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Copper, lead and zinc sulfide concentrates — Experimental methods for checking the precision of sampling

Concentrés sulfurés de cuivre, de plomb et de zinc — Méthodes expérimentales de contrôle de la fidélité de l'échantillonnage

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 12744 was prepared by Technical Committee ISO/TC 183, *Copper, lead and zinc ores and concentrates.*

Annexes A and B of this International Standard are for information only.

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Copper, lead and zinc sulfide concentrates — Experimental methods for checking the precision of sampling

1 Scope

This International Standard specifies methods for checking the precision of primary sampling, sample processing, chemical analysis, physical testing and determination of moisture content of copper, lead and zinc sulfide concentrates being carried out in accordance with the methods specified in ISO 12743, expressed in terms of standard deviations.

2 Normative reference

The following standard contains provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the edition indicated was valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 12743:—[1], *Copper, lead and zinc sulfide concentrates — Sampling procedures for determination of metal and moisture content.*

3 General conditions

3.1 General

The determination of precision of primary sampling is based on collecting pairs of interleaved samples from each lot. If sample processing and measurement are also carried out in duplicate, it is possible to determine the precision of sample processing and analysis.

3.2 Number of lots

It is recommended that pairs of interleaved samples be collected from more than 20 lots of the same type of concentrate in order to reach a reliable conclusion. The lot size shall be chosen to ensure this requirement is met.

3.3 Number of increments and number of samples

The minimum number of increments for checking precision should preferably be twice the number determined in accordance with ISO 12743. Hence, if the number of increments required for routine sampling is n and one lot sample is constituted, the minimum number of increments should be $2n$, and two interleaved samples shall be constituted.

Alternatively, if the precision is being checked as part of routine sampling, n increments may be taken and two interleaved samples constituted, each comprising $n/2$ increments. The sampling precision thus obtained must be divided by $\sqrt{2}$ to obtain the sampling precision for lot samples comprising n increments.

3.4 Sample processing and analysis

Sample processing shall be carried out in accordance with ISO 12743. The analysis of samples shall be carried out according to the methods specified in the relevant International Standards.

3.5 Frequency of precision checks

It is recommended that, even after a precision check has been conducted, further checks be carried out at regular intervals. Precision checks should also be carried out when there is a change in equipment.

Because of the large amount of work involved in checking precision, it is recommended that checks be carried out as a part of routine sampling and analysis.

1) To be published.

4 Definition of symbols

Symbol	Term
k	Number of lots
n	Number of increments
R_1	Absolute difference between duplicates for interleaved samples A and B
$\overline{R}_1$	Mean absolute difference between duplicates for interleaved samples A and B for k lots
R_2	Absolute difference between means for divided interleaved samples A_1 and A_2, and B_1 and B_2
$\overline{R}_2$	Mean absolute difference between means for divided interleaved samples A_1 and A_2, and B_1 and B_2, for k lots
R_3	Absolute difference between means for interleaved sample A and interleaved sample B
$\overline{R}_3$	Mean absolute difference between means for interleaved sample A and interleaved sample B for k lots
s	Estimated value of standard deviation, σ
s_1^2	Estimated variance from $\overline{R}_1$
s_2^2	Estimated variance from $\overline{R}_2$
s_3^2	Estimated variance from $\overline{R}_3$
s_A	Estimated standard deviation of analysis
s_P	Estimated standard deviation of sample processing
s_{S_1}	Estimated standard deviation of primary sampling
s_{SP}	Estimated standard deviation of primary sampling and sample processing
s_T	Estimated total standard deviation of primary sampling, sample processing and analysis
x_{i1}	First duplicate result for interleaved sample, where i = 1 and 2 and indicates interleaved sample A or B
x_{i2}	Second duplicate result for interleaved sample, where i = 1 and 2 and indicates interleaved sample A or B
x_{ij1}	First duplicate result for interleaved sample, where i = 1 and 2 and indicates interleaved sample A or B, and j = 1 or 2 and indicates laboratory samples A_1 or A_2, and B_1 or B_2
x_{ij2}	Second duplicate result for sample, where i = 1 and 2 and indicates interleaved sample A or B, and j = 1 or 2 and indicates laboratory samples A_1 or A_2, and B_1 or B_2
$\overline{x}$	Mean value of duplicate results
$\overline{\overline{x}}$	Mean of mean of duplicate results
$\overline{\overline{\overline{x}}}$	Mean of $\overline{\overline{x}}$ values, and grand mean for sample processing method 3
$\overline{\overline{\overline{\overline{x}}}}$	Grand mean of all results for sample processing methods 1 and 2

