

Repræsentativ prøvetagning – Horizontal standard

Representative sampling – Horizontal standard

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I denne 2. udgave er referencen til ITRC (2012) fjernet, idet DS er blevet gjort bekendt med, at der er skabt tvivl om validiteten af det tekniske indhold i ITRC (2012).

National foreword

In this 2nd edition, reference to ITRC (2012) has been removed as DS has been informed that with doubt has been raised about the validity of the technical content in ITRC (2012).

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Foreword

This standard outlines a practical, self-controlling approach for representative sampling with minimal complexity, based on the Theory of Sampling (TOS). The generic sampling process described and all elements involved are necessary and sufficient for the stated objective, in order to be able to document sampling representativity under the conditions specified. It is always necessary to consider the full pathway from primary sampling to analytical aliquot in order to be able to guarantee a reliable and valid analytical outcome. This standard, including the normative annexes and further, optional references in the Bibliography, constitute a complete competence basis for this purpose. The present approach will ensure appropriate levels of accuracy and precision for both primary sampling as well as for all sub-sampling procedures and mass-reduction systems at the subsequent laboratory stages before analysis.

A sampling process needs to be structurally correct (see 3.7) in order for the essential accuracy requirement to be fulfilled, with no exceptions allowed. For the process also to be sufficiently precise it is often necessary to proceed through iterative stages, until the effective sampling variance has been brought below an a priori given threshold; this is also known as 'fit-for-purpose' representativity. In this endeavour, the key feature is the heterogeneity of the target lot, which is to be identified and quantified. Heterogeneity characterisation forms the key element of this standard. When both the accuracy and precision demands have been met properly, all types of solid lots and two-phase (solid-liquid) materials can be sampled representatively (gasses are excluded from this standard), and the derived quality assurance of the sampling process is thereby subject to open public inspection and assessment. Without informed commitment to such an empirical heterogeneity characterisation, all prospects of being able to document representativity will remain out of reach.

This standard outlines a systematic scientific basis for improving sampling procedures, which will lead to increased reliability for decision-making based on empirical measurement results. Not all existing standards are in compliance with the appropriate TOS requirements, although partial elements can be found in many places (see Bibliography). Relationships to other standards, guidelines, good practices as well as regulatory and legal requirements shall be handled with insight. Where found in opposition to other, less TOS-compliant stipulations, it will be necessary to start a process of revision or updating of the relevant standards or norm-giving documents which may be a lengthy process. While this takes place, or when dictated by documented sampling variances that are too high (a key issue in the present standard), it is always an option to employ more stringent quality criteria with a TOS-based approach, than what may be presently codified. As there are serious economic and societal consequences of non-representative sampling, these are also appropriately described and illustrated in this standard, which emphasises impacts caused by inferior analytical results and related non-reliable decision-making.

The overall objective of this standard is to establish comprehensive motivation and competence only relying on fully TOS-compliant sampling procedures and equipment irrespective of the theoretical, practical, technological, industrial or societal context under the law.¹⁾

¹⁾ No standard is a legal document on its own and is therefore not legally binding. To the extent that European Community (EC) law on the subject treated in this standard has been adopted, EC law shall be adhered to. EC law implemented in national law takes precedence to non-legal documents in case of conflict.

Introduction

The importance of reliable, i.e. representative sampling, is self-evident. Many societal, political, economic, environmental, and other important decisions are based on the necessary assumption of relevant and reliable measurement results. But a narrow focus on the analytical stage alone is a very dangerous mistake; the preceding sampling stages should be included as well, because the effects from inferior sampling most often completely overshadow other contributions to the total uncertainty budget. The objective of this standard is to ensure global adherence to principles for representative sampling by outlining a set of simple requirements for procedures and documentation that will allow everybody to evaluate whether a given sampling procedure is representative or not, and thereby how reliable the reported analytical results are. The principles described in this standard outline all necessary relationships between a priori sampling criteria, sampling conditions and a posteriori quality results (Quality Objectives, QO).

This standard covers representative sampling of all types of solid and two-phase (solid-liquid) lots and material types, as well as derived demands for the necessary types of sampling equipment. Relevant aspects regarding analytical error, quality control, quality assurance, traceability, measurement uncertainty (MU) and process analytical technologies (PAT) are, however, only treated in their relationship with sampling as they are treated comprehensively in other relevant guidelines, e.g. (Bakeev 2010) and (Ramsey and Ellison 2007). This standard only deals with the critical success factors for sampling representativity and how to ensure a valid sampling quality assurance without which analysis cannot be undertaken on an uncompromised basis.

The target group for this standard is all professional individuals from top to bottom (managers, supervisors, technicians, samplers), companies, organisations and regulatory bodies responsible for sampling, first line samplers, process engineers, laboratory personnel, academic and industrial scientists. The principles of representative sampling are generic and are essentially only dependent on lot heterogeneity, the specific sampling procedure employed and the sampling competence of the operative personnel (as well as their supervisors). These principles are scalable with respect to lot size but are not dependent of material type (only their heterogeneity matters) and are independent of equipment brands (it is only the function of the sampling equipment that matters). Representative sampling shall specifically also be independent with regard to economic, market and trade interests as these issues do not have an impact with respect to representativity. Reliable criteria for representativity follow from the objective framework called the Theory of Sampling (TOS), which is the only existing complete framework that leads to operative procedures for sampling error elimination and/or appropriate reduction where and when needed. The principles of Measurement Uncertainty (MU) lead to a relevant total uncertainty estimation only if/when the relevant sampling errors have been correctly dealt with first. For this reason, this standard can also be seen as a complement requirement for proper MU assessment.

The context behind this standard is that a minimum TOS understanding and practical competence is needed in order for any agent or agency to be able to perform and document, representative sampling – it is emphatically not enough to rely on one, or more specific pieces of equipment, nor on rigid sampling schemes purporting to apply to all situations. In general it will not be acceptable to carry over sampling procedures, or sampling plans, from one commodity type (material type) to another without specific validation. The important issues pertaining to representativity – sampling process, sampling equipment, and the resulting samples and analytical results – require full transparency and traceability.

There exists a singular characteristic associated with every material, which is the critical determinant for all sampling related issues – heterogeneity (Gy 1998, Pitard 1993, Esbensen & Minkinen (Eds) 2004). Material heterogeneity interacts with every sampling procedure in use, be it representative or not, giving rise to several types of sampling errors (quantified as the Total Sampling Error, TSE), which should always be included in a total measurement error estimate. Thus, the influencing factors regarding sampling are both the sampling procedure as well as heterogeneity. How to counteract these adverse error effects constitutes the proactive objective in this standard. Only when full adherence to the principles and procedures laid out in this standard is achieved, can all stakeholders trust that sampling has been performed in such a way that it can be unambiguously documented as representative.

Sampling addresses both stationary targets, i.e. 1-D (one dimensional) piles, stacks, 2-D and 3-D lots, as well as moving lots (the latter also known as process sampling, or sampling of dynamic 1-D lots). Lot dimensionality is both related to the physical geometrical appearance, but is in a practical context also related to the way the lot can be sampled, e.g. a conveyor belt is 1-D if all increments cover the two transverse dimensions completely (width/ thickness), but inferior, superficial grab sampling in the same context makes it a 3-D lot. Lot characteristics are defined in clause 3.18.

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The case of 'sampling in the plane' is especially important in many contexts (environment science, soil remediation, risk assessment): 2-D sampling (constant increment/sample length in the Z-direction) necessitates a geometric/geographic sampling plan, and specific 2-D approaches have been developed. But although this is important, it is not to be elevated to the status of a special case. There is nothing in 2-D sampling that justifies deviation from any of the general principles promulgated in this standard - each increment (or sample) in a 2-D pattern shall still be representative, unless the same bias-generating error effects will occur also here as in 1-D and 3-D stationary and dynamic 1-D lot sampling.

This standard stipulates a general quality objective threshold level (see 5.3), which, if transgressed, results in failure of the representativity of the sampling procedure tested - and which should then be improved, with no exceptions. The scientific background for this procedural approach only guarantees representativity, if this threshold is not transgressed. This quality objective only has validity if based on structurally correct sampling (see 3.7). This standard makes it mandatory to disclose the operative quality objective employed and its quantitative estimate (%), or to report fully and voluntarily on specific reasons why deviating thresholds have been employed, in order for all parties to be able to assess the non-standard decision-making uncertainty and risks so incurred. Decision-making based on analytical data can only be said to be appropriately informed if all sampling and analytical errors involved are known and quantified.

When a sampling procedure has been QO-approved for a certain material, it can be carried out or repeated by any other sampling agent for the same specific material/analyte combination without reservation. There may be a certain carrying-over applicability to similar materials as well, but only within reasonable bracketed material classes at large. This standard makes it mandatory always to perform relevant QO-testing (an empirical heterogeneity characterisation) for every new material, new analyte, new sampling procedure or any new combination hereof.

Because representative sampling is the singular criterion for reliable decision making, no exception from the requirements and stipulations in this standard can be allowed. Deviating quality standards (guidelines, good practice, norm-giving documents), material sampling standards (guidelines etc.) for specific materials, sample preparation standards and analytical standards (guidelines etc.) are therefore to take second place in the authority hierarchy, because these are matrix-dependent and may not be fully TOS-compliant. In case of discrepancies regarding sampling specifications, this standard is therefore to take precedence (see Figure1).

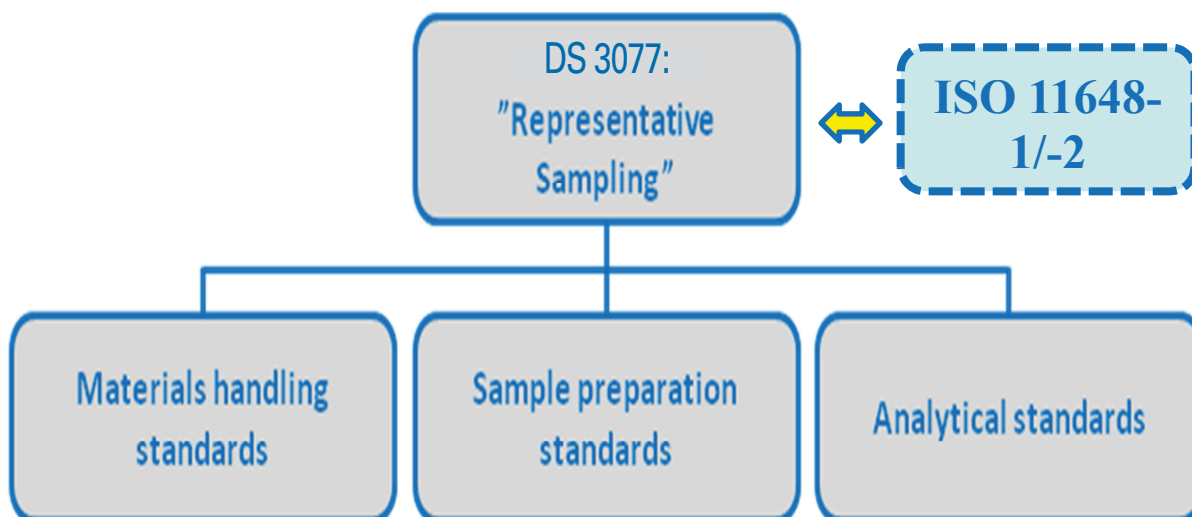


Figure 1 – Relationships between sampling standards and materials handling, sample preparation and analytical standards

ISO 11648-1 and -2 adopt only TOS partially.

Sampling rationale

All sampling is subject to appropriate, comprehensive and sufficient problem-definition, e.g. what is the purpose of analysis at the end of the entire sampling-analysis pathway? For what purpose will the analytical results be used, e.g. trade/contract issues, environmental decision-making, resource management, ecological, medical, or toxicity threshold assessments? Such purposes are many and diverse. Equally important: What is the operative lot definition? How is the lot defined geometrically and sampling-wise (1-D, 2-D, 3-D) and/or temporarily: Does lot composition change over time, space or mass? In 2-D sampling, 'sampling in the plane', the overlying context is focused on the areal 'Decision Units' (DU) involved (2-D or simplified 3-D lot definitions).

The nature of material heterogeneity is all-pervasive: all materials are irregular, at all scales, at all locations (and sometimes changing over time). All lots are heterogeneous from the local scale (commensurate with the increment volume extracted) to the complete lot volume (which can never be sampled in its entirety). It is not conducive to view all lots as but a population of (potential) analytical results; such a notion is not able to capture the full complexity of heterogeneous real-world materials and lots, but rather invites neglect for how samples should be extracted (focus is too early on producing the analytical results). Heterogeneity has two conceptual aspects, distributional (or spatial) heterogeneity (DH) and compositional (or constitutional) heterogeneity (CH); both concepts are necessary in order to understand the interaction of a specific sampling process with a specific material. TOS is the only theory to make this essential distinction and analyses all consequences hereof.

