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Hard coal and coke — Mechanical sampling —

Part 7:
Methods for determining the precision of sampling, sample preparation and testing

Houille et coke — Échantillonnage mécanique —

Partie 7: Méthodes pour la détermination de la fidélité de l'échantillonnage, de la préparation de l'échantillon et de l'essai

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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.

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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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT), see the following URL: Foreword - Supplementary information

The committee responsible for this document is ISO/TC 27, *Solid mineral fuels*, Subcommittee SC 4, *Sampling*.

This second edition cancels and replaces the first edition (ISO 13909-7:2001), which has been technically revised.

ISO 13909 consists of the following parts, under the general title *Hard coal and coke — Mechanical sampling*:

- *Part 1: General introduction*
- *Part 2: Coal — Sampling from moving streams*
- *Part 3: Coal — Sampling from stationary lots*
- *Part 4: Coal — Preparation of test samples*
- *Part 5: Coke — Sampling from moving streams*
- *Part 6: Coke — Preparation of test samples*
- *Part 7: Methods for determining the precision of sampling, sample preparation and testing*
- *Part 8: Methods of testing for bias*

Introduction

Two different situations are considered when a measure of precision is required. In the first, an estimate is made of the precision that can be expected from an existing sampling scheme and, if this is different from that desired, adjustments are made to correct it. In the second, the precision that is achieved on a particular lot is estimated from the experimental results actually obtained using a specifically designed sampling scheme.

The formulae developed in this part of ISO 13909 are based on the assumption that the quality of the fuel varies in a random manner throughout the mass being sampled and that the observations will follow a normal distribution. Neither of these assumptions is strictly correct. Although the assumption that observations will follow a normal distribution is not strictly correct for some fuel parameters, this deviation from assumed conditions will not materially affect the validity of the formulae developed for precision checking since the statistics used are not very sensitive to non-normality. Strictly speaking, however, confidence limits will not always be symmetrically distributed about the mean. For most practical uses of precision, however, the errors are not significant.

NOTE In the text, the term “fuel” is used where both coal and coke would be applicable in the context and either “coal” or “coke” where that term is exclusively applicable.

Hard coal and coke — Mechanical sampling —

Part 7:
Methods for determining the precision of sampling, sample preparation and testing

1 Scope

In this part of ISO 13909, formulae are developed which link the variables that contribute to overall sampling precision. Methods are described for estimating overall precision and for deriving values for primary increment variance which can be used to modify the sampling scheme to change the precision. Methods for checking the variance of sample preparation and testing are also described.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 13909-1, *Hard coal and coke — Mechanical sampling — Part 1: General introduction*

ISO 13909-2, *Hard coal and coke — Mechanical sampling — Part 2: Coal — Sampling from moving streams*

ISO 13909-3, *Hard coal and coke — Mechanical sampling — Part 3: Coal — Sampling from stationary lots*

ISO 13909-4, *Hard coal and coke — Mechanical sampling — Part 4: Coal — Preparation of test samples*

ISO 13909-5, *Hard coal and coke — Mechanical sampling — Part 5: Coke — Sampling from moving streams*

ISO 13909-6, *Hard coal and coke — Mechanical sampling — Part 6: Coke — Preparation of test samples*

ISO 13909-8, *Hard coal and coke — Mechanical sampling — Part 8: Methods of testing for bias*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 13909-1 apply.

4 General

When designing a sampling scheme in order to meet a required precision of results, formulae are necessary that link certain fuel and sampling characteristics to that precision. The main factors to be considered are the variability of primary increments, preparation and testing errors, the number of increments and samples taken to represent the lot, and the mass of the samples. These formulae are derived in Clause 5. Methods for estimating the parameters used in those formulae are given in Clause 6.

Once a sampling system has been designed and installed, the precision which is being achieved on a routine basis should be checked. An estimate of the precision can be obtained from the primary increment variance, V_I, the numbers of increments, n, and sub-lots, m, (see Clause 5) and the preparation and testing variance, V_{PT}. The preparation component of V_{PT} is made up of on-line sample processing and off-line sample preparation.

Sampling variance is a function of product variability, so the same number of increments, sub-lots, and preparation and testing errors will yield different precision with fuels that exhibit different product variability.

Depending on the extent to which serial correlation exists and which method of estimating primary increment variance is used, such an estimate could represent a considerable overestimate of the numerical value of the precision (i.e. indicate that it is worse than is really the case). In addition, in order for the results to be meaningful, large numbers of increments (in duplicate) would need to be prepared and analysed for the estimation of V_I and V_{PT}.

Quality variations obtained in the form of primary increment variances on existing systems are not absolute and therefore designers should exercise caution when using such results in a different situation. The estimated value of the primary increment variance, V_I, should be derived experimentally for each fuel and at each sampling location.

Whenever a sampling scheme is used for determining increment variance, the operating conditions should be as similar as possible to the conditions known, or anticipated, to prevail during the sampling for which the increment variance is needed, whether it be carried out by the same or by a different sampling system.

An estimate of the precision actually achieved can be obtained by taking the sample in a number of parts and comparing the results obtained from these parts. There are several methods of doing this, depending on

a) the purpose of the test, and

b) the practical limitations imposed by the available sampling procedures and equipment.

Where a sampling system is in existence, the purpose of the test is to check that the scheme is in fact achieving the desired precision (see Clause 7). If it is not, it may need to be modified and rechecked until it meets the precision required. In order to do this, a special check scheme should be devised which may be different from the regular scheme but which measures the precision of the regular scheme.

For regular sampling schemes, the most rigorous approach is that of duplicate sampling of sub-lots. In many existing mechanical sampling systems, however, the capacity of individual components and the interval between increments in the regular scheme is insufficient to allow the taking of extra increments. In such cases, duplicate samples can be constituted from the normal number of increments and the result adjusted for the smaller number of increments in each sample (see 7.3).

The need may arise to sample a particular lot and to know the precision of the result obtained (see Clause 8). Once again, a special check scheme needs to be devised, but in this case, it is the precision achieved by that scheme on that lot which is required. For the measurement of the precision achieved for a particular lot, replicate sampling is the best method.

Methods for detailed checking of preparation and testing errors are given in Clause 9. The results may also be used to provide data for the formulae used in Clause 5.

5 Formulae relating to factors affecting precision

5.1 General

Precision is a measure of the closeness of agreement between the results obtained by repeating a measurement procedure several times under specified conditions and is a characteristic of the method used. The smaller the random errors of a method, the more precise the method is. A commonly accepted index of precision is two times the sample estimate of the population standard deviation and this index of precision is used throughout this part of ISO 13909.

If a large number of replicate samples, *j*, are taken from a sub-lot of fuel and are prepared and analysed separately, the estimated precision, *P*, of a single observation is given by Formula (1):

$$P = 2s = 2\sqrt{V_{\mathrm{SPT}}} \qquad (1)$$

where

s is the sample estimate of the population standard deviation;

V_{SPT} is the total variance.

The total variance, V_{SPT}, in Formula (1) is a function of the primary increment variance, the number of increments, and the errors associated with sample preparation and testing.

NOTE The components of primary increment variance are the variance of sample extraction and the variance contributed by product variability. The variance contributed by product variability is generally, but not always, the largest source of variance in sampling.

For a single sample, this relationship is expressed by Formula (2):

$$V_{\mathrm{SPT}} = \frac{V_{\mathrm{I}}}{n} + V_{\mathrm{PT}} \qquad (2)$$

where

V_{I} is the primary increment variance;

V_{PT} is the preparation and testing variance;

n is the number of primary increments in the sample.

5.2 Sampling

Where the test result is the arithmetic mean of a number of samples, resulting from dividing the lot into a series of sub-lots and taking a sample from each, Formula (2) becomes:

$$V_{\mathrm{SPT}} = \frac{V_{\mathrm{I}}}{mn} + \frac{V_{\mathrm{PT}}}{m} \qquad (3)$$

where

m is the number of sample results used to obtain the mean.

Since a sample is equivalent to one member of a set of replicate samples, by combining Formulae (1) and (3), it can be shown that:

$$P = 2\sqrt{\frac{V_{\mathrm{I}}}{mn} + \frac{V_{\mathrm{PT}}}{m}} \qquad (4)$$

Formula (4) gives an estimate of the precision that can be expected to be achieved when a given sampling scheme is used for testing a given fuel, the variability of which is known or can somehow be estimated. In addition, Formula (4) enables the designer of the sampling scheme to determine, for the desired precision and with fuel of known or estimated variability, the combination of numbers of increments and samples, respectively, which will be most favourable considering the relative merits of the sampling equipment and the laboratory facilities in question. For the latter purpose, however, it is more convenient to use either or both Formulae (5) and (6), both of which have been derived by rearranging Formula (4).

$$n = \frac{4V_I}{mP^2 - 4V_{PT}} \tag{5}$$

$$m = \frac{4\left(V_I + nV_{PT}\right)}{nP^2} \tag{6}$$

NOTE Results obtained from solid mineral fuels flowing in a stream will frequently display serial correlation, i.e. immediately adjoining fuel tends to be of similar composition, while fuel further apart tends to be of dissimilar composition. When this is so, the estimates of precision of the result of a single sample based on primary increment variance and the variance of preparation and testing would indicate precision that is worse, i.e. numerically higher, than the precision actually achieved. The effect of serial correlation can be taken into account using the variographic method of determining variance given in informative Annex A.

6 Estimation of primary increment variance

6.1 Direct determination of individual primary increments

The direct estimation of primary increment variance can be accomplished with a duplicate sampling scheme comprised of several hierarchical levels which allows both the overall variance and the variance of preparation and testing to be estimated. The estimated variance of primary increments can then be obtained by subtraction of the variance of preparation and testing from the estimated overall variance. A number of primary increments is taken systematically and either divided into two parts or prepared so that duplicate samples are taken at the first division stage. Each part is prepared and tested for the quality characteristic of interest, using the same methods that are expected to be used in routine operations. The mean of the two results and the difference between the two results are calculated for each pair.