5 Method of experiment

5.1 Interleaved samples

Each alternate primary increment shall be diverted so that pairs of interleaved samples A and B are formed. The number of divided increments per primary increment should be the same as for routine sampling. An example of a sampling plan for producing pairs of interleaved samples A and B is shown in figure 1.

5.2 Sample processing and analysis

The pairs of interleaved samples A and B taken in accordance with 5.1 shall be divided separately and subjected to either method 1, method 2 or method 3 sample processing and analysis as described in 5.2.1, 5.2.2 or 5.2.3.

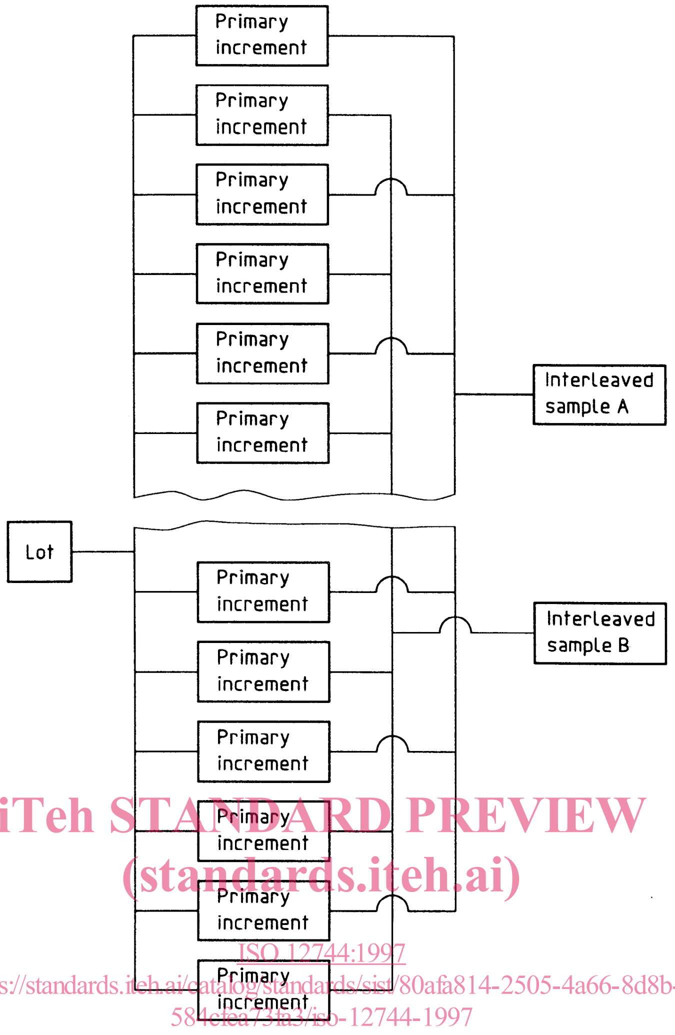

Figure 1 — Example of a plan for interleaved duplicate sampling

5.2.1 Sample processing method 1 (see figure 2)

The two interleaved samples A and B shall be divided separately to prepare four laboratory samples, A_1, A_2, and B_1, B_2. These laboratory samples shall each be analysed in duplicate, and the duplicates designated x_{111} and x_{112} for sample A_1, x_{121} and x_{122} for sample A_2, x_{211} and x_{212} for sample B_1 and x_{221} and x_{222} for sample B_2. The eight determinations shall be run in random order by the same analyst on the same day using the same analytical equipment. An example is given in annex A.

NOTE 1 By using method 1, the estimated precisions of primary sampling, sample processing and analysis can be obtained separately.

5.2.2 Sample processing method 2 (see figure 3)

Sample A shall be divided to prepare two laboratory samples, A_1 and A_2. From sample B, only one laboratory sample shall be prepared. The laboratory samples shall each be analysed in duplicate, and the duplicates designated x_{111} and x_{112} for sample A_1, x_{121} and x_{122} for sample A_2, and x_{21} and x_{22} for sample B. The six determinations shall be run in random order by the same analyst on the same day using the same analytical equipment.

NOTE 2 By using method 2, the estimated precisions of primary sampling, sample processing and analysis can be obtained separately. However, the estimated values will be less precise than those obtained using method 1.

5.2.3 Sample processing method 3 (see figure 4)

From each of the two interleaved samples A and B, one laboratory sample shall be prepared. The two laboratory samples A and B shall be analysed in duplicate and the measurements obtained shall be designated x_{11} and x_{12} for sample A and x_{21} and x_{22} for sample B. The four determinations shall be run in random order by the same analyst on the same day using the same analytical equipment.

NOTE 3 By using method 3, only the estimated precision of analysis and the combined precision of primary sampling and sample processing are obtained.

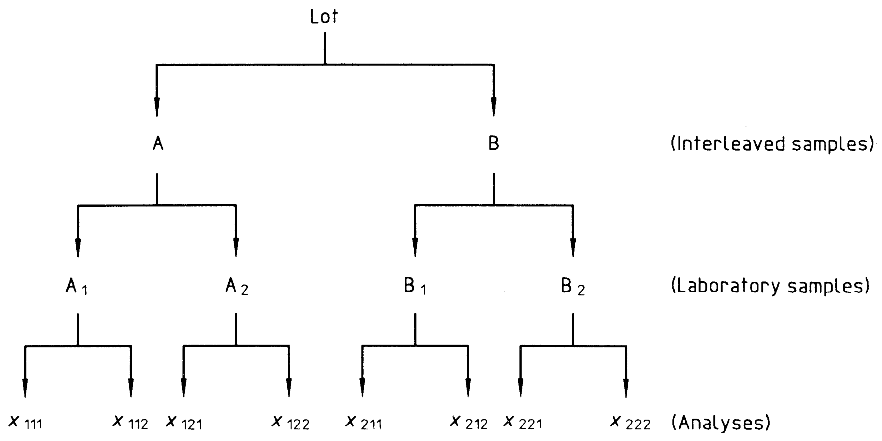

Figure 2 — Flowsheet for sample processing method 1

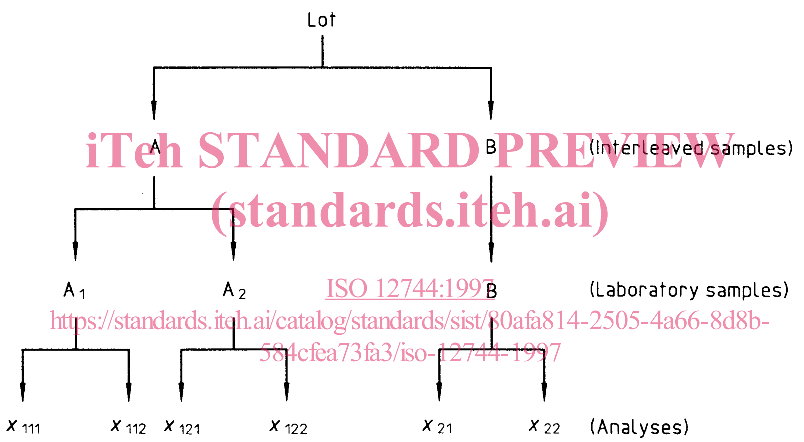

Figure 3 — Flowsheet for sample processing method 2

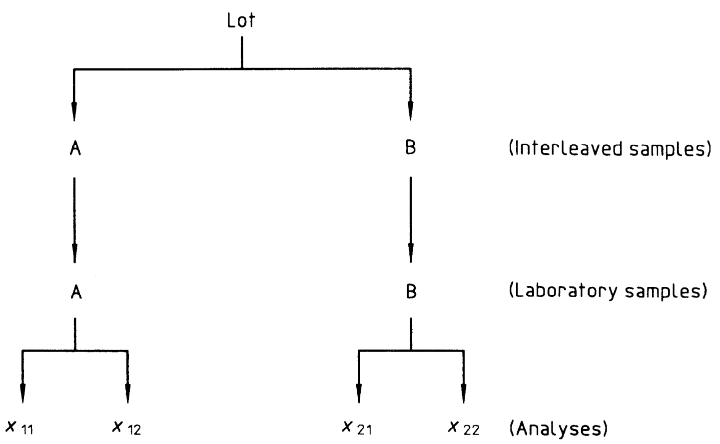

Figure 4 — Flowsheet for sample processing method 3

6 Evaluation of experimental data

6.1 General

The method for evaluation of experimental data shall be as specified below, depending on the method of sample processing selected.

6.2 Sample processing method 1

The estimated standard deviations of primary sampling, sample processing and analysis shall be calculated in accordance with the following procedure.

a) Calculate the mean and range for each pair of duplicates:

$$\bar{x}_{ij} = \frac{1}{2}(x_{ij1} + x_{ij2}) \quad \ldots (1)$$

$$R_1 = \left| x_{ij1} - x_{ij2} \right| \quad \ldots (2)$$

where

i = 1 and 2 representing interleaved samples A and B respectively;

j = 1 and 2 representing laboratory samples A_1 and A_2 or B_1 and B_2.

b) Calculate the mean of the mean and range for each pair of duplicates:

$$\bar{\bar{x}}_i = \frac{1}{2}(\bar{x}_{i1} + \bar{x}_{i2}) \quad \ldots (3)$$

$$R_2 = \left| \bar{x}_{i1} - \bar{x}_{i2} \right| \quad \ldots (4)$$

c) Calculate the mean and range for each pair of interleaved samples, A and B:

$$\bar{\bar{\bar{x}}} = \frac{1}{2}(\bar{\bar{x}}_1 + \bar{\bar{x}}_2) \quad \ldots (5)$$

$$R_3 = \left| \bar{\bar{x}}_1 - \bar{\bar{x}}_2 \right| \quad \ldots (6)$$

d) Calculate the grand mean and the means of ranges R_1, R_2 and R_3:

$$\bar{\bar{\bar{\bar{x}}}} = \frac{1}{k}\sum \bar{\bar{\bar{x}}} \quad \ldots (7)$$

$$\bar{R}_1 = \frac{1}{4k}\sum R_1 \quad \ldots (8)$$

$$\bar{R}_2 = \frac{1}{2k}\sum R_2 \quad \ldots (9)$$

$$\bar{R}_3 = \frac{1}{k}\sum R_3 \quad \ldots (10)$$

where k is the number of lots.

e) Calculate the variances s_1^2, s_2^2 and s_3^2 from the means of ranges $\bar{R}_1$, $\bar{R}_2$ and $\bar{R}_3$:

$$s_1^2 = \frac{\pi}{4}\left(\bar{R}_1\right)^2 \quad \ldots (11)$$

$$s_2^2 = \frac{\pi}{4}\left(\bar{R}_2\right)^2 \quad \ldots (12)$$

$$s_3^2 = \frac{\pi}{4}\left(\bar{R}_3\right)^2 \quad \ldots (13)$$

where $\pi/4$ is a statistical factor relating range to variance for a pair of measurements.

f) Conduct F-tests on the variances s_1^2, s_2^2 and s_3^2 to determine whether their differences are statistically significant using the following procedure:

1) calculate the variance ratios s_2^2/s_1^2 and s_3^2/s_2^2;

2) compare these ratios with the 95 % confidence F-ratios given in table 1 for the number of degrees of freedom applicable to each variance estimate;

3) if the calculated variance ratio exceeds the F-ratio, partition the two variances into variance components as their difference is statistically significant.

If the calculated variance ratio does not exceed the F-ratio, the variances s_2^2 and/or s_3^2 cannot be meaningfully partitioned into variance components and more data need to be collected.

g) Assuming the F-tests conducted in f) indicate that the differences between the variances s_1^2, s_2^2 and s_3^2 are significant, calculate the estimated values of the variance of analysis (s_A^2), sample processing (s_P^2) and primary sampling ($s_{S_1}^2$) as follows:

$$s_A^2 = s_1^2 \quad \ldots (14)$$

$$s_P^2 = s_2^2 - \frac{1}{2}s_1^2 \quad \ldots (15)$$

$$s_{S_1}^2 = s_3^2 - \frac{1}{2}s_2^2 \quad \ldots (16)$$

h) Calculate the total variance of primary sampling, sample processing and analysis (s_T^2) as follows:

$$s_T^2 = s_{S_1}^2 + s_P^2 + s_A^2 \quad \ldots (17)$$

Table 1 — F-ratios at the 95 % confidence level for comparison of two variances

Degrees of freedom (smaller variance)	Degrees of freedom (larger variance)						
	20	24	30	40	60	120	∞
20	2,12	2,08	2,04	1,99	1,95	1,90	1,84
24	2,03	1,98	1,94	1,89	1,84	1,79	1,73
30	1,93	1,89	1,84	1,79	1,74	1,68	1,62
40	1,84	1,79	1,74	1,69	1,64	1,58	1,51
60	1,75	1,70	1,65	1,59	1,53	1,47	1,39
120	1,66	1,61	1,55	1,50	1,43	1,35	1,25
∞	1,57	1,52	1,46	1,39	1,32	1,22	1,00

i) Calculate the estimated values of the total standard deviation (s_T) and the standard deviations of primary sampling (s_{S_1}), sample processing (s_P) and analysis (s_A).

j) Compare the values of s_T, s_{S_1}, s_P and s_A thus obtained with the desired standard deviations.

6.3 Sample processing method 2

The estimated standard deviations of primary sampling, sample processing and analysis shall be calculated in accordance with the following procedure:

a) Calculate the mean and range for each pair of duplicates:

$$\bar{x} = \frac{1}{2}(x_{111} + x_{112}), \frac{1}{2}(x_{121} + x_{122}), \frac{1}{2}(x_{21} + x_{22}) \qquad \ldots (18)$$

$$R_1 = |x_{111} - x_{112}|, |x_{121} - x_{122}|, |x_{21} - x_{22}| \qquad \ldots (19)$$

b) Calculate the mean and range for duplicates A_1 and A_2:

$$\bar{\bar{x}} = \frac{1}{4}(x_{111} + x_{112} + x_{121} + x_{122}) \qquad \ldots (20)$$

$$R_2 = \frac{1}{2}|(x_{111} + x_{112}) - (x_{121} + x_{122})| \qquad \ldots (21)$$

c) Calculate the mean and range for each pair of interleaved samples, A and B:

$$\bar{\bar{\bar{x}}} = \frac{1}{2}\left[\bar{\bar{x}} + \frac{1}{2}(x_{21} + x_{22})\right] \qquad \ldots (22)$$

$$R_3 = \left|\bar{\bar{x}} - \frac{1}{2}(x_{21} + x_{22})\right| \qquad \ldots (23)$$

d) Calculate the grand mean and the means of ranges R_1, R_2 and R_3:

$$\bar{\bar{\bar{x}}} = \frac{1}{k}\sum \bar{\bar{\bar{x}}} \qquad \ldots (24)$$

$$\bar{R}_1 = \frac{1}{3k}\sum R_1 \qquad \ldots (25)$$

$$\bar{R}_2 = \frac{1}{k}\sum R_2 \qquad \ldots (26)$$

$$\bar{R}_3 = \frac{1}{k}\sum R_3 \qquad \ldots (27)$$

where k is the number of lots.

e) Calculate the variances s_1^2, s_2^2 and s_3^2 from the means of ranges $\bar{R}_1$, $\bar{R}_2$ and $\bar{R}_3$:

$$s_1^2 = \frac{\pi}{4}\left(\bar{R}_1\right)^2 \qquad \ldots (28)$$

$$s_2^2 = \frac{\pi}{4}\left(\bar{R}_2\right)^2 \qquad \ldots (29)$$

$$s_3^2 = \frac{\pi}{4}\left(\bar{R}_3\right)^2 \qquad \ldots (30)$$

where $\pi/4$ is a statistical factor relating range to variance for a pair of measurements.

f) Conduct F-tests on the variances s_1^2, s_2^2 and s_3^2 to determine whether their differences are statistically significant using the following procedure:

1) calculate the variance ratios s_2^2/s_1^2 and s_3^2/s_2^2;

2) compare these ratios with the 95 % confidence F-ratios given in table 1 for the num-

ber of degrees of freedom applicable to each variance estimate;

3) if the calculated variance ratio exceeds the F-ratio, partition the two variances into variance components as their difference is statistically significant.

If the calculated variance ratio does not exceed the F-ratio, the variances s_2^2 and/or s_3^2 cannot be meaningfully partitioned into variance components and more data need to be collected.

g) Assuming the F-tests conducted in f) indicate that the differences between the variances s_1^2, s_2^2 and s_3^2 are significant, calculate the estimated values of the variance of analysis (s_A^2), sample processing (s_P^2) and primary sampling ($s_{S_1}^2$) as follows:

$$s_A^2 = s_1^2 \qquad \ldots (31)$$

$$s_P^2 = s_2^2 - \frac{1}{2} s_1^2 \qquad \ldots (32)$$

$$s_{S_1}^2 = s_3^2 - \frac{3}{4} s_2^2 \qquad \ldots (33)$$

h) Calculate the total variance of primary sampling, sample processing and analysis (s_T^2) as follows:

$$s_T^2 = s_{S_1}^2 + s_P^2 + s_A^2 \qquad \ldots (34)$$

i) Calculate the estimated values of the total standard deviation (s_T) and the standard deviations of primary sampling (s_{S_1}), sample processing (s_P) and analysis (s_A).

j) Compare the values of s_T, s_{S_1}, s_P and s_A thus obtained with the desired standard deviations.

6.4 Sample processing method 3

Although the estimated standard deviation of analysis can be obtained, the estimated standard deviations of primary sampling and sample processing cannot be separated using sample processing method 3. The estimated standard deviations shall be calculated in accordance with the following procedure.

a) Calculate the mean and range for each pair of duplicates:

$$\bar{x}_i = \frac{1}{2}(x_{i1} + x_{i2}) \qquad \ldots (35)$$

$$R_1 = \left| x_{i1} - x_{i2} \right| \qquad \ldots (36)$$

where $i = 1$ and 2 representing interleaved samples A and B respectively.

b) Calculate the mean and range for each pair of interleaved samples, A and B:

$$\bar{\bar{x}} = \frac{1}{2}(\bar{x}_1 + \bar{x}_2) \qquad \ldots (37)$$

$$R_3 = \left| \bar{x}_1 - \bar{x}_2 \right| \qquad \ldots (38)$$

c) Calculate the grand mean and the means of ranges R_1 and R_3:

$$\bar{\bar{\bar{x}}} = \frac{1}{k} \sum \bar{\bar{x}} \qquad \ldots (39)$$

$$\bar{R}_1 = \frac{1}{2k} \sum R_1 \qquad \ldots (40)$$

$$\bar{R}_3 = \frac{1}{k} \sum R_3 \qquad \ldots (41)$$

where k is the number of lots.

d) Calculate the variances s_1^2 and s_3^2 from the means of ranges $\bar{R}_1$ and $\bar{R}_3$:

$$s_1^2 = \frac{\pi}{4} \left(\bar{R}_1\right)^2 \qquad \ldots (42)$$

$$s_3^2 = \frac{\pi}{4} \left(\bar{R}_3\right)^2 \qquad \ldots (43)$$

where $\pi/4$ is a statistical factor relating range to variance for a pair of measurements.

e) Conduct F-tests on the variances s_1^2 and s_3^2 to determine whether their differences are statistically significant using the following procedure:

1) calculate the variance ratio s_3^2/s_1^2;

2) compare this ratio with the 95 % confidence F-ratio given in table 1 for the number of degrees of freedom applicable to each variance estimate;

3) if the calculated variance ratio exceeds the F-ratio, partition the two variances into variance components as their difference is statistically significant.

If the calculated variance ratio does not exceed the F-ratio, the variance s_3^2 cannot be meaningfully partitioned into variance components and more data need to be collected.