TOS's comprehensive theoretical analysis outlines why it is necessary, indeed imperative, always to assume a significant heterogeneity²⁾. This allows universal principles to be applied for all types of materials and lots, eliminating the otherwise practically infinite number of matrix-versus-analyte combinations (there are at present already a multitude of analytical standards, one for each compound – in addition to several standards that address different analytes in these different materials). If this combinatorial hierarchy should be augmented by different sampling standards for each material, this would only create unnecessary confusion. One of the aims of this standard is to help simplify the task of representative sampling in view of the bewildering number of materials that first need to be appropriately sampled in science, technology and industry. TOS furthers one common set of universal principles and derived practical sampling procedures for all these cases.

TOS's comprehensive General Principles (GP) and Sampling Unit Operations (SUO), as codified in this standard (see 5.2), together with its normative and related references and an extensive bibliography, guarantee that representative sampling is always possible – and that this can be fully documented.

²⁾ In the vanishingly small number of cases dealing with uniform materials (materials with very low heterogeneity), nothing is lost by also here observing the universal principles that guarantee representative sampling throughout all the vastly higher number of significant heterogeneity cases.

DS 3077:2013**1 Scope**

This standard is a matrix-independent standard for representative sampling. Compliance with the principles herein ensures that a specific sampling method (procedure) is representative.

This standard sets out a minimum competence basis for reliable planning, performance and assessment of existing or new sampling procedures with respect to representativity.

This standard invalidates grab sampling³⁾ and other incorrect sampling operations, by requiring conformance with a universal set of seven governing principles and unit operations (see 5.2).

This standard specifies two simple quality assurance measures (Quality Objectives, QO) regarding:

- 1) sampling of stationary lots, the Relative Sampling Variability test (RSV)
- 2) sampling of dynamic lots, Variographic Analysis (VA), also known as variographic characterisation, with an analogous RSV_{1-dim}. (This standard contains a variographic software program (freeware) making variographic characterisation available to all users).

This standard stipulates maximum threshold levels for both of these quality assurance measures (QO).

This standard is based on the Theory of Sampling (TOS). A comprehensive background for TOS can be found in clause 2. This standard also contains a full complement of additional references and background literature (see Bibliography).

This standard enforces professional self-control by stipulating mandatory disclosure of one of two comprehensive quality assurance approaches as produced by RSV or variographic characterisation to all parties involved.

This standard specifies documentation and reporting of sampling representativity and efficiency for each analyte in combination with a specific class of materials respectively. Any deviation from this standard's QO shall be justified and reported.

This standard employs a dual acceptance approach: items not mentioned are not acceptable as modifications in any sampling procedure or sampling plan, unless specifically tested and assessed by the QO's described herein – while all modifications successfully passing this test requirement are acceptable.

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 11648-1:2003, *Statistical aspects of sampling from bulk materials – Part 1: General Principles*

ISO 11648-2:2001, *Statistical aspects of sampling from bulk materials – Part 2: Sampling of particular materials*

NOTE – ISO 11648-1 and -2 constitute a comprehensive basis for sampling, but are restricted to treating all of sampling exclusively from a statistical point of view (examples: sampling only from a population of units; no distinction between compositional and distributional heterogeneity; no concept of incorrect vs. correct sampling errors). This standard augments this approach with the necessary, full conceptual theory and practice of sampling (TOS), without which ISO 11648-1 and -2 are incomplete.

[WCSB1 Proceedings] Esbensen, K.H. & P. Minkkinen (2004) (Eds). *Special Issue: 50 years of Pierre Gy's Theory of Sampling. Proceedings: First World Conference on Sampling and Blending (WCSB1). Tutorials on Sampling: Theory and Practise. Chemometrics and Intelligent Laboratory Systems*, vol. 74, Issue 1, 236 p. ISSN 0169-7439

Petersen, L., C. Dahl, K.H. Esbensen (2004). Representative mass reduction in sampling – a critical survey of techniques and hardware. In: *Special Issue: 50 years of Pierre Gy's Theory of Sampling. Proceedings: First World Conference on Sampling and Blending (WCSB1)*. Esbensen & Minkkinen (Eds). *Chemometrics and Intelligent Laboratory Systems*, vol. 74, Issue 1, p. 95-114

3) "Grab sampling" and all other technical terms: see clause 3: Terms and definitions.

Esbensen, K.H. & Mortensen, P. (2010). Process Sampling (Theory of Sampling, TOS) – the Missing Link in Process Analytical Technology (PAT). In: Bakeev, K. A. (Ed.) *Process Analytical Technology*. 2nd Edition. pp. 37-80. Wiley. ISBN 978-0-470-72207-7

EN 14899:2005, *Characterization of waste – Sampling of waste materials – Framework for the preparation and application of a Sampling Plan*

3 Terms and definitions

For the purpose of this document, the following terms and definitions apply:

3.1

accuracy

difference between true lot concentration, a_L , and the measured sample concentration, a_S . a_S is an estimate of a_L

NOTE 1 to entry – The analytical concentration is preferentially based on a composite sample (see 3.6). True lot concentration refers to the notion of the average lot concentration. True lot concentration is used in theoretical deliberations which further the basis for practical sampling procedures, as laid out in the Theory of Sampling, TOS (see 3.40). The relative accuracy is reflected by the Sampling Error, SE (see 3.31). For practical applications, true lot concentration, a_L , is estimated in the given context, e.g. as the mean of several, structurally correct determinations, using an appropriately high number of individual representative samples. See also replication experiment (3.25) and variographic characterisation (3.42).

NOTE 2 to entry – See Note 1 to entry of 3.3 on the possible alternative abolition of the term accuracy according to the rationale behind the Measurement Uncertainty (MU) approach. TOS specifically retains the concepts of accuracy and reproducibility (precision); argumentation can be found in TOS literature.

3.2

analyte, constituent

chemical or physical measurand (metrology), the quantity of which is estimated by the analysis employed subsequent to sampling

NOTE 1 to entry – "Analyte" (that which is analysed and quantified) can be used synonymously with chemical compound, physical parameter, mass, etc.

3.3

analytical uncertainty, measurement uncertainty (MU_{analysis})

inherent uncertainties stemming exclusively from the specific analytical method employed

NOTE 1 to entry – The analytical uncertainty MU_{analysis} reflects the difference of the analytical result from the true concentration value in the analytical aliquot – whereas the full measurement uncertainty (MU) is viewed as caused both by the Total Sampling Error (TSE) and the Total Analytical Error (TAE). TSE is the combined effects from sampling along the entire flow path from the moment the primary sample is defined and sampled, until the analytical quantification, or testing, is completed. $MU_{\text{TSE} + \text{TAE}}$ should not be confused with MU_{analysis} .

3.4

bias

see 3.37, sampling bias

3.5

comminution

preferential reduction of the top particle sizes in an aggregate material subjected to crushing (or cutting)

NOTE 1 to entry – Comminution is a technical term that describes the effect of crushing of an increment or a sample.

DS 3077:2013**3.6
composite sample**

sample made up of a number of increments (this number is termed Q)

NOTE 1 to entry – The ISO equivalent of composite sample is bulk sample. There is full conceptual consistency between the definition of composite (TOS) and bulk sample (ISO), but a composite sample shall either be representative or not, according to the characteristics of how its increments have been extracted, a distinction only made in TOS.

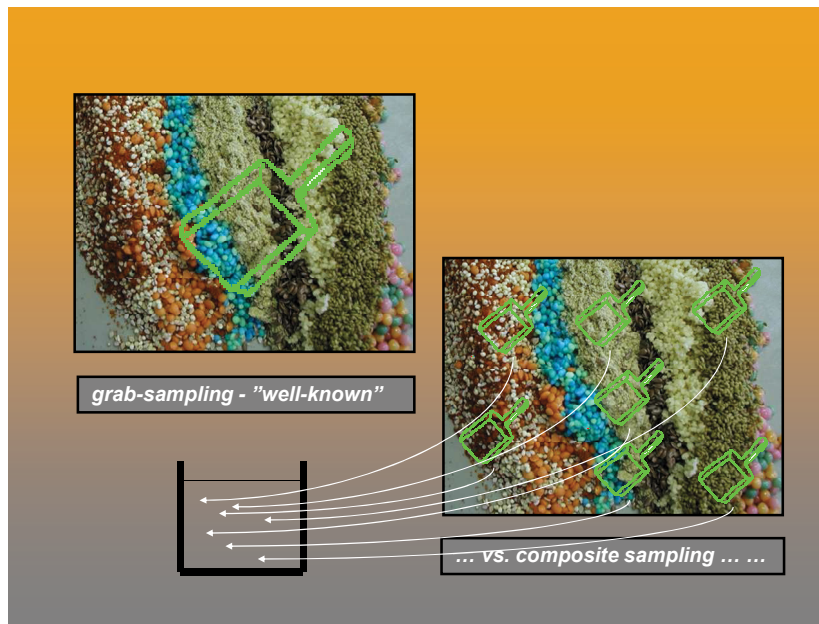
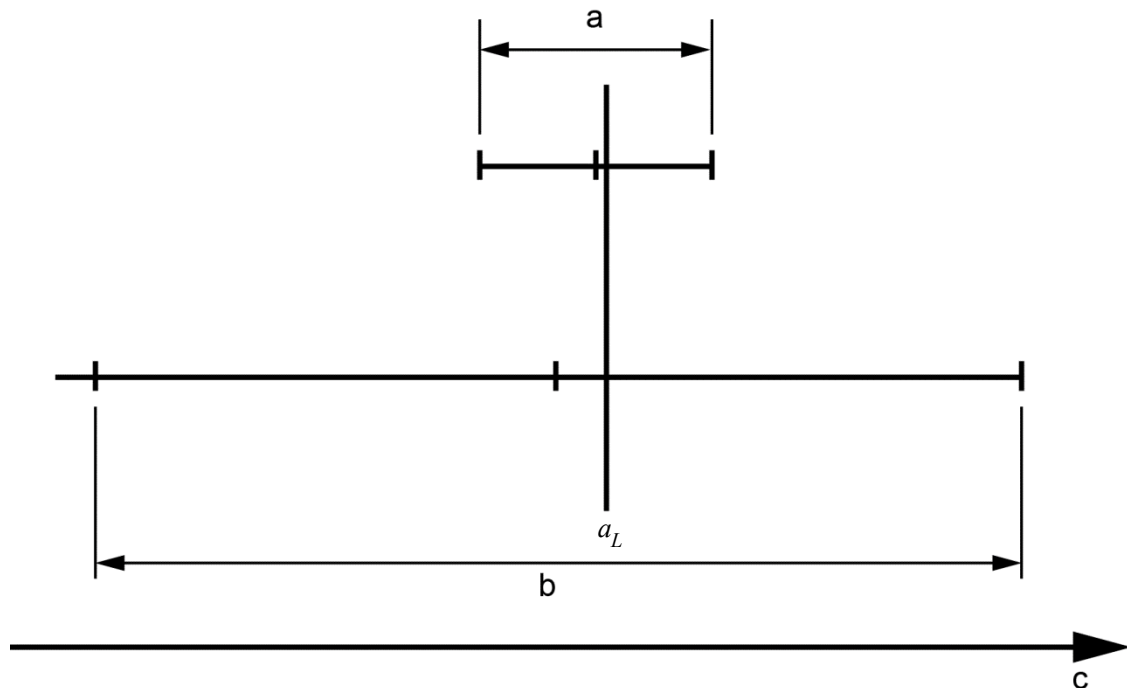


Figure 2 – Composite sampling of significantly heterogeneous material

Irrespective of scale, a composite sample (Q increments) is able to represent material/lot heterogeneity far better than a sample originating from a single extraction operation (grab sampling), see Figure 2.

NOTE 2 to entry – The primary purpose of composite sampling is to cover spatial and/or compositional heterogeneity of the lot as best possible subject to given logistical and practical conditions and a specific sampling procedure, see Figure 2. The same sampling tool volume (e.g. a scoop) can be significantly better as a provider of a composite sample than when used for grab sampling (single sample operation). In principle, and in practice, informed and competent use of composite sampling will result in a considerably reduced sampling variance (TSE) compared to grab sampling; the average will in general also lie closer to the true lot composition for composite sampling, see Figure 3 and 3.11.

NOTE 3 to entry – Composite sampling can also be used for more local purposes, i.e. for minimizing the effect of local heterogeneity (segregation or otherwise) of a single localised sample – for example when expressing or modeling concentration gradients in 1-D, 2-D or 3-D geometrical contexts, e.g. trend surface analysis.