It is recommended that at least 30 increments be taken, spread if possible over an entire lot or even over several lots of the same type of fuel.

The procedure is as follows.

a) Calculate the preparation and testing variance, V_{PT}.

$$V_{PT} = \frac{\sum d^2}{2n_p} \tag{7}$$

where

d is the difference between pair members;

n_p is the number of pairs.

b) Calculate the primary increment variance, V_I.

$$V_I = \frac{\sum x^2 - \frac{1}{n_p}\left(\sum x\right)^2}{\left(n_p - 1\right)} - \frac{V_{PT}}{2} \tag{8}$$

where

x is the mean of the two measurements for each increment.

An alternative method for estimating primary increment variance, V_I, is as follows:

$$V_I = \frac{\sum D^2}{2h} - \frac{V_{PT}}{2} \tag{9}$$

where

D is the difference between the means of successive pairs;

h is the number of successive pairs.

This method avoids the overestimation of sampling variance when there is serial correlation (see Note in 5.2) but can only be used if the primary-increment sampling interval at which the increments are taken is more than or approximately equal to the primary-increment sampling interval used when the scheme is implemented in routine sampling operations.

The most rigorous treatment of serial correlation is to use the variographic method given in Annex A. This takes into account both serial correlation and sampling interval effects, thereby avoiding overestimation of sampling variance and number of primary increments due to these factors.

6.2 Determination using the estimate of precision

The primary increment variance can be calculated from the estimate of precision obtained either using the method of duplicate sampling given in 7.2 or replicate sampling given in Clause 8 according to Formula (10) which is derived by rearranging the terms of Formula (4).

$$V_I = \frac{mnP^2}{4} - nV_{PT} \tag{10}$$

This value can then be used to adjust the sampling scheme if necessary.

7 Methods for estimating precision

7.1 General

For all the methods given in this Clause, the following symbols and definitions apply:

- n_0 is the number of increments in a sub-lot for the regular scheme;
- m_0 is the number of sub-lots in a lot for the regular scheme;
- P_0 is the desired precision for the regular scheme;
- P_W is the worst (highest absolute value) precision to be permitted.

In all cases, the same methods of sample preparation shall be used as for the regular scheme.

7.2 Duplicate sampling with twice the number of increments

Twice the normal number of increments ($2n_0$) are taken from each sub-lot and combined as duplicate samples (see Figure 1), each containing n_0 increments. This process is repeated, if necessary, over several lots of the same fuel, until at least 10 pairs of duplicate samples have been taken.

A parameter of the fuel is chosen to be analysed, e.g. ash content (dry basis) for coal, or Micum 40 index for coke. The standard deviation within duplicate samples for the test parameter is then calculated using Formula (11):

$$s = \sqrt{\frac{\sum d^2}{2n_\mathrm{p}}} \tag{11}$$

where

d is the difference between duplicates;

n_p is the number of pairs of duplicates being examined.

An example of results for coal ash is given in Table 1.

Table 1 — Results of duplicate sampling, % ash, dry basis

Sample pair no.	Duplicate values %		Difference between duplicates	
	A	B	$\lvert A - B \rvert = d$	d^2
1	11,1	10,5	0,6	0,36
2	12,4	11,9	0,5	0,25
3	12,2	12,5	0,3	0,09
4	10,6	10,3	0,3	0,09
5	11,6	12,5	0,9	0,81
6	11,8	12,0	0,2	0,04
7	11,8	12,2	0,4	0,16
8	10,8	10,0	0,8	0,64
9	7,9	8,2	0,3	0,09
10	10,8	10,3	0,5	0,25
			Total	2,78

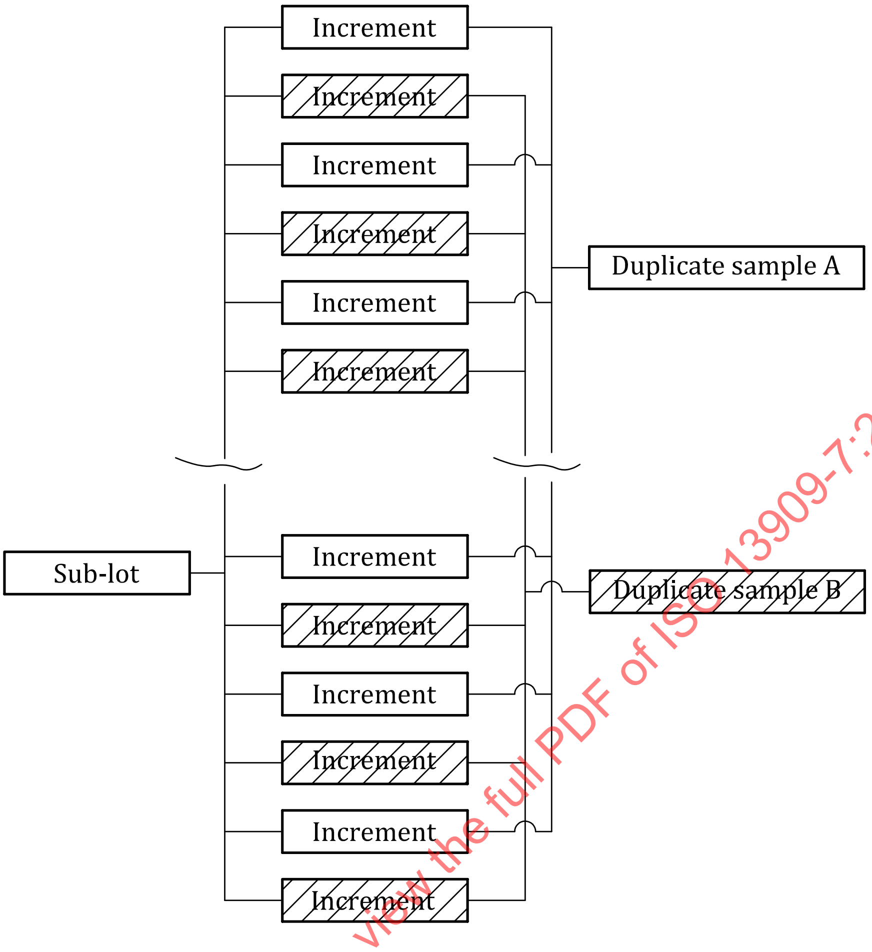
The number of pairs, n_p is 10. The variance of the ash content is therefore

$$s^2 = \frac{\sum d^2}{2n_\mathrm{p}}$$

$$= \frac{2{,}78}{20} = 0{,}139$$

and the standard deviation is:

$$s = \sqrt{0{,}139\,0} = 0{,}373$$



Key

☐ increment from regular scheme

▨ extra increment for precision check scheme

Figure 1 — Example of a plan of duplicate sampling

The precision of the result for a single sub-lot is therefore:

$$
\begin{aligned}
P &= 2s \\
&= 2\left(0{,}373\right) = 0{,}75\ \%\,\text{ash}
\end{aligned}
$$

The precision achieved for the mean ash of a normal lot sampled as m sub-lots is given by $2s/\sqrt{m}$. For example, if $m = 10$, then:

$$
P = \frac{2\left(0{,}373\right)}{\sqrt{10}} = 0{,}235\ 9\ \%
$$

These values of P have been calculated using point estimates for the standard deviation and represent the best estimate for precision.

If an interval estimate for the standard deviation is used, then on a 95 % confidence level, the precision is within an interval with upper and lower limits. These limits are calculated from the point estimate of precision and factors which depend on the degrees of freedom (f) used in calculating the standard deviation (see Table 2).

Table 2 — Factors used for calculation of precision intervals

f (number of observations)	5	6	7	8	9	10	15	20	25	50
Lower limit	0,62	0,64	0,66	0,68	0,69	0,70	0,74	0,77	0,78	0,84
Upper limit	2,45	2,20	2,04	1,92	1,83	1,75	1,55	1,44	1,38	1,24

NOTE The factors in Table 2 are derived from the estimate of s^2 obtained from the squared differences of n pairs of observations. Since there is no constraint in this case, the estimate as well as d^2 will have n degrees of freedom. The values in Table 2 are derived from the relationship:

$$\frac{ns^2}{\chi^2_{n,0,025}} < s^2 < \frac{ns^2}{\chi^2_{n,0,0975}}$$

The body of Table 2 gives the values for $\sqrt{n/\chi^2}$, which are multiplied by s to obtain the confidence limits.

For example, for the lot with 10 sub-lots used in the example above:

Upper limit = 1,75 (0,235 9) = 0,41 %

Lower limit = 0,70 (0,235 9) = 0,17 %

where the factors are obtained from Table 2 using $f = n_P$, i.e. 10. The true precision lies between 0,17 % and 0,41 % ash at the 95 % confidence level.

7.3 Duplicate sampling during routine sampling

If operational conditions do not allow the taking of $2n_0$ increments from each normal sub-lot or precision is to be determined during normal sampling, then, provided that all increments can be kept separate, adopt the following procedure for estimating precision.

Take the normal number of increments, n_0, from each sub-lot and combine them as duplicate samples each comprising $n_0/2$ increments (see Figure 2). Repeat this process, if necessary, over several lots of the same fuel until at least 10 pairs of duplicate samples have been obtained. In this case, the precision obtained using the procedure in 7.2 will be for $n_0/2$ increments. This estimate of precision is divided by the square root of 2 to obtain the estimate of precision for sub-lot samples comprising n_0 increments.

