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Standard Guide for Interpretation and Use of Results from Interlaboratory Testing of Chemical Analysis Methods¹

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1. Scope

1.1 This guide covers procedures to help a task group interpret interlaboratory study (ILS) statistics to state precision and accuracy of a test method and make judgments concerning its range of use.

1.2 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*²

D6512 Practice for Interlaboratory Quantitation Estimate

E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials

E1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method

E1763 Guide for Interpretation and Use of Results from Interlaboratory Testing of Chemical Analysis Methods

E1914 Practice for Use of Terms Relating to the Development and Evaluation of Methods for Chemical Analysis

3. Terminology

3.1 For definitions of terms used in this guide, refer to Terminology E135.

3.2 For descriptions of terms used in this guide, refer to Practice E1914.

4. Significance and Use

4.1 A written test method is subjected to an ILS to evaluate its performance. The ILS produces a set of statistical estimates

that depend upon the method, but also are influenced by the laboratories and test materials involved in the study. For that reason, the ILS task group must interpret these estimates, aided by this guide and using analytical judgment, to decide if the method is suitable to be balloted for publication as a standard. The task group may use this guide to help them prepare the precision and bias statements that are a required part of the method.

5. Interlaboratory Studies

5.1 The following statement is required in each test method:

5.1.1 This test method has been evaluated in accordance with Practice E1601 and Guide E1763. Unless otherwise noted in the precision and bias section, the lower limit in the scope of each method specifies the lowest analyte content that may be analyzed with acceptable error (defined as a nominal 5 % risk of obtaining a 50 % or larger relative difference in results on the same test sample in two laboratories).

NOTE 1—this guide has been found to be useful for calculation of the interlaboratory quantitation estimate in accordance with Practice D6512, using known reference values in place of the measured values for application to that practice. It has been found necessary to replace the zero value for the blank with a very small number in order to apply this practice to that method to avoid the divide by zero computational error.

6. Required Statistical Information

6.1 A task group satisfies the requirement for statistical information if the method includes a table of the ILS statistics prepared in accordance with 6.2 and 6.3 and a summary statement selected from the model statements in Section 9. If the task group wishes to provide further statistical information, it may do so in accordance with the provisions of Section 7.

6.2 *Variability Data*—List the variability statistics for each analyte in a separate table arranged by increasing analyte content. List the number of independent data sets used in the calculations and the ILS statistics calculated in accordance with Practice E1601. Where appropriate, list the material type and reference material identification. Follow the examples of Table 1, Table 2, and Table 3.

6.2.1 If the analytical method includes optional conditions extending the analyte range (for example, decreased sample portions or multiple calibration curves,) list the ILS statistics for each option separately as shown in Table A3.1 and Table A3.3.

¹ This guide is under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores, and Related Materials and is the direct responsibility of Subcommittee E01.22 on Laboratory Quality.

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For Annual Book of ASTM Standards volume information, refer to the standard's Document Summary page on the ASTM website.

TABLE 1 Gold in Bullion by the Fire Assay Method

Test Material	Number of Laboratories	Gold found, %	Minimum SD (s_M , E1601)	Reproducibility SD (s_R , E1601)	Reproducibility Index (R , E1601)	$R_{rel\%}$
6	7	26.350	0.0089	0.0318	0.089	0.34
4	10	65.744	0.0236	0.0439	0.123	0.25
2	10	73.831	0.0261	0.0296	0.083	0.20
3	10	76.484	0.0275	0.0543	0.152	0.19
1	10	78.392	0.0200	0.0689	0.193	0.11
5	7	99.060	0.0189	0.0368	0.103	0.10

TABLE 2 Manganese in Iron Ores by the Permanganate Titrmetric method

Test Material	Number of Laboratories	Man gane se found, %	Minimum SD (s_M , E1601)	Reproducibility SD (s_R , E1601)	Reproducibility Index (R , E1601)	$R_{rel\%}$
1	8	0.62	0.0047	0.0069	0.0193	3.11
2	8	1.17	0.0189	0.0219	0.0614	5.25
3	8	1.72	0.0237	0.0244	0.0683	3.97
4	8	2.83	0.0218	0.0244	0.0683	2.41
5	8	3.73	0.0218	0.0360	0.1007	2.70
6	8	5.55	0.0275	0.0724	0.2026	3.65