**Key**

- a composite sampling variance
- b single grab sampling variance
- c concentration
- a_L grade

Figure 3 – Sampling variance comparison: composite sampling vs. grab sampling of significantly heterogeneous materials (see below)

Composite samples in Figure 3 each consist of Q increments respecting the Fundamental Sampling Principle, FSP (see 3.10), collected so as to display maximal spatial "coverage" of the lot (see 3.6), while each grab sample is the result of a single sampling operation at one location only. Error bars represent the empirical sampling variance obtained by 10-fold replication of each sampling procedure, RE (see 3.25).

3.7**correct sampling**

a sampling procedure for which all incorrect sampling errors have been eliminated (see 3.14 and 5.2). Fit-for-purpose is content with minimising (ISE, see 3.16) according to a given criterion

3.8**due diligence (sampling due diligence)**

operations that will ensure a correct, and hence an accurate enough sampling process, in order to minimise/eliminate the bias-generating incorrect sampling errors (ISE, see 3.16), also involving competence with respect to subsequent reduction of the correct sampling errors

NOTE 1 to entry – Sampling errors can be minimised only at the willingness to select and employ the appropriate equipment and invest in the competence-building and labor efforts needed. There is no universal sampling 'technological fix' solution that is applicable to all material types and sampling procedures.

DS 3077:2013**3.9
experimental variogram**

empirical process (or stationary 1-D lot) sampling assessment involving 60 increments (minimum) resulting in a variographic characterization (60 is a consensus value from TOS literature, with various alternatives ranging from 40 to 100). Experience with variographics is imperative. Often existing historical chronological data are available for variographic characterization, making specific experimental work unnecessary. Data mining is often a very valuable source for variographics

NOTE 1 to entry – The information in an empirical variogram can be expressed by three parameters only; range, nugget effect (Y-axis intercept) and sill, RSV 1-dim is the proper QO for process sampling.

**3.10
fundamental sampling principle
FSP**

all potential increments of a lot shall have identical, non-zero, probability and practical possibility to end up as the physically extracted increment (or sample)

NOTE 1 to entry – Areas, volumes, parts of a lot, which are not physically accessible with a given sampling procedure are not allowed, since representativity is impossible to achieve on such a restricted lot basis.

NOTE 2 to entry – ISO 11648-1 uses the designation "simple random sampling" for the same characteristic.

**3.11
grab sample**

single-increment sample resulting from a unitary sampling operation (literally "grabbing"), almost always emphasising alleged efficiency, inexpensiveness, effort-minimising desirability (see Figure 4 and 3.39)

NOTE 1 to entry – Grab sampling can result in representative samples only in the rarest of instances. If a grab sampling procedure is contemplated, it is mandatory to test and document it by one of the two heterogeneity characterization methods in this standard, RSV or variographic characterization.

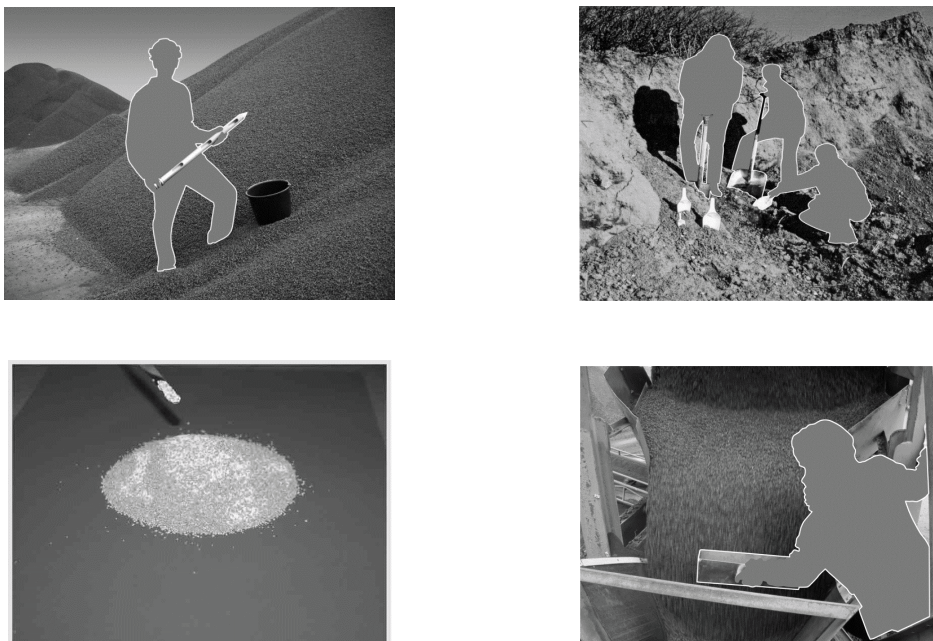


Figure 4 – Grab sampling illustration across all scales of interest (from macroscopic storage piles to powders) for both stationary and dynamic lots

The possibility for any single-increment extraction operation to achieve representativity is virtually zero since the lot cannot be covered with respect to its intrinsic heterogeneity (DH), see Figure 4.

Grab sampling constitutes the world's most misused sampling operation. All single-sample approaches for heterogeneous materials are in conflict with the Fundamental Sampling Principle, FSP (see 3.10) and militate against the necessary heterogeneity counteraction. Compare (see 3.6).

NOTE 2 to entry – Grab sampling is applicable at all sampling scales, from the field, in the industrial plant to the analytical laboratory, but completely fails to comply with the fundamental sampling principle (see 3.10). This standard mandates composite sampling for all situations in which grab sampling has not been approved by a pertinent validation, either RSV or by variographic analysis.

3.12

grade (lot), a_L

mass of the constituent present in the lot divided by the total mass of the lot, M_L

NOTE 1 to entry – What is defined as grade in TOS is often referred to as concentration in many other contexts (which can alternatively be volume based).

3.13

grade (sample), a_S, a_i

mass of the constituent present in the sample (or increment) divided by the total mass of the sample, M_S (or increment, M_i)

NOTE 1 to entry – In this respect, the definition of grade in TOS is referred to as concentration in many ISO contexts.

3.14

heterogeneity contribution, h_i

derived measure of contribution to the full lot heterogeneity arising from an individual increment (indexed i below), sample or composite sample

NOTE 1 to entry – The heterogeneity contributions of increments, or samples, can be calculated either as relative (dimensionless) or absolute values (retaining the original unit of measurement).

$$\text{Relative heterogeneity } h_i = \frac{a_i - a_L}{a_L} \frac{M_{si}}{\bar{M}_s} \quad (1a)$$

$$\text{Absolute heterogeneity: } h_i^a = (a_i - a_L) \frac{M_{si}}{\bar{M}_s} \quad (1b)$$

M_{si} is the increment/sample mass, size or mean flow-rate

\bar{M}_s is mean increment/sample mass, size or mean flow-rate increment.

3.15

increment

a partial sample unit, which specifically is intended to be combined with other increments to form a composite sample. A composite sample is made up of Q increments

NOTE 1 to entry – The designation sample vs. increment is a critical determinant with respect to subsequent use, as an increment is always supposed to be physically aggregated and mixed with other increments to make up a composite sample. TOS is the only framework, which distinguishes between two possible outcomes of a sampling process: representative samples vs. non-representative specimens (see 3.39). An individual increment can sometimes temporarily serve in the capacity of a sample in variographic analysis (6.3), but after subsequent process sampling optimisation, process samples will most often be made up of several increments.

3.16

incorrect sampling error ISE

includes the following four errors, IDE, IEE, IPE, IWE (described below)

DS 3077:2013**3.16.1*****increment delimitation error******IDE***

occurs when the boundaries of an intended increment cannot be assured to be correct and identical to those for other increments. For 1-D sampling, an increment shall be delineated by parallel boundaries and shall provide a complete cross section of the moving flux of matter, i.e. covering both transverse dimensions (width, thickness). IDE occurs when all parts of the lot do not have an exactly identical chance of becoming part of the sample. IDE is an increment delimitation problem

3.16.2***increment extraction error******IEE***

occurs when the sampling tool is selective on what is extracted and therefore is not covering all parts of the delineated increments identically; particles hitting the boundary wall of the increment tool shall be forced to obey the center-of-gravity rule (particles having their center-of-gravity inside the delimited tool boundaries shall be included in the increment) – and vice versa for particles for which the center-of-gravity falls on the outside, such particles shall be forced not to be included. IEE is an increment recovery, or extraction, problem

3.16.3***increment preparation error******IPE***

post-sampling alterations as a result of e.g. contamination, losses, alteration (physical constitution or chemical composition), human errors, ignorance, carelessness, fraud or sabotage. IPE is not strictly speaking a sampling issue, as IPE effects only occur between – or after sampling. However there is good reason to categorise IPE with the other ISE as the resulting effects also add to TSE before analysis

3.16.4***increment weighting error******IWE***

occurs when all collected increments are not proportional to the contemporary flow rate (1-dimensional) or to the thickness of a stratum (2-dimensional) at the time or place of collection

3.17***lag******LAG***

for 1-D sampling the lag is the between-increment distance (or between-sample distance); see Figure 10

3.18***lot (stationary, dynamic)***

sampling target, the specified material subjected to the sampling procedure

NOTE 1 to entry – The term lot refers to both the material itself as well as to its size, its physical and geometric features and form. Lots are here distinguished into stationary and dynamic lots. The latter is a material flux, where sampling is usually carried out at one, or more fixed sampling locations. For stationary lots, the sampler should negotiate the entire lot volume in order that the Fundamental Sampling Principle is respected.

3.19***mass reduction***

sample reduction resulting in one or more sub-samples all of which being representative with respect to the original sample

NOTE 1 to entry – All sampling operations will lead to mass reduction. However, the critical issue is whether the particular mass reduction equipment and procedures are structurally correct, i.e. able to produce accurate sub-samples (the mass reduction should also be sufficiently precise). A comprehensive benchmark survey of procedures and equipment types for mass reduction was reported by Petersen et al (2004) covering nearly every major approach found in science, technology and industry.

3.20 material class

related material types, for which new specific heterogeneity characterisation and sampling QO quantification is not necessary, e.g. related commodity types or aggregate material specifically with closely related grain size distribution

NOTE 1 to entry – In all likelihood, it is very often easier and less expensive to perform a proper heterogeneity characterization for all new materials not sampled before, given the economic and other potential consequences of relying on undocumented sampling procedures.

3.21 measurement uncertainty (MU) [metrology]

a non-negative parameter characterising the dispersion of the values attributed to a measured quantity. The uncertainty has a probabilistic basis and reflects incomplete knowledge of the quantity. All measurements are subject to uncertainty, and a measured value is only complete if it is accompanied by a statement of the associated uncertainty. MU also designates a conceptual metrological approach, codified in GUM (2008) and GUIDE (2007)

NOTE 1 to entry – Currently, a debate is unfolding in the specialist literature as to whether MU or TOS shall have priority. It is not possible to contribute meaningfully, far less provide a final resolution of this issue in this standard. TOS is primarily oriented towards empowering samplers to eliminate or reduce as much as possible the inflationary effects from unwanted and unnecessary sampling errors before MU estimation. Rather than to add to a partially confrontational debate, DS 3077 adopts a view of a constructive call for reconciliation between TOS and MU. MU is treated thoroughly in GUM (2008) and GUIDE (2007).

3.22 nugget effect

minimum variance in the variogram $V(0)$; intercept of the variogram Y-axis at lag = 0

NOTE 1 to entry – $V(0)$ is the sum of all stationary sampling as well as the total analytical error variance. The nugget effect indicates the absolute Minimum Possible Error (MPE) in any practical process sampling situation (only achievable with very frequent incremental sampling (lag = 1)).

3.23 quality objective QO

quantitative sampling variability index, usually expressed as a unit-less ratio (relative standard deviation %, for stationary lot sampling), or as a fraction of a variance ratio (also expressed as a relative %, for dynamic lot sampling). (See also 3.25, 3.27 and 3.29)

3.24 range

the lag at which the variogram becomes effectively constant (i.e. a flat variogram). Within the range, increment pairs are progressively more correlated with each other, the smaller their lag

NOTE 1 to entry – At lags beyond the range, the variance effectively becomes a constant maximum magnitude. The range constitutes the boundary for practical process sampling systems, which should use a smaller lag.

3.25 replication experiment RE

procedure for estimating RSV for a stationary lot being sampled by a specific sampling procedure

NOTE 1 to entry – A replication experiment can also be used, with proper lot coverage, for a lot which is transformed into an elongated 1-D lot. In this case the RE grades into a variographic characterisation, only depending on the number of samples taken [$Q := 10, 20, 30, 40, 50 \dots$]. Proper variographics is strongly recommended.