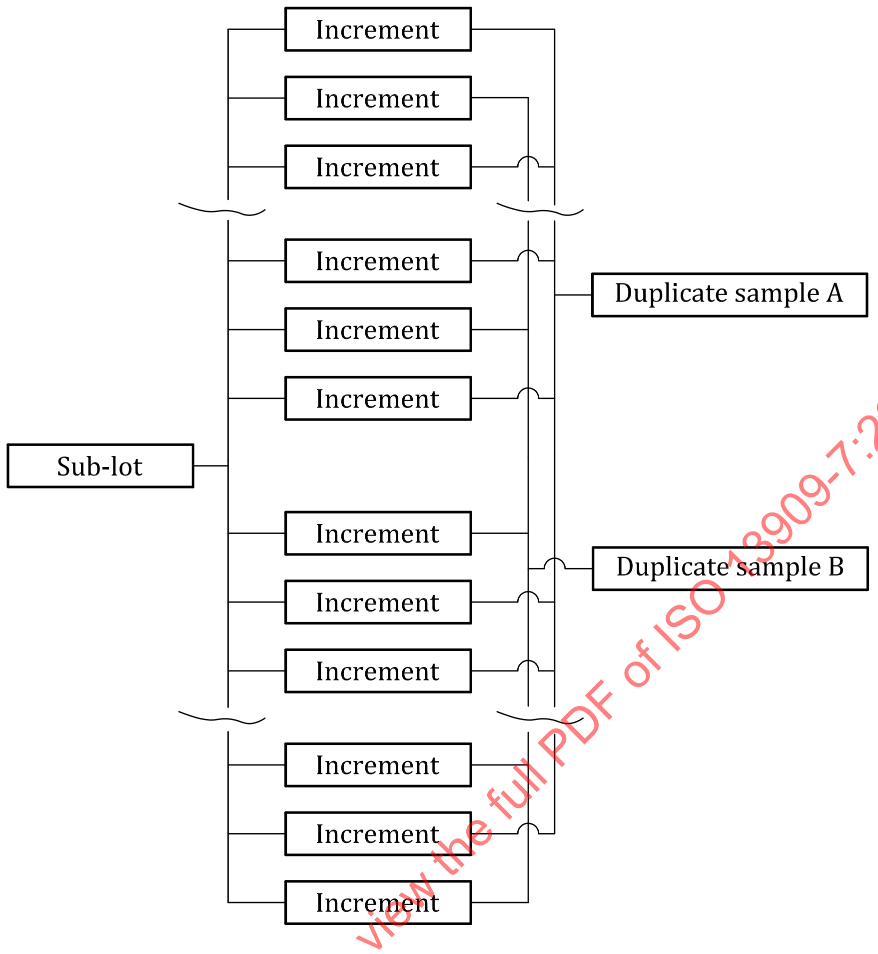


Figure 2 — Example of a plan of duplicate sampling where no additional increments are taken

7.4 Alternatives to duplicate sampling

At some locations, operational conditions of a sampling system do not allow duplicate samples to be collected with the assurance that no cross-contamination of sample material from adjacent primary increments occurs. In such cases, other methods have been found useful. An example of such a method, using Grubbs estimators, is given for information in Annex B.

This method involves collecting three samples from each of a minimum of 30 sub-lots of fuel. One sample is collected using the normal sampling scheme and two mutually independent systematic samples are collected by stopping a main fuel handling belt for collection of stopped-belt increments at preselected intervals.

7.5 Precision adjustment procedure

If the desired level of precision, P_0, for the lot lies within the confidence limits, then there is no evidence that this precision is not being achieved. However, if the confidence interval is wide enough to include both P_0 and P_W, the test is inconclusive and further data shall be obtained. The results shall be combined with the original data and the calculation done on the total number of duplicate samples.

NOTE The expected effect is reduction of the width of the confidence limits since the value of *f* in Table 2 will be greater.

This process can be continued until either P_W is above the upper confidence limit or the value of P_0 falls outside the confidence limits. In the latter case, adjustment may be necessary.

NOTE If the precision obtained differs from the desired precision, a cost/benefit analysis will indicate whether it is worthwhile to proceed with any modifications to the sampling system and sampling programme because the costs incurred in making the changes and retesting may not be worthwhile.

Before making changes to the sampling scheme, the errors of preparation and testing shall be examined using the procedures given in Clause 9. It should then be possible to decide whether to make the changes to the sampling or the sample preparation using the formulae in 5.2.

If it is decided to design a new sampling scheme, the first step is the calculation of the primary increment variance. This can be done using Formula (12) which is derived by rearranging Formula (4) and substituting n_0 for *n.*

$$V_\mathrm{I} = \frac{m n_0 P^2}{4} - n_0 V_\mathrm{PT} \qquad (12)$$

where

P is the measured precision obtained from the test and is not P_0;

V_PT is either the original value or one estimated using the methods in Clause 9.

Using the new value for the primary increment variance, design a new scheme following the procedures specified in ISO 13909-2, ISO 13909-3 or ISO 13909-5, as relevant, depending on whether the sampling is of coal or coke and from moving or stationary fuels.

When the new scheme is in operation, carry out a new precision check, discarding the previous results and continue in this fashion until the precision is satisfactory.

Thereafter, it is not necessary to check the precision for every lot but periodic checks should be carried out. For example, one sub-lot in five may be examined or, alternatively, 10 consecutive sub-lots if using method 7.2, or the equivalent if using method 7.3.

When 10 pairs of results have been accumulated, they shall be examined as described in 7.2, ignoring any intervening samples not taken in duplicate.

8 Calculation of precision

8.1 Replicate sampling

Establish the parameter to be analysed, e.g. ash (dry basis), and establish the sampling scheme for the required precision in accordance with ISO 13909-2, ISO 13909-3 or ISO 13909-5 as appropriate, depending on whether the sampling is of coal or coke and from moving streams or stationary lots.

Instead of forming a sample from each sub-lot, combine the total number of increments, $n \cdot m$, as replicate samples. The number of replicate samples, j, shall be not less than the number of sub-lots, m, used in the calculation (see the relevant part of ISO 13909), and not less than 10.

If there are 10 such samples and the sample containers are labelled A, B, C, D, ... J, then successive increments will go into the containers as follows: A, B, C, D, E, F, G, H, I, J, A, B, C, D, ...

A typical calculation for coal is given below using the results in Table 3.

The number of replicate samples, j, is 10.

The mean result is 165/10 = 16,5 % ash

Table 3 — Results of single lot sampling, % ash, dry basis

Sample no.	Sample value %	(Sample value)^2
A	15,3	234,09
B	17,1	292,41
C	16,5	272,25
D	17,2	295,84
E	15,8	249,64
F	16,4	268,96
G	15,7	246,49
H	16,3	265,69
I	18,0	324,00
J	16,7	278,89
Totals	165,0	2 728,26

The sample estimate of the population standard deviation, *s*, is:

$$s = \sqrt{\frac{\left[\sum x_\text{i}^2 - \frac{\left(\sum x_\text{i}\right)^2}{n}\right]}{\left(n-1\right)}}$$

$$= \sqrt{\frac{2\,728{,}26 - \frac{165^2}{10}}{9}} = 0{,}800$$

The best estimate for the precision, *P*, achieved for the lot is given by:

$$P = \frac{2s}{\sqrt{j}} \tag{13}$$

i.e.

$$P = \frac{2\left(0{,}800\right)}{\sqrt{10}} = 0{,}506\ \%\ \text{ash}$$

Hence, using Table 2, the true precision lies between 0,35 % and 0,89 % at the 95 % confidence level. It should be noted, however, that the procedure given in this subclause tends to overstate the variance to the extent that it includes variance components of sample preparation and analysis.

8.2 Normal sampling scheme

If it is desired to design a regular sampling scheme based on the results of the procedure specified in 8.1, the estimate of precision obtained, the number of increments per sample and the number of replicate samples can be substituted into Formula (12) and the value for increment variance estimated. The procedures specified in ISO 13909-2, ISO 13909-3 or ISO 13909-5, as appropriate, can then be followed to design the regular sampling scheme.

9 Methods of checking sample preparation and testing errors

9.1 General

The methods described in this Clause, for checking the precision of sample preparation and testing, are designed to estimate the variance of random errors arising in the various stages of the process. The errors are expressed in terms of variance. Separate tests are necessary to ensure that bias is not introduced either by contamination or by losses during the sample preparation process (see ISO 13909-8).

As described in ISO 13909-4, sample preparation for general analysis of coal will normally be carried out in at least two stages, each stage consisting of a reduction in particle size, possible mixing, and division of the sample into two parts, one of which is retained and one rejected. All the errors occur in the course of the division, in the selection of the final 1 g of 212 µm size and in the analysis. The most important factors are the size distribution of the samples before division and the masses retained after division.

The preparation of coke samples is generally carried out with fewer stages but the same basic principle of checking for errors applies.

For convenience, the remainder of this Clause refers to coal ash only. If the variance is satisfactory for ash, it will normally be so for the other characteristics of the proximate and ultimate analyses, except possibly for errors in moisture and calorific value, which should be checked. If desired, all characteristics may be checked.

Methods are described for checking the overall errors of preparation and testing and also the errors incurred at individual stages.

The methods were originally developed for manual and non-integrated mechanical preparation. If some sample preparation is carried out within an integrated primary sampling/sample preparation system, it may not be practicable to determine the errors for the individual components, except by artificial means such as re-feeding reject streams through the system, which would be totally unrepresentative of normal operations. The variances of the integrated preparation stages may therefore have to be compounded with the primary increment variance and measured as such.

9.2 Target value for variance of sample preparation and analysis

9.2.1 General

The overall preparation and testing variance, V_{PT}, estimated by the procedure described in 9.3, is evaluated in relation to a previously determined target, V_{PT}^{0}. This target is normally laid down by the body responsible for sample preparation.

The individual division errors are estimated directly. These may be evaluated either in relation to a target or as a proportion of the overall variance.

NOTE As a rough guide, a division-stage variance is generally twice the analytical variance so that, for example, for a three-stage preparation and testing process, the overall value of V_{PT}^{0} is divided in the ratio 2:2:1 to obtain the two-division stage variance targets and the analytical variance.

The final-stage analysis variance target can be determined from the relevant analytical standard from Formula (14):

$$V_{\text{T}}^{0} = \frac{r^{2}}{8} \tag{14}$$

where

V_{T}^{0} is the final sample extraction and analytical variance target;

r is the repeatability limit of the analytical method.