TABLE 3 Boron in Steel by the Curcumin Spectrophotometric Method

Test Material	Number of Laboratories	Boron found, %	Minimum SD (s_M , E1601)	Reproducibility SD (s_R , E1601)	Reproducibility Index (R , E1601)	$R_{rel\%}$
1-D1,1	14	0.00023	0.000036	0.000064	0.00018	78.3
2-B1,2	21	0.00023	0.000082	0.000102	0.00028	124
3-B1,1	21	0.00026	0.000046	0.000084	0.00024	90.4
4-D1,7	14	0.00045	0.000046	0.000150	0.00042	63.3
5-B1,3	21	0.00046	0.000061	0.000107	0.00030	65.2
6-D1,2	14	0.00108	0.000054	0.000100	0.00028	25.9
7-B1,4	21	0.00136	0.000068	0.000189	0.00053	39.0
8-D1,3	14	0.00275	0.000104	0.000129	0.00036	12.1
9-D1,4	14	0.00315	0.000104	0.000129	0.00036	11.4
10-B1,5	21	0.00362	0.000111	0.000214	0.00060	13.3
11-D1,5	14	0.00378	0.000104	0.000257	0.00072	19.0
12-B1,6	21	0.00432	0.000143	0.000189	0.00053	12.3
13-D1,8	14	0.00432	0.000096	0.000171	0.00048	11.1
14-D1,6	14	0.00639	0.000132	0.000471	0.00132	15.2
15-B1,7	21	0.00904	0.000179	0.000482	0.00135	14.9
16-B1,8	21	0.0114	0.00035	0.000625	0.00175	15.4

	Certified Boron, %	B-value, %	Material Identification (Source)	Description
1	...	...	...	non-alloyed steel
2	0.0003	-0.00007	ERMC 097-1	high purity iron
3	0.0003	-0.00007	ERMC 283-1	high speed steel
4	...	...	...	alloyed steel
5	0.0004	0.00006	BAM 187-1	low alloyed steel
6	...	...	...	non-alloyed steel
7	0.0015	-0.00014	BCS 456/1	mild steel
8	...	...	...	non-alloyed steel
9	...	...	...	non-alloyed steel
10	0.0038	-0.00018	BAM 284-1	stainless steel
11	...	...	...	non-alloyed steel
12	0.0041	0.00022	BAM 178-1	low alloyed steel
13	...	...	...	alloyed steel
14	...	...	...	non-alloyed steel
15	0.0090	-0.00004	JSS 175-5	mild steel
16	0.0118	-0.0004	BCS 459/1	carbon steel

6.3 Bias Data—If the ILS includes one or more test materials having an accepted reference value, include the accepted value(s) and b-value(s) as shown in [Table 3](#).

7. Models for Error in Analytical Methods

7.1 An estimate of the reproducibility index, R , is obtained in an ILS for each individual test material. These are the discrete values of R listed in a statistical information table. Users need an estimate of R at the analyte level, which may lie anywhere within the range of the scope of the test method. If the task group conducted the ILS properly and employed good quality test materials having compositions that cover the application range, that information may be provided by following the procedures in this section.

7.1.1 If the analytical method includes sample portion or calibration options, treat the ILS statistics for each option as a separate method.

7.2 The task group must decide if the statistics for the test materials in the ILS exhibit trends that follow one of the three error models included in this section. The use of a model is essential if the task group intends to describe the behavior of the reproducibility index, R , as a function of analyte content. If the task group cannot agree on one model, it should not attempt to relate R to analyte content. The keys to identifying the model are the trends in R and $R_{rel\%}$ as the analyte content increases. [Annex A1](#) includes a more detailed discussion of these analytical error models.