DS 3077:2013**3.26
representative sampling**

a multi-stage process ensuring that all sampling units (increments or samples) of the lot have an equal probability of being selected and not altered in any way that would change the analytical result, while all sampling units that do not belong to the lot shall have zero probability of being selected. Representative sampling signifies that the sampling process is both correct (accurate) and sufficiently precise (3.26). Representativity is a characteristic that can only be attributed to a sampling process; the representativity status of individual samples cannot be ascertained by any attribute pertaining to the sample in isolation. Representative samples only occur as a result of a representative sampling process

**3.27
relative sampling variation
RSV**

standard variation in relation to the average of analytical results from repeated sampling, e.g. from a replication experiment (3.24). RSV is calculated based on the analytical measurements. RSV is the proper quality objective (QO) for the replication experiment (RE)

NOTE 1 to entry – It is imperative that RSV is estimated only for structurally correct sampling procedures, as bias cannot be detected whether by RSV or any other estimation procedure. If not eliminated/minimised, a sampling bias will cause RSV to attain unnecessarily inflated, significantly varying magnitudes for repeated estimation. It is not possible to estimate the excess variability incurred.

**3.28
representativity, r**

squared sampling error, r^2 (SE), sufficient for the intended use. r^2 is defined as

$$r^2(\text{SE}) = m^2(\text{SE}) + s^2(\text{SE}) \leq r_{\text{threshold}}^2$$

where:

$m^2(\text{SE})$ is the squared sampling bias,

$s^2(\text{SE})$ is the variance of the random sampling error and

$r_{\text{threshold}}^2$ is the maximum tolerable total squared sampling error (variance) defined by the user of the analytical results.

NOTE 1 to entry – As sampling bias is difficult, if not impossible to estimate in practice, all efforts to eliminate or minimise it can only be through the use of structurally correct sampling equipment and procedures. However, the variance of random sampling errors can be easily estimated and reduced, as shown in this standard and the general TOS literature i.e. sampling precision, or sampling reproducibility (TOS).

**3.29
RSV_{1-dim}**

ratio of $V(0)$, the nugget effect, to the sill in a variogram, expressed as a percentage

NOTE 1 to entry – RSV_{1-dim} is a variance ratio whereas RSV_{0-D} is a ratio between an empirically estimated standard variation in relation to the average of properly repeated stationary sampling operations.

**3.30
sample**

a correctly extracted fraction of the lot so as to be representative, subject to a precision requirement

NOTE 1 to entry – Representative samples can only be the result of a representative sampling process. Representativity cannot be declined: either a particular sample is or is not representative (see also 3.26).

3.31
sampling error (relative sampling error)
SE

$$SE = \frac{a_s - a_L}{a_L}$$

3.32
sampling correctness principle
SCP

minimisation (preferentially full elimination) of all incorrect sampling errors (ISE, see 3.16)

3.33
sampling operation

specific physical sampling task for example as described in a sampling procedure

NOTE 1 to entry – Sampling operations are divided into two types, singular, or unitary (one only operation) or sequential multi stage operations.

3.34
sampling plan

all information pertinent to a particular sampling activity, predetermined procedures for selection, extraction, preservation, transportation and preparation of the portions sampled from a lot

[EN 14899:2005, IUPAC:1990].

3.35
sampling procedure

specific and detailed description of the operations that together comprise valid sampling when performed in accordance with defined principles and using defined equipment

3.36
sampling unit operation(s)
SUO

system of governing principles and sampling operations defining TOS' main requirements to practical sampling

[Esbensen & Minkinen (2004), Esbensen & Julius (2009)].

NOTE 1 to entry – If need be, strict division into Governing Principles (GP) and proper SUOs can be invoked, but no confusion need arise when both are collectively termed as SUOs.

NOTE 2 to entry – GPs and SUOs are recent additions to the didactics of TOS intended to provide a succinct minimum practical framework for representative sampling (see 5.2).

3.37
sampling bias

difference between the true lot concentration (or grade) a_L and the average of several sample concentrations a_S (however performed); bias is also known as the systematic error effect

3.38
sill

average variance of a variogram

NOTE 1 to entry – In the case of a sufficient number of increments/samples (50-60), the sill usually takes on the appearance of a 'ceiling' to the variogram.

DS 3077:2013**3.39
specimen**

an incorrectly extracted portion of a lot, i.e. an invalid 'sample' resulting from a biased sampling operation

NOTE 1 to entry – Specimens cannot be documented to be accurate and can therefore never be representative.

NOTE 2 to entry – Specimens are essentially unspecified lumps of matter from a lot with no specific provenance. TOS emphasizes that no theoretical analysis is possible for specimens. From a specimen it is not possible to draw valid conclusions concerning the properties of the whole lot specifically not regarding a lot a_L .

**3.40
theory of sampling
TOS**

a body of theoretical work initiated in 1950 by the French scientist Pierre Gy, who over a period of 25 years developed a complete theory of heterogeneity, sampling procedures and sampling equipment assessment (design principles, operation and maintenance requirements)

NOTE 1 to entry – TOS was further elaborated by Gy into a coherent didactic framework but also added to by later generations especially in the last two decades. Gy's personal account of TOS and its development history can be found in Esbensen & Minkkinen (2004).

NOTE 2 to entry – Pierre Gy has published over 275 papers and seven books on sampling, in later years joined by several other international sampling experts (Pitard, Bongarcon, Minkkinen, Holmes, Lyman, Smith, Carrasco).

The bibliography contains a selected range of background TOS references.

**3.41
variogram**

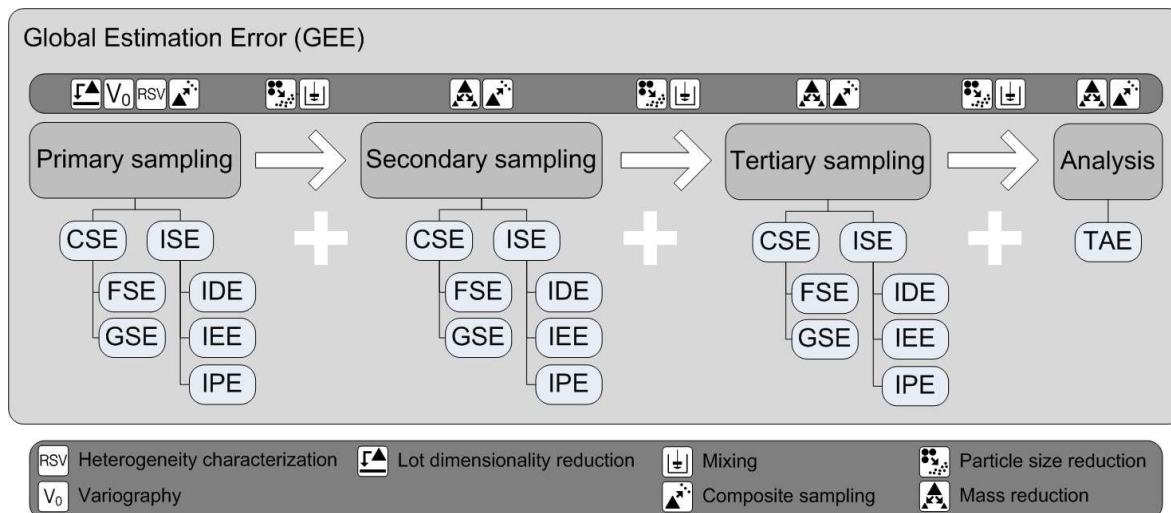
comprehensive delineation of total process variance, expressed as a function of the lag, $V(j)$

**3.42
variography**

estimation of total variance at increasing lag intervals for process sampling for both stationary as well as dynamic 1-D lots

4 TOS overview and special application domains**4.1 TOS, synoptic overview**

Figure 5 shows a didactic synopsis of all essential relationships between sampling stages, sampling errors, four sampling unit operations (SUO) and three Governing Principles (GP).



Fundamental Sampling Principle (FSP)

IDE: Increment Delineation Error

IEE: Increment Extraction Error

IPE: Increment Preparation Error

Replication experiment (RSV)

FSE: Fundamental Sampling Error

GSE: Grouping and Segregation Error

TAE: Total Analytical Error

Sampling Correctness Principle (SCP)

CSE: Correct Sampling Errors

ISE: Incorrect Sampling Errors

Figure 5 – A minimum sampling competence encompasses FSP, TOS' paradigm of sampling correctness, five sampling errors (CSE/ISE) and seven Sampling Unit Operations (SUO)

Empirical heterogeneity testing, RSV (see 3.27) is universally applicable both for the total sampling process as well as for specific sampling stages. For 1-D lots variographic characterisation apply.

Process sampling relies on variographic analysis (VA) for heterogeneity characterisation, sample mass (composite sampling) and sampling rate optimisation. There are two additional sampling errors especially related to process sampling (trend process sampling error; cyclic process sampling error), which can be brought under control relatively easily. Within the framework of this standard, sampling from either stationary or dynamic lots covers a necessary basis with which to address nearly all sampling issues (see clause 2 and the Bibliography).

4.2 Special TOS application domains

There are TOS application domains, in which sampling takes place under apparently "special conditions", some of which have been considered as justification for introducing "special sampling procedures", or as reasons why the general TOS requirements can be relaxed.

In special TOS application domains the objectives may not necessarily concern how to get an optimal estimate of the average lot composition, but serve other purposes for example related to mapping heterogeneity in a specific 1-D, 2-D or 3-D context.

Examples abound, e.g.:

- sampling natural processes (downstream rivers or along soil, or forestry transects); and
- sampling variable thickness horizons or formations (stacks, soils, layered materials).

However, for such and similar cases there is no justification for deviating from the general TOS principles. Such cases just constitute non-standard frameworks within which the principles for representative sampling should still be fully respected.

A case in point would be the Incremental Sampling Method (ISM), in which some issues (sampling plan, decision units) are indeed 2-D specific, but which do not legitimise deviations from TOS concerning primary increment sampling or mass-reduction.

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Another case is related to skewed concentration distributions, often lumped together under the term 'log-normal distributions' although often significantly more irregular in the distribution tail. In many natural sciences and industry, odd high values ('outliers') are often discarded for no specific reason other than the fact that conventional Gaussian or log-normal statistics may then better apply. However unless Poisson statistics are well understood as applied to the sampling process, this *modus operandi* will more often be fundamentally wrong than otherwise as outliers often contain essential information. All lots shall be treated individually and with utmost respect for the potential complexity involved. In the many cases in which an apparent single analyte sampling issue is in fact embedded in a multi-analyte context, it is prudent and highly advantageous to adopt a fully multivariate approach to outlier characterisation, detection and deletion; a comprehensive initiation can be found in Esbensen & Geladi (2010).

5 Requirements**5.1 General**

It is a general requirement that sampling shall be performed correctly, enforcing minimisation, or elimination of all bias-generating sampling errors (see WCSB1 Proceedings, Esbensen, K.H. & P. Minkkinen (2004)). Securing bias-minimised sampling is the primary imperative, which is termed TOS's preventive paradigm. There are many overlapping features between this standard and ISO 11648-1 and -2, but the real-world heterogeneity of the type of lots met within science, technology and industry does not in general comply with the pure statistical notion of 'sampling from a population' (of 'sampling units') without a broader understanding of the defining issues in TOS, i.e. the complementary duality between CH (compositional heterogeneity) and DH (distributional heterogeneity), incorrect vs. correct sampling errors (and their effects), the special sampling bias issues, which are essential for theoretical completeness and which are the only guarantee for full practical sampling representativity.

5.2 Correct sampling – Sampling unit operations (SUO)

Correct sampling requires that the extraction probability for all fragments (grains) or groups of fragments (increments) shall be strictly identical (non-zero), which shall be realised by the sampling procedure and the sampling equipment in use. In practical sampling the correctness imperative shall never be compromised. No concession can be allowed lest the bias-generating errors (incorrect sampling errors) remain out of control, which will invariably result in an unknown, varying sampling bias which cannot be compensated by any known means (statistical, data analytical, or other). For this reason, collection and preservation of increments shall each be structurally correct, minimising the incorrect sampling error effects IDE, IEE, IWE and IPE. This rule applies to sampling of all types of materials: grains, liquids with suspended solids, waste, soil (polluted or not), sediments, powders, high purity materials, pharmaceutical products and all other material types. The normative references and the Bibliography describe all necessary measures involved in complying with these requirements.

All representative sampling shall comply with the Governing Principles (SUO 1-3) and practical procedures (SUO 4-7) *inter alia* termed Sampling Unit Operations (SUO):

- SUO 1** Lot dimensionality transformation from stationary lots to a 1-D configuration can advantageously be performed because of the ease with which optimal process sampling can be performed on this basis (described in SUO 3).
- SUO 2** Heterogeneity characterisation (stationary lots) is carried out via a replication experiment (see 3.25), resulting in a QO in the form of the RSV [%] sampling quality index.
- SUO 3** Heterogeneity characterisation (dynamic lots: moving material streams, or elongated stationary 1-D lots). Variographic analysis (VA) performs a task similar to heterogeneity characterisation for process sampling as does RSV for stationary lots. Variographic analysis allows a much more informative characterisation of the sampling process and the heterogeneity of the lot material, and is always to be preferred. Variographic analysis is explained in 5.3. A proper RSV_{1-dim} quality objective can only be derived from a variogram.
- SUO 4** Lot or sample homogenisation by mixing (or blending) shall be conducted before or at each sampling step, as appropriate (Petersen et al. 2004). Note, however, that forceful mixing is not by itself all-pervasive, and is indeed not always an effective process, depending upon the nature of the lot. Excessive mixing can actually lead to increased segregation, especially when the lot is close to its natural minimum residual heterogeneity status. Mixing is far from an automatic guarantee for sampling success, but it is always helpful.