The division errors for moisture content may be unavoidably greater than those for ash content because of the need to avoid excessive handling which could in turn result in bias. Such errors may, however, be acceptable if the overall precision can be achieved due to the lower primary increment variances normally encountered for moisture content.

9.2.2 Off-line preparation

The methods of sample preparation recommended for coal in ISO 13909-4, using the masses specified, should achieve, for coal ash, a sample preparation and testing variance of 0,2 or less. For many coals, much lower variances will be achievable, particularly, if mechanical dividers are used that take a great many more than the minimum number of cuts. Similar considerations will apply to the methods of preparation for coke in ISO 13909-6. If possible, therefore, a more stringent overall target should be set in the light of experience with similar coals prepared on similar equipment.

Smaller preparation errors will reduce the number of samples required to be taken and tested.

The worst-case individual division-stage variance (for coal 0,08) should be treated as a maximum which may be improved by using mechanical division.

9.2.3 On-line preparation

Where some elements of sample preparation are carried out in a system integral with the primary sampler, the errors involved may be compounded with the primary increment variance, V_{I}. In such cases, it should be expected that the residue of V_{PT} will be less than it would have been had all the sample preparation been done off-line.

It is recommended that realistic overall targets be obtained from relevant experience. As a worst-case target, however, use the worst-case individual division-stage variance for each division stage plus the appropriate analytical variance (see 9.2.1).

9.3 Checking procedure as a whole

The first step is to check that the overall variance of preparation and testing does not exceed the target set, V_{PT}^{0} (see 9.2). The method provides a test of whether the difference between the estimated value and the target value is statistically significant.

This is done by taking duplicate samples at the first division of the sample; these are thereafter treated entirely separately to give the two test samples (see Figure 3). The two samples provide an unbiased estimate of the variance of sample preparation and analysis. Ten pairs of test samples are obtained in this way.

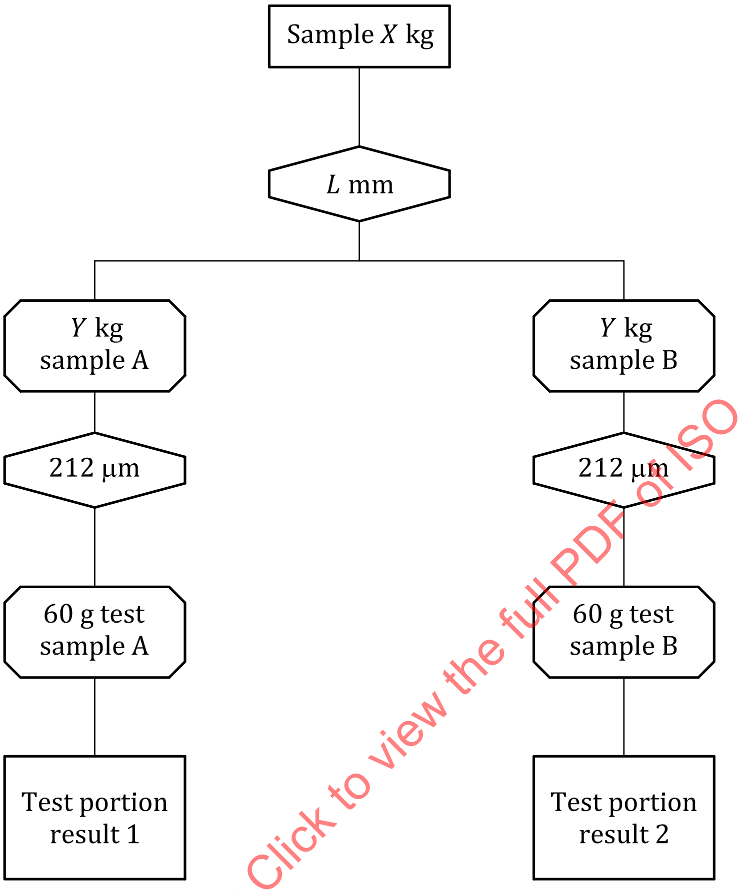
If the mean observed absolute difference between the 10 pairs of results is y, then 0,886 2 y should lie between $0{,}7\sqrt{V_{\mathrm{PT}}^{0}}$ and $1{,}75\sqrt{V_{\mathrm{PT}}^{0}}$ (see Table 2).

NOTE The factor 0,886 2 is derived from the relationship for converting the mean differences between pairs to the standard deviation.

Provided that the standard deviations of two successive sets of 10 duplicate samples fall between these upper and lower limits, it may be assumed that the procedure is satisfactory.

If the standard deviation is below $0{,}7\sqrt{V_{\mathrm{PT}}^{0}}$, the variance is low but no adjustment is necessary since it is always desirable to have the variance as low as possible.

If the standard deviation is greater than $1{,}75\sqrt{V_{\mathrm{PT}}^{0}}$, the variance is too high and the masses retained at various stages of the sample-preparation process are probably insufficient. Therefore, the variance of the errors arising at each stage should be estimated as described in 9.4 so that steps may be taken to improve the procedures shown to be necessary.



Key

⬡ reduce to particle size specified (*L* is the nominal top size after first-stage reduction)

▢ divide to mass specified (*Y* is the value give in Table 3)

Figure 3 — Overall test of sample preparation

9.4 Checking stages separately

9.4.1 General

The following two procedures are commonly used.

a) Procedure 1 (see 9.4.2), where analysis is inexpensive relative to the cost of sampling.

b) Procedure 2 (see 9.4.3), which is slightly less accurate but involves fewer analyses.

Using the principles of 9.4.2.2 or 9.4.3.2 as appropriate, schemes with more than two division stages can normally be examined.

For example, the errors arising from a three-stage preparation scheme can be separated as follows:

a) the errors in taking Y kg from X kg = variance V_1;

b) the errors in taking 60 g from Y kg = variance V_2;

c) the analytical errors, which include the error of taking 1 g from the bottle of fuel crushed to 212 µm = variance V_T.

The total variance of the procedure, V, is given by Formula (15):

$$V = V_1 + V_2 + V_T \tag{15}$$

If duplicates are extracted at an intermediate stage, the total variance of these samples will be the sum of errors at this and later stages. For example, if in a three-stage procedure, duplicates are taken at the second stage, then the variance of the duplicates is $V_2 + V_T$.

In order to separate the component variances, it is necessary to take duplicates at each stage, calculate the total variance at each stage and then, by working backwards from the analysis stage, separate the individual stage variances.

The same procedures may be used to measure the errors at different stages when installing a new piece of equipment or when considering the introduction of a new kind of procedure. Particular care is needed in the interpretation of the results, especially in estimating errors at each stage of division.

9.4.2 Procedure 1

9.4.2.1 Method

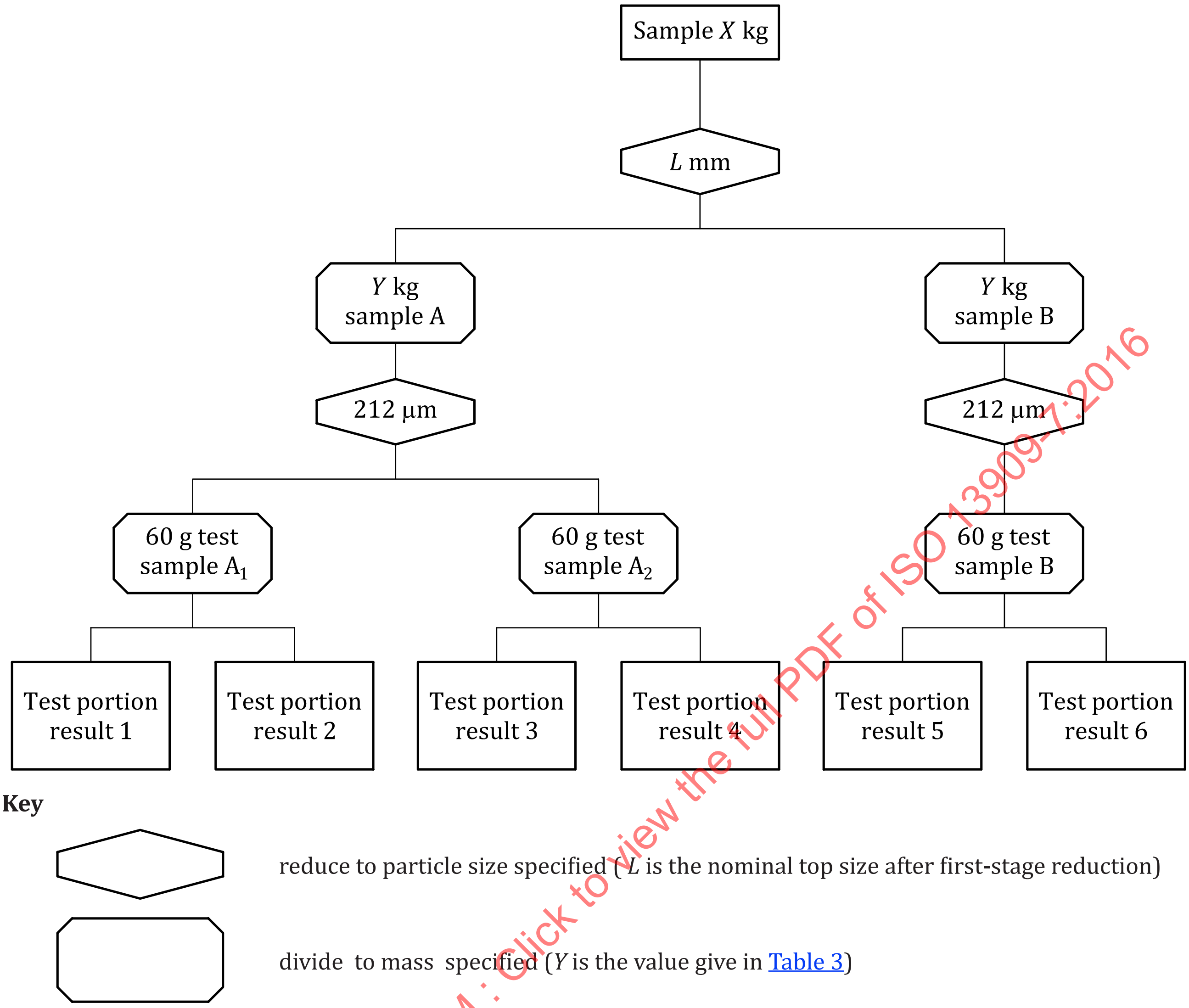
The method is based on that given by R. C. Tomlinson.[1]

At the first stage of division, two samples (see Figure 4, A and B) each of mass Y kg are taken as described in 9.5 and the remainder of the material is discarded. Sample B is then treated in the normal manner to give a general-analysis test sample.

