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Fluorspar — Experimental methods for checking the bias of sampling and sample preparation

Spaths fluor — Méthodes expérimentales pour la vérification du biais de l'échantillonnage et de la préparation des échantillons

Reference number
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Foreword

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Fluorspar — Experimental methods for checking the bias of sampling and sample preparation

1 Scope

This International Standard specifies the experimental methods for checking the bias of the sampling and sample preparation of similar types of fluorspar carried out in accordance with the methods specified in ISO 8868.

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 edition of the standard indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 8868:1989, *Fluorspar — Sampling and sample preparation.*

3 General conditions

3.1 In the experimental methods given here, the results obtained from the method to be checked (referred to as Method B) are compared with the results of a reference method (referred to as Method A) which, for all practical purposes, is considered to produce practically unbiased results, from technical and empirical viewpoints.

3.2 In the event that there is no significant difference in a statistical sense between the results obtained from Method B and Method A, then Method B may be adopted as a routine method, provided that agreement is reached between the parties concerned.

NOTE 1 In this International Standard, bias is assessed by application of the Student t-test (one-sided) at the 5 % level of significance, by determining whether the difference between the results of Method A and Method B is due to random variations or whether the results are statistically different.

3.3 The number of lots shall not be less than 20. The number of tests required depends on the standard deviation of the differences based on 20 tests and the value of the bias, δ, to be detected, as specified in clause 5.

The value of the bias (δ) to be detected shall be decided by agreement between the parties concerned, taking into account, from the technical and economical viewpoints, the precision of the various methods to be adopted in the experiment, i.e. sampling, sample preparation and measurement. As a guide, a bias value of half the precision specified in ISO 8868:1989, table 1 may be appropriate unless otherwise agreed.

3.4 Quality characteristics such as calcium fluoride (CaF_2) content, silica (SiO_2) content, moisture content, particle size distribution and others may be used as the basis of bias determination.

4 Sampling and sample preparation methods

4.1 Sampling

The reference method (Method A) for checking the bias of sampling is the stopped belt method. The method to be checked (Method B) shall be compared with this reference method on the same material. Examples for the experiments are given below.

EXAMPLE 1: Sampling from conveyors

Method A: Take each increment from the stopped conveyor at a specified place for the full width of the belt and the full thickness of the fluorspar stream; the minimum width of the cut shall be more than three times the nominal top size of the fluorspar and should exceed the width of the smallest increment shovel, as shown in ISO 8868:1989, table 4.

Method B (The method to be checked): Take each increment from a point selected each time at random within the fluorspar, according to ISO 8868:1989, 4.4.

EXAMPLE 2: Mechanical sampling

Method A: Take each increment according to Method A of Example 1.

Method B: Take each increment from the moving conveyor, using a mechanical sampler, close to where the increment was taken by Method A.

EXAMPLE 3: Sampling from wagons

Method A: Take each increment according to Method A of Example 1.

Method B: Take each increment at random from the new surface of the fluorspar exposed during loading into or discharging from a wagon.

EXAMPLE 4: Sampling from stockpiles

Method A: Take each increment according to Method A of Example 1.

Method B: Take each increment from new surface of the fluorspar exposed during reclaiming.

4.2 Sample preparation

Methods for composing a pair of gross samples, preparation of samples and testing shall be as given below.

a) Increments obtained from one lot in accordance with Method A and Method B are grouped, respectively, so as to compose a pair of gross samples A and B.

b) The gross samples A and B are prepared separately in accordance with ISO 8868 and tested in accordance with relevant International Standards.

c) The above procedure is performed on 20 or more lots (see 3.3).

NOTE 2 The bias of the sampling method can be checked either on pairs of increments or on pairs of gross samples. It is recommended that this experiment be repeated for several types of fluorspar.

5 Analysis of experimental data

The method of analysis of experimental data shall be as given below.

5.1 Determination of the standard deviation of the differences

a) Denote individual measurements obtained in accordance with Method A and Method B by x_{Ai}, x_{Bi}, respectively.

b) Calculate the difference, d_i between x_{Ai} and x_{Bi} from the following equation:

$$d_i = x_{Bi} - x_{Ai} \qquad i = 1,2, ..., k \qquad \text{... (1)}$$

where k is the number of paired sets of measurements.

c) Calculate the mean of the differences, $\bar{d}$, to one decimal place further than that used in the measurements themselves:

$$\bar{d} = \frac{1}{k} \sum d_i \qquad \text{... (2)}$$

d) Calculate the sum of the squares, SS_d, and the standard deviation (s_d) of the difference:

$$SS_d = \sum d_i^2 - \frac{1}{k}\left(\sum d_i\right)^2 \qquad \text{... (3)}$$

$$s_d = \sqrt{SS_d/(k-1)} \qquad \text{... (4)}$$

5.2 Determination of the required number of lots n_r for experiment

Calculate the value of the standardized difference, D, as follows:

$$D = \frac{\delta}{s_d} \qquad \text{... (5)}$$

Then determine, using table 1, the value of n_r corresponding to the value of D.