7.3 General Model for Error in Analytical Methods—The ILS data follows the general model if, with increasing analyte concentration, R increases (most noticeably at higher concentrations) while $R_{rel\%}$ decreases (most noticeably at lower concentrations.) Data for the boron method in [Table 3](#) show this behavior. To interpret statistics that follow this model, select a procedure from [Annex A2](#) for calculating estimates of the constants K_R and $K_{rel\%}$. Substituted in [Eq 1](#), the constants define an equation representing the expected values of R for the method as a function of analyte concentration. The task group may use the relationship to estimate R for the method at any concentration, C , within the scope of the method.

$$\hat{R}_C = \sqrt{K_R^2 + (C \times K_{rel\%}/100)^2} \quad (1)$$

The boron ILS data in [Table 3](#) yield estimates of $K_R = 0.00026\%$ boron and $K_{rel\%} = 14.6\%$. The following equation predicts R at analyte contents from 0 % to approximately 0.012 % boron.

$$\hat{R}_C = \sqrt{0.00026^2 + (\%B \times 0.146)^2} \quad (2)$$

7.4 Constant Model for Error in Analytical Methods—The ILS data follows the constant error model if, with increasing analyte concentration, R neither increases nor decreases but $R_{rel\%}$ continually decreases. The gold method ILS data in [Table 1](#) show this behavior. For statistics that follow this model, use [Eq 3](#) to calculate the root-mean-square (RMS) estimate of K_R . This value predicts R at all analyte contents within the scope of the method:

$$\hat{K}_R = \sqrt{\sum R^2/n} \quad (3)$$

where:

$\sum R^2$ = sum of the squares of R over all test materials, and
 n = number of test materials.



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The six values for R , squared and added, equal 0.100901. Dividing by the number of materials, $n = 6$, and taking the square root gives an estimate for K_R of 0.13 %. This estimate applies from 0 to 100 % gold.

7.5 Relative Model for Error in Analytical Methods—The ILS data follows the relative error model, if with increasing analyte concentration, $R_{rel\%}$ neither increases nor decreases but R continually increases. The manganese method ILS data in Table 2 show this behavior. For statistics that follow this model, use Eq 4 to calculate an RMS estimate of $K_{rel\%}$. This value predicts $R_{rel\%}$ only within the analyte content range tested during the ILS:

$$\hat{K}_{rel\%} = \sqrt{\sum (R_{rel\%})^2 / n} \quad (4)$$

where:

$\sum (R_{rel\%})^2$ = sum of the squares of $R_{rel\%}$ over all test materials, and
 n = number of test materials.

The six values for $R_{rel\%}$, squared and added, equal 79.4161. Dividing by the number of test materials, $n = 6$, and taking the square root gives an estimate for $K_{rel\%}$ of 3.7 %. This estimate applies from approximately 0.5 % to 6 % manganese.

8. Calculation of the Low Scope Limit of the Method

NOTE 2—Refer to Annex A4.

8.1 A method is always written for a nominal analyte concentration range expected to cover the anticipated applications. If the low scope limit calculated from the ILS statistics is lower than the low limit specified in the draft method, the task group need not lower the scope of the method unless it wishes to do so. However, if the calculated low limit is higher than the value specified in the draft method, the task group shall raise the low limit to the calculated value. For methods with sample portion or calibration options, calculate the low scope limit from the data for the option covering the lowest range.

8.2 The task group must establish the appropriate value for R_L , the lowest estimated reproducibility index from the ILS, and select e_{max} , the maximum allowable percent relative error. These constants are used to calculate L , the lowest analyte content for which the method is expected to give quantitative results.

8.2.1 R_L —For an ILS evaluated in accordance with the general error model (7.3) or the constant error model (7.4), set R_L equal to the estimate of K_R . Otherwise, set R_L equal to the estimated R for the test material with the lowest analyte content. If several have nearly equal values for R , set R_L equal to the square root of the sum of their squares.

8.2.2 Maximum Allowable Error, e_{max} —Set e_{max} equal to 50 %, a value that has been found satisfactory for most methods used to test materials at low analyte contents.

8.3 Use Eq 5 to calculate L , the lower limit as follows:

$$L = \frac{100 \times R_L}{e_{max}} \quad (5)$$

where:

R_L and e_{max} have the values selected in accordance with 8.2. Eq 5 becomes $L = 2 R_L$ for the usual case in which $e_{max} = 50$ %.