From sample A, however, two samples of 60 g each are taken as described in 9.5 at the second step of sample division and each of these constitutes a general-analysis test sample.

The three test samples (two from A and one from B) can conveniently be labelled A_1, A_2 and B; and a duplicate determination of a property, e.g. ash, is then made from each of these three samples.

At least 10 samples should be treated in this way, giving 10 sets of six results.



Key

reduce to particle size specified (L is the nominal top size after first-stage reduction)

divide to mass specified (Y is the value give in Table 3)

Figure 4 — Detailed check of sample preparation — Procedure 1

9.4.2.2 Calculation of variance from individual stages

The variances of duplicate samples separated at each stage of the preparation, i.e. first stage, V_z, second stage, V_y and third stage, V_x, are calculated from the general Formula (16):

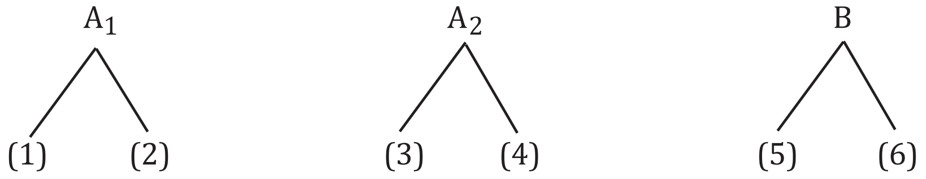
$$V = \frac{\sum d^2}{2n_p} \qquad (16)$$

where

d is the difference between duplicates;

n_p is the number of pairs of duplicates.

For each of the 10 samples, there are six analyses denoted by the symbols (1) to (6) as follows:



a) For each test sample, calculate the difference between duplicates. Call these differences *x* and calculate

$$V_x = \frac{\sum x^2}{60}$$

b) For sample A, calculate the difference between A_1 and A_2, i.e.

$$\frac{(1)+(2)}{2} - \frac{(3)+(4)}{2}$$

Call these differences *y* and calculate

$$V_y = \frac{\sum y^2}{20}$$

c) Calculate the difference between A and B, i.e.

$$\frac{(1)+(2)+(3)+(4)}{4} - \frac{(5)+(6)}{2}$$

Call these differences *z* and calculate

$$V_z = \frac{\sum z^2}{20}$$

9.4.2.3 Calculation of cumulative variance at each stage

Calculate the stage variances V_1, V_2 and V_T, starting with the third (analysis) stage, taking into account at the second and first stages that the duplicate results are the means of more than one determination, and thus have a component of later stages included in their total variance.

a) Third stage

Since there are no other errors involved, $V_T = V_x$.

b) Second stage

Since the results compared are the means of two analyses, the third stage component is $V_T/2$.

$$V_y = V_2 + \frac{V_T}{2}$$

and therefore

$$V_2 = V_y - \frac{V_x}{2}$$

c) First stage

For sample A, the results are the mean of four analyses; therefore, the third-stage component is $V_T/4$. Two samples are involved at the second stage; therefore, the second stage component is $V_2/2$.

The variance for sample A is therefore $V_1 + \frac{V_2}{2} + \frac{V_T}{4}$.

For sample B, the results are the mean of two analyses; therefore, the third-stage component is $V_T/2$. Only one sample is involved; therefore, the second-stage component is V_2.

The variance for sample B is therefore $V_1 + V_2 + \frac{V_T}{2}$.

Averaging the two sample (A and B) variances as (A+B)/2 gives:

$$V_z = \frac{\left(V_1 + \frac{V_2}{2} + \frac{V_T}{4} + V_1 + V_2 + \frac{V_T}{2}\right)}{2}$$

$$= V_1 + 3\frac{V_2}{4} + 3\frac{V_T}{8}$$

$$= V_1 + 3\frac{V_y}{4}$$

Hence:

$$V_1 = V_z - 3\frac{V_y}{4}$$

It is possible, because of the errors of estimates based on a limited number of results, for one of the estimated parameters to be negative. In this case, assume negative variances to be zero in all subsequent calculations.

9.4.3 Procedure 2

9.4.3.1 Method

If analysis is expensive relative to the cost of sampling, a second procedure can be considered which is slightly less accurate but involves fewer analyses. The method is illustrated in Figure 5. The procedure is the same as that described in 9.4.2.1, except that only sample A_1 is analysed in duplicate. Ten samples are prepared, giving 10 sets of results.

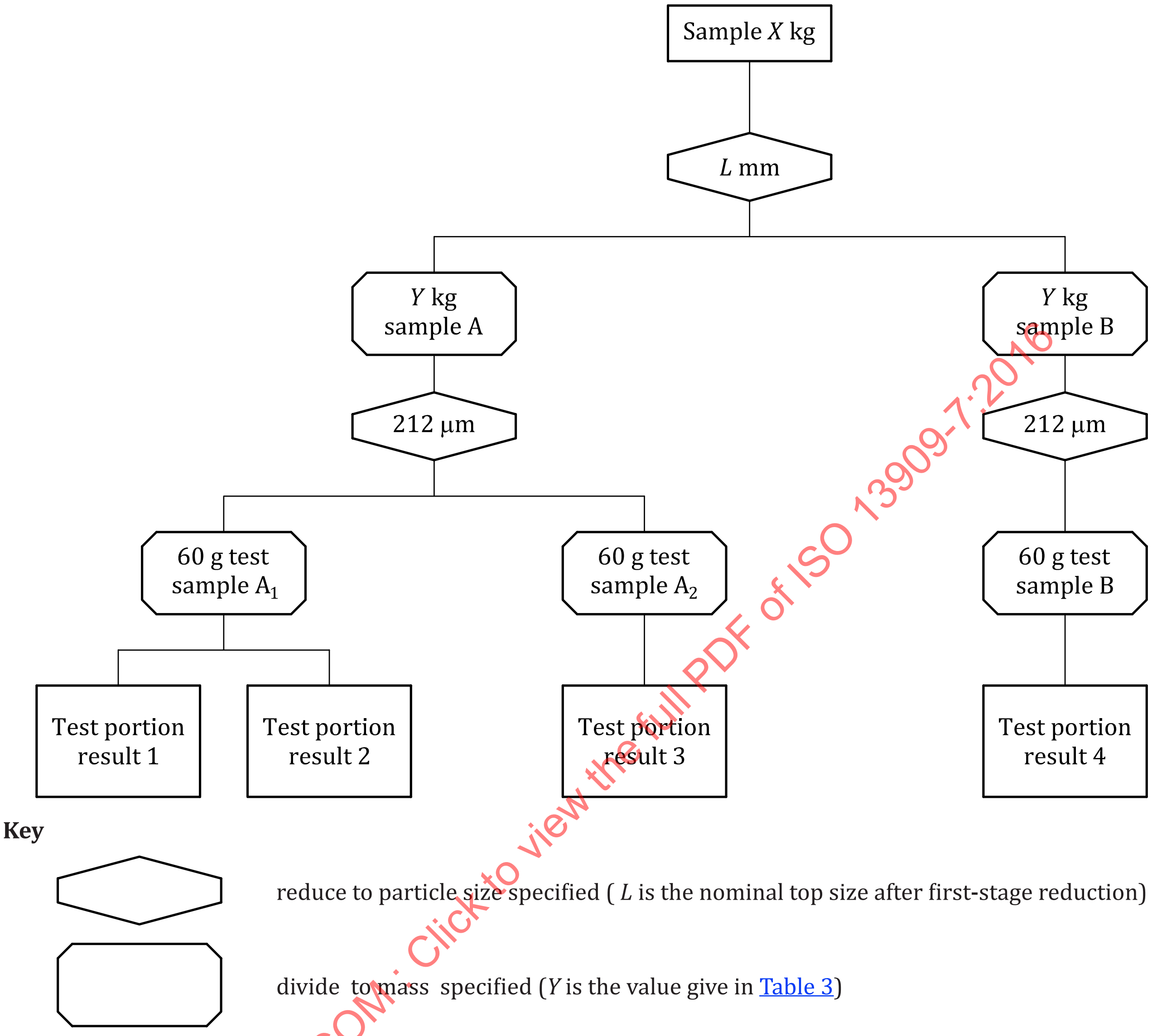


Figure 5 — Detailed check of sample preparation — Procedure 2

9.4.3.2 Calculation of variance arising from individual stages

Calculate the variances from the stages as follows.

a) Calculate the differences between the duplicate analyses, i.e.

(1) − (2)

Call these differences x and calculate

$$V_x = \frac{\sum x^2}{20}$$

b) Calculate the differences between samples A_1 and A_2, i.e.

$$\frac{(1)+(2)}{2} - (3)$$

Call these differences y and calculate

$$V_y = \frac{\sum y^2}{20}$$

c) Calculate the differences between A and B, i.e.

$$\frac{\frac{(1)+(2)}{2}+(3)}{2}-(4)$$

Call these differences *z* and calculate

$$V_z = \frac{\sum z^2}{20}$$

9.4.3.3 Calculation of cumulative variance at each stage

Calculate the cumulative stage variances as follows.

a) Third stage

$$V_T = V_x$$

b) Second stage

For A_1, the result is from two analyses; the third-stage component is therefore $V_T/2$.