SUO 5 All primary sampling directed at securing an optimal estimate of a_L shall employ composite sampling (unless it has been specifically proven that acceptable sampling quality can be otherwise achieved based on e.g. grab samples or drill core sections). The only acceptable verification of a proposed grab sampling approach for primary sampling is by a replication experiment RSV [%] or by a variographic analysis (VA), the usage of which shall always be specifically justified and described.

SUO 6 Comminution (preferential particle top-size reduction) shall be applied between each sampling step as appropriate (Petersen et al. 2004).

NOTE – Comminution results in a material state with considerable smaller top particle size and a much reduced grain size dispersion. This allows for much more efficient mixing, thereby also contributing to a significantly reduced sampling variability.

SUO 7 Representative mass reduction is a critical success factor at all sampling stages. Benchmark guidelines and suggested principles for assessment of procedures and equipment are available (Petersen et al. 2004), (see clause 2 and the Bibliography).

NOTE – The full sampling-laboratory handling-analysis pathway ('from lot to aliquot') can be understood as a two-step process: i) primary sampling, followed by ii) representative mass-reduction. The latter covers all aspects of mass-reduction (sub-sampling, splitting) needed in order to produce the analytical aliquot from the primary sample, which is necessarily a multi-staged process. It is emphasised that the qualified sampler should be fully competent with respect to SUO 7. All necessary guidelines are present in the references given above.

Deviations, modification or avoidance of any GP/SUO shall be justified, described and reported in full and any modified sampling procedure shall be characterised by a pertinent QO quantification.

5.3 Quantifying empirical sampling variance

Sampling variability, sampling variance or sampling reproducibility (TOS) shall be characterised by a quantitative measure, a quality objective (QO). For all lots, empirical experiments shall be performed in order to estimate the effective level of sampling variability. For all stationary lots, a replication experiment shall be used to express the RSV [%] associated with the sampling procedure employed (see 6.2). For dynamic lots a variographic characterisation shall be conducted (see 6.3). For stationary lots transformed to dynamic lots under SUO 1, a 1-D replication experiment may alternatively be performed, in which case full disclosure (why, how) is mandatory, as this will result in a first order quantitative assessment of the total sampling and analysis error involved. This should preferentially be complemented by a proper variographic analysis as soon as possible.

The quality objectives RSV [%], or the equivalent in variographics, RSV_{1-dim} (nugget effect-to-sill ratio), express a quantitative measure of the effective material heterogeneity as manifested with the specific sampling procedure employed. All quality objectives relate to a specific interaction between lot heterogeneity and the specific sampling procedure employed. The QO will change for a different heterogeneity and/or for a different sampling procedure. It is only by characterising a lot by one (or other) specific sampling procedure that we can gain insight into the manifestations of the particular lot heterogeneity. Sampling a different lot material with an already tested procedure thus still necessitates a new QO estimation (because the heterogeneity is new, and may be significantly different) unless it can be proved that the new target resembles the same lot material, or a closely related material class (see 3.20). Changing to another sampling procedure always requires a new QO assessment.

This standard outlines necessary and sufficient criteria derived from the Theory of Sampling and two practical tools – the replication experiment and variographic analysis – to establish reliable empirical estimates of the effects of TSE and (TSE+TAE) for any sampling procedure applicable to nearly all types of materials (gases and gas-mixtures excluded). SUO 1 allows transformation of a stationary lot to a dynamic lot (or to a 1-dimensional elongated lot), upon which to perform a replication experiment (RSV analysis) instead of a full variographic analysis – but the variogram approach is always preferable. When such a proxy approach is used, it is a critical condition that the complete lot is thus transformed and that an absolute minimum of 10 single primary samples are deployed in such a fashion to cover the lot, compositionally and spatially as best possible, in a fully documentable fashion. 10 replicate sampling operations are a strict minimum, but it is strongly recommended to use a higher number.

The basic requirements for proper incremental process sampling build on identical principles as for stationary lots situations, with addition of two specific process sampling errors, as is elucidated in Gy (1996), Pitard (1993), Esbensen & Mortensen (2010). (See also clause 2 and the Bibliography).

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There is always a significant economic savings potential in recognising that both a replication experiment, and a variographic experiment, can be analysed for an unlimited number of analytes without any additional effort (if the sample mass is large enough and the analysis is not destructive). It is the same set of samples, which is sent to the analytical laboratory for determination of the series of analytes involved. Properly planned and organised experiments can thus be made relevant and valid for many analytes simultaneously.

From TOS' concept of heterogeneity, it is clear that the critical sampling conditions shall be those corresponding to the most heterogeneously distributed analyte. Accomodating the demand for this analyte guarantees that this sampling will be optimal for all other analytes as well.

5.4 Sampling competences

Individuals involved in sampling shall be competent. Sampling competences include a comprehensive understanding of the terms and basic principles in TOS, practical sampling skills, knowledge of sampling purpose, and familiarity with the matrix to be sampled. Different competences are required in different steps of a sampling procedure. Planning and performing sampling is often undertaken by more than one person; each sampling step shall be undertaken by a competent, or competently educated, person, but there shall be a unified sampling responsibility (see 5.5).

5.5 Sampling responsibility

One legal person shall be appointed as responsible for all parties involved in sampling, who shall each be competent with respect to the principles of representative sampling. This entity shall ensure an appropriate educational level and correct instructions to be distributed, interpreted and acted upon by all individuals involved in a specific sampling operation. In order to fulfil the requirements of this standard, a unified sampling responsibility shall be established across all scales, i.e. from primary sampling to production of the analytical aliquot, after which the specific analysis responsibility takes over, the latter shall be compliant with the principles delineated in Measurement Uncertainty, MU.

The legal person shall also be responsible for all documentation and quality control involved in matching the requirements specified in this standard and related background material. In cases where suitably experienced parties and agents are involved, e.g. in professional laboratories or similar, it may nevertheless be considered expedient to divide the sampling responsibility – in which case an authoritative supervising entity needs to be defined.

5.6 Documentation

All steps in the sampling process shall be documented. The following records shall be available in a relevant form:

- sampling plan;
- field observations;
- sampling report.

A sampling plan shall be designed and completed prior to undertaking any sampling process. The sampling plan shall meet all the necessary requirements for:

- correct sampling (the sampling procedure will be affected by minimal bias);
- clear formulation of sampling objectives and a priori quality objectives (QO);
- requirements arising from analysis as well as requirements for testing;
- recording of, or reference to information on all necessary safety precautions to be taken in order to protect the sampler.

The principles for preparation of a sampling plan laid out in EN 14899:2005 can be used to produce a sampling plan for any sampling or testing program.

The sampling plan shall include a clear description of the sampling procedure or shall refer to the sampling procedure appropriately. An example of a TOS-compliant sampling procedure documentation can be found in Annex A⁴⁾.

Field observations shall be recorded and documented when the sampling process is executed. Field observations include all relevant auxiliary information needed for full understanding of the performance of the practical sampling. Foreseen data collection problems, as well as unforeseen observations, events and changes in plans shall be reported in full.

A sampling report shall be completed after the sampling processes have been executed. The sampling report shall contain all information relevant to the evaluation of the results and the decision-making based upon the results.

6 Test methods

6.1 General

To follow the requirement in clause 5.2, either of the two following procedures in 6.2 or 6.3 shall apply.

6.2 Relative Sampling Variability (RSV) – the Replication Experiment

The variability of repeated sampling can be quantified by extracting and analysing a number of replicate samples. These shall specifically have the aim to cover the entire spatial geometry of the lot as best as possible, i.e. spanning the volume of the primary lot in an optimal fashion (given the circumstances), and calculating the resulting empirical variability of the resulting analytical results a_s . This procedure is termed a Replication Experiment (RE). Often a relatively small number of primary samples will suffice for a first survey, though whenever the number is as low as 10 to 20, there will always be a significant risk for not quantifying the full heterogeneity impact. It is essential that the primary sampling operations are fully realistic replications of the routine sampling procedure used, i.e. they shall not be extracted at the same general location (which would result in a local characterisation only), but instead the chosen number of replications shall each interact with the lot in such a fashion so as to optimally comply with the fundamental sampling principle⁵⁾ (see 3.10).

A replication experiment can be applied to an existing (routine) sampling procedure, which is to be evaluated – or it can be applied to an improved sampling procedure. In the latter case, the difference between the two QO furthers a quantitative measure of the effects of the improvements or modifications made of the initial sampling procedure. An example could be RE1 [87%] → RE2 [13%].

The replication experiment shall be carried out by a fixed procedure that also specifies precisely how the following sub-sampling, mass reduction and analysis are to be carried out (SUO 7). It is essential that primary sampling, as well as all sub-sampling and mass-reduction stages including sample preparation, are replicated in a identical fashion.

As neither RSV nor any other estimation procedure can detect a sampling bias with certainty (without significant, large experimental efforts, nearly always exceeding all practical and economical limits), TOS stipulates that all bias-generating errors, ISE (see 3.16), shall be eliminated or sufficiently suppressed, before application of RSV to any sampling process (sampling correctness) can be considered definitive and reliable⁵⁾.

⁴⁾ Annex A is an example of an industrial sampling procedure, which, although not TOS-compliant in every detail, is nevertheless deemed generally acceptable because of its integrated quality control RSV [%] disclosure. Note how a few minor deviations from the principles in the standard are freely and clearly disclosed. Every aspect of the performance of this sampling procedure is fully available for public insight, discussion and evaluation.

⁵⁾ Parties may occasionally wish to try to test a current sampling procedure in which the above requirement has been only partially fulfilled for whatever reason, e.g. sampling not covering the entire log volume, or using a non-standard composite procedure – or even grab sampling. The purpose of such a tentative survey could be that it is deemed worthwhile to test an existing procedure before establishing a more TOS-compliant procedure. The replication experiment will then include error effects from whatever incorrect factors involved. Even though this apparently would open the door for the possibility of avoiding (some of) the stringent requirements of this standard, there is an inherent guarantee against voluntary misuse: Should the QO for this exploratory survey exceed the acceptable threshold, the need for complete fulfilment of the requirements in this standard is now documented and therefore mandated, with no exceptions. There are good reasons to start validation by testing and existing sampling procedure: i) there is always the possibility it may turn out to fall below the pertinent QO threshold, and thus be acceptable as is; in all cases where this is not the case, modification is imperative, and cannot be negotiated. ii) A QO for the existing procedure is needed in order to quantify the effects of the improvements/modifications carried out in this procedure.

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It has been found convenient to employ a standard statistic to the results from a replication experiment. The statistical coefficient of variation, CV, is an informative measure of the relative magnitude of the standard deviation (STD) in relation to the average (X_{avr}) of a set of replicated analytical results, expressed as a percentage [%]:

$$CV = \left[\frac{STD}{X_{avr}} \right] \times 100 = RSV \text{ [%]} \quad (2)$$

RSV [%] is called the Relative Sampling Variability (or Relative Sampling Standard Deviation).

RSV [%] encompasses all sampling and analytical errors combined as manifested by a minimum 10 times replication of the entire 'field-to-aliquot' path way being assessed. RSV [%] measures the total empirical sampling variance influenced by the specific heterogeneity of the lot material, as expressed by the current sampling procedure. RSV is comprised by both the primary, secondary and tertiary sampling errors, including all errors incurred by mass reduction as well as the Total Analytical Error (TAE).

The general consensus acceptance threshold for RSV shall be 20%. RSV [%] values higher than this level signify a high sampling-plus-analysis variability with the consequence that the procedure tested shall be improved, see Figure 6. All exceptions from this requirement shall be justified and made public to ensure full transparency for all stakeholders.

It is obvious that a single universal RSV threshold that is supposed to apply to all types of materials and lots interacting with very different sampling processes is much to wish for. It violates the very nature of heterogeneity and its almost unlimited manifestations. A consensus threshold of 20% (rel.) is therefore only proposed as a recommended maximum total error – if a singular threshold for all materials is desired or if no other criterion is in effect. There is clearly a limit to the validity of a completely general threshold. A 20% threshold may be appropriate e.g. in a geological context, while a metallurgist would perhaps have to opt for 5% and a commodity trader could insist on 1%. Industrial situations will vary tremendously. It is recommended that end-users educate themselves so as to be able to decide on a possible different level (indeed also a higher level is conceivable in particular cases).

