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Petroleum and related products — Precision of measurement methods and results —

Part 3: Monitoring and verification of published precision data in relation to methods of test

Produits pétroliers et connexes — Fidélité des méthodes de mesure et de leurs résultats —

Partie 3: Surveillance et vérification des données de fidélité publiées relatives aux méthodes d'essai

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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This document was prepared by Technical Committee ISO/TC 28, *Petroleum and related products, fuels and lubricants from natural or synthetic sources*, in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 19, *Gaseous and liquid fuels, lubricants and related products of petroleum, synthetic and biological origin*, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

A list of all parts in the ISO 4259 series can be found on the ISO website.

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Introduction

ISO 4259-1 specifies the methodology for the design, execution and data processing of a one-time snapshot statistical study to arrive at precision estimates achieved by a random sampling of laboratories. This snapshot estimate is published in the standard test method as the expected precision.

This document explains the methodology for the utilisation of proficiency testing schemes (as defined in ISO 4259-2) to test the hypothesis that the precision achieved by the laboratories in the proficiency testing scheme is statistically consistent with the published precision derived from the ISO 4259-1 study described above. It is therefore a logical follow-up on the other parts.

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Petroleum and related products — Precision of measurement methods and results —

Part 3: Monitoring and verification of published precision data in relation to methods of test

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1 Scope

This document specifies the methodology for the regular monitoring of the test method precision achieved versus the precision published in the standard test method using data from proficiency testing schemes (PTSs) supported by the regular users of standard test methods.

The procedures in this document are designed specifically for proficiency testing (PT) conducted on standard test methods, having a published reproducibility, for petroleum and petroleum-related products, which are presumed to be homogeneous, and where the data distribution is approximately normal. In addition, it is applicable to properties of interest that are (known to be) stable over time and transport.

This document specifies the methodology for the statistical comparison of standard deviation under reproducibility conditions achieved in PT programmes versus that published.

The purpose of this comparison is to find out if the published reproducibility precision is representative of that achievable by the regular participants in the PT programmes.

This document also provides guidance on how to use a PT z-score to monitor an individual participant's performance over time (see Annex B).

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 4259-1, *Petroleum and related products — Precision of measurement methods and results — Part 1: Determination of precision data in relation to methods of test*

ISO 13528:2015, *Statistical methods for use in proficiency testing by interlaboratory comparison*

ISO/IEC 17043, *Conformity assessment — General requirements for proficiency testing*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 4259-1, ISO 13528, ISO/IEC 17043 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

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3.1
proficiency testing
PT
evaluation of participant performance against pre-established criteria by means of interlaboratory comparisons

3.2
proficiency testing scheme
PTS
programme designed for the periodic evaluation of participating laboratories' proficiency in the execution of a standard test method through the statistical analysis of their test results obtained on aliquots prepared from a single batch of homogeneous material

Note 1 to entry: The frequency of such testing varies in accordance with the scheme objective. Each execution of testing involves testing of a single batch of material. Materials typically vary from test to test.

Note 2 to entry: This is also commonly referred to as the "Inter Laboratory Cross Check Programme".

4 Proficiency testing scheme requirement

4.1 PTS provider

The PTS provider shall conform to the technical and management requirements as outlined in ISO/IEC 17043.

4.2 PT homogeneity and stability of proficiency test items

4.2.1 Property homogeneity

The assessment of property homogeneity shall be performed after the proficiency test items have been packaged in the final form and before distribution to participants. Consult and follow ISO 13528:2015, Annex B, as appropriate.

4.2.2 PT data and statistics requirement

The comparison methodology in this document is intended for PT data and statistics meeting the following requirements.

a) The PT data requirements are as follows.

   1) Data are obtained using a common standard test method with a published reproducibility obtained in accordance with ISO 4259-1 or equivalent.

   2) Data are all numeric (i.e. do not contain results such as < xxx or > xxx).