For A_2, there is a single analysis and the third-stage component is therefore V_T. Combining these gives:

$$\frac{\frac{V_T}{2}+V_T}{2} = \frac{3V_T}{4}$$

Since

$$V_y = V_2 + \frac{3V_T}{4}$$

and

$$V_T = V_x$$

Therefore

$$V_2 = V_y - \frac{3V_x}{4}$$

c) First stage

For sample A, the result is the mean of two samples, A_1 and A_2. Therefore, the second- and third-stage components are:

$$\frac{V_2 + \frac{3V_T}{4}}{2} = \frac{V_2}{2} + \frac{3V_T}{8}$$

For sample B, there is only one result; therefore, the second- and third-stage components are:

$V_2 + V_T$

Combining these two and adding V_1 gives:

$$V_Z = V_1 + \frac{\left(\frac{V_2}{2} + \frac{3V_T}{8}\right) + \left(V_2 + V_T\right)}{2}$$

$$= V_1 + \frac{3\left(V_y - \frac{3V_x}{4}\right)}{4} + \frac{11V_T}{16}$$

$$= V_1 + \frac{3V_y}{4} + \frac{V_x}{8}$$

Therefore

$$V_1 = V_z - \frac{3V_y}{4} - \frac{V_x}{8}$$

9.4.4 Interpretation of results

Compare the variances estimated by the procedures described in 9.4.2 or 9.4.3 with the previously determined targets for each stage (see 9.2).

It is difficult to assess variances of this type for accuracy and, since only a small number of tests is carried out, each variance obtained has a considerable margin of error. If a variance for either stage is particularly large, it can be asserted that the errors are high and an attempt needs to be made to reduce them, but if a variance is low it is better not to assume that the results are so satisfactory that the procedure can be relaxed.

Examine the values obtained from 9.4.2 or 9.4.3 and make a decision as to which one is too high and needs attention. In general, this would be the stage of the procedure which gives the highest value of the variances V_1, V_2 or V_T obtained from the calculation in 9.4.2.3 or 9.4.3.3.

If the variance of analysis is too high, the equipment shall be carefully examined, particularly, the accuracy of the mixing procedures, the weighing devices and the control of temperatures, where appropriate. Also, the procedure being used shall be carefully checked against the appropriate specification.

If the excessive variance arises from a stage of sample preparation, the procedure at the stage concerned shall be carefully examined to confirm that it is in accordance with the appropriate part of ISO 13909, i.e. ISO 13909-4 for coal or ISO 13909-6 for coke. In particular, the size analysis after reduction shall be checked.

If these examinations fail to reveal any discrepancy, the procedure shall be improved by adopting one or both of the following alternatives:

a) crush the sample to a smaller particle size;

b) retain a larger sample mass for the next stage.

Then repeat the general test described in 9.3 to determine whether the procedure as a whole is now satisfactory. If it is not, the detailed stage-check test described in 9.4 shall be repeated. This cycle of tests shall be continued, as necessary, until the mean of the differences between 10 pairs of results lies between $0{,}70\sqrt{V_{PT}^0}$ and $1{,}75\sqrt{V_{PT}^0}$ for two successive sets of 10 samples.

The detailed test described in 9.4 should not be repeated immediately after a change has been made as this procedure is complicated. Moreover, because of the margin of error mentioned above, it is difficult to tell whether a smaller value for the variance of a particular stage represents a significant improvement or not. Therefore, it is better to test the procedure as a whole to see if successive sets of 10 samples are satisfactory.

9.5 Procedure for obtaining two samples at each stage

9.5.1 With a riffle

Perform mixing with the riffle in a normal manner, then proceed in the usual way to obtain sample A.

Collect all the residue and repeat the entire procedure to obtain a second sample B. Samples A and B shall not come from the halves of the first division.

9.5.2 With a mechanical sample divider

With a mechanical sample divider, either

a) arrange the sample divider in such a way that two receptacles are available for taking two samples of the appropriate mass, then discard the rest of the material, or

b) if the sample divider is of such a design that only one sample can be taken at a time, take one sample of the appropriate mass, then return the whole of the discard to the divider and take a second sample of the same mass.

9.6 Example

An engineer decided to check the plant sample-preparation procedures on a coal of ash content of about 25 %, with a required precision of 1 %. It was found that in order to achieve this precision, 15 increments were required in the sample. It was decided that the target for the overall preparation and testing error, V_{PT}^{0}, should be 0,2 (see 9.2).

Sampling was carried out in the usual manner and 10 successive samples were treated as described in 9.3 so that a pair of results was obtained from each sample. Thus, 10 pairs of duplicate test samples were obtained and the ash content of each test sample was determined.

These sample values were tabulated as shown in the first two columns of Table 4.

NOTE The values in all the tables are % ash, dry basis.

The difference between each pair was calculated and the mean difference obtained. This is shown in column 4 of Table 4.

Table 4 — Overall test of sample preparation errors

Sample	Sample A	Sample B	Difference $\lvert A-B \rvert$
1	25,7	25,0	0,7
2	24,3	25,1	0,8
3	25,6	25,0	0,6
4	28,1	27,1	1,0
5	27,8	28,7	0,9
6	25,1	25,8	0,7
7	25,6	24,8	0,8
8	24,4	25,2	0,8
9	27,8	27,1	0,7
10	26,3	27,3	1,0
		Total	8,0
		Mean	0,80
		Estimated within-pair standard deviation	0,71

The estimated within-pair standard deviation was 0,71. Although this does not exceed the upper limit of $1{,}75\sqrt{V_{\mathrm{PT}}^{0}}$ (i.e. 0,78), the variance of the sample preparation was nevertheless high and therefore an experiment was arranged as described in 9.4.2 so that the variance of the errors arising at each stage could be estimated. The results which were obtained are shown in Table 5.

Table 5 — Detailed test of sample preparation errors

Sample	A1		A2		B	
	1	**2**	**3**	**4**	**5**	**6**
1	26,8	26,6	26,1	26,6	25,3	25,2
2	26,5	26,6	26,5	26,5	25,4	25,5
3	25,4	25,3	25,4	25,3	25,2	25,3
4	28,8	28,5	28,7	28,6	28,3	28,2
5	29,4	30,1	30,1	29,8	28,7	28,7
6	25,7	25,3	25,7	25,7	25,2	25,3
7	24,5	24,4	24,3	24,4	24,6	24,7
8	26,1	25,9	26,6	26,3	25,7	25,8
9	23,1	23,2	23,5	23,3	23,1	23,1
10	31,5	31,6	30,8	30,9	30,8	30,9

The differences, x, between duplicates of samples A_1, A_2 and B were tabulated as in Table 6. From these differences, $\sum x^2$ was calculated [see 9.4.2.2 a)]. Similarly, the differences y [see 9.4.2.2 b)] between mean results were tabulated as in Table 7 and $\sum y^2$ calculated and the differences z [see 9.4.2.2 c)] were tabulated as in Table 8 and $\sum z^2$ calculated.

Table 6 — Calculation of values of x

Sample	A_1 (1) − (2)	A_2 (3) − (4)	B (5) − (6)
1	0,2	0,5	0,1
2	−0,1	0,0	−0,1
3	0,1	0,1	−0,1
4	0,3	0,1	0,1
5	−0,7	0,3	0,0
6	0,4	0,0	−0,1
7	0,1	−0,1	−0,1
8	0,2	0,3	−0,1
9	−0,1	0,2	0,0
10	−0,1	−0,1	−0,1
$\sum x^2 = 1,46$			

Table 7 — Calculation of values of y

Sample	A_1 $\frac{(1)+(2)}{2}$	A_2 $\frac{(3)+(4)}{2}$	$A_1 - A_2$ y
1	26,70	26,35	0,35
2	26,55	26,50	0,05
3	25,35	25,35	0,00
4	28,65	28,65	0,00
5	29,75	29,95	−0,20
6	25,50	25,70	−0,20
7	24,45	24,35	0,10
8	26,00	26,45	−0,45
9	23,15	23,40	−0,25
10	31,55	30,85	0,70
$\sum y^2 = 0,97$			

Table 8 — Calculation of values of z

Sample	A $\frac{(1)+(2)+(3)+(4)}{4}$	B $\frac{(5)+(6)}{2}$	A – B z
1	26,52	25,25	1,27
2	26,52	25,45	1,07
3	25,35	25,25	0,10
4	28,65	28,25	0,40
5	29,85	28,70	1,15
6	25,60	25,25	0,35
7	24,40	24,65	−0,25
8	26,23	25,75	0,48
9	23,28	23,10	0,18
10	31,20	30,85	0,35
$\sum z^2 = 4{,}820\ 6$			

V_x, V_y and V_z were calculated as follows:

$$V_x = \frac{\sum x^2}{60} = 0{,}024\ 33$$

$$V_y = \frac{\sum y^2}{20} = 0{,}048\ 50$$

$$V_z = \frac{\sum z^2}{20} = 0{,}241\ 03$$

V_T, V_2 and V_1 (see 9.4.2.3) were estimated as follows:

$V_T = V_x = 0{,}024\ 33 = 0{,}02$ (corrected to two decimal places)

$V_2 = V_y - 0{,}50V_x = 0{,}036\ 34 = 0{,}04$ (corrected to two decimal places)

$V_1 = V_z - 0{,}75V_y = 0{,}204\ 66 = 0{,}20$ (corrected to two decimal places)

Thus, it is clear that V_1 is the largest and that the errors occurring at the first stage of sample division require investigation.

The progress of improvement to the first stage should initially be assessed by checking the procedure as a whole, as described in 9.3.

Annex A
(informative)

Variogram method for determining variance

A.1 General

The method for estimating primary increment variance described in 6.2 does not take into account the possible serial correlation between increments and may lead to a greater calculated number of increments than would be necessary to obtain a given sampling precision. The variogram method may be used as an alternative means of estimating the number of primary increments needed to attain a given level of precision.

The variogram is a plot of the mean squared difference in the quality of increments, i.e. variance, as a function of the interval, or lag, between them. The distance between neighbouring increments is called lag 1, and the distance between neighbouring odd and even increments is called lag 2, etc. This is illustrated in Figure A.1.