8.4 Set the lower limit of the method to L .

9. Interpretation of ILS Statistics

9.1 A properly conducted ILS program often provides more information than is apparent from visual inspection of the statistics. Typically, when the test program is completed, the participants have recent experience with the behavior of the method as applied to different test materials. The task group may use this knowledge to clarify trends in the performance of the method at different analyte contents. If the task group agrees upon an error model that is both consistent with the observed values of R and $R_{rel\%}$ and representative of their experience with the method and equipment, they may use the model to calculate the expected value for R at various analyte contents within the scope of the method as a guide to users.

9.2 Precision Statements—Select a statement from the following example formats:

9.2.1 ILS in Which No Model has Been Adopted: [Insert the number of laboratories with data used in the ILS] laboratories participated in testing this method, providing [number of data sets actually used] sets of data. Table ____ summarizes the precision information.

9.2.2 ILS in Which Constant Error Model has Been Adopted: [Insert the number of laboratories with data used in the ILS] laboratories participated in testing this method, providing [number of data sets actually used] sets of data. Table ____ summarizes the precision information. Within the scope of the method, the reproducibility index, R , is approximately [insert the estimated K_R from 7.4].

9.2.3 ILS in Which Relative Error Model has Been Adopted: [Insert the number of laboratories with data used in the ILS] laboratories participated in testing this method, providing [number of data sets actually used] sets of data. Table ____ summarizes the precision information. Within the scope of the method, the relative reproducibility index, $R_{rel\%}$ is approximately [insert the estimated $K_{rel\%}$ from 7.5].

9.2.4 ILS in Which General Analytical Error Model has been Adopted: [Insert the number of laboratories with data used in the ILS] laboratories participated in testing this method, providing [number of data sets actually used] sets of data. Table ____ summarizes the precision information. The following equation predicts the approximate value of R at any concentration, C , within the scope of the method:

$$R_C = \sqrt{K_R^2 + \left(C \times \frac{K_{rel\%}}{100} \right)^2} \quad (6)$$

Insert values for K_R and $K_{rel\%}$ obtained in 7.3.

9.2.5 For 9.2.3 or 9.2.4, the task group may also wish to show and refer to a table of expected values for R , calculated for various analyte contents by $K_{rel\%}$ or Eq 1, respectively.

9.2.6 For ILS with optional sample portions or calibration curves, the task group may need expert assistance to properly display the statistics for various concentrations.

9.3 Accuracy—The difference between the calculated mean for an analyte and its accepted value for each test material is the statistic b -value, the task group may use to judge the accuracy of a method. Include the bias information in the same table used for the precision information. Screen the b -values to eliminate any that are characteristic of the test material rather than the method. If the b -value for any material/analyte combination is much larger than for materials with similar analyte contents, look for a reason, such as poor homogeneity or a large uncertainty in the certified value. Be particularly critical of materials for which both b -value and R are exceptionally large. If a cause is found, remove the data for that analyte/material combination from the ILS table and recalculate the ILS statistics for that analyte. Examine each b -value separately to decide if the size of the estimated bias is so large that it creates a technical or commercial problem at the corresponding analyte content. If the task group fails to find either type of problem, the accuracy of the method shall be deemed satisfactory and no purely statistical consideration shall be advanced to question that finding.

9.4 Bias Statements—Select the appropriate statement from the following examples:

9.4.1 ILS in Which No Accepted Reference Materials were Available for Testing: No information on the accuracy of this method is known because, at the time it was tested, no accepted reference materials were available [if other reasons apply, for example, satisfactory reference materials cannot be produced, state the applicable reason.] Users are encouraged to employ suitable reference materials, if available, to verify the accuracy of the method in their laboratories.

9.4.2 ILS in Which One (or More) Accepted Reference Material was Tested: The accuracy of this method has been deemed satisfactory based upon the bias information in Table _____. Users are encouraged to use these or similar reference materials to verify that the method is performing accurately in their laboratories.