   3) A single result only is reported by each participant (i.e. no repeat).

b) The PT statistics requirements are as follows.

   The following statistics are required to be provided as part of the PTS report for each round.

   a) PT statistics (average and standard deviation) shall be based on at least 10 results, where at least 16 is strongly recommended, with at least 6 uniquely different values, after outlier rejection in accordance with the generalized extreme studentized deviation (GESD) as described in ISO 4259-1 or an equivalent technique.

      NOTE 1 PT data with insufficient resolution due to rounding (e.g. cold flow properties of diesel fuel) can invalidate the last requirement (a minimum of six uniquely different values).

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b) Data distribution is approximately normal as assessed by a generally accepted statistical technique such as Anderson-Darling (AD) or Shapiro-Wilk at the 0,01 significance level.

NOTE 2 PT data with insufficient resolution due to rounding can overestimate the normality assessment statistics.

c) PT standard deviation is calculated using the root-mean-square technique.

d) z-scores are as defined in ISO 13528:2015, 9.4.

5 Comparison of PT precision achieved to published precision

5.1 General

The comparison of PT precision achieved to published precision is carried out via a formal hypothesis test.

The parameter of interest is the standard deviation under reproducibility conditions as defined in ISO 4259-1.

The null hypothesis (H_0) to be tested against an alternate hypothesis (H_1) is outlined as follows:

— H_0: standard deviation under reproducibility conditions achieved from the PT round (S_{R_PT}) is not different from that published (S_{R_pub});

— H_1: S_{R_PT} is different from S_{R_pub}.

The statistical test to be used is the F-test on the variance ratio.

5.2 Perform F-test on the variance ratio

NOTE See Annex A for worked examples of the variance ratio construction and F-test described in this subclause.

5.2.1 Construction of the variance ratio to be used for the F-test

The F-test is performed on the variance ratio constructed using $(S_{R\_pub})^2$ and $(S_{R\_PT})^2$.

S_{R_pub} is obtained by first calculating the published reproducibility (R_{pub}) at the property level for the specific PT round using the published reproducibility equation in the standard test method.

Then, divide R_{pub} by the k-value provided in Table 1 if the associated degree of freedom (df) is known.

If the df for the published reproducibility is not known, divide R_{pub} by 2,888.

NOTE Division by 2,888 is based on the minimum required df of 30 for R_{pub}.

S_{R_PT} is obtained from the PT report for the specific round. This is the sample standard deviation calculated using the root-mean-square method applied to all non-rejected results.

The F-ratio is constructed by placing the numerically larger quantity in the numerator as follows:

— if S_{R_pub} is numerically larger or equal to S_{R_PT}, the variance ratio to be tested = $(S_{R\_pub})^2$ / $(S_{R\_PT})^2$;

— otherwise, the variance ratio to be tested = $(S_{R\_PT})^2$ / $(S_{R\_pub})^2$.

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Table 1 — k-value for different degrees of freedom