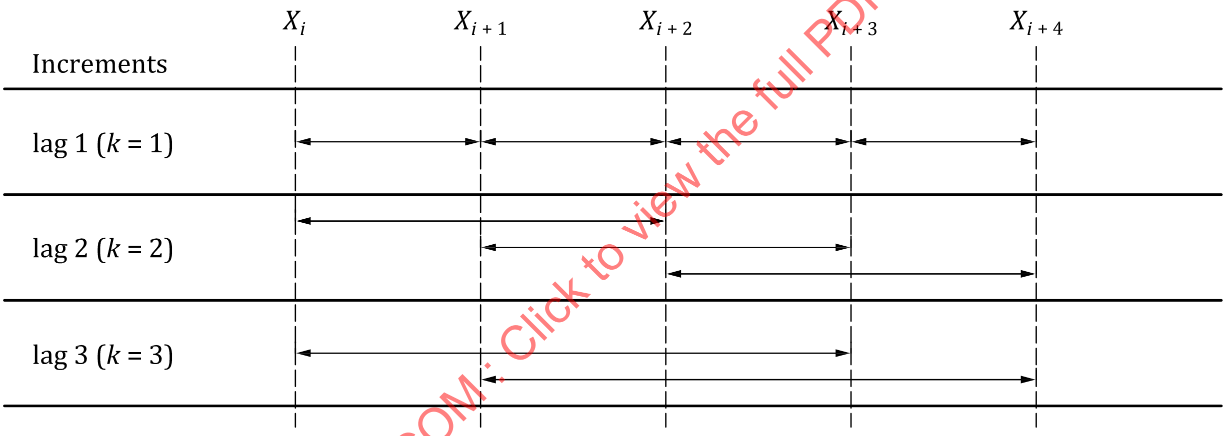


Figure A.1 — Graphical representation of elements used for the calculation of the experimental variance V_e (k)

Lag may be a time interval for time-basis sampling or a mass interval for mass-basis sampling. The data are obtained by collecting n increments from a sub-lot and analysing each increment separately.

The increments should be collected at about half the sampling interval calculated from ISO 13909-2:2016, 5.2.2, Formula (8) or ISO 13909-2:2016, 5.3.2, Formula (9) using the number of increments estimated using ISO 13909-2:2016, 4.3.4.2, Formula (2) or that normally used for sampling the particular fuel in question.

The value of the variance V (k) at lag k is calculated from Formula A.1:

$$V\left(k\right)=\sum_{i=1}^{i=N_k}\frac{\left(x_{i+k}-x_i\right)^2}{2N_k} \tag{A.1}$$

where

x_i is the analysis for increment i;

x_{i+k} is the analysis for increment $i + k$;

N_k is the number of pairs of increments at lag k apart.

The principal features of a variogram are shown in Figure A.2. The intercept V_R on the vertical axis is the random component of variance. The other component of variance is the temporal component, which increases with lag and may reach a maximum.

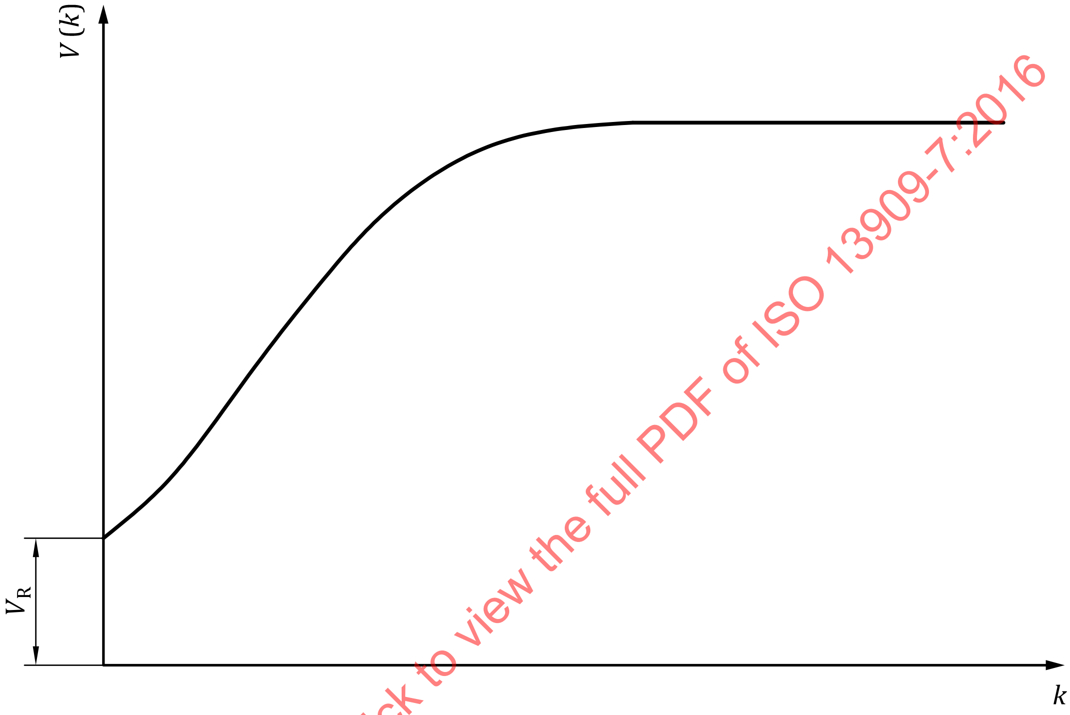


Figure A.2 — General features of variograms

The variances $V(k)$ obtained using Formula (A.1) include the sample preparation and testing variance V_{PT}, which is constant, as well as the sampling variance. This is also a component of the variogram intercept, V_R, and consequently a correction is made to obtain the sampling variance (see A.3). An estimate of V_{PT} can be obtained by extracting two duplicate divided samples from each increment at the first off-line division stage and preparing and analysing both.

Experience shows that a variogram for usual sampling intervals can be adequately approximated by a straight line over the range $k = 1$ to about $k = 5$, according to Formulae (A.2) and (A.3) for time-basis and mass-basis sampling, respectively:

$$V(t) = V_R + Bk\Delta t \qquad \text{(A.2)}$$

$$V(m) = V_R + Bk\Delta m \qquad \text{(A.3)}$$

where

V_R is the random component of variance (the intercept) of the variogram;

B is the gradient (or slope) of the variogram;

Δt is the sampling interval (lag 1) for time-basis sampling;

Δm is the sampling interval (lag 1) for mass-basis sampling.

A.2 Calculation and fitting the variogram

A.2.1 General

Calculate the value of the variance $V(k)$ for the first 10 lags using Formula (A.1) and plot the variogram of variance $V(k)$ versus lag k.

Estimate the values of V_R and B in Formulae (A.2) or (A.3) by fitting a straight line to the linear portion of the variogram, i.e. lag 1 to k_{lin}. The linear portion is typically about the first five lags and the straight line can be fitted either by eye or by linear regression.

A.2.2 Variogram fit by eye

Set V_R to the value of $V(k)$ where the straight line intercepts the y-axis.

Calculate the gradient of the variogram using either Formula (A.4) or Formula (A.5) for time-basis and mass-basis sampling, respectively:

$$B = \frac{V\left(k_{lin}\right) - V_R}{k_{lin}\Delta t} \qquad (A.4)$$

$$B = \frac{V\left(k_{lin}\right) - V_R}{k_{lin}\Delta m} \qquad (A.5)$$

A.2.3 Variogram fit by linear regression

Set $y = V(k)$ and $x = k\Delta t$ or $x = k\Delta m$ for time-basis or mass-basis sampling, respectively.

Calculate B and V_R as follows:

$$B = \frac{k_{lin}\sum xy - \sum x \sum y}{k_{lin}\sum x^2 - \left(\sum x\right)^2} \qquad (A.6)$$

$$V_R = \frac{\sum y - B\sum x}{k_{lin}} \qquad (A.7)$$

A.2.4 Calculation of corrected variance

Subtract the sample preparation and testing variance V_{PT} from the value of V_R to obtain the corrected variance V_C as follows:

$$V_C = V_R - V_{PT} \qquad (A.8)$$

The variance V_C provides information on sampling errors only.

A.3 Calculation of sampling variance

After determining V_C and B, calculate the sampling variance V_S as follows.

For systematic sampling:

$$V_{\mathrm{S}} = \frac{V_{\mathrm{C}}}{n} + \frac{Bm_{\mathrm{SL}}}{6n^2} \tag{A.9}$$

and for stratified random sampling:

$$V_{\mathrm{S}} = \frac{V_{\mathrm{C}}}{n} + \frac{Bm_{\mathrm{SL}}}{3n^2} \tag{A.10}$$

where

m_{SL} is the mass of the sub-lot;

n is the number of increments taken from the sub-lot.

NOTE For time-basis sampling, m_{SL} is replaced by T, the total sampling time.

A.4 Calculation of number of increments

Calculate the number of increments required to achieve the desired sampling variance V_{S} by transposing Formulae (A.9) and (A.10) and solving for n using Formulae (A.11) and (A.12).

For systematic sampling:

$$n = \frac{V_{\mathrm{C}} + \sqrt{V_{\mathrm{C}}^2 + \frac{2}{3} Bm_{\mathrm{SL}} V_{\mathrm{S}}}}{2V_{\mathrm{S}}} \tag{A.11}$$

and for stratified random sampling:

$$n = \frac{V_{\mathrm{C}} + \sqrt{V_{\mathrm{C}}^2 + \frac{4}{3} Bm_{\mathrm{SL}} V_{\mathrm{S}}}}{2V_{\mathrm{S}}} \tag{A.12}$$

A.5 Calculation of total variance

Assuming that all the increments are combined into a single sample for the sub-lot, calculate the total variance V_{SPT} for sampling, preparation and testing using Formulae (A.13) and (A.14).