10. Keywords

10.1 error models for analytical methods; interpretation of interlaboratory studies; use of interlaboratory statistics

ANNEXES

(Mandatory Information)

A1. PRECISION MODELS FOR METHODS OF CHEMICAL ANALYSIS

A1.1 Interlaboratory studies of methods are designed to partition the total variability of the study into two or more components using analysis of variance. The total variance is broken up into the component parts revealed by the variable levels included in the statistical design. An ILS produces a separate set of statistics for each analyte in each test material (analyte/material combination.) The total variance includes all sources of variability that operate during the experiment. The statistics s_R , and R are the standard deviation and reproducibility index for differences between laboratories, the highest level in the ILS design. Consequently, they encompass all sources of error in the ILS.

A1.2 The total variance may also be partitioned into two mutually exclusive parts in a different manner: The first component, characteristic of the method but independent of analyte concentration, has a constant value for all test materials. The second, a function of analyte concentration, increases in materials with higher analyte contents. All constant variability sources are summed into a single variable, s_K^2 , and all concentration-dependent sources into another variable, s_v^2 . Because every variability source that is not constant with respect to analyte concentration must be dependent upon concentration, the total variance, s_T^2 , is represented as follows:

$$s_T^2 = s_K^2 + s_v^2 \quad (\text{A1.1})$$

Analyte concentration is implicitly included in the final term of Eq A1.1. The simplest relationship between precision of a method and analyte concentration asserts that the percent standard deviation is constant relative to concentration:

$$s_{\text{rel}\%} = 100 \times s_v / C. \quad (\text{A1.2})$$

A1.2.1 Substitution into Eq A1.1 yields Eq A1.3, a general relationship between observed standard deviation and analyte concentration:

$$s_T^2 = s_K^2 + \left(C \times \frac{s_{\text{rel}\%}}{100} \right)^2 \quad (\text{A1.3})$$

Note that s_K and $s_{\text{rel}\%}$ are both constants by definition. Because the reproducibility index, R , is a simple function of the standard deviation, s , Eq A1.4 follows from Eq A1.3. It represents R at a discrete concentration, R_C , as a function of the analyte concentration, C , and involves the two constants, K_R and $K_{\text{rel}\%}$, which are characteristic of the method:

$$R_C = \sqrt{K_R^2 + \left(C \times \frac{K_{\text{rel}\%}}{100} \right)^2} \quad (\text{A1.4})$$

A1.3 General Model for Analytical Methods—Eq A1.4 represents a model which many ILS data sets follow. The plot of R for each test material in the ILS against its concentration has the following general characteristics:

A1.3.1 For analyte concentrations below a certain level, R becomes asymptotic to the horizontal line at $R = K_R$. The model shows K_R as the lowest possible value for R .

A1.3.2 For analyte concentrations above a certain level, R becomes asymptotic to a line through the origin with its slope equal to $K_{\text{rel}\%}/100$. The model shows $K_{\text{rel}\%}$ as the lowest possible value for $R_{\text{rel}\%}$.

A1.3.3 The unique concentration in A1.3.1 and A1.3.2 is the transition concentration, C_{trans} . At that concentration, both constant and concentration-dependent sources contribute equally to the observed variability. Eq A1.5 predicts the transition concentration:

$$C_{\text{trans}} = 100 \times \frac{K_R}{K_{\text{rel}\%}} \quad (\text{A1.5})$$

A1.3.4 These theoretical relationships are shown in Fig. A1.1. The ILS statistics estimate the parameters of the method only at the discrete analyte concentrations of the test materials. Plots of R versus mean C , both ILS statistics, always exhibit a scatter about the fitted line. The extent of the scatter varies greatly among ILS for different methods and is affected by many factors, some of which may not be directly related to the precision of the analytical method under test. Eq A1.4 is useful because it represents the part of the data variability that can be “explained” by changes in analyte concentration between materials. Variability not related to analyte concentration is caused either by random variability in measurements or by inhomogeneity in test materials. The constants in Eq A1.4 are

