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Copper, lead, zinc and nickel concentrates — Experimental methods for checking the bias of sampling

Concentrés de cuivre, de plomb, de zinc et de nickel — Méthodes expérimentales de contrôle de l'erreur systématique d'échantillonnage

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Foreword

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The main task of technical committees is to prepare International Standards. 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.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 13292 was prepared by Technical Committee ISO/TC 183, *Copper, lead, zinc and nickel ores and concentrates*.

This second edition cancels and replaces the first edition (ISO 13292:1997), which has been technically revised.

Copper, lead, zinc and nickel concentrates — Experimental methods for checking the bias of sampling

WARNING — This International Standard may involve hazardous materials, operations and equipment. It is the responsibility of the user of this International Standard to establish appropriate health and safety practices and determine the applicability of regulatory limitations prior to use.

1 Scope

This International Standard specifies methods for checking whether there is any bias in the sampling of copper, lead, zinc and nickel concentrates, where the sampling is carried out in accordance with the methods specified in ISO 12743. These methods can also be used for comparing alternative sampling regimes, checking whether there is any bias in sample processing and for checking possible significant differences in sampling at different places, e.g. at loading and discharge points, or the analysis of exchange samples. Numerical examples are given in Annex A.

2 Normative references

The following referenced documents are indispensable for the application 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 12743, *Copper, lead, zinc and nickel concentrates — Sampling procedures for determination of metal and moisture content*

3 General requirements and recommendations

The procedures specified in this International Standard are applicable to paired data only. The results obtained from the method to be checked for bias (referred to as Method B) are compared with the results for a reference method (referred to as Method A), which is considered to produce unbiased results from technical and empirical viewpoints. If there is no significant difference between the results obtained using Method B and Method A, then Method B may be adopted as a routine method.

While the procedures specified in Clause 5 are principally designed for checking bias against a reference method, separate measurements of quality characteristics, e.g. using different sampling regimes, sampling at loading (Method A) and discharge (Method B), or analyses of exchange samples, may also be compared to check whether there is a statistically significant difference between the results.

Mechanical sampling systems, or manual sampling methods, are tested for bias by comparing the test results for final system or manually collected samples (Method B) with the test results for reference increments collected from a stopped conveyor belt (Method A). Analytical methods or test procedures are checked against certified reference materials.

The standard method of taking reference increments from a stopped conveyor belt presents operational difficulties, even if the handling system is capable of being restarted with a fully loaded belt. The main problems are losses in production tonnage and the difficulty experienced in the sequence of starting the handling system. During a ship's loading or unloading operation, this can cause delays in the turnaround time of the ship.

Alternative reference methods, which are also expensive, divert the ore flow onto a transfer conveyor belt to produce a material bed section identical to that from the main belt on which the mechanical primary sampler (Method B) is installed. Stopped-belt sampling is then carried out on the transfer belt to collect reference increments (Method A). The transfer conveyor belt should be of sufficient length to allow the establishment of a material bed section that is not influenced by any longitudinal segregation introduced by the diversion plate. The primary sampler and the point of diversion to the transfer belt should be as close as possible.

Sampling and sample processing procedures are more prone to bias than analytical techniques and test methods. As system samples and reference increments are progressively reduced in mass and particle size, lot samples, subsamples and test samples become increasingly vulnerable to sample loss and contamination. Therefore, systematic errors occur more frequently during sample processing than during sampling, so different stages of the sample processing procedure may require testing for bias.

Where testing for bias, the number of paired sets of measurements (data sets) shall be not less than 20. The number of data sets required depends on the variance of the differences between the two methods and on the value of the bias, δ, to be detected.

Any chemical or physical characteristic may be used to check whether any bias is present, e.g. copper, lead, zinc, nickel or moisture content. Bias may not always be present for just one parameter. Therefore, several parameters to reduce the effect of short-term variations in quality, preferably including all those that are likely to be of interest, should be examined to determine whether bias exists. Characteristics to be tested for the presence of bias need to be decided before the test work begins.