Figure 6 describes the RSV threshold(s).

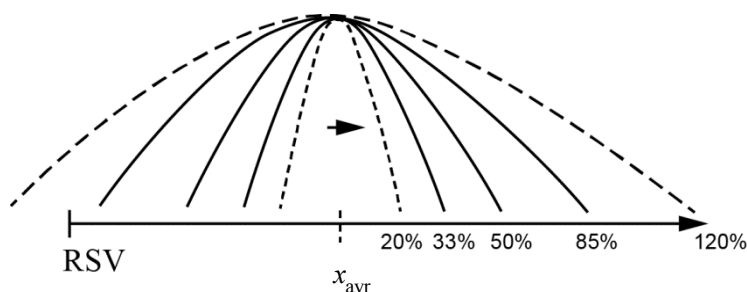


Figure 6 – Schematic illustration of replication experiment thresholds RSV e.g. 20%, 33%, 50%, 85% and 120% (see text for full explanation)

Figure 6 shows that very large relative standard deviations (higher than approx. 85%), when fitted to a standard normal distribution, give rise to apparent negative concentration values. This has no physical meaning however; these are only model fitting artifacts of no practical consequence (in fact for such large variances the proper model would be the Poisson distribution). However, the critical information for the sampler is manifested already when RSV exceeds 20%, namely that the total estimation procedure shall be improved (TOS).

Certainly, there are materials and material classes that may merit a higher (or a lower) threshold, for which the proposed RSV [20%] value is less appropriate and shall not necessarily be applied. For such cases, a material-dependent quantification, RSV [%], shall be developed, dependent upon the samplers own competence and diligence. All deviations from the general threshold shall however always be justified, described and reported in full.

Quality control of a replication experiment is strongly influenced by the degree to which a realistic compositional and spatial coverage of the entire lot has been achieved. It is fully possible to try to circumvent this issue by deliberately replicating the primary sampling based on a very restricted "local footprint" only. Users of this standard should not have such intentions. The normative references and the Bibliography present several examples on how to address many practical challenges and how to implement correct procedures in general.

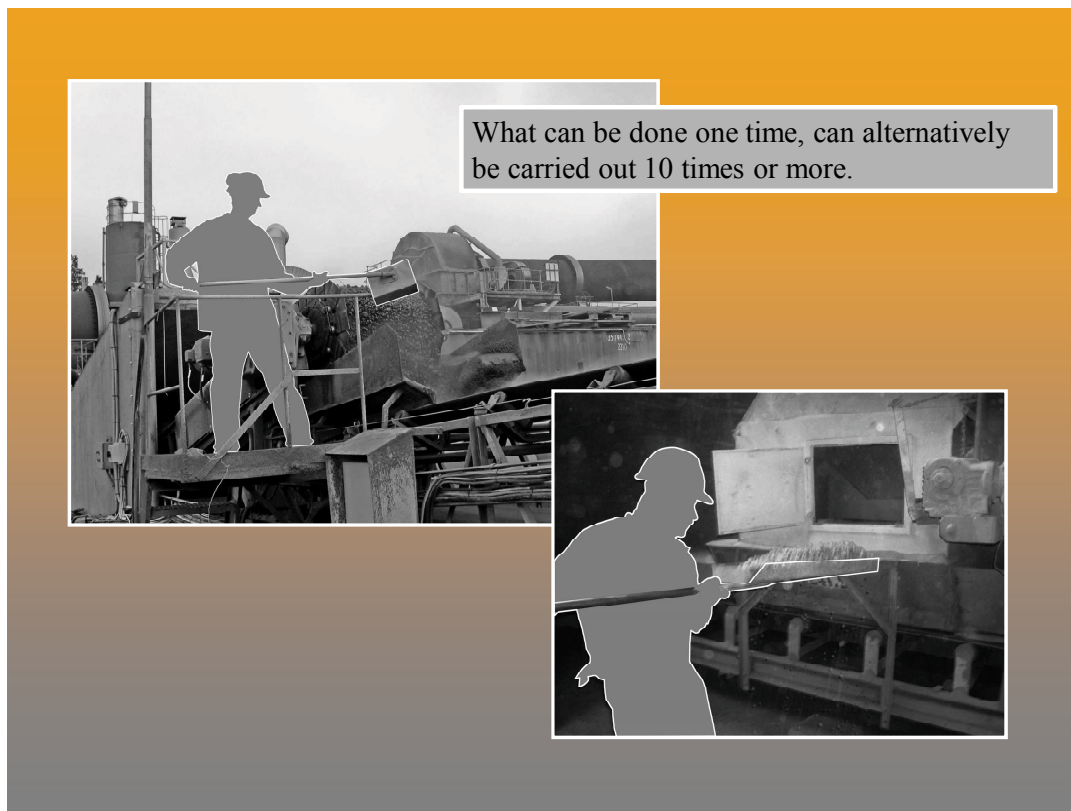


Figure 7 – Selected examples of a replication experiment (RE) setup for a dynamic lot sampling case (left illustration) and for a static case (right illustration)

Figure 7 shows typical industrial lot sampling (left: dynamic, process lot; right: stationary lot), both in the form of manual grab sampling. Uncontrolled delimitation (IDE) and extraction errors (IEE) obviously occur, leading to a significant inconstant sampling bias. Replication experiments will establish an undisputable RSV[%] basis for rejection or acceptance. The process sampling example (left) could alternatively, indeed easily, have been subjected to a proper variogram analysis instead (see 6.3).

Figure 8 shows two examples of a manual, incorrect sampling procedure (significant IDE/IEE) applied to stationary heterogeneous lot materials, for which an RSV experiment estimate higher than 20% would disqualify continued use.

NOTE – Materials from science, technology and industry manifestly show a very large range of heterogeneities. This standard only reluctantly accepts a general QO threshold (20%), and specifies that many materials and lots likely are in need of a lower threshold (less heterogeneous materials), or even higher (e.g. mineralisations, ores, wastes) levels. It is fully acceptable to establish such differing threshold levels for specific materials/lots, but each such case shall be thoroughly justified, described, validated and disclosed to all relevant parties.

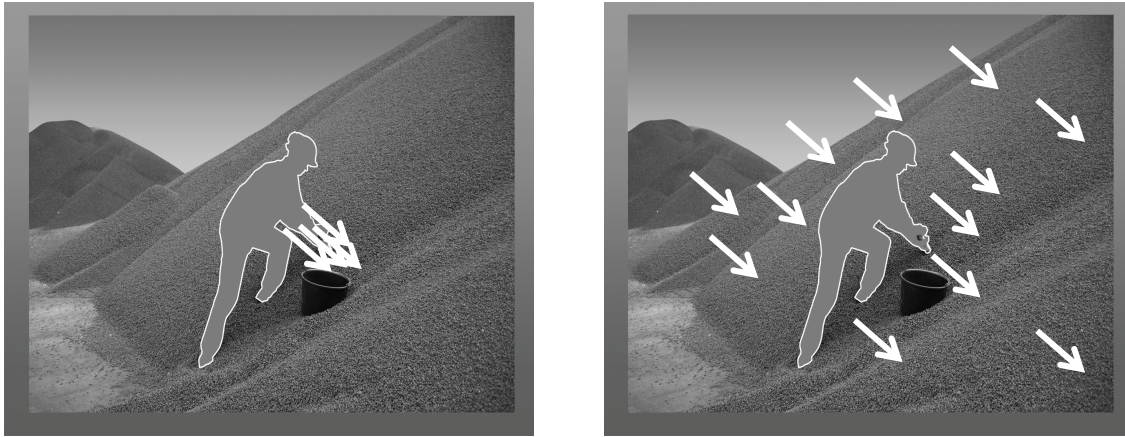


Figure 8 – Illustration of primary composite sampling showing a too narrow "local footprint" (left), and an apparently more appropriate areal coverage (right)

Note the application of composite sampling in Figure 8. While "appropriate lot coverage" cannot easily be universally defined nor quantified in a standardised form, the ultimate requirement is simpler: There shall be full adherence to the Fundamental Sampling Principle (FSP, see 3.10). It is observed that neither of the sampling plans displayed in Figure 8 comply with FSP – neither procedure is therefore acceptable, as none of them allows sampling from the interior of the lot⁶⁾.

The principle warnings from the examples in Figures 6 - 8 can be generalised to many other materials and lot types.

It is noteworthy that analytical procedures occasionally can have significantly large TAE, e.g. in the order of 10% (relative) or even more, which should be factored in when evaluating the RSV threshold limit.

While all illustrations above relate to a single analyte only, in many practical situations several analytes are quantified simultaneously. Instead of making appropriate moves regarding sampling error elimination and reduction for all these elements, it is enough to base TOS principles and requirements only on the analyte that shows the largest variability, i.e. the analyte for which the heterogeneity is the largest. By fulfilling the requirements for this analyte, a similar TOS guarantee is issued for all other analytes as well.

6.3 Dynamic lots: Variographic analysis

Variographic analysis is an integral part of process sampling, e.g. Pitard (1993), Gy (1998), Minkkinen (2004) and Esbensen & Mortensen (2010). The variogram of a one-dimensional measurement series (representing a 1-D lot) can be estimated either from historical data or from an active variographic experiment. It is often highly advantageous if a historical database exists, because this can be intelligently mined by problem-dependent variographic analysis.

For a variographic experiment (variographic characterisation), N increments are typically collected using a systematic sample selection mode. The collected increments are first treated as individual samples and are consequently analysed individually, resulting in a series of N analytical results, a_s . These results may later, after the variographic analysis, be aggregated in various fashions, when they are used to simulate various optional composite sampling schemes. In variographic analysis therefore, the terms increments and samples are sometimes used inter alia without undue confusion.

Increments (samples) shall be sampled correctly; it is imperative not to induce IDE and/or IEE sampling errors, as indicated in Figure 9, which is a principal illustration of increment outline traces across a conveyor belt (two correct delineations, and five incorrect) outlining the parallel sides demand for the cutting tool trajectory. Identical rules apply for example to crosscutting sampling of pipelines where the traces shown represent 3-D slices.

⁶⁾ If the general nature of the lot material has been previously investigated and for example found to be of acceptable heterogeneity in a given context, the "wide footprint" composite sampling illustrated in Figure 8 (right) *may* be deemed acceptable. Note however that such acceptance is not contingent on the specific sampling plan alone (superficial composite sampling), but is fully dependent on a correct and representative pre-qualification of the material involved. Any indication that the inherent lot heterogeneity is changing disqualifies further acceptance.

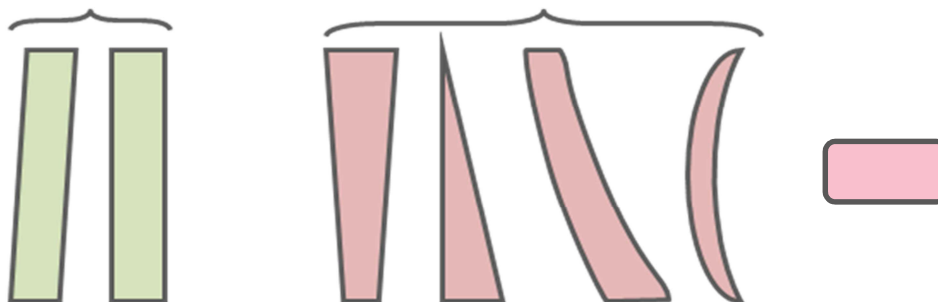


Figure 9 – Illustration of two correct, and five incorrect sampling traces across flowing streams of matter (conveyor belt, pipeline, other)

The five rightmost increments will all cause a significant IDE (the rightmost trace represents a completely inappropriate grab sample). All examples may also suffer from IEE effects, or not, pertaining to the specific sampling extraction process involved.

If and whenever possible, always mine historical data as a basis for a variographic analysis; it is astounding how often high value archival data exist, from which the equivalent of a new complete variographic experiment can be deduced, but which have never been put to use. If this option is not possible, the active variographic experiment comes to the fore. Active variographic experiments will always be needed to verify the existing procedures at appropriate times.

The cost for a variographic experiment is that associated with taking the N primary increments (samples) and analysing all of these in the laboratory; there are no other costs and the experiment need not be repeated in order to investigate the possible improvement effects from composite sampling etc. This is a powerful advantage and a very great savings potential. Variographic analysis can also answer questions of the type: "What will be the (TSE+TAE) associated with composite sampling alternatives to the single increment/full analytical costs baseline, using Q increment compositing?" Indeed the same variographic analysis provides an answer for all Q in the interval $[2,3,4,5 \dots N]$ – and will also furnish an estimate for different optional sampling rates as well (see for example Gy (1998), Pitard (2003), Minkinen (2004) and Esbensen et al (2009)). By judiciously using "too small" increment masses as the starting point (as assessed by existing knowledge), the subsequent composite sampling investigation allows a reliable determination of the "optimal sample mass" expressed as an optimal Q (composite sampling is also the ultimate best solution for 1-D sampling). If too small masses had not been chosen in the specification of the variographic experiment, sample mass optimisation would be much more difficult, if not impossible.