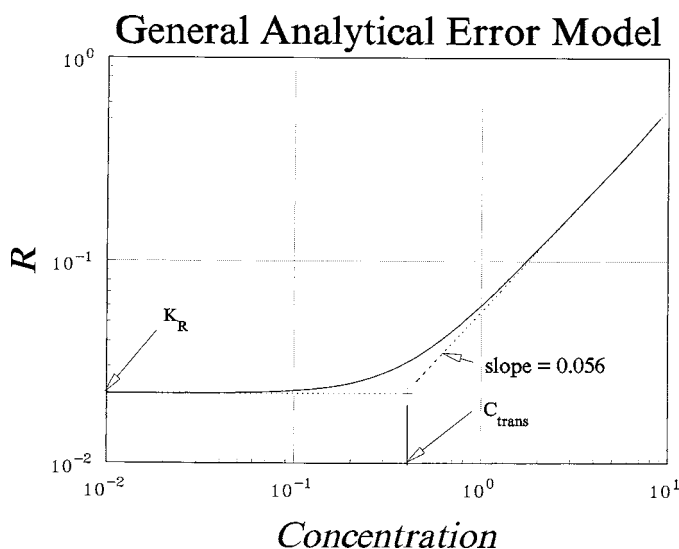


FIG. A1.1 Plot of R for a Hypothetical Method with $K_R = 0.022$ and $K_{\text{rel}\%} = 5.6\%$

estimated by commonly available curve-fitting techniques, several of which are explained in Annex A2.

A1.3.5 The constants of the general model have the following physical significance: K_R defines the minimum value of R a user may expect at low analyte contents; $K_{\text{rel}\%}$ defines the lowest $R_{\text{rel}\%}$ a user may expect for materials with higher analyte contents.

A1.4 *Constant Precision Model*—If a method is tested with materials containing less than about $\frac{1}{2} C_{\text{trans}}$, R will appear to be independent of analyte concentration. Some methods follow this model at all attainable analyte contents. Fire-assay methods seem to exhibit this behavior. The chemical reactions are carried out at elevated temperatures, so that the kinetics and equilibria are not significant sources of variability in comparison with weighing errors. Weighing errors are constant at all analyte contents. This explains why the ILS for a fire assay method (see Table 1) shows a constant value for R over the tested content range of 25 to 100 % gold. When a task group applies this model to its ILS results, it should state in the research report the chemical and physical aspects of the method causing the constant variability. This model is also implied if the estimate of $K_{\text{rel}\%}$ from the general analytical model is zero. Because R is independent of analyte content, the R value for every material is an equally probable estimate of R . Report the root-mean-square (RMS) average R of all test materials as the estimate of R for the method, from zero to the highest level tested in the ILS.

A1.5 *Relative Precision Model*—Many methods of chemical analysis exhibit constant relative precision over a restricted range of analyte concentrations. If the intended applications of a method lie within this range, the task group need not test the method at lower analyte levels. This model is also implied if the estimate of K_R from the general analytical model is zero. Because the relative reproducibility index is proportional to analyte concentration, the $R_{\text{rel}\%}$ of each test material is an equally probable estimate of the relative reproducibility of the method. Report the RMS average $R_{\text{rel}\%}$ of all test materials as the estimate of $R_{\text{rel}\%}$ for the method over the concentration range tested in the ILS. The lower limit of the scope is set by the requirements of the applications.

A2. PROCEDURES FOR ESTIMATING THE CONSTANTS OF THE GENERAL ANALYTICAL MODEL

A2.1 *Linear Regression Procedures*—Do not use ordinary linear regression programs, such as those provided with electronic calculators. They are not suitable for ILS data because they assume that R is a linear function of concentration and has constant variability over the entire range of the independent variable. In general, these assumptions are not valid for ILS data.

A2.2 *Nonlinear Curve Fitting Procedures*—Many statistical and data-plotting software packages contain procedures for fitting the nonlinear Eq A1.4 to data. The results from one

program may differ from others, but the differences ordinarily are small and may usually be ignored. Always verify that the curve is a reasonable fit to the data by plotting R versus C . Use log-log coordinates to enhance visibility of the low-concentration data.

A2.3 *Least-Squares Procedures with Variable Precision*—Two calculation programs have been specifically developed to estimate the constants in Eq A1.4 for ILS data sets. The first program minimizes the squares of the differences relative to the observed values of R . The second minimizes the squares of the differences relative to the observed values of $R_{\text{rel}\%}$.