df	0	1	2	3	4	5	6	7	8	9
30	2,888	2,884	2,881	2,877	2,874	2,871	2,868	2,865	2,863	2,861
40	2,858	2,856	2,854	2,852	2,850	2,848	2,847	2,845	2,843	2,842
50	2,841	2,839	2,838	2,837	2,835	2,834	2,833	2,832	2,831	2,830
60	2,829	2,828	2,827	2,826	2,825	2,824	2,824	2,823	2,822	2,821
70	2,821	2,820	2,819	2,819	2,818	2,817	2,817	2,816	2,815	2,815
80	2,814	2,814	2,813	2,813	2,812	2,812	2,811	2,811	2,810	2,810
90	2,810	2,809	2,809	2,808	2,808	2,808	2,807	2,807	2,806	2,806
100	2,806	2,805	2,805	2,805	2,804	2,804	2,804	2,804	2,803	2,803
110	2,803	2,802	2,802	2,802	2,802	2,801	2,801	2,801	2,801	2,800
120	2,800	2,800	2,800	2,799	2,799	2,799	2,799	2,798	2,798	2,798
130	2,798	2,798	2,797	2,797	2,797	2,797	2,797	2,797	2,796	2,796
140	2,796	2,796	2,796	2,795	2,795	2,795	2,795	2,795	2,795	2,795
150	2,794	2,794	2,794	2,794	2,794	2,794	2,793	2,793	2,793	2,793
160	2,793	2,793	2,793	2,793	2,792	2,792	2,792	2,792	2,792	2,792
170	2,792	2,792	2,791	2,791	2,791	2,791	2,791	2,791	2,791	2,791
180	2,791	2,790	2,790	2,790	2,790	2,790	2,790	2,790	2,790	2,790
190	2,790	2,789	2,789	2,789	2,789	2,789	2,789	2,789	2,789	2,789
200	2,789	2,789	2,789	2,788	2,788	2,788	2,788	2,788	2,788	2,788

5.2.2 Comparison of variance ratio to be tested to a critical value $F_{\_crit\_,025}$

Compare the appropriate variance ratio to be tested (see 5.2.1) to the critical value ($F_{\_crit\_,025}$) in Tables 2 and 3 using the following degrees of freedom.

— For S_{R_pub}, use the achieved df from ISO 4259-1 or equivalent analysis that the published reproducibility is based on. If this is not available, use 30 as the df.

— For S_{R_PT}, the df = (no. of non-rejected results used to calculate S_{R_PT}) − 1.

NOTE Because the numerically larger term is always placed in the numerator of the F-ratio, for a 5 % significant test, the critical value to use is the upper 97,5 percentile of the F-distribution.

If the variance ratio is less than or equal to the critical value from Tables 2 and 3, do not reject the null hypothesis, H_0, as there is insufficient evidence to reject the null hypothesis as formulated in 5.1.

If variance ratio exceeds the critical value from Tables 2 and 3, the null hypothesis, H_0, is rejected in favour of the alternate hypothesis, H_1, as formulated in 5.1. That is, the conclusion is that there is sufficient statistical evidence to suggest the standard deviation under reproducibility conditions as achieved by the participants in the PT round is inconsistent (different) than that published, for that specific PT round.

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Table 2 — $F_{\text{critical (0,025, df\_numerator, df\_denominator)}}$ — 10 to 29 degrees of freedom

