports, and known limitations of the test method or equipment can give a preliminary notion of the PLOQ. An LOQ can be estimated in a single laboratory.

6.2.2 *Select Sample Materials*—Normally, use sample materials that are typical of those to which the test method is applied. In special cases, the method of standard additions (spiking) can be necessary to achieve the selected test levels. Synthetic blends may be required because of cost or other

---

[1] This practice is under the jurisdiction of Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.94 on Quality Assurance and Statistics.

Current edition approved April 10, 1998. Published July 1998.

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

[3] Keith, L. H., et al, "Principles of Environmental Analysis," *Analytical Chemistry*, American Chemical Society, Vol 55, 1983, p. 227.

practical considerations.

6.2.2.1 Plan to determine the PLOQ of each important test result of a multicomponent test. The PLOQs are not additive.

6.2.3 *Select Number of Laboratories*—Determine the PLOQ with the precision during an interlaboratory study so that it will tend to be representative of industry wide experience.

NOTE 4—Just as it is possible to obtain a preliminary estimate of test method repeatability by performing a study in one laboratory, so it is possible to estimate the LOQ of the test method in one laboratory.

6.2.4 *Determine Number of Runs Per Sample*—If a blank measurement is required to calculate the measured level of analyte, the analyst must obtain a separate blank measurement for each sample aliquot analyzed.

NOTE 5—At least six degrees of freedom are required. When a precision study is done, the relevant standard deviation is the repeatability standard deviation. The number of degrees of freedom here equals the number of participating laboratories times the number of repetitions less one by each laboratory. When one laboratory is used, the relevant standard deviation is that obtained by repeating the test seven or more times on portions of one sample.

6.3 Continue with 6.3.1. However, since the PLOQ depends on the attainable precision, there can be cases where a laboratory-specific precision and LOQ are needed by an individual laboratory for a special purpose. If the decision is made to determine the LOQ in a single laboratory, proceed to 6.3.2.

6.3.1 *Interlaboratory*—Conduct the interlaboratory study to determine precision in a normal fashion making sure that appropriate samples are included. Proceed to the calculation steps (Section 7).

6.3.2 *One Laboratory*:

6.3.2.1 Select an initial sample. This initial sample and a second sample (6.2.3) should be selected to bracket an expected LOQ broadly.

6.3.2.2 Run the entire test method on seven aliquots and calculate mean, standard deviation, and the ratio mean/standard deviation.

6.3.2.3 Select a second sample and repeat the determinations and calculations.

6.3.2.4 Repeat 6.3.2.1-6.3.2.3 and, for example by a binary search process, converge on the LOQ. Exceptional situations include those where cases of practical interest are either all above or all below the LOQ as evidenced by the mean to standard deviation ratios.

6.4 An LOQ should be redetermined when there are substantive changes in the operator experience level, test method, instrumentation, or the sample types to which it is deemed applicable, and another interlaboratory study becomes necessary.

7. Calculation

7.1 Arrange the means and corresponding standard deviations in ascending order of the mean.

7.2 Divide each mean by the corresponding standard deviation to obtain a ratio.

7.3 The level at which these ratios becomes greater than ten and remains so is the PLOQ. A more precise value may be obtained by regression but not by extrapolation.

8. Reporting Low-level Data

8.1 Should a test result be reported that is below the PLOQ, give the PLOQ in parentheses after the data, for example, chlorine content = 110 mg/kg (PLOQ=1000 mg/kg).

8.2 A statement about the PLOQ should appear in the test method as a footnote to the Scope.

9. Examples

9.1 Examples from an interlaboratory study are provided in Table 1.

9.1.1 The PLOQ itself might be estimated at 1000 mg/kg. Tables similar to Table 1 are generated by the D-2 computer software program.[4]

9.2 *Study in One Laboratory*—The abbreviated example in Table 2 illustrates one possible way to tabulate the data.

9.2.1 It would seem that the LOQ is at or above the level of Sample A. Nevertheless, it is recommended that at least another sample at a lower level be run to make sure this is not an outlier.

10. Keywords

10.1 limit of quantitation; pooled limit of quantitation

TABLE 1 Interlaboratory Study Examples

Sample	Mean	Within Laboratories		Ratio Mean/Standard Deviation
		Standard Deviation	Degrees of Freedom	
S8[A]	110.0	44.72	10	2.5
S1[A]	640.0	100.0	10	6.4
S3[A]	870.0	89.44	10	9.7
S6	1180	94.87	10	12.4
S2	1272	78.17	9	16.3
S7	2505	136.0	10	18.4
S4	3165	125.0	8	25.3
S5	3338	112.4	10	29.6

[A]Ratio of mean to standard deviation is less than ten and is, therefore, lower than the PLOQ.

TABLE 2 Abbreviated Example—One Laboratory

Run\Sample	A	Blank	A-Blank	B	Blank	B-Blank
1	800	10	790	1050	20	1030
2	900	5	895	1250	20	1230
3	900	10	890	1250	5	1245
4	800	0	800	1300	0	1300
5	750	0	750	1200	5	1195
6	950	20	930	1100	10	1090
7	1000	5	995	1150	5	1145
Mean			864.3			1176.4
Standard Deviation			87.29			94.06
Ratio Mean/ Standard Deviation		-	9.9[A]		-	12.5

[A]Ratio of the mean of sample A to its standard deviation is less than ten and is, therefore, lower than the LOQ.

[4] Calculation of Precision Data: Petroleum Test Methods Software Program (D2PP), release 2.0. Available from ASTM. Request PCN 13-402000-12.