When n_r is 20 or less, proceed as in 5.3. When n_r is more than 20, carry out additional experiments on ($n_r - 20$) lots.

This procedure shall be repeated until the number of paired sets of data becomes equal to or less than the n_r specified in table 1.

5.3 Statistical test

Calculate the value of Student's t_0 to the nearest third decimal place:

$$t_0 = \frac{\bar{d}}{s_d/\sqrt{k}} \qquad \text{... (6)}$$

When the absolute value of t_0 is smaller than the value of t corresponding to k as given in table 2, conclude that the difference is not significant and Method B can be adopted as a routine method.

Table 1 — Required number of paired sets of data, n_r, determined by the value of the standardized difference, D

Range of standardized difference, D	Required number of paired sets of data, n_r	Range of standardized difference, D	Required number of paired sets of data, n_r
$0,30 \leqslant D < 0,35$	122	$1,1 \leqslant D < 1,2$	11
$0,35 \leqslant D < 0,40$	90	$1,2 \leqslant D < 1,3$	10
$0,40 \leqslant D < 0,45$	70	$1,3 \leqslant D < 1,4$	8
$0,45 \leqslant D < 0,50$	55	$1,4 \leqslant D < 1,5$	8
$0,50 \leqslant D < 0,55$	45	$1,5 \leqslant D < 1,6$	7
$0,55 \leqslant D < 0,60$	38	$1,6 \leqslant D < 1,7$	6
$0,60 \leqslant D < 0,65$	32	$1,7 \leqslant D < 1,8$	6
$0,65 \leqslant D < 0,70$	28	$1,8 \leqslant D < 1,9$	6
$0,70 \leqslant D < 0,75$	24	$1,9 \leqslant D < 2,0$	5
$0,75 \leqslant D < 0,80$	21	$2,0 \leqslant D$	5
$0,80 \leqslant D < 0,85$	19		
$0,85 \leqslant D < 0,90$	17		
$0,90 \leqslant D < 0,95$	15		
$0,95 \leqslant D < 1,00$	14		
$1,00 \leqslant D < 1,10$	13		

NOTE — Table 1 is taken from DAVIES, O.L. (ed.) *The Design and Analysis of Industrial Experiments*, 1956, pp. 606-607, and lists values of n_r for D at $\alpha = 0,05$ and $\beta = 0,05$, where α is the chance of assuming a statistical difference when none exists (i.e. the confidence level of the one-sided t-test) and β is the chance of assuming no statistical difference when a bias δ is present.

Table 2 — Value of t at 5 % level of significance (one-sided test)

Number of paired sets of measurements, k	t	Number of paired sets of measurements, k	t
20	1,729	40	1,685
21	1,725	41	1,684
22	1,721	42	1,683
23	1,717	43	1,682
24	1,714	44	1,681
25	1,711	45	1,680
26	1,708	46	1,679
27	1,706	47	1,679
28	1,703	48	1,678
29	1,701	49	1,677
30	1,699	50	1,677
31	1,697	51	1,676
32	1,696	61	1,671
33	1,694	81	1,664
34	1,692	121	1,658
35	1,691	241	1,651
36	1,690	∞	1,645
37	1,688		
38	1,687		
39	1,686		

NOTE — Table 2 is taken from JSA *Statistical Tables and Formulas with Computer Applications*, Tokyo, Japanese Standards Association, 1972.

6 Numerical examples from an experiment

6.1 Numerical example 1 on gravel of metallurgical-grade fluorspar (δ: 0,50 % CaF_2)

Table 3 shows the results of an experiment on a mechanical sampler carried out in accordance with example 2 given in 4.1.

The magnitude of bias to be detected in the experiment has been agreed by the parties concerned as 0,50 % in calcium fluoride (CaF_2) content.

Table 3 — Numerical example 1

Lot No.	Source of fluorspar	Calcium fluoride (CaF_2) content, %			
		x_{Bi}	x_{Ai}	$d_i = x_{Bi} - x_{Ai}$	d_i^2
1	F	72,26	72,96	– 0,70	0,490 0
2	E	74,92	74,07	0,85	0,722 5
3	C	81,85	80,93	0,92	0,846 4
4	B	85,45	86,03	– 0,58	0,336 4
5	B	86,43	87,05	– 0,62	0,384 4
6	E	74,45	73,47	0,98	0,960 4
7	B	86,31	85,47	0,84	0,705 6
8	A	76,23	76,86	– 0,63	0,396 9
9	E	75,80	75,13	0,67	0,448 9
10	D	74,94	75,52	– 0,58	0,336 4
11	D	76,98	76,18	0,80	0,640 0
12	E	75,73	74,84	0,89	0,792 1
13	F	73,66	74,10	– 0,44	0,193 6
14	C	79,09	78,41	0,68	0,462 4
15	F	73,99	73,15	0,84	0,705 6
16	A	76,20	76,76	– 0,56	0,313 6
17	B	86,23	85,37	0,86	0,739 6
18	E	74,56	73,78	0,78	0,608 4
19	B	85,45	86,21	– 0,76	0,577 6
20	A	76,53	75,75	0,78	0,608 4
			Sum	5,02	11,269 2