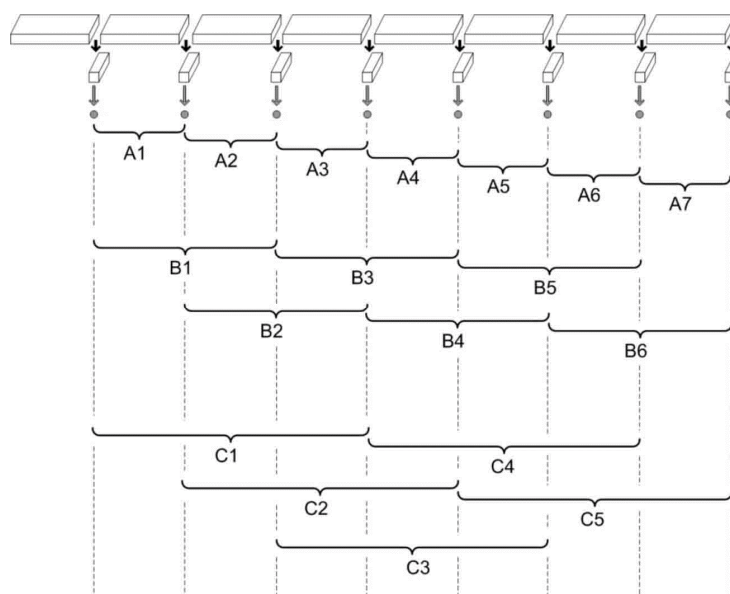


Figure 10 – Definition of increments and lags

Each increment shall be cut from the dynamic lot in a correct fashion. Subsequent variographic modelling uses an increasing "lag" definition, A: lag = 1; B: lag = 2; C: lag = 3 etc.

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The smallest lag (A-series) forms the basis for the variographic evaluation. Doubling this base-lag (B-series), or tripling (C-series) indicates how progressively larger lags can also be established, all sets covering the entire measurement series (N analyses). The lag basis covers the interval $[1, 2, \dots, N/2]$. After correct extraction, processing and analysis, increments are to be compared pair-wise in several systematic sets, each characterised by a specific lag (inter-increment distance, Figure 10), in which the three sets of paired increments/samples with lag = 1 (A), lag = 2 (B) or with lag = 3 (C) are illustrated (larger lags are also employed in the variogram calculation below). Full dots represent individual analytical results a_s . Note the systematic sampling mode, which is always used in a variographic experiment.

Irrespective of the nature of the 1-D lot heterogeneity, the practical minimum number of increments, N , needed for a valid variographic experiment shall not be smaller than 60 (experts, with considerable TOS experience may occasionally succeed with a smaller number). In general, however, it is recommended that N lies in the interval 60 – 100 samples in view of the highly informative results that can be gained (see TOS literature).

NOTE – To eliminate a weighing error (IWE), increments should be proportional to the flow-rate of the sampling target, or alternatively, if the target consists of a liquid or slurry flow, or where the analytical results are given volume based units (kg/m³, g/dm³, mol/dm³, etc.), the flow-rate at the time of sampling should be recorded. For constant flux streams, collecting constant weight increments will suffice. The collected samples are mass-reduced and subsequently analysed individually in identical fashion (SUO 7). The most reliable estimate of the true lot concentration, the effective lot mean, can be calculated as the statistically weighted mean from these analytical results:

$$a_L = \frac{\sum M_{sj} a_j}{\sum M_{sj}} \quad (3)$$

a_i is the analytical result of sample i and M_{sj} the size of the sample (or the flow-rate) at the time of sampling. Also, in the situation where the material flux is relatively constant (varying below +/- 20% rel.), a simple average calculation will often suffice.

TOS shows how it is advantageous to use heterogeneity contributions (defined below) instead of just analytical results for all types of heterogeneity characterisation.

The experimental variogram can be calculated using either relative or absolute heterogeneity contributions (3.14), for increasing sample lags from 1 to maximum of $N/2$. Equation 4 uses the relative heterogeneity contributions, which is strongly recommended.

$$V_j = \frac{1}{2(N-j)} \sum_{i=1}^{N-j} (h_{i+j} - h_i)^2, \quad j = 1, 2, \dots, \frac{N}{2} \quad (4)$$

Sill = $V(j > R)$, the sill is also designated $V(P)$.

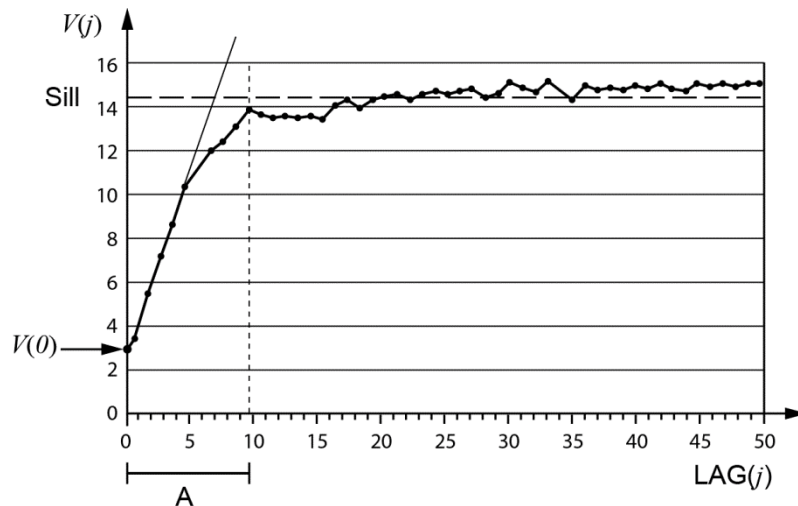
$V(0)$, also termed the 'nugget effect' (a term borrowed from geostatistics⁷⁾).

$V(0)$ contains the sum-total of all stationary sampling and analytical errors: TAE, ISE, and CSE.

$$RSV_{1dim} = [V(0) / \text{sill}] \times 100.$$

Figure 11 shows the relevant parameters in a variogram.

⁷⁾ The nugget effect is not a variance that exists physically in the lot but is a product of practical sampling, laboratory mass-reduction, to which is added the analytical error component as well (TAE). The nugget effect is unavoidable because one cannot sample two increments from the exact same volume.



Key

A range

Figure 11 – Generic experimental variogram with its three fundamental parameters, range, sill and nugget effect

The nugget effect, $V(0)$, corresponds to what is called the Minimum Possible Error variance, MPE (see 3.22), i.e. the limiting minimum sampling error possible, not achievable in practice without the ultimate costs of sampling the entire process by back-to-back increments. While thus only an ideal, MPE serves well as a yardstick with which to assess how well low-lag sampling will perform. In the example shown in Figure 11, $V(0)$ is satisfactorily low (approximately 20% of the sill value). This means that about 80% of the total variability in the data series is true process variation.

The range is the lag at which the variogram $V(j)$ becomes effectively constant ("flat"), characterised by the maximum variance, the sill (S). From the variogram, especially from the rising variogram part corresponding to the lowest lags, an impression can be obtained as to the effects of sampling with optional smaller lags than the range. This is equivalent to using a higher sampling rate. Note that the sampling variance, reflected in $V(j)$ is reduced as a function of more frequent sampling, i.e. by sampling more often it is possible to force the resulting TSE + TAE to be reduced.

Using variographic analysis effectively requires a non-trivial level of competence and experience. The present description constitutes a first initiation. Annex B is a program that performs all necessary calculations (including a brief embedded program description). A more comprehensive introduction to variographic characterisation can be found in the normative references and in the following references in the Bibliography: Gy (1998), Pitard (1993), Lyman (1986), Pitard (2009), Minkinen (2004) and Esbensen & Mortensen (2010).

The objectives of a variographic analysis are many:

- 1) characterisation of $V(0)$, the Minimum Possible Error variance (MPE), i.e. TSE+TAE at lag = 0, especially as a proportion of the total process variation (sill), $RSV\%_{1-dim}$. With just a little experience, it is easy to develop a graphical understanding of acceptable vs. unacceptable (TSE+TAE) in relation to the sill; Esbensen & Mortensen 2010, and the literature cited, gives several examples from many diverse sectors in science, technology and industry;
- 2) establishing a basis for changing the existing sampling rate, if needed;
- 3) establishing a basis for introducing alternative composite sampling schemes, e.g. using a different number of increments (Q) than in an existing procedure, which has been found wanting.

If the variographic experiment points out that the pertinent QO is not respected, inspection of the variogram suggests ways and means of how to modify the existing procedure in terms of the relative effects possible by changing the only two parameters involved, the sampling frequency and/or the number of increments composited, Q .

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From a variographic analysis it is easy to derive a relative variance measure ($RSV\%_{1\text{-dim}}$) of the magnitude of the nugget effect in relation to the sill. This is an essential QO for process sampling, equivalent to RSV for stationary lots.

The required consensus threshold level for $RSV\%_{1\text{dim}}$ is 33%⁸⁾.

If the nugget effect exceeds 33% of the sill (both measures estimated from the same variographic experiment), the pertinent sampling procedure enters a zone of a too low signal-to-noise ratio to validly monitor/characterise the true process variations, which is the prime target of any process sampling/analysis. $RSV\%_{1\text{dim}}$ is a variance proportion measure.

The special situation of a flat variogram, in which the nugget effect is equal to the sill, is characteristic of a situation in which the entire process variation is made up of the Global Estimation Error: $(GEE) = (TSE + TAE)$ for all lags (scales). Usually this precludes any meaningful monitoring or control, as there is simply no effective process information available, irrespective of the apparent (large) variations present in the series of analytical results. In such a case no special help can be gained from the process context; the lot can just as well be sampled as if it was a 0-D or a 3-D lot.

NOTE – A notable exception is the special case in which the sill is decidedly low, a case which is always easy to identify in the practical process context, e.g. because the variogram characterises a clearly stationary, stable process/product with very low variability.

It is possible to choose a different threshold than 33% in process sampling (as well as one may choose a different RSV [%] criterion for stationary lot sampling). If/when a deviation from 33% is decided upon, this standard specifies as a non-negotiable requirement that this alternative QO is made public in order for users of the samples and their analytical results to be able to make informed judgement of the validity of the procedure(s) or equipment(s) involved.

There is a very large economic savings potential in recognising that a variographic experiment can be analysed for any number of analytes in the same set of increments (60-100) sent to the analytical laboratory. Also here, it shall be the analyte exhibiting the largest heterogeneity that sets the standard regarding the necessary sampling procedure and its parameters (sampling rate, number of increments, Q , in composite samples).

7 Priority

It shall be mandatory to disclose the operative quality objectives employed and their quantitative estimates (percentage) for any specific sampling procedure applied to a specific lot material. It is also mandatory to fully report the specific reasons why deviating quantitative thresholds have optionally been decided on. There shall be no valid reasons not to accept the requirement for full disclosure.

ISO 11648-1 and -2 constitute a comprehensive basis for sampling, but are restricted to treating all sampling from a statistical point of view exclusively. This standard augments this approach with the necessary, full conceptual Theory and Practice of Sampling foundation (TOS) needed for completion. ITRC (2012) forms a solid foundation for practical 2-D sampling, also advantageously completed by applying this standard.

In case of conflicting criteria or requirements in other standards or guiding documentation, which are not sufficiently described, documented, or which are not in full compliance with TOS, this standard shall take precedence in all matters regarding representative sampling.

Failure to comply with these priorities is a breach of due diligence.


NOTE – Tracing illustrations, Figures 4, 7 and 8, are included with permission from the publisher Wiley – VCH. Illustrations originate from Esbensen & Minkkinen: "Representative Sampling – In Science, Technology and Industry", to be published.

⁸⁾ $RSV\%_{1\text{dim}}$ is a variance proportion measure. This %-level is different from that of $RSV_{0\text{-D}}$ because there are many more degrees of freedom available in a variographic setting with which to monitor, assess and evaluate the true process variation above the $V(0)$ level.