For systematic sampling:

$$V_{\mathrm{SPT}} = \frac{V_{\mathrm{C}}}{n} + \frac{Bm_{\mathrm{SL}}}{6n^2} + V_{\mathrm{PT}} \tag{A.13}$$

and for stratified random sampling:

$$V_{\mathrm{SPT}} = \frac{V_{\mathrm{C}}}{n} + \frac{Bm_{\mathrm{SL}}}{3n^2} + V_{\mathrm{PT}} \tag{A.14}$$

A.6 Example of calculation of sampling and total variance

The data for ash content in Table A.1 were obtained by collecting and analysing individual increments taken at 0,25 min intervals. The preparation and testing variance V_{PT} was determined separately and found to be 0,01.

Table A.1 — Ash content of individual increments taken at 0,25 min intervals

Increment number	Ash content % (*m*/*m*)
1	14,6
2	13,8
3	14,7
4	16,1
5	15,6
6	15,6
7	15,8
8	15,3
9	15,8
10	15,4
11	15,9
12	16,1
13	15,3
14	16,0
15	15,2
16	15,5
17	14,6
18	14,9
19	15,3
20	15,4
21	15,4
22	15,4
23	16,0
24	15,5
25	15,5
26	15,4
27	15,4
28	14,7
29	15,2
30	14,9

Calculate the experimental variogram points $V(k)$ using Formula (A.1). For lag 1 ($k = 1$), the variance is calculated as follows:

$$V(1) = \frac{(13{,}8 - 14{,}6)^2 + (14{,}7 - 13{,}8)^2 + \ldots + (14{,}9 - 15{,}2)^2}{2 \times 29}$$

$$= \frac{9{,}03}{58} = 0{,}156$$

For lag 2 ($k = 2$), the variance is calculated as follows:

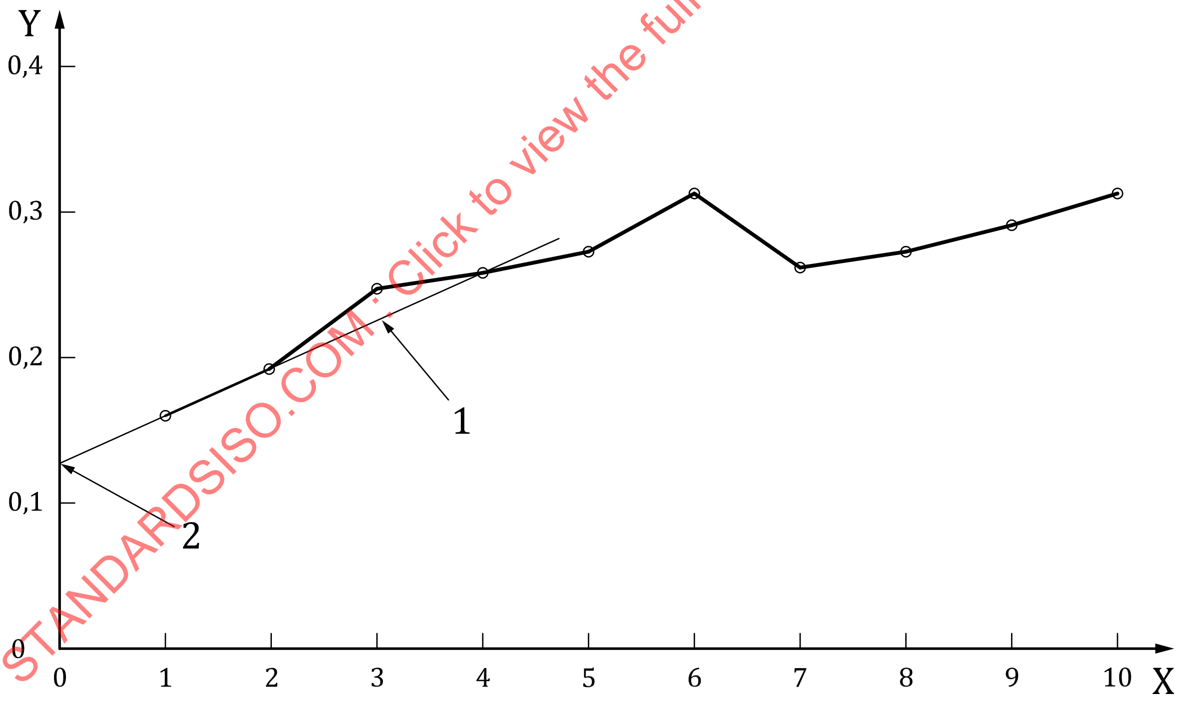
$$V(2) = \frac{(14{,}7 - 14{,}6)^2 + (16{,}1 - 13{,}8)^2 + \ldots + (14{,}9 - 14{,}7)^2}{2 \times 28}$$

$$= \frac{10,31}{56} = 0,184$$

The first 10 variogram points are tabulated in Table A.2 and plotted in Figure A.3.

Table A.2 — Variogram points for the data in Table A.1

Integer lag k	Lag in minutes $k\Delta t$	Variance $V(k) = y$
1	0,25	0,156
2	0,50	0,184
3	0,75	0,235
4	1,00	0,245
5	1,25	0,258
6	1,50	0,297
7	1,75	0,247
8	2,00	0,261
9	2,25	0,280
10	2,50	0,297



Key

1 variogram fit by eye

2 intercept V_R (eye) = 0,125

X lag, k

Y variance

Figure A.3 — Variogram for the data in Table A.2

Fit a straight line to the first five points of the variogram (see A.2.2) by first calculating the following summations:

$$\sum y = 1{,}078$$

$$\sum x = 3{,}750$$

$$\sum xy = 0{,}874\ 8$$

$$\sum x^2 = 3{,}437\ 5$$

Calculate B using Formula (A.6):

$$B = \frac{5 \times 0{,}874\ 8 - 3{,}75 \times 1{,}078}{5 \times 3{,}437\ 5 - 3{,}75^2} = 0{,}11$$

Calculate V_R using Formula (A.7):

$$V_\mathrm{R} = \frac{1{,}078 - 0{,}11 \times 3{,}75}{5} = 0{,}13$$

The alternative method of fitting a straight line to the variogram by eye (see A.2.2) gives very similar results. As shown in Figure A.3, a straight line has been drawn from V (4) through V (2) and V (1) to intercept the Y-axis. The intercept is 0,125, so V_R = 0,125. The gradient of the variogram can then be calculated using Formula (A.4) as follows:

$$B = \frac{V\left(4\right) - 0{,}125}{4 \times 0{,}25} = \frac{0{,}245 - 0{,}125}{1} = 0{,}12$$

Completing the calculation of sampling and total variance using the results for the linear regression fit to the variogram, calculate V_C using Formula (A.8):

$$V_\mathrm{C} = 0{,}13 - 0{,}01 = 0{,}12$$

Assuming that systematic sampling is to be used and that 30 increments are to be taken from a sub-lot at 1 min intervals (i.e. m_SL = 30), calculate the sampling variance from the above values for V_C and B using Formula (A.9):

$$V_\mathrm{S} = \frac{0{,}12}{30} + \frac{0{,}11 \times 30}{6 \times 30^2} = 4{,}6 \times 10^{-3}$$

Calculate the overall variance by adding the preparation and testing variance using Formula (A.15):

$$V_\mathrm{SPT} = V_\mathrm{S} + V_\mathrm{PT} \tag{A.15}$$

$$= 0{,}004\ 6 + 0{,}01$$

$$= 0{,}014\ 6$$

Finally, calculate the precision of the result for a single sub-lot using Formula (1) as follows:

$$\begin{aligned} P &= 2\sqrt{V_{\mathrm{SPT}}} \\ &= 2 \times 0{,}121 \\ &= 0{,}24\ \%\ \text{ash} \end{aligned}$$

Annex B
(informative)

Grubbs' estimators method for determining sampling precision

B.1 General

At some locations, operational conditions of a sampling system do not allow duplicate samples to be collected with the assurance that no cross-contamination of sample material from adjacent primary increments occurs. In such cases, the sampling precision being obtained may be checked by collecting three samples from each of a minimum of 30 sub-lots of fuel. One sample is collected using the normal sampling scheme (system sample) and two mutually independent systematic samples are collected by stopping a main fuel-handling belt for collection of stopped-belt increments at preselected intervals (reference samples A and B).

B.2 Selection of sub-lot size for measuring precision

The sub-lot size should be such that

a) the mass of material collected by the on-line sampling and sample preparation system is at least twice the minimum mass given in ISO 13909-2:2016, Table 1, and

b) the minimum fuel-conveying time for each sub-lot is 1 h. The time during which the fuel-handling belts are shut down for collection of stopped-belt increments is not included as fuel-conveying time.

B.3 Selection of number of stopped-belt increments and collection intervals

Each of the two reference samples, stopped-belt sample A and stopped-belt sample B, consists of a minimum of three stopped-belt increments and preferably more to ensure that the overall precision of the reference methods is comparable to that of the sampling system under test. Obtain the sampling interval for each reference sample by dividing the sub-lot fuel-running time, in minutes, by the number of stopped-belt increments to be collected. For example, with a sub-lot size of 900 tonnes during which the expected fuel-conveying time is 90 min, and with three stopped-belt increments collected from each sub-lot, the stopped-belt systematic sampling interval for each stopped- belt reference sample will be 30 min.

To ensure that reference samples and system samples are mutually independent, it is necessary that true systematic sampling be employed for collection of reference samples. Thus, for both reference sample A and reference sample B from each sub-lot, a random number table or pseudo-random generator is used to select a time for collection of the first stopped-belt increment, in 0,5 min intervals, from all possibilities within the stopped-belt sampling interval. For a 30 min stopped-belt sampling interval, there will be 60 possibilities upon each choice. The time for collection of each subsequent stopped-belt increment for each reference sample is determined by repeatedly adding the systematic sampling interval until all increments have been collected.

The results of this procedure are illustrated in Table B.1, where the sub-lot size is the quantity of fuel conveyed during a 90 min interval and three stopped-belt increments are collected for each reference sample.