$$\bar{d} = \frac{1}{k}\sum d_i = +5{,}02/20 = +0{,}251$$

$$SS_d = \sum d_i^2 - \frac{1}{k}\left(\sum d_i\right)^2 = 11{,}269\ 2 - \frac{(5{,}02)^2}{20} = 10{,}009$$

$$s_d = \sqrt{SS_d/(k-1)} = \sqrt{10{,}009/19} = 0{,}726$$

Thus

$$D = \frac{\delta}{s_d} = \frac{0{,}50}{0{,}726} = 0{,}689$$

From table 1, $n_r = 28$ is obtained, and thus $k = 20$ in the experiment is not sufficient. Therefore, an additional eight sets of experiments are carried out in accordance with 5.2. These data sets are shown in table 4.

Table 4 — Numerical example 1 — Additional data

Lot No.	Source of fluorspar	Calcium fluoride (CaF_2) content, %			
		x_{Bi}	x_{Ai}	$d_i = x_{Bi} - x_{Ai}$	d_i^2
21	A	75,31	75,85	– 0,54	0,291 6
22	A	76,14	75,33	0,81	0,656 1
23	C	79,43	79,92	– 0,49	0,240 1
24	B	82,36	81,62	0,74	0,547 6
25	E	74,52	73,59	0,93	0,864 9
26	F	72,81	73,43	– 0,62	0,384 4
27	F	74,19	74,76	– 0,57	0,324 9
28	B	84,86	84,13	0,73	0,532 9
			Sum	6,01	15,111 7

$$\bar{d} = \frac{1}{k} \sum d_i = +6{,}01/28 = +0{,}215$$

$$SS_d = \sum d_i^2 - \frac{1}{k}\left(\sum d_i\right)^2 = 15{,}111\ 7 - \frac{(6{,}01)^2}{28} = 13{,}821\ 7$$

$$s_d = \sqrt{SS_d/(k-1)} = \sqrt{13{,}821\ 7/27} = 0{,}715$$

Thus

$$D = \frac{\delta}{s_d} = \frac{0{,}50}{0{,}715} = 0{,}699$$

From table 1, $n_r = 28$ is obtained, and thus $k = 28$ in the experiment is sufficient.

$$t_0 = \frac{\bar{d}}{s_d/\sqrt{k}} = \frac{0{,}215}{0{,}715/\sqrt{28}} = -1{,}591$$

$t = 1{,}703$ for $k = 28$ from table 2.

$$|t_0| < t$$

Therefore, the bias is not significant and Method B is adopted as a routine method.

6.2 Numerical example 2 on acid-grade fluorspar (δ: 0,25 % CaF_2)

Table 5 shows the results of an experiment carried out according to example 3 given in 4.1.

The magnitude of bias to be detected in the experiment has been agreed between the parties concerned as 0,25 % in calcium fluoride (CaF_2) content.

Table 5 — Numerical example 2

Lot No.	Source of fluorspar	Calcium fluoride (CaF_2) content, %			
		x_{Bi}	x_{Ai}	$d_i = x_{Bi} - x_{Ai}$	d_i^2
1	A	96,65	96,92	– 0,27	0,072 9
2	A	98,01	98,15	– 0,14	0,019 6
3	A	97,33	97,24	0,09	0,008 1
4	A	98,99	98,60	0,39	0,152 1
5	A	98,79	99,12	– 0,33	0,108 9
6	A	97,92	97,48	0,44	0,193 6
7	A	99,05	99,18	– 0,13	0,016 9
8	A	97,65	97,34	0,31	0,096 1
9	A	97,86	97,93	– 0,07	0,004 9
10	A	97,90	97,53	0,37	0,136 9
11	A	97,94	97,88	0,06	0,003 6
12	A	98,03	97,62	0,41	0,168 1
13	A	96,70	96,99	– 0,29	0,084 1
14	A	97,86	97,44	0,42	0,176 4
15	A	96,82	96,78	0,04	0,001 6
16	A	97,57	97,81	– 0,24	0,057 6
17	A	98,05	97,70	0,35	0,122 5
18	A	97,77	97,88	– 0,11	0,012 1
19	A	98,97	99,06	– 0,09	0,008 1
20	A	97,92	97,64	0,28	0,078 4
			Sum	1,49	1,522 5