If the purpose of the bias check is to assess the performance of the sampling equipment, it is recommended that increments for Method A and Method B be taken from closely adjacent portions of the concentrate to reduce the effect of short-term variations in quality, and that sample processing and analysis be carried out on each increment individually. This is likely to reduce the number of data sets required to detect a given bias in the sampling equipment.

On the other hand, if the purpose of the bias check is to determine whether the selected sampling regime is biased, e.g. due to the presence of periodic variations in quality, it is recommended that increments for Method A and Method B be taken completely independently.

Even after a bias check has been conducted, further checks should be carried out at regular intervals. Bias checks should also be carried out when sampling equipment is changed.

4 Sampling and sample processing methods

4.1 Sampling

4.1.1 General

The method to be checked (Method B) shall be compared with a designated reference method (Method A) using the same type of concentrate. Method A may also be an alternative method that is being compared with Method B. As specified in Clause 3, at least 20 pairs of samples shall be collected following the procedures detailed in ISO 12743.

4.1.2 Checking bias in mechanical sampling

Method A: Reference increments are taken by stopped-belt sampling.

Method B: System increments are taken from a moving stream with a mechanical sampler.

4.1.3 Checking difference between sampling at different locations

Method A: Increments are taken from a moving stream with a mechanical sampler at a loading location.

Method B: Increments are taken from a moving stream with a mechanical sampler at a discharge location.

4.2 Sample processing and analysis

The procedure for constituting pairs of samples and carrying out the subsequent sample processing and analysis shall be as follows.

a) Constitute two samples (sample A and sample B), consisting of one or a number of individual increments obtained in accordance with Method A and Method B.

b) Subject sample A and sample B to similar sample processing and analysis procedures, as specified in ISO 12743 and other relevant International Standards, to obtain sets of measurements for the characteristics of interest. It is recommended that analyses of paired samples be carried out under repeatability conditions, to decrease the analytical variance.

5 Analysis of experimental data

5.1 Statistical basis

It is helpful at this point to review the definitions of Type I and Type II risks in bias testing. Consider the null hypothesis, H_0, that there is no positive or negative bias in Method B compared with Method A. The alternative hypothesis, H_1, is that there is either positive or negative bias. A Type I error occurs if H_0 is rejected on the basis of the sample data falling into the critical region of a statistical test when, in reality, H_0 is true. A Type II error occurs if H_0 is accepted on the basis of the statistical test on the sample data when, in reality, H_1 is true.

In this International Standard, the statistical test for accepting H_0 is that the absolute value of the difference between the mean of the quality characteristics for the reference (or alternative) set of increments (Method A) and the mean for the corresponding set of system increments (Method B) is smaller than a specified bias detection limit, BDL.

A bias can be either positive or negative, so for a positive bias:

$$\bar{x}(\mathrm{B}) - \bar{x}(\mathrm{A}) > +\,\mathrm{BDL} \tag{1}$$

while for a negative bias:

$$\bar{x}(\mathrm{B}) - \bar{x}(\mathrm{A}) < -\,\mathrm{BDL} \tag{2}$$

where $\bar{x}(\mathrm{A})$ and $\bar{x}(\mathrm{B})$ are the means for the reference (or alternative) set of increments (Method A) and the system set of increments (Method B), respectively.

The bias detection limit is defined as the minimum bias that can be detected at the 95 % confidence level using the data available. It is calculated using the method described in 5.3.

By convention, a symmetrical, two-sided 5 % probability (α = 0,05) is assigned to the risk (Type I) of rejecting the null hypothesis, H_0, when in fact it is true (see [1] and [2] in the Bibliography). In addition, an asymmetrical 10 % probability (β = 0,10) is assigned to the risk of accepting the null hypothesis, H_0, when in fact it is not true. Thus, sufficient data sets shall be collected to ensure that there is a small risk α = 0,05 of concluding that there is a statistical difference between Method A and Method B when none exists (Type I risk), and a small risk β = 0,10 of concluding that there is no statistical difference when a bias δ is present (Type II risk). A Student's t-test (two-sided) shall then be applied at the 5 % level of significance. If the result is significant, it is concluded that a bias exists. However, if the result is not significant, it is concluded that no bias as large as δ exists.

5.2 Determination of the mean difference and its standard deviation

Determine the standard deviation of the differences between Method A and Method B using the following procedure.

a) Denote individual measurements for the ith sample pair using Method A and Method B as x_{A_i} and x_{B_i}, respectively.

b) Calculate the difference, d_i , between $x_{\mathrm{B}i}$ and $x_{\mathrm{A}i}$, i.e.

$$d_i = x_{\mathrm{B}_i} - x_{\mathrm{A}_i} \tag{3}$$

where

i = 1, 2, ..., k

k is the the number of paired sets of measurements.

c) Calculate the mean, $\overline{d}$, of the differences using the following equation:

$$\overline{d} = \frac{\sum_{i=1}^{k} d_i}{k} = \overline{x}(\mathrm{B}) - \overline{x}(\mathrm{A}) \tag{4}$$

d) Calculate the sum of the squares, SS_d, and the standard deviation, s_d, of the difference using the following equations, where summations are over i = 1,2,..., k:

$$\mathrm{SS_d} = \sum {d_i}^2 - \frac{1}{k}\left(\sum d_i\right)^2 \tag{5}$$

$$s_\mathrm{d} = \sqrt{\frac{\mathrm{SS_d}}{k-1}} \tag{6}$$

5.3 Determination of the required number of data sets

a) Specify the magnitude of the bias (or difference), δ, to be detected.

b) Calculate the bias detection limit for the combined risk of Type I and Type II errors using the following equation:

$$\mathrm{BDL} = \left(t_{0,05;\ k-1} + t_{0,10;\ k-1}\right)\frac{s_\mathrm{d}}{\sqrt{k}} \tag{7}$$

where $t_{0,05;k-1}$ and $t_{0,10;k-1}$ are the tabulated Student's t-values for $k - 1$ degrees of freedom corresponding to α = 0,05 and β = 0,10 as given in Table 1.

The bias detection limit, BDL, is the minimum bias that can be detected using the data available.

c) If BDL $\leqslant \delta$, the number of data sets is sufficient and the statistical test in 5.4 can be applied.

d) If BDL $> \delta$, calculate the standardized difference, D, and the required number of data sets, n_r, corresponding to this value of D using Equations 8 and 9 below. These equations are based on the strategy of adjusting the number of data sets in Equation 7 until BDL = δ, while avoiding the rigour of adjusting the corresponding degrees of freedom in the t-tests:

$$D = \frac{\delta}{s_d} \tag{8}$$

$$n_r = \frac{\left(t_{0,05;k-1} + t_{0,10;k-1}\right)^2}{D^2} \tag{9}$$

Calculated values of n_r for k = 20 and different values of the standardized difference D are given in Table 2.

e) Collect an additional ($n_r - k$) data sets and repeat steps b) to d) until the number of data sets exceeds n_r.

Table 1 — Values of t at 5 % and 10 % levels of significance (two-sided test)

Number of data sets, k	$t_{0,05;k-1}$	$t_{0,10;k-1}$
20	2,093	1,729
21	2,086	1,725
22	2,080	1,721
23	2,074	1,717
24	2,069	1,714
25	2,064	1,711
26	2,060	1,708
27	2,056	1,706
28	2,052	1,703
29	2,048	1,701
30	2,045	1,699
31	2,042	1,697
41	2,021	1,684
61	2,000	1,671
121	1,980	1,658
∞	1,960	1,645

Table 2 — Required number of data sets determined from the initial 20 measurements for given standardized differences D and α = 0,05 and β = 0,10

Standardized difference D	Required number of data sets n_r
0,35	119
0,40	91
0,45	72
0,50	58
0,55	48
0,60	41
0,65	35
0,70	30
0,75	26
0,80	23
0,85	20

NOTE The required number of data sets in this table is calculated using Equation 9 with $t_{0,05;19}$ = 2,093 and $t_{0,10;19}$ = 1,729 (from Table 1).

5.4 Statistical test

Calculate the value of a parameter t_0 (which is assumed to have a t-distribution with $k-1$ degrees of freedom) using the following equation:

$$t_0 = \frac{\overline{d}\,\sqrt{k}}{s_d} \tag{10}$$

If the absolute value of t_0 is smaller than the value of $t_{0,05;k-1}$ given in Table 1 for k data sets ($k-1$ degrees of freedom), the difference between Method A and Method B is not larger than δ, the value of the bias (or difference) to be detected. Therefore, Method A and Method B can be considered equivalent and hence Method B could be adopted as a routine method, if Method A is a designated reference method.

However, if the absolute value of t_0 is larger than the value of $t_{0,05;k-1}$ in Table 1, there is a significant difference between Method A and Method B, and hence a significant bias in Method B, if Method A is a designated reference method. Action should be taken to eliminate this bias .

Annex A
(informative)

Numerical examples of determining the bias of sampling

A.1 Example 1 (δ = 0,2 % copper)

The numerical example shown in Table A.1 is the result of an experiment comparing stopped-belt sampling with a mechanical sampler carried out in accordance with 4.1. The magnitude of bias to be detected is 0,2 % copper (m/m).

Table A.1 — Numerical example 1 (copper concentrate)

Data set	Copper content, % (m/m)		$d_i = x_{B_i} - x_{A_i}$	d_i^2
	x_{B_i}	x_{A_i}		
1	29,20	29,00	0,20	0,040 0
2	29,75	29,67	0,08	0,006 4
3	31,00	30,74	0,26	0,067 6
4	31,62	32,16	− 0,54	0,291 6
5	30,96	31,26	− 0,30	0,090 0
6	30,02	29,92	0,10	0,010 0
7	31,17	31,11	0,06	0,003 6
8	31,91	31,87	0,04	0,001 6
9	29,98	30,42	− 0,44	0,193 6
10	31,21	31,13	0,08	0,006 4
11	31,26	31,30	− 0,04	0,001 6
12	28,98	29,22	− 0,24	0,057 6
13	28,95	29,09	− 0,14	0,019 6
14	31,97	31,89	0,08	0,006 4
15	29,36	28,88	0,48	0,230 4
16	30,74	31,24	− 0,50	0,250 0
17	30,74	31,14	− 0,40	0,160 0
18	30,47	30,33	0,14	0,019 6
19	30,55	31,03	− 0,48	0,234 4
20	30,80	30,94	− 0,14	0,019 6
Sum			− 1,70	1,706 0
Mean	30,53	30,62	− 0,085	

Substituting into equations 4 and 5 gives:

$$\overline{d} = \frac{1}{k}\sum d_i = \frac{-1{,}70}{20} = -0{,}085$$

$$\mathrm{SS_d} = \sum {d_i}^2 - \frac{1}{k}\left(\sum d_i\right)^2 = 1{,}706\,0 - \frac{\left(-1{,}70\right)^2}{20} = 1{,}561\,5$$

Hence, using Equation 6:

$$s_\mathrm{d} = \sqrt{\frac{\mathrm{SS}_d}{k-1}} = \sqrt{\frac{1{,}561\,5}{19}} = 0{,}286\,7$$

Using Equation 7, the bias detection limit is given by:

$$\mathrm{BDL} = \left(t_{0{,}05;\,19} + t_{0{,}10;\,19}\right)\frac{s_\mathrm{d}}{\sqrt{\mathrm{k}}} = \left(2{,}093 + 1{,}729\right)\frac{0{,}286\,7}{\sqrt{20}} = 0{,}245$$

Because BDL $> \delta$, the number of data sets is insufficient. Hence, calculate the standardized difference, D, and the required number of data sets, n_r , using equations 8 and 9.

$$D = \frac{\delta}{s_\mathrm{d}} = \frac{0{,}2}{0{,}286\,7} = 0{,}697\ 6$$

$$n_r = \frac{\left(t_{0{,}05;\,19} + t_{0{,}10;\,19}\right)^2}{D^2} = \frac{\left(2{,}093 + 1{,}729\right)^2}{0{,}697\ 6^2} = 30$$

Hence, an additional 10 data sets should be collected and the significance test carried out on the 30 data sets.

A.2 Example 2 (δ = 0,15 % lead)

The numerical example shown in Table A.2 is also the result of an experiment comparing stopped-belt sampling with a mechanical sampler carried out in accordance with 4.1. The magnitude of bias to be detected is 0,15 % lead (*m/m*).

Table A.2 — Numerical example 2 (lead concentrate)

Data set	Lead content, % (m/m)		$d_i = x_{B_i} - x_{A_i}$	d_i^2
	x_{B_i}	x_{A_i}		
1	49,50	49,00	0,50	0,250 0
2	50,05	49,67	0,38	0,144 4
3	52,10	51,74	0,36	0,129 6
4	53,32	53,16	0,16	0,025 6
5	53,26	53,06	0,20	0,040 0
6	50,32	49,92	0,40	0,160 0
7	53,47	53,11	0,36	0,129 6
8	53,91	53,57	0,34	0,115 6
9	50,28	50,02	0,26	0,067 6
10	51,51	51,13	0,38	0,144 0
11	51,56	51,30	0,26	0,067 6
12	49,28	49,02	0,26	0,067 6
13	48,95	48,75	0,20	0,040 0
14	51,97	51,59	0,38	0,144 4
15	49,36	48,88	0,48	0,230 4
16	54,04	53,75	0,29	0,084 1
17	53,04	52,80	0,24	0,057 6
18	50,77	50,42	0,35	0,122 5
19	52,85	52,62	0,23	0,052 9
20	53,80	53,53	0,27	0,072 9
Sum			6,30	2,146 8
Mean	51,67	51,35	+ 0,315	

Substituting into Equations 4 and 5 gives:

$$\overline{d} = \frac{1}{k}\sum d_i = \frac{6{,}30}{20} = +0{,}315$$

$$\mathrm{SS_d} = \sum {d_i}^2 - \frac{1}{k}\left(\sum d_i\right)^2 = 2{,}148\ 6 - \frac{(6{,}30)^2}{20} = 0{,}162\ 3$$

Hence, using Equation 6:

$$s_\mathrm{d} = \sqrt{\frac{\mathrm{SS}_d}{k-1}} = \sqrt{\frac{0{,}162\ 3}{19}} = 0{,}092\ 4$$

Using Equation 7, the bias detection limit is given by:

$$\mathrm{BDL} = \left(t_{0{,}05;\,19} + t_{0{,}10;\,19}\right)\frac{s_\mathrm{d}}{\sqrt{\mathrm{k}}} = \left(2{,}093 + 1{,}729\right)\frac{0{,}092\ 4}{\sqrt{20}} = 0{,}079$$

Because BDL $< \delta$, the number of data sets is sufficient. The statistical test can therefore be carried out in accordance with Equation 10.

$$t_0 = \frac{\overline{d}\sqrt{k}}{s_d} = \frac{0{,}315\sqrt{20}}{0{,}092\,4} = 15{,}24$$

Using Table 1, $t_{0,05;19}$ = 2,09, i.e. for 20 data sets. Thus,

$$|t_0| > t_{0,05;\,19}$$

Therefore, there is a significant bias in Method B and action should be taken to eliminate this bias.

Bibliography

[1] MERKS, J.W., *Sampling and Weighing of Bulk Solids*, Clausthal-Zellerfeld, Trans. Tech. Publications, 1st Edition, 1985

[2] DAVIES, O.L. (Ed.), *Design and Analysis of Industrial Experiments*, London, Oliver and Boyd, 1956

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