df_ denominator	df_numerator																			
	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29
10	3,72	3,66	3,62	3,58	3,55	3,52	3,50	3,47	3,45	3,44	3,42	3,40	3,39	3,38	3,37	3,35	3,34	3,34	3,33	3,32
11	3,53	3,47	3,43	3,39	3,36	3,33	3,30	3,28	3,26	3,24	3,23	3,21	3,20	3,18	3,17	3,16	3,15	3,14	3,13	3,13
12	3,37	3,32	3,28	3,24	3,21	3,18	3,15	3,13	3,11	3,09	3,07	3,06	3,04	3,03	3,02	3,01	3,00	2,99	2,98	2,97
13	3,25	3,20	3,15	3,12	3,08	3,05	3,03	3,00	2,98	2,96	2,95	2,93	2,92	2,91	2,89	2,88	2,87	2,86	2,85	2,85
14	3,15	3,09	3,05	3,01	2,98	2,95	2,92	2,90	2,88	2,86	2,84	2,83	2,81	2,80	2,79	2,78	2,77	2,76	2,75	2,74
15	3,06	3,01	2,96	2,92	2,89	2,86	2,84	2,81	2,79	2,77	2,76	2,74	2,73	2,71	2,70	2,69	2,68	2,67	2,66	2,65
16	2,99	2,93	2,89	2,85	2,82	2,79	2,76	2,74	2,72	2,70	2,68	2,67	2,65	2,64	2,63	2,61	2,60	2,59	2,58	2,58
17	2,92	2,87	2,82	2,79	2,75	2,72	2,70	2,67	2,65	2,63	2,62	2,60	2,59	2,57	2,56	2,55	2,54	2,53	2,52	2,51
18	2,87	2,81	2,77	2,73	2,70	2,67	2,64	2,62	2,60	2,58	2,56	2,54	2,53	2,52	2,50	2,49	2,48	2,47	2,46	2,45
19	2,82	2,76	2,72	2,68	2,65	2,62	2,59	2,57	2,55	2,53	2,51	2,49	2,48	2,46	2,45	2,44	2,43	2,42	2,41	2,40
20	2,77	2,72	2,68	2,64	2,60	2,57	2,55	2,52	2,50	2,48	2,46	2,45	2,43	2,42	2,41	2,40	2,39	2,38	2,37	2,36
21	2,73	2,68	2,64	2,60	2,56	2,53	2,51	2,48	2,46	2,44	2,42	2,41	2,39	2,38	2,37	2,36	2,34	2,33	2,33	2,32
22	2,70	2,65	2,60	2,56	2,53	2,50	2,47	2,45	2,43	2,41	2,39	2,37	2,36	2,34	2,33	2,32	2,31	2,30	2,29	2,28
23	2,67	2,62	2,57	2,53	2,50	2,47	2,44	2,42	2,39	2,37	2,36	2,34	2,33	2,31	2,30	2,29	2,28	2,27	2,26	2,25
24	2,64	2,59	2,54	2,50	2,47	2,44	2,41	2,39	2,36	2,35	2,33	2,31	2,30	2,28	2,27	2,26	2,25	2,24	2,23	2,22
25	2,61	2,56	2,51	2,48	2,44	2,41	2,38	2,36	2,34	2,32	2,30	2,28	2,27	2,26	2,24	2,23	2,22	2,21	2,20	2,19
26	2,59	2,54	2,49	2,45	2,42	2,39	2,36	2,34	2,31	2,29	2,28	2,26	2,24	2,23	2,22	2,21	2,19	2,18	2,17	2,17
27	2,57	2,51	2,47	2,43	2,39	2,36	2,34	2,31	2,29	2,27	2,25	2,24	2,22	2,21	2,19	2,18	2,17	2,16	2,15	2,14
28	2,55	2,49	2,45	2,41	2,37	2,34	2,32	2,29	2,27	2,25	2,23	2,22	2,20	2,19	2,17	2,16	2,15	2,14	2,13	2,12
29	2,53	2,48	2,43	2,39	2,36	2,32	2,30	2,27	2,25	2,23	2,21	2,20	2,18	2,17	2,15	2,14	2,13	2,12	2,11	2,10
30	2,51	2,46	2,41	2,37	2,34	2,31	2,28	2,26	2,23	2,21	2,20	2,18	2,16	2,15	2,14	2,12	2,11	2,10	2,09	2,08
35	2,44	2,39	2,34	2,30	2,27	2,23	2,21	2,18	2,16	2,14	2,12	2,10	2,09	2,07	2,06	2,05	2,04	2,03	2,02	2,01
40	2,39	2,33	2,29	2,25	2,21	2,18	2,15	2,13	2,11	2,09	2,07	2,05	2,03	2,02	2,01	1,99	1,98	1,97	1,96	1,95
45	2,35	2,29	2,25	2,21	2,17	2,14	2,11	2,09	2,07	2,04	2,03	2,01	1,99	1,98	1,96	1,95	1,94	1,93	1,92	1,91
50	2,32	2,26	2,22	2,18	2,14	2,11	2,08	2,06	2,03	2,01	1,99	1,98	1,96	1,95	1,93	1,92	1,91	1,90	1,89	1,88
55	2,29	2,24	2,19	2,15	2,11	2,08	2,05	2,03	2,01	1,99	1,97	1,95	1,93	1,92	1,90	1,89	1,88	1,87	1,86	1,85
60	2,27	2,22	2,17	2,13	2,09	2,06	2,03	2,01	1,98	1,96	1,94	1,93	1,91	1,90	1,88	1,87	1,86	1,85	1,83	1,82
65	2,25	2,20	2,15	2,11	2,07	2,04	2,01	1,99	1,97	1,95	1,93	1,91	1,89	1,88	1,86	1,85	1,84	1,83	1,82	1,81

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Table 2 *(continued)*

df_ denominator	df_numerator																			
	10	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**
70	2,24	2,18	2,14	2,10	2,06	2,03	2,00	1,97	1,95	1,93	1,91	1,89	1,88	1,86	1,85	1,83	1,82	1,81	1,80	1,79
75	2,22	2,17	2,12	2,08	2,05	2,01	1,99	1,96	1,94	1,92	1,90	1,88	1,86	1,85	1,83	1,82	1,81	1,80	1,78	1,77
80	2,21	2,16	2,11	2,07	2,03	2,00	1,97	1,95	1,92	1,90	1,88	1,87	1,85	1,83	1,82	1,81	1,79	1,78	1,77	1,76
85	2,20	2,15	2,10	2,06	2,02	1,99	1,96	1,94	1,91	1,89	1,87	1,86	1,84	1,82	1,81	1,80	1,78	1,77	1,76	1,75
90	2,19	2,14	2,09	2,05	2,02	1,98	1,95	1,93	1,91	1,88	1,86	1,85	1,83	1,81	1,80	1,79	1,77	1,76	1,75	1,74
95	2,19	2,13	2,08	2,04	2,01	1,98	1,95	1,92	1,90	1,88	1,86	1,84	1,82	1,81	1,79	1,78	1,77	1,75	1,74	1,73
100	2,18	2,12	2,08	2,04	2,00	1,97	1,94	1,91	1,89	1,87	1,85	1,83	1,81	1,80	1,78	1,77	1,76	1,75	1,74	1,72
120	2,16	2,10	2,05	2,01	1,98	1,94	1,92	1,89	1,87	1,84	1,82	1,81	1,79	1,77	1,76	1,75	1,73	1,72	1,71	1,70
140	2,14	2,09	2,04	2,00	1,96	1,93	1,90	1,87	1,85	1,83	1,81	1,79	1,77	1,76	1,74	1,73	1,72	1,70	1,69	1,68
160	2,13	2,07	2,03	1,99	1,95	1,92	1,89	1,86	1,84	1,82	1,80	1,78	1,76	1,74	1,73	1,72	1,70	1,69	1,68	1,67
180	2,12	2,07	2,02	1,98	1,94	1,91	1,88	1,85	1,83	1,81	1,79	1,77	1,75	1,73	1,72	1,71	1,69	1,68	1,67	1,66
200	2,11	2,06	2,01	1,97	1,93	1,90	1,87	1,84	1,82	1,80	1,78	1,76	1,74	1,73	1,71	1,70	1,68	1,67	1,66	1,65

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Table 3 — $F_{\text{critical}\,(0,025,\,\text{df\_numerator},\,\text{df\_denominator})}$ — 30 to 200 degrees of freedom

df_ denominator	df_numerator																			
	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	120	140	160	180	200
10	3,31	3,28	3,26	3,24	3,22	3,21	3,20	3,19	3,18	3,18	3,17	3,16	3,16	3,16	3,15	3,14	3,13	3,13	3,12	3,12
11	3,12	3,09	3,06	3,04	3,03	3,01	3,00	2,99	2,99	2,98	2,97	2,97	2,96	2,96	2,96	2,94	2,94	2,93	2,92	2,92
12	2,96	2,93	2,91	2,89	2,87	2,86	2,85	2,84	2,83	2,82	2,82	2,81	2,81	2,80	2,80	2,79	2,78	2,77	2,77	2,76
13	2,84	2,80	2,78	2,76	2,74	2,73	2,72	2,71	2,70	2,70	2,69	2,68	2,68	2,68	2,67	2,66	2,65	2,64	2,64	2,63
14	2,73	2,70	2,67	2,65	2,64	2,63	2,61	2,60	2,60	2,59	2,58	2,58	2,57	2,57	2,56	2,55	2,54	2,54	2,53	2,53
15	2,64	2,61	2,59	2,56	2,55	2,54	2,52	2,51	2,51	2,50	2,49	2,49	2,48	2,48	2,47	2,46	2,45	2,44	2,44	2,44
16	2,57	2,53	2,51	2,49	2,47	2,46	2,45	2,44	2,43	2,42	2,42	2,41	2,40	2,40	2,40	2,38	2,37	2,37	2,36	2,36
17	2,50	2,47	2,44	2,42	2,41	2,39	2,38	2,37	2,36	2,35	2,35	2,34	2,34	2,33	2,33	2,32	2,31	2,30	2,29	2,29
18	2,44	2,41	2,38	2,36	2,35	2,33	2,32	2,31	2,30	2,30	2,29	2,28	2,28	2,27	2,27	2,26	2,25	2,24	2,23	2,23
19	2,39	2,36	2,33	2,31	2,30	2,28	2,27	2,26	2,25	2,24	2,24	2,23	2,23	2,22	2,22	2,20	2,19	2,19	2,18	2,18
20	2,35	2,31	2,29	2,27	2,25	2,24	2,22	2,21	2,20	2,20	2,19	2,18	2,18	2,17	2,17	2,16	2,15	2,14	2,13	2,13
21	2,31	2,27	2,25	2,23	2,21	2,19	2,18	2,17	2,16	2,16	2,15	2,14	2,14	2,13	2,13	2,11	2,10	2,10	2,09	2,09
22	2,27	2,24	2,21	2,19	2,17	2,16	2,14	2,13	2,13	2,12	2,11	2,10	2,10	2,09	2,09	2,08	2,07	2,06	2,05	2,05
23	2,24	2,20	2,18	2,15	2,14	2,12	2,11	2,10	2,09	2,08	2,08	2,07	2,07	2,06	2,06	2,04	2,03	2,02	2,02	2,01
24	2,21	2,17	2,15	2,12	2,11	2,09	2,08	2,07	2,06	2,05	2,05	2,04	2,03	2,03	2,02	2,01	2,00	1,99	1,99	1,98
25	2,18	2,15	2,12	2,10	2,08	2,06	2,05	2,04	2,03	2,02	2,02	2,01	2,01	2,00	2,00	1,98	1,97	1,96	1,96	1,95
26	2,16	2,12	2,09	2,07	2,05	2,04	2,03	2,02	2,01	2,00	1,99	1,98	1,98	1,97	1,97	1,95	1,94	1,94	1,93	1,92
27	2,13	2,10	2,07	2,05	2,03	2,01	2,00	1,99	1,98	1,97	1,97	1,96	1,95	1,95	1,94	1,93	1,92	1,91	1,90	1,90
28	2,11	2,08	2,05	2,03	2,01	1,99	1,98	1,97	1,96	1,95	1,94	1,94	1,93	1,93	1,92	1,91	1,90	1,89	1,88	1,88
29	2,09	2,06	2,03	2,01	1,99	1,97	1,96	1,95	1,94	1,93	1,92	1,92	1,91	1,91	1,90	1,89	1,88	1,87	1,86	1,86
30	2,07	2,04	2,01	1,99	1,97	1,95	1,94	1,93	1,92	1,91	1,90	1,90	1,89	1,89	1,88	1,87	1,86	1,85	1,84	1,84
35	2,00	1,96	1,93	1,91	1,89	1,87	1,86	1,85	1,84	1,83	1,82	1,82	1,81	1,81	1,80	1,79	1,77	1,77	1,76	1,75
40	1,94	1,90	1,88	1,85	1,83	1,82	1,80	1,79	1,78	1,77	1,76	1,76	1,75	1,75	1,74	1,72	1,71	1,70	1,70	1,69
45	1,90	1,86	1,83	1,81	1,79	1,77	1,76	1,75	1,74	1,73	1,72	1,71	1,70	1,70	1,69	1,68	1,66	1,66	1,65	1,64
50	1,87	1,83	1,80	1,77	1,75	1,74	1,72	1,71	1,70	1,69	1,68	1,67	1,67	1,66	1,66	1,64	1,63	1,62	1,61	1,60
55	1,84	1,80	1,77	1,74	1,72	1,71	1,69	1,68	1,67	1,66	1,65	1,64	1,64	1,63	1,62	1,61	1,59	1,58	1,58	1,57
60	1,82	1,78	1,74	1,72	1,70	1,68	1,67	1,65	1,64	1,63	1,63	1,62	1,61	1,60	1,60	1,58	1,57	1,56	1,55	1,54
65	1,80	1,76	1,72	1,70	1,68	1,66	1,65	1,63	1,62	1,61	1,60	1,60	1,59	1,58	1,58	1,56	1,55	1,53	1,53	1,52

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Table 3 *(continued)*

df_denominator	df_numerator																			
	30	**35**	**40**	**45**	**50**	**55**	**60**	**65**	**70**	**75**	**80**	**85**	**90**	**95**	**100**	**120**	**140**	**160**	**180**	**200**
70	1,78	1,74	1,71	1,68	1,66	1,64	1,63	1,62	1,60	1,59	1,59	1,58	1,57	1,56	1,56	1,54	1,53	1,52	1,51	1,50
75	1,76	1,72	1,69	1,67	1,65	1,63	1,61	1,60	1,59	1,58	1,57	1,56	1,55	1,55	1,54	1,52	1,51	1,50	1,49	1,48
80	1,75	1,71	1,68	1,65	1,63	1,61	1,60	1,59	1,57	1,56	1,55	1,55	1,54	1,53	1,53	1,51	1,49	1,48	1,47	1,47
85	1,74	1,70	1,67	1,64	1,62	1,60	1,59	1,57	1,56	1,55	1,54	1,53	1,53	1,52	1,51	1,49	1,48	1,47	1,46	1,45
90	1,73	1,69	1,66	1,63	1,61	1,59	1,58	1,56	1,55	1,54	1,53	1,52	1,52	1,51	1,50	1,48	1,47	1,46	1,45	1,44
95	1,72	1,68	1,65	1,62	1,60	1,58	1,57	1,55	1,54	1,53	1,52	1,51	1,51	1,50	1,49	1,47	1,46	1,45	1,44	1,43
100	1,71	1,67	1,64	1,61	1,59	1,57	1,56	1,54	1,53	1,52	1,51	1,50	1,50	1,49	1,48	1,46	1,45	1,44	1,43	1,42
120	1,69	1,65	1,61	1,59	1,56	1,55	1,53	1,52	1,50	1,49	1,48	1,47	1,47	1,46	1,45	1,43	1,42	1,41	1,40	1,39
140	1,67	1,63	1,60	1,57	1,55	1,53	1,51	1,50	1,48	1,47	1,46	1,45	1,45	1,44	1,43	1,41	1,39	1,38	1,37	1,36
160	1,66	1,62	1,58	1,55	1,53	1,51	1,50	1,48	1,47	1,46	1,45	1,44	1,43	1,42	1,42	1,39	1,38	1,36	1,35	1,35
180	1,65	1,61	1,57	1,54	1,52	1,50	1,48	1,47	1,46	1,44	1,43	1,43	1,42	1,41	1,40	1,38	1,36	1,35	1,34	1,33
200	1,64	1,60	1,56	1,53	1,51	1,49	1,47	1,46	1,45	1,44	1,42	1,42	1,41	1,40	1,39	1,37	1,35	1,34	1,33	1,32

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5.2.3 Multiple comparisons overtime

The repeated rejection of H_0 from multiple rounds suggests that the published precision is not representative of the precision achieved by the participating laboratories for the materials tested in those PT rounds.

In addition, the status of which standard deviation source is numerically larger (S_{R_pub} or S_{R_PT}) should be tracked. Five successive rounds where the same standard deviation source is numerically larger, regardless if there has been no rejection of H_0, also suggest that the published precision is not representative of the precision achieved by the participating laboratories for the materials tested in those PT rounds.

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Annex A
(informative)

Worked examples of F-test

A.1 General

This annex presents some examples in line with 5.2.

For these examples, a 30 df for S_{R_pub} is used. For each PT round, the numerically larger S is in bold font.

A.2 Example A

Total aromatics (vol %); $R_{pub} = 0{,}244(X)^{\wedge 0{,}75}$

Average PT	S_{R_PT}	n	**AD**	$R_{PT} = 2{,}8\sigma$	R_{pub} **at average PT**	S_{R_pub}	**F-ratio**	$F_{crit\_,025}$	**Reject H_0 ?**
16,437	**0,874**	23	0,5	2,448	1,992	0,690	1,61	2,16	n
8,317	0,267	84	0,78	0,748	1,195	**0,414**	2,40	1,75	y
20,151	**0,978**	20	0,41	2,738	2,321	0,803	1,48	2,21	n
14,817	0,570	22	0,37	1,597	1,843	**0,638**	1,25	2,31	n

A.3 Example B

Benzene (volume %); $R_{pub} = 0{,}13(X) + 0{,}05$

Average PT	S_{R_PT}	n	**AD**	$R_{PT} = 2{,}8\sigma$	R_{pub} **at average PT**	S_{R_pub}	**F-ratio**	$F_{crit\_,025}$	**Reject H_0 ?**
0,692	0,034	29	0,3	0,10	0,140	**0,048**	1,98	2,11	n
0,618	0,027	29	0,42	0,08	0,130	**0,045**	2,73	2,11	y
0,240	0,016	23	0,79	0,04	0,081	**0,028**	3,28	2,27	y
0,497	0,023	26	0,79	0,06	0,115	**0,040**	2,99	2,18	y

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Annex B
(informative)

Use of z-scores to monitor an individual participant's PT performance

B.1 z-score calculation

Consistent with ISO 13528:2015, Formula (14), a z-score for participant *i* in a single PT round is defined as shown in Formula (B.1):

$$z_i = \left(x_i - P_{\text{avg}}\right) \Big/ \left(S_{R\_\text{PT}}\right) \tag{B.1}$$

where

x_i is participant *i*'s single result for the PT round;

P_{avg} is the arithmetic average for the specific PT round;

S_{R_PT} is the standard deviation under reproducibility conditions achieved from the PT round.

In this annex, all references to z relate for participant *i*, hence there is no further use of the subscript *i*.

B.2 Run-sum calculation using participant *i*'s z-scores from multiple PT rounds

NOTE An assessment of systematic bias from run-sum is only meaningful for "high" frequency PT schemes (e.g. monthly).

Let:

— n denote the chronological identification of the PT round, with the largest value being the most recent PT round;

— z_n denote the z-score of participant *i* for the n^{th} PT round;

— S_{n} denote the run-sum to be computed after examination of z_n.

Calculate S_{n} as shown in Formula (B.2) or (B.3).

a) If z_n is of the same arithmetic sign (+ or −) as $z_{(n-1)}$:

$$S_{\text{n}} = z_n + S_{(n-1)} \tag{B.2}$$

b) If z_n is of a different arithmetic sign (+ or −) from $z_{(n-1)}$:

$$S_{\text{n}} = z_n \tag{B.3}$$

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