Annex A

(informative)

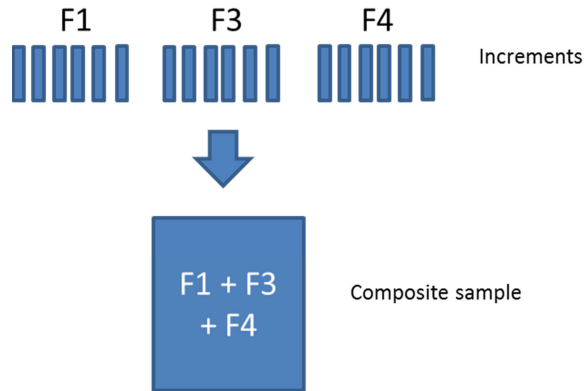
Sampling plan and sampling procedure – Example

Sampling procedure for fly ash	
Application	This procedure describes sampling of fly ash from big bags.
Comments	This procedure is prepared in collaboration with "Company X" taking into account current daily work routines and the specific production conditions for this material.
Sampling purpose	Samples taken according to this procedure constitute the basis for the mandated characterization of fly ash (see below).
References	Danish Statutory order 719:2011 – Statutory order on landfills EN 14899:2006 – Characterization of waste – Sampling of waste materials – Framework for the preparation and application of a Sampling Plan
Information about fly ash production and handling	<p>Fly ash is separated from flue gas in electrostatic filters and collected together with boiler ash and ash from the economizer in large bags, so-called big bags. For two of the furnaces (F1 and F3), fly ash is collected separately via a common bag station. For each furnace the collection system thus consists of six bags per system, (two times three bags), see illustration below. A similar facility exists for furnace F4.</p> <div style="text-align: center;">  </div> <p><i>Fly ash collection system from furnace F4.</i></p> <p>Fly ash is discharged via a closed system into big bags, which are attached directly to the outlet pipes. When a bag is full, it is closed and dumped into a container, which is removed and transported to the landfill. Approximately 8,000 tons of fly ash is produced annually.</p> <p>Since collection of fly ash is carried in a closed system the only option for sampling is to extract increments directly from the bags immediately after they are full. Sampling can be performed using a sampling probe (sampling spear), which is pushed through the top of the bag and all the way to the bottom. N.B. it is important to ensure that the material from the bottom of the bag is included in the sample in the appropriate proportion.</p>

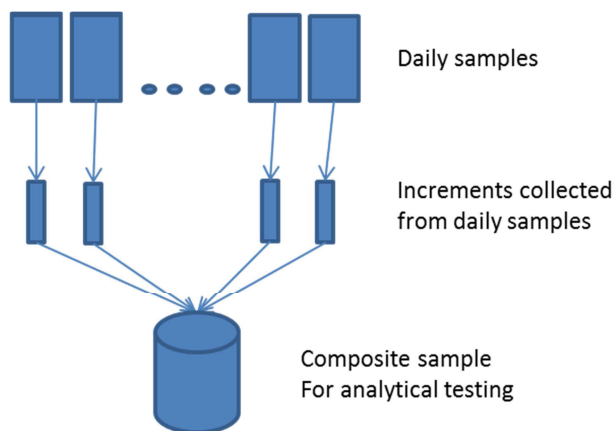
Sampling procedure for fly ash



Sampling strategy

Over ten consecutive working days (interrupted only by weekends) daily samples are extracted from big bags from all active collection stations. Sampling is carried out by means of sampling spears. Increments are mixed every day to form a one-day composite sample – following the chart below




After the sampling period is completed, increments are taken from each one-day sample and again mixed to make up a meta-composite sample. This sample, from which the ultimate analytical sample originates, is supposed to be representative of fly ash produced over the entire stipulated ten sampling days – see figure below. A ten-day composite sample is constituted in the following fashion:



Sampling procedure for fly ash	
Equipment	<p><i>Primary sampling:</i></p> <ul style="list-style-type: none"> • Sampling probe (spear) with removable plug • Plastic buckets with airtight lid for storage of one-day samples • Scales for registration of one-day sample weight <p><i>Secondary sampling:</i></p> <ul style="list-style-type: none"> • Sampling probe (plastic or plexiglas) • Scales for registration of laboratory sample weight • Plastic buckets with airtight lid for storage of laboratory sample
Primary sampling	<p>During a production day several sets of six big bags are filled with fly ash. At the end of every weekday a random container with a set of six bags is selected for sampling, which is performed immediately before the big bags are cut and separated from the collection system.</p> <p>By means of a sampling probe (sampling spear; cylindrical tube) increments are extracted from all six big bags from each furnace.</p> <p>The sampling probe is pushed vertically down through the bag all the way to the bottom of the bag. The probe is turned in both directions and gently pulled back. The plug is removed and the sample contained in the probe (approx. 150 g) is transferred to a plastic bucket.</p> <p>All samples, taken from the three furnaces on the same day, are combined to a one-day sample, which is mixed well and weighed.</p> <p>These one-day samples are stored under dry conditions until the sampling period is completed.</p> <p>The person who carries out primary sampling completes and signs (with initials) a data sheet as documentation (Appendix 1).</p> <div style="display: flex; justify-content: space-around; margin-top: 10px;">   </div>

Sampling procedure for fly ash

<p>Secondary sampling (pre-treatment and sub-sampling of laboratory sample)</p>	<p>When the ten-day sampling period is completed, increments are extracted from each one-day sample with a tubular sampling probe (see illustration below). The number of increments to be sampled shall be calculated based on how much material can be extracted with this sampling probe compared with the stipulated weight of the analytical laboratory sample.</p> <p>The laboratory samples should consist of 10 l material. The calculated number of increments is recorded. An identical number of increments (equivalent to approximately the same amount of material) shall be taken from each one-day sample.</p> <p>Increments are taken by passing the sampling probe vertically through the material and to the bottom of the bucket. The tube is closed at the top with a tightly fitting plug and gently pulled back. Loss of material from the bottom end probe must be avoided.</p> <div style="text-align: center;">  </div> <p>All increments are combined to form the laboratory sample; the weight of the analysis sample is recorded.</p> <p>The person conducting the secondary sampling completes and signs (with initials) a data sheet as documentation (Appendix 1).</p>
<p>Preservation and packaging</p>	<p>All one-day samples are stored in a dry place in tightly sealed plastic containers until the sampling period is completed. The samples are to be clearly marked with date and product name.</p> <p>The laboratory sample is labeled with date and product name as "analytical laboratory sample".</p> <p>The laboratory sample is stored in a tightly sealed plastic bucket for a maximum period of one month.</p>
<p>Transport</p>	<p>The sample / samples are sent for analysis within one month after extraction. It is to be ensured that samples are transported safely, so that packaging and content cannot be damaged or cross contaminated en route.</p>
<p>Quality assurance</p>	<p>This sampling procedure has been validated in spring 2010 by repeating the process of sampling, sub-sampling, testing and analysis 8 times (a so-called "replication experiment"). The result of the validation is shown in Appendix 2.</p>
<p>Documentation</p>	<p>The following documentation shall be recorded each time the sampling procedure is performed:</p> <ul style="list-style-type: none"> - Sampling plan (shall be prepared before sampling) - Field report (attached as appendix 1 and filled in by the person conducting the sampling) - Sampling report (shall be prepared after sampling)

**Appendix 1 – Data registration sheet for sampling of fly ash
(Field report)**

Sampling period	
Primary sampling Sampler	Primary sampling is carried out by N.N. (affiliation).
Notes	

Primary sampling					
Sampling date	Number of increments			Collective weight of one-day sample	Initials
	F1	F3	F4		

Secondary sampling	
Date	
Responsible	Secondary sampling was carried out by N.N. (affiliation)
Labelling of samples used to produce laboratory sample	
Number of increments per one-day sample	
Weight of laboratory sample	
Comments	

Appendix 2 – Validation results: Replication experiment

Procedure for sampling of fly ash product

Results from replicate testing

Sample no	P0009908-00	P0009909-00	P0009910-00	P0009911-00	P0009912-00	P0009913-00	P0009914-00	P0009915-00
Sample ID	Sample A	Sample B	Sample C	Sample D	Sample E	Sample F	Sample G	Sample H
Leaching	LS=2	LS=2	LS=2	LS=2	LS=2	LS=2	LS=2	LS=2
pH	6,58	6,79	6,84	6,81	6,86	6,79	6,88	6,65
Conductivity mS/m	15000	16000	16000	16000	16000	16000	17000	16000
Redox mV	245	236	235	235	230	232	230	234
Chloride mg/l	19516	22576	23108	19435	22577	24148	22374	22204
Fluoride mg/l	<500	<500	<500	<500	<500	<500	<500	<500
Bromide mg/l	13364	11213	11519	14094	13858	13458	17944	12948
Sulfate mg/l	122344	127968	126378	127829	129588	131315	133572	127615
NPOC mg/l	3,29	3,52	3,59	4,23	0,8	1,71	1,1	2,2
Al µg/l	114,7	92,9	81,1	63,4	80,9	65,5	80,8	97,4
As µg/l	<10	<10	<10	<10	<10	<10	<10	<10
Ba µg/l	188,2	190	184	174,2	168,7	165,4	163,8	167,4
Cr µg/l	508,5	950	1106	795,9	850,5	937,8	1050	838,9
Cd µg/l	20000	19700	23360	17410	15150	19310	12570	18170
Cu µg/l	13000	7129	6524	8075	7356	7607	8446	9498
Pb µg/l	385,4	409,3	4472	429,6	455	396,3	426,9	447,1
Ni µg/l	6722	6704	6739	6058	6678	6272	4916	6414
Mo µg/l	3253	2358	2049	1683	1877	1903	2138	2147
Mn µg/l	30000	29530	27920	26880	27570	26630	29450	27990
Fe µg/l	129	319	321	<50	35,7	308	<50	<50
V µg/l	59,1	49,2	46,4	<50	<50	<50	<50	<50
Se µg/l	112,5	142,1	154,1	105,58	127,3	124,3	125,8	122,3
Sb µg/l	94	79	100	100	74	90	83	74
Hg µg/l	36	13	9	11	13	17	22	15
Si mg/l	12,5	10	15	15	10	15	10	15
Ca mg/l	121	101	102	113	111	104	81	113
K mg/l	36320	36500	37440	36340	36010	36530	42790	35440
Na mg/l	46910	44020	45830	44620	45580	43380	47540	45180
Zn mg/l	3200	3272	3462	2363	2296	3635	2574	3095

Calculation of averages and relative standard deviations (RSV), 8 replications

		No. results	Average	Standard deviation	Relative Standard Deviation %	Minimum	Maximum
pH		8	6,8	0,11	1,6	6,6	6,9
Conductivity	mS/m	8	16000	535	3,3	15000	17000
Redox	mV	8	235	4,8	2,0	230	245
Chloride	mg/l	8	21992	1666	8	19435	24148
Fluoride	mg/l	0	< 500				
Bromide	mg/l	8	13550	2059	15	11213	17944
Sulfate	mg/l	8	128326	3349	3	122344	133572
NPOC	mg/l	8	2,6	1,3	50	0,80	4,2
Al	µg/l	8	85	17	20	63	115
As	µg/l	0	< 10				
Ba	µg/l	8	175	11	6	164	190
Cr	µg/l	8	880	184	21	509	1106
Cd	µg/l	8	18209	3273	18	12570	23360
Cu	µg/l	8	8454	2046	24	6524	13000
Pb	µg/l	8	425	25	6	385	455
Ni	µg/l	8	6313	617	10	4916	6739
Mo	µg/l	8	2176	481	22	1683	3253
Mn	µg/l	8	28246	1269	4	26630	30000
Fe	µg/l	5	223	132	59	36	321
V	µg/l	3	52	6,7	13	46	59
Zn	µg/l						
Se	µg/l	8	127	15	12	106	154
Sb	µg/l	8	87	11	12	74	100
Hg	µg/l	8	17	8,6	51	9,0	36
Si	mg/l	8	13	2,5	19	10	15
Ca	mg/l	8	106	12	11	81	121
K	mg/l	8	37171	2338	6	35440	42790
Na	mg/l	8	45383	1400	3	43380	47540
Zn	mg/l	8	2987	510	17	2296	3635

NOTE – RSV, Relative Sampling Variation, should be below 20%.

Bibliography

Standards, guidelines, reports

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NOTE – There are numerous examples of partial introduction of the principles in the Theory of Sampling in many ISO standards, in particular regarding the requirement for correct design of cutters for sampling iron ore, coal and coke, as well as copper, lead, zinc and nickel concentrates. An appreciable TOS impact can also be found for some sectors within the cement industry a.o. An illuminating review of the persistent activity for incorporation of correct sampling theory and practice into ISO sampling standards for the international trade of mineral commodities can be found in Holmes (2012) [In: WCSB5, Proceedings].

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Annex B (informative)

Variogram software (MS-Excel)

In this standard Annex B comprises an MS Excel file provided together with the electronic version.

This freeware variogram calculator is not warranted; it is for personal use only. DS assumes no responsibility for the use of this software, nor any results based hereupon. While the correctness of the variogram results has been checked internally, there is no legal guarantee for its use in any scientific, commercial or other enterprise. For such use, referral to a number of commercial variogram software packages can be found in the standard, but DS cannot recommend any specific software.

Egne notater/Notes: