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Characterization of waste — Sampling of waste materials —

Part 1: Guidance on selection and application of criteria for sampling under various conditions

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National foreword

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Charakterisierung von Abfall - Probenahme - Teil 1: Richtlinien zur Auswahl und Anwendung von Kriterien für die Probenahme unter verschiedenen Bedingungen

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Contents

Foreword

This Technical Report (CEN/TR 15310-1:2006) has been prepared by Technical Committee CEN/TC 292 “Characterization of waste”, the secretariat of which is held by NEN.

This Technical Report has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association.

This Technical Report is one of a series of five Technical Reports dealing with sampling techniques and procedures, and provides essential information and instructions for the application of the EN-standard:

EN 14899 Characterisation of Waste - Sampling of waste materials - Framework for the preparation and application of a Sampling Plan

The principal component of the EN Standard is the mandatory requirement to prepare a Sampling Plan. This EN 14899 standard can be used to:

- produce standardised sampling plans for use in regular or routine circumstances (i.e. the elaboration of daughter/derived standards dedicated to well defined sampling scenarios);
- incorporate specific sampling requirements into national legislation;
- design and develop a Sampling Plan on a case by case basis.

The Technical Reports display a range of potential approaches and tools to enable the project manager to tailor his sampling plan to a specific testing scenario (i.e. a ‘shop shelf’ approach to sampling plan development for waste testing). This approach allows flexibility in the selection of the sampling approach, sampling point, method of sampling and equipment used.

This Technical Report describes the statistical principles related to sampling, and provides methods based on these principles enabling a testing programme to be defined that will produce results sufficiently reliable for the decision-making process for which they are required.

Wastes arise in a wide variety of types (e.g. pastes, liquids, granular materials, mixes of different materials) and sampling situations (e.g. during a waste production process, stockpiles, tanks, drums). There can also be a variety of sampling objectives within each of the three broad categories (basic characterisation, compliance testing and on-site verification). Consequently the Report cannot provide definitive instructions for each and every case on the practical details of the testing programme, such as the required number of samples, the size of these samples, and whether they should be spot or composite samples. Instead, its aim is to expose the factors that influence the choice of these detailed components of the sampling exercise, and to provide statistical tools that can then be applied to determine the most appropriate testing programme for any given sampling scenario.

Introduction

Wastes are materials, which the holder discards, or intends or is required to discard, and which may be sent for final disposal, reuse or recovery. Such materials are generally heterogeneous and it will be necessary therefore to specify in the testing programme the amount of material for which the characteristics of interest need to be defined. The testing of wastes allows informed decisions to be made on how they should be treated (or not), recovered or disposed of. In order to undertake valid tests, some sampling of the waste is required.

The principal component of the standard EN 14899 is the mandatory requirement to prepare a Sampling Plan, within the framework of an overall testing programme as illustrated in Figure 1 of EN 14899:2005 and can be used to:

- produce standardised sampling plans for use in regular or routine circumstances (elaboration of daughter/derived standards dedicated to well defined sampling scenarios);
- incorporate the specific sampling requirements of European and national legislation;
- design and develop a Sampling Plan for use on a case by case basis.

The development of a Sampling Plan within this framework involves the progression through three steps or activities:

1) define the Sampling Plan;

2) take a field sample in accordance with the Sampling Plan;

3) transport the laboratory sample to the laboratory.

This Technical Report provides information to support Key Step 1 of the Sampling Plan process map and describes the selection of sampling approach that can be used in the recovery of a sample for a wide variety of waste types and arisings. Specifically this Technical Report provides information to support 4.2.7 (Select sampling approach) of the Framework Standard. Due consideration and selection of statistical criteria is of key importance in the production of a Sampling Plan as it provides the sole means of ensuring that, wherever possible, the type and number of samples taken will address a clearly identified objective and will provide results that achieve a tolerable level of reliability.

Table 1 - Main statistical steps in defining a sampling plan for a testing programme

Step	Subject
Specify the objective of the Testing Programme	
1	Specify the objective of the Testing Programme
Develop the Technical Goals from the objective	
2	Define the population to be sampled
3	Assess variability
4	Select the sampling approach
5	Identify the scale
6	Choose the required statistical approach
7	Choose the desired reliability
Determine the practical instructions	
8	Choose the sampling pattern
9	Determine the increment/ sample size
10	Determine the use of composite or individual samples
11	Determine required number of samples
Define the Sampling Plan	
12	Define the Sampling Plan

To illustrate the application of these principles, a series of 14 examples of sampling scenarios for a single waste stream are provided in Annex E.

This Technical Report should be read in conjunction with the Framework Standard for the preparation and application of a Sampling Plan as well as the other Technical Reports that contain essential information to support the Framework Standard. The full series comprises:

- EN 14899 Characterization of waste - Sampling of waste materials - Framework for the preparation and application of a Sampling Plan;
- CEN/TR 15310-1, Characterization of waste – Sampling of waste materials – Part 1: Guidance on selection and application of criteria for sampling under various conditions;
- CEN/TR 15310-2, Characterization of waste – Sampling of waste materials – Part 2: Guidance on sampling techniques;
- CEN/TR 15310-3, Characterization of waste – Sampling of waste materials – Part 3: Guidance on procedures for sub-sampling in the field;
- CEN/TR 15310-4, Characterization of waste – Sampling of waste materials – Part 4: Guidance on procedures for sample packaging, storage, preservation, transport and delivery;
- CEN/TR 15310-5, Characterization of waste – Sampling of waste materials – Part 5: Guidance on the process of defining the Sampling Plan.

The Technical Reports contain procedural options (as detailed in Figure 2 of EN 14899:2005) that can be selected to match the sampling requirements of any testing programme.

1 Scope

This Technical Report discusses the statistical principles of sampling, and provides a number of statistical tools to assist in the design of testing programmes for application to sampling under various conditions.

NOTE 1 Given the great variety of waste types, sampling situations and objectives, this Technical Report cannot provide definitive instructions that cover all scenarios. Instead, it discusses the basic statistical approach to be followed, and provides statistical tools that can be applied to determine the amount and type of sampling (e.g. number of samples and sample size) in any given situation to achieve results of adequate reliability (i.e. precision and confidence).

NOTE 2 The document provides considerable detail on current best practice, but is not exhaustive.

NOTE 3 To clarify the text, the document provides a number of worked examples.

2 Terms and definitions

For the purposes of this Technical Report, we have used or adapted the definitions of ISO 3534 Parts 1, 2 and 3 wherever possible. In a minority of cases, however, those definitions are couched in technical statistical language, which is likely to be unhelpful to the intended readership. In these instances we have either supplemented the formal definition with an additional note, or provided an alternative simpler definition.

NOTE In order to keep the list of definitions as compact as possible, some terms that are used only occasionally in the main text have been omitted. B.1 provides an additional list of definitions that are specifically relevant to the various annexes.

2.1

analytical error

collective term for the imprecision and bias associated with the analytical method

2.2

characteristic

property, which helps to identify or differentiate between items of a given population
[ISO 3534-1]

NOTE The characteristic may be either quantitative (by variables) or qualitative (by attributes).

2.3

coefficient of variation

for a non-negative characteristic the ratio of the standard deviation to the average
[ISO 3534-1]

2.4

compliance (and non-compliance)

compliance is achieved when the sample values from a monitoring programme meet a pre-defined set of criteria. Conversely, non-compliance occurs when the sample values fail to meet the pre-defined criteria

NOTE Examples of compliance criteria are:

- The estimated mean should be ≤ 20 mg/kg;
- Fewer than 3 sample values out of 20 should exceed 50 μg/l.

2.5

composite sample

two or more increments / sub-samples mixed together in appropriate proportions, either discretely or continuously (blended composite sample), from which the average value of a desired characteristic may be obtained
[ISO 11074-2]

2.6

confidence interval

interval within which a particular population parameter may be stated to lie at a specified confidence level. The bounds of the confidence interval are termed the upper and lower confidence limits

2.7

fundamental variability

inherent variability shown by a material at the smallest scale of measurement

2.8

heterogeneity

degree to which a property or a constituent is not uniformly distributed throughout a quantity of material

NOTE 1 A material may be heterogeneous with respect to one analyte or property but not with respect to another.

NOTE 2 The degree of heterogeneity is a key-determining factor in sampling error.

2.9

increment

individual portion of material collected by a single operation of a sampling device

NOTE 1 Increments may be reduced and tested individually or combined with other increments, with the resulting composite reduced in size and tested as a single unit.

NOTE 2 Increments are created by the sampling operation and are usually taken from parts of a lot separated in time or space.

2.10

judgemental sampling

samples collected using at best a partially-probabilistic procedure and at worst a non-probabilistic approach. Usually these samples are taken from a sub-population which is substantially more restrictive than the overall population.

2.11

mean (arithmetic mean)

sum of values divided by the number of values
[ISO 3534-1]

NOTE For example, the arithmetic mean of the five values 12, 4, 11, 9 and 6 is 8.4.

2.12

overall population

entire volume of material about which information is required.

NOTE 1 For example, the overall population might be the output of waste over the whole lifetime of the plant.

NOTE 2 See ‘population’.

2.13

percentile

P-percentile of a population is the value below which P% of the values in the population fall, and hence is exceeded by (100-P)% of the population.

NOTE For example, 95 % of the values in a population are less than or equal to the 95-percentile, and 5 % of the population values exceed it.

2.14

physical sampling error

error attributable to the activity of taking the sample

2.15

population

totality of items under consideration. [ISO 3534-1:1993, definition 2.3]

NOTE The population will generally be a convenient, well-defined subset of the overall population (e.g. a year's production of waste) that is believed to be typical of that wider population.

2.16

precision

closeness of agreement between independent test results obtained under stipulated conditions
[ISO 3534-1]

NOTE 1 Precision depends only on the distribution of random errors and does not relate to the true value or the specified value.

NOTE 2 The measure of precision usually is expressed in terms of imprecision and computed as a standard deviation of the test results. A lower precision is reflected by a larger standard deviation.

2.17

probabilistic sampling

sampling conducted according to the statistical principles of sampling

NOTE 1 The essential principle of probabilistic sampling is that every individual particle or item in the population has an equal chance of being sampled.

NOTE 2 Probabilistic sampling results in boundary conditions for the type of sampling equipment used, the method of sampling (where, when, how) and the minimum size of increments and (composite) samples.

2.18

probability

real number in the scale 0 to 1 attached to a random event
[ISO 3534-1]

NOTE An event with a probability close to zero is very unlikely to happen. For example, the probability of obtaining 'heads' in each of 10 consecutive spins of a coin is about 0.001. Conversely, an event with probability close to 1 is very likely to happen. For example, the event of obtaining at least one 'six' when rolling 25 dice is about 0.99.

2.19

probability distribution (of a random variable)

function giving the probability that a random variable takes any given value or belongs to a given set of values
[ISO 3534-1]

NOTE The probability distribution is a mathematical description of the relative frequencies with which different values arise in the population. It is commonly represented graphically, and can be thought of as the curve that the histogram of random sample values would tend towards as the number of samples becomes indefinitely large.

2.20

random sample

sample of n sampling units taken from a population in such a way that each of the possible combinations of n sampling units has a particular (known) probability of being taken
[ISO 3534-1]

2.21

random sampling

process of taking a random sample
[ISO 3534-1]

2.22

reliability

collective term for the degree of precision and confidence achieved by a given sampling scheme

2.23

representative

sample resulting from a sampling plan that can be expected to reflect adequately the properties of interest in the parent population
[ISO 11074-2]

2.24

representative sample

sample in which the characteristic(s) of interest is (are) present with a reliability appropriate for the purposes of the testing programme

2.25

sample

portion of material selected from a larger quantity of material. [ISO 11074-2:1998, definition 1.5]

NOTE 1 The manner of selection of the sample should be described in a sampling plan.

NOTE 2 The use of the term ‘sample’ should be supported with a preface as far as possible as it does not indicate to which step of the total sampling procedure it is related when used alone e.g. field sample, laboratory sample.

2.26

sample size

number of items or the quantity of material constituting a sample.

NOTE In statistical sampling theory, the term ‘sample size’ is commonly used to denote the *number* of samples. To lessen the risk of confusion, that usage has been avoided in this Technical Report; thus ‘sample size’ refers unambiguously to the volume or mass of any one sample.

2.27

sampling error

that part of the estimation error, which is due to the fact that only a sample of size less than the population size, is observed
[ISO 3534-1]

2.28

sampling pattern

collective term for the method of sampling to be adopted, such as random, systematic, stratified random or judgemental

2.29

scale

stated size or volume that is considered appropriate for assessing the material

NOTE 1 It follows that variations occurring in the material on any finer scale than this are deemed not to be of relevance.

NOTE 2 Annex A provides further explanation of the concept of scale.

2.30

simple random sample

sample of *n* sampling units taken from a population in such a way that all possible combinations of n sampling units have the same probability of being taken
[ISO 3534-1]

2.31

spatial variability

general term for the variability between locations in the material to be sampled

2.32

spot sampling

sample of a specified number or size taken from a specified place in a material or at a specified place and time in a stream of material and representative of its own immediate or local environment
[ISO 11074-2]

NOTE Form of sampling in which each sample is individually analysed (in contrast to composite sampling).

2.33

standard deviation

positive square root of the variance
[ISO 3534-1]

NOTE This is the most commonly used measure of variability of a data set or statistical population. For example, the standard deviation of the values 3.7, 5.5, 2.8, 9.1 and 6.0 is 2.43.

2.34

stratum/strata

strata are mutually exclusive and exhaustive parts of a population. They are identified either, because they are believed to be different from each other or for the purposes of sampling

2.35

stratified sampling

in a population which can be divided into mutually exclusive and exhaustive strata (i.e. sub-populations), sampling carried out in such a way that specified proportions of the sample are drawn from the different strata and each stratum is sampled with at least one sampling unit
[ISO 3534-1]

NOTE The objective of taking stratified samples is to obtain a more representative sample than that which might otherwise be obtained by random sampling.

2.36

sub-population

defined part of the population that will be targeted for the purposes of sampling

2.37

systematic error (or Bias)

difference between the expectation of the test results and an accepted reference value
[ISO 3534-1]

NOTE Bias is a systematic tendency for the observations in a set of samples to be displaced above or below the true or accepted value.

2.38

systematic sampling

sampling by some systematic method
[ISO 3534-1]

NOTE Examples are where samples are taken at regular intervals through time (e.g. weekly) or through space (e.g. every tenth skip).

2.39

temporal variability

general term for the variability through time

2.40

uncertainty

an estimate attached to a test result, which characterises the range of values within which the true value is asserted to lie
[ISO 3534-1]

NOTE In general, uncertainty of measurement comprises many components. Some of these may be estimated on the basis of the statistical distribution of the results of a series of measurements and can be characterised by standard deviations. Estimates of other components can only be based on experience or other information.

2.41

within-population variability

dispersion of observations or test results obtained within a population
[ISO 3534-2]

NOTE The within-population variation may be estimated from data from a single population, or by pooling the estimates for several populations, as appropriate.

3 Specify the objective of the Testing Programme

The objective of the Testing Programme consists of a general statement of overall purpose. The objective should be made clear prior to selecting a sampling strategy, as it is an essential first step towards defining the type and quality of the information that is to be obtained through sampling. A clearly defined objective is required to identify the material population that will be characterized through sampling.

NOTE 1 In most cases a Testing Programme can only have one objective. In other words, each single objective will generally result in a separate Testing Programme.

NOTE 2 Examples of possible objectives of the Testing Programme are:

– to compare the quality of the test material with quality levels defined in national or international legislation;

- to characterise the test material following a change in ownership;
- to determine the reusability of the test material;
- to determine the leachability of the test material;
- to assess the human health and / or environmental risks posed by the test material.

NOTE 3 The Landfill Directive (1999/31/EC) requires technical instruments to fulfil its role in setting European policy goals on waste disposal. The technical instruments on sampling are provided by CEN/TC 292 (WG1), which has developed the Framework Standard EN 14899 on waste sampling supported by a series of Technical Reports (see the Introduction). Examples of testing requirements relating to the Landfill Directive are:

- basic (comprehensive) characterisation, consisting of a thorough determination of the behaviour and properties of interest of the material.
- compliance testing, consisting of (periodic) testing to determine compliance with specific conditions or reference conditions e.g. legislation or contract.
- on-site verification, consisting of 'quick check' methods to establish consistency with other tests or other formulated documentation.

This Technical Report can be applied to meet the needs of the Landfill Directive but has not been written exclusively for that purpose, as it deals with the sampling of wastes and associated materials in a wider context.

NOTE 4 Sampling will not be necessary in every case for meeting the objective. For example, the objective of an on-site verification may be simply to establish the identity of the waste material received. (Is it a liquid? Is its colour blue?)

In the majority of cases, the objective is too general and non-specific for it to lead directly to the detailed instructions necessary for the Sampling Plan. It is therefore necessary to translate the objective into technical goals. These provide a more detailed specification of the sampling activity, and are sufficiently comprehensive to enable all aspects of the sampling plan to be determined - the type, size, scale and number of samples to be taken, the way they are selected from the material under investigation, and so on. The process of developing the technical goals from the objective is discussed in detail in Clause 4.

4 Develop the technical goals from the objective

4.1 General

Once the objective of the Sampling Plan has been agreed (see Clause 3), the next step is to develop the technical goals. This is a critical step, because once the technical goals have been defined, we can determine specific sampling and data analysis requirements and identify the statistical analytical tools that will provide a consistent means of assessing and interpreting testing data. Such tools ultimately provide the means of verifying whether or not the technical goals have been met.

In the process of deriving the technical goals from the objective, it is important to remain focussed on the conclusions that the sampling is intended to deliver, and their implications for the technical specification of the testing programme.

In some cases the translation from the objective to the technical goals is straightforward because details such as the type of sample to be taken, or the statistical parameter to be determined from the results, may already be laid down in national or international legislation. Otherwise, however, the project manager needs to define the technical goals in close consultation with all involved parties, as the technical goals will lead directly to the practical instructions that are given to the sampler prior to sampling. Conflicts can often arise between (a) the desired reliability and scope of the sampling, and (b) the available resources, in which case compromises will be necessary. This makes it all the more essential that the involved parties do agree on the technical goals and their implications prior to sampling.

Some technical goals can be sufficiently well defined that they can be directly implemented into the Sampling Plan (for example, the material to be sampled and the constituents to be tested), whilst

other technical goals (for example the scale and confidence level) may require further 'translation' into practical instructions to the sampler.

Define the population to be sampled	See 4.2 and CEN/TR 15310-5
Assess variability	See 4.3
Select the sampling approach	See 4.4
Select constituents to be studied	See CEN/TR 15310-5
Identify the scale	See 4.5, Annex A and CEN/TR 15310-5
Choose the required statistical parameter	See 4.6
Choose the desired reliability	See 4.7

4.2 Define the population to be sampled

4.2.1 General

The term 'population' is a statistical term for defining the total volume of material about which information is required through sampling. Specification of the population should be one of the first steps in defining the Sampling Plan.

It is important to check in the process of defining the Sampling Plan that all involved parties are talking about 'the same amount of material'.

4.2.2 Overall population

4.2.3 Population

Commonly it is impractical to sample from the overall population. Difficulties arise particularly where the overall population relates to the whole lifetime's operation of a plant. Any associated sampling programme would then need to cover broadly that same period, and it would clearly be unhelpful if the operator had to wait until nearly all the waste had been produced before being able to make an assessment of its characteristics.

It is customary, therefore, to define the 'population' as a convenient sub-set of the overall population that is believed to be typical of that wider overall population. For example, one month's ash production might be thought typical of overall incinerator performance; the contents of a lagoon on a particular date might be thought typical of the contents on any other day in the year. It is important to appreciate that an appropriate choice of population relies on *the experience and judgement of the interested parties*: it is not a statistical task.

It is also important to define the population explicitly over space and/or time; if this is not done, it is impossible to say whether a particular sampling exercise will result in representative samples.

NOTE For some sampling objectives, spatial variation may not be relevant (e.g. when sampling liquid from a pipeline at intervals through time), whilst for other objectives, temporal variation may not be relevant (e.g. when sampling from a number of heaps in a disposal site).

In defining the population for sampling it is important to consider the issue of 'scale' (see 4.5).

4.2.4 Sub-population

Cases arise where it is difficult or even impossible to sample certain parts of the population due to access restrictions. In such circumstances it is useful to define a subset of the population - termed the 'sub-population' - which restricts sampling to a more convenient region. The sub-population is therefore the specific part of the population that will be targeted for sampling, and which is thought to be sufficient to characterise the population. Sampling may therefore be carried out on either the

population or sub-population depending on the volume of, and access to, the waste under consideration.

The definition of a number of sub-populations may be useful where a large population is under investigation. These might be based on known changes in the production process or expected concentration levels. Alternatively the sub-population may be based on a characteristic of the material, such as any 'deviating parts' (e.g. white particles in a black material).

NOTE 1 A variety of terms could be used to define a sub-population according to the context, including 'lot', 'sub-population', 'drum' or 'stockpile'. Whatever terms are used, their interpretation might easily be confusing and will be highly dependent on the definition of the testing programme. For stockpile sampling, for example, the population will often be the same as the lot or sub-population to be sampled, while a sub-population would be a part of that lot. In other cases, however, a number of individual stockpiles may be related to each other - for example, through being the daily arisings from a treatment plant. The stockpiles might then be viewed collectively as the population, while an individual stockpile is the sub-population. Alternatively, it might be appropriate to define the collective of stockpiles as the overall population and each individual stockpile as a population.

NOTE 2 Given this risk of multiple interpretations, the EN and CEN/TRs in this series only use the terms 'overall population', 'population' and 'sub-population'.

4.2.5 Examples

Some examples illustrating how it is possible to define overall population, population and sub-population for various categories of material are as follows:

Example 1: Liquids

Overall population:	The total amount of liquid that passes through the slurry lagoon during a year
Population:	The total liquid held in a slurry lagoon on a particular date.
Sub-population:	The volume of liquid accessible from a bridge across part of the lagoon.

Example 2: Sludges

Overall population:	The entire contents of all sludge tankers leaving a treatment works in a year.
Population:	The entire contents of all sludge tankers leaving a treatment works in a particular week.
Sub-population:	The columns of sludge accessible from the top inspection hatches of all tankers leaving the works in a particular week.

Example 3: Powders and crystals

Population:	All air pollution control (APC) residues from an incinerator over a calendar year.
Sub-population:	All APC residues produced during four selected weeks in the year.

Example 4: Granular materials

Population:	The contents of a spoils heap over a specified area.
Sub-population:	All material within 2 metres of the perimeter of the heap.

Example 5: Granular materials

Overall population:	All bottom ash produced by an incinerator since it started incinerating waste.
Population:	All bottom ash from an incinerator over a particular month.
Sub-population:	All bottom ash produced through the month during the working day (e.g. 08:00 to 16:00).

It is important to appreciate that the resulting samples can only be representative in relation to the defined sub-population. Their relevance to the population is dependent on the validity of the assumptions made by the Project Manager. Due consideration of scale is required when defining the sub-population (see 4.5 and especially Annex A).

The Sampling Plan should contain a specified description of the population or sub-population to be sampled to avoid possible ambiguities in sample collection.

Prior to sampling the sampler should check if the material matches the detailed description of the population or sub-population as specified in the Sampling Plan.

NOTE It is suggested that the sampler takes photographs of the waste material to be sampled in order that evidence of its identity can subsequently be provided if required.

4.3 Assess variability

4.3.1 General

A key element in testing programme design is a requirement to understand the main components of variability in the population being sampled. In general, variability is a characteristic of the waste that cannot be changed without intensive manipulation of the waste. Its investigation is important because the more that is understood about the types of spatial and temporal variability affecting the material under investigation, the greater will be the opportunity for that knowledge to be exploited in designing the sampling programme.

NOTE Example 1:
suppose a preliminary sampling exercise shows that the day-to-day variation in the drums from a production process is much greater than the variation within any one day's drums. This indicates that, to characterise a week or months, it would be a waste of effort to take several samples in any one day. The most reliable result would be obtained by taking a sample from a single drum from as many different days as possible.
Example 2:
depending on the purpose of sampling, knowledge of a marked temporal cycle would give an option to (a) sample systematically over the cycle to smooth out that component of variation, or (b) target the sampling to the worst point in the cycle.

The impact of variability on the sampling exercise is heavily influenced by choice of scale - that is, the mass or volume of material that is taken into account to undertake an assessment of that material, where variations on a smaller scale than this are deemed to be unimportant. For more information see 4.5 and especially Annex A.

4.3.2 Spatial variability

4.3.2.1 General

Visualised in bulk, most materials exhibit some degree of heterogeneity. The origin of this spatial variability will often be the physically different locations from which the material has arisen. However, in other cases it may actually be due to *temporal* variations in the industrial process producing the material. The spatial variability is an inherent characteristic of the population, which will not change without manipulation of the material (e.g. by stirring a drum of settled liquid, or mixing a spoils heap).

NOTE 1 Strata are a number of sub-populations that collectively cover the population. The term sub-population is used to denote an accessible part of the population for the purposes of sampling. This implies that when only part of the population is accessible for sampling, that part is termed the sub-population.

NOTE 2 Example 1: the spatial variation shown by pollutant concentrations of a liquid in a lagoon may reflect concentration variations through time in the pollutant, coupled with imperfect mixing of the liquid in the lagoon itself. Example 2: a major source of spatial variability within a stockpile may be the substantial differences from day to day in the average contaminant concentrations in the process.

4.3.2.2 Within-stratum variability

Within-stratum variability is the term for the variation seen between samples taken from the same stratum - assuming that, in the case of sampling granular material, the sample size is sufficiently large for the effect of fundamental variability (see A.2) to be negligible. It is important to distinguish carefully between within-stratum and between-stratum variability, as their relative magnitudes have a critical bearing on how a given amount of sampling effort is best deployed.

4.3.2.3 Between-strata variability

Between-strata variability is the component of spatial variability that is introduced when there is spatial variability between different parts (strata) of the population.

NOTE 1 Examples of between-strata variation are the differences in the average concentration of a contaminant between:

- heaps of sludge in a disposal area;
- skips of bottom ash from different incinerators; and
- bags of material over a week's arisings.

NOTE 2 The distinction between within-stratum and between-strata variation is most obviously relevant when the material is in physically distinct parts. However, the concept of within-stratum variability is of equal relevance and importance to the Testing Programme design when the material arises or accumulates sequentially through time - as, for example, with material on a conveyor belt.

4.3.3 Temporal variability

4.3.3.1 General

Temporal variability can be considered as being of three main types: cyclic, 'driven', and random.

4.3.3.2 Cyclic variability

This is where the material characteristic exhibits a regular temporal pattern - for example, according to time of day, day of week, or time of year.

NOTE Example 1:
the sludge from a sewage works may show a seasonal pattern of variation because of the effect of temperature on the efficiency of the treatment process.

Example 2:
the cadmium concentrations in arisings from an industrial plant may routinely be higher on Fridays because of its regular production schedule.

4.3.3.3 'Driven' variability

This is the term given to temporal variability that is caused or 'driven' by known factors.

NOTE Bottom ash from a clinical waste incinerator may be found to have consistently different properties on those days when material received from a particular pharmaceutical company is incinerated. Or it may be consistently different on shifts following a period of plant downtime for planned maintenance.

4.3.4 Random variability

Many other factors (mostly unknown) will additionally be influencing the material characteristics through time. Random variability is most often related to a (large) number of different (small) sources. The net effect of all these appears as unaccountable or random temporal variation.

NOTE Whenever temporal variability is expected, good knowledge is necessary of the production process of the waste and its relation to the point and/or moment of sampling.

4.4 Select the sampling approach

4.4.1 General

There are two primary approaches to sampling. For the purposes of the Framework standard and this supporting TR these are termed 'probabilistic' and 'judgemental' sampling.

The use of probabilistic sampling should always be preferred where a quantifiable level of reliability is required in the results of the population being tested, because any deviation from probabilistic sampling will result in the loss of information on the reliability of the results.

4.4.2 Probabilistic sampling

The basis of probabilistic sampling is that each element within the population to be assessed has an equal chance of being selected by the sampling process. This implies that the whole population is accessible for sampling - even if, for example, it is a large stockpile. The key benefit of taking this 'statistical' approach to sampling is that the reliability of the resulting conclusions can be quantified (see 4.7.3).

The selection of appropriate sampling equipment is also important to ensure that a representative sample can be collected, for example, the entire particle size distribution for particulate materials.

NOTE 1 Probabilistic sampling can be adopted in a stepwise approach: where the results from a sampling exercise are unacceptably imprecise, additional random samples can be taken to provide an improved measure of uncertainty. However, this approach will obviously increase the testing cost.

NOTE 2 In the case of a sub-population exhibiting segregation and consisting of several wastes, it is more efficient to consider each of the different strata separately (Stratified sampling).

4.4.3 Judgemental sampling

With 'judgemental' sampling, in contrast to probabilistic sampling, samples are collected using at best a partially-probabilistic procedure, and at worst a non-probabilistic approach. The most common reason for selecting judgemental sampling is that representative sampling from the whole population is practically impossible, given the available resources in time and/or money. In addition, judgemental sampling may also be undertaken to deliberately target a specific item or point within the population (this type of sampling is commonly referred to as spot sampling).

The use of judgemental sampling will result in samples being taken from a sub-population, which is nearly always substantially more restrictive than the whole population. Within that sub-population, however, it might be feasible for the sampling to be probabilistic. This option should be adopted wherever possible, as it will mean that the results are at least representative for the part of the population sampled - though they still of course run the risk of being biased for the whole population.

NOTE 1 For example, samples might be taken at random from the top 50 cm of a stockpile, or from the fringe of a lagoon within 1 m of the banks. The advantage of doing this is that it allows statistically sound information to be generated for at least the sub-population sampled. This makes it easier to assess the possible errors involved in extrapolating to the whole population (i.e. stockpile, or lagoon), whilst also making explicit the way in which the sampling is unrepresentative. Errors should also be assessed in the light of available knowledge for the methodology adopted.

NOTE 2 The adoption of judgemental sampling at this level may therefore have severe financial and/or environmental consequences.

Given these unquantifiable uncertainties, the usefulness of the results from judgemental sampling is highly dependent on the reliability of the waste material background information - on which any expert judgement, and ultimately the Sampling Plan, is based. The limitations of judgemental sampling will therefore be especially acute for new sampling scenarios where there is an absence of relevant information or validation results.

4.5 Identify the scale

The 'scale' is a crucially important element in defining a sampling programme. It defines the minimum quantity (mass or volume) of material below which variations are judged to be unimportant. For example, if the scale is defined to be ' a drum of waste', then variations in any characteristic of the waste within the volume of a drum are declared to be of no concern. The scale is discussed more fully in Annex A.

The amount of spatial variability in the population cannot be quantified without defining the scale on which that variability occurs. For example, the variability from gram to gram of material in a sub-population is likely to be larger than the variability from kilogram to kilogram. If variations in concentration on so fine a scale as this are believed to be important, then that is the scale on which

the sampling must operate. If, conversely, concentration variations within any one kilogram of material are irrelevant, the primary aim of the sampling should be to quantify variability solely on the kilogram-to-kilogram scale. It is therefore of vital importance that the scale is stated explicitly.

NOTE When the scale of interest is 1 kg, a much higher degree of variability might be expected within the stockpile than for a scale of, for example, 5 tons. Thus, if the purpose of sampling were to test compliance with a limit, the resulting data might lead to rejection of the stockpile on the scale of 1 kg, but acceptance of the stockpile on the scale of 5 tons.

Conversely, a given scale represents the quantity or magnitude of waste on which you intend to base your measurement or that the measurement need to relate to.

It follows that when obtaining information about a waste material at the specified scale, each numerical value is a mean for the volume or mass of material at that scale.

4.6 Choose the required statistical parameter

A ‘statistical parameter’ is any numerical characteristic of a population - for example, its mean or its standard deviation. A key step in planning a testing programme is to specify the statistical parameter that is required to be estimated. It is important to do this because the choice generally has a critical bearing on both the type of sampling and the number of samples needed.

For a number of commonly used parameters, Annex B provides statistical expressions both for estimating the parameter itself, and for calculating the uncertainty associated with that estimate. The second of these is a critical piece of information, because it provides the quantitative link between the number of samples and the achievable reliability (see 4.7 and Annex C).

For estimating percentiles, as Annex B indicates, the choice of method depends on what can be assumed about the underlying ‘probability distribution’ - a statistical term used to describe the relative frequencies with which different values arise in a given population. Two probability distributions are particularly useful - the Normal and logNormal distributions. Annex B accordingly provides a brief description of these. It also introduces the binomial distribution because of its importance to the handling and interpretation of ‘presence/absence’ data.

The objective of the testing programme will guide the selection of the most appropriate statistical parameter. Three generic levels of testing are commonly distinguished:

- basic Characterisation;
- compliance testing;
- on-site verification.

NOTE 1 Other definitions might apply.

When testing is aimed at basic characterisation, the investigation is likely to require measures of (a) variability and (b) extreme behaviour of key constituents. A large number of samples may be needed to meet these requirements. However, such a sampling exercise would also be useful more widely in providing a good indication of the overall statistical distribution of those key constituents.

Depending on the statistical distribution the mean may not provide the most useful estimate of the ‘central characteristic’. For example, where the statistical distribution is positively skewed, the median (or 50-percentile; see Annex B, B 2.1.4) may be a useful estimator than the mean. This will depend on the objective of the testing programme.

When the objective is compliance testing, the choice of statistical parameter will usually have already been designated by the compliance rules defined by the regulator, as will the scale at which the material is required to comply (see Annex A). Commonly mean and percentile values are used in this type of testing.

In the case of on-site verification the investigation will focus on either the measured value in relation to a compliance level that should not be exceeded (making it a simple type of compliance testing), or simple 'presence/absence' attribute measurements.

NOTE 2 On-site verification does not necessarily require actual (analytical) measurements. It might well need only a visual inspection of the material in order to determine if it is indeed the type of material that was expected.

4.7 Choose the desired reliability

4.7.1 General

The reliability of a Testing Programme is a general term embracing three statistical concepts: 'bias', 'precision', and 'confidence'. The objective of the Testing Programme will influence the degree of reliability that is regarded as acceptable, but the final selection of reliability criteria will nearly always need to be a compromise between cost and expectation. The process of defining the Sampling Plan, may well, therefore be an iterative process.

Given the important decisions that are likely to rest on the findings of a basic characterisation exercise, it is suggested that the reliability should be as high as possible. Conversely, given the 'quick check' format envisaged for on-site verification, the achievable reliability for any one assessment will in many cases be low. However, this could be offset to some extent where a large number of similar checks are available.

4.7.2 Precision and Confidence

A unique property of probabilistic sampling (see 4.4) is that it allows an error band - known as a 'confidence interval' - to be placed around any parameter estimate. The semi-width of the confidence interval is usually known as the 'precision'. This depends on:

- the desired degree of confidence;
- the variability in the population or sub-population;
- the sampling pattern (see 5.2);
- the chosen number of samples;
- the assumed statistical probability distribution followed by the population (see Annex A).

The key benefit of being able to estimate the achievable confidence and precision associated with any proposed Testing Programme is that it provides a quantitative link between the sampling resources used and the reliability of the resulting answers.

4.7.3 Errors in the Testing Programme

- **Systematic error** (also known as bias). A Testing Programme with a systematic error is one that has a persistent tendency either to under-estimate or to over-estimate the parameter of interest. Systematic errors might easily occur when sampling takes place from a sub-population.

NOTE 1 For example, a daytime sampling programme will tend to underestimate the mean concentration of a contaminant in the incinerator ash if the most toxic materials tend to be burnt at night time.

- **Random error**. As the Testing Programme never samples more than a very small fraction of the whole population, the composition of the samples is to some degree determined by chance. Consequently the composition of the sample will never be exactly the same as the composition of the whole population. The difference between sample and population resulting from this chance process is known as the random error.

- **Statistical sampling error.** Statistical sampling error, or more commonly 'sampling error', occurs as a consequence of the fact that only part of the population is sampled. Consequently the calculated characteristic will differ from the 'true' value of the whole population - that is, the value that would have been obtained if the whole population could have been sampled. This difference is known as the sampling error. This might either be a systematic error or a random error (or a combination of both), depending on the adopted sampling procedure. For a correctly applied probabilistic sampling exercise, the sampling error will be due solely to random error.
- **Physical sampling error.** In addition to statistical sampling error, which arises as an inevitable consequence of the random sample selection process, the sampling activity may itself introduce an additional error. This can be termed 'physical sampling error', and may take the form of either systematic or random error (or a combination of both). To minimise this type of sampling error, the most appropriate sampling device for the task should be selected, and the standards laid down for its correct use adhered to.

NOTE 2 Example 1:
suppose a cross-sectional sample is taken from the entire width of a conveyor, and the scoop fails to catch all of the fines (perhaps because of unevenness of the surface). The resulting sample will tend to consistently under-represent the fines component of the material (systematic error).

Example 2:
suppose a mixed sample is taken from the end of a pipeline by collecting portions of the exit stream at regular intervals. This technique assumes that flow is constant over the whole time of sampling; thus error will be introduced if flow is in fact varying over the period. If the variations in flow are random, then the physical sampling error will be random in nature, but in most situations the resulting errors are likely to be both random and systematic.

Example 3:
suppose a 3 cm diameter auger is used when sampling a spoils heap in which particle size may be as large as 5 cm. The larger particles cannot be sampled and will therefore have no contribution to the measurements. As a consequence there will be a systematic error in the measurements.

- **Analytical error**

Analytical error is the collective term for the errors that arise during the analytical activities necessary to obtain the desired results, including the sample pre-treatment, extraction or destruction of the sample and the subsequent analysis of the extract, destruate or eluate. A reliable estimate of the random component of analytical error, and an upper limit on the possible bias, will generally be available from the laboratory through its Analytical Quality Control (AQC) procedures.

5 Determine the Practical Instructions

5.1 General

Clause 4 has discussed the steps needed to develop the objective of the Sampling Plan into a number of more detailed technical goals. The technical goals must now be translated into practical instructions that are given to the sampler prior to sampling. The practical issues that should be considered in identifying these instructions are as follows:

- choose the sampling pattern — See 5.2
- determine the minimum increment and sample size — See 5.3
- the use of composite versus individual samples — See 5.4
- determine the required number of increments and samples — See 5.5

5.2 Sampling pattern

5.2.1 General

The sampling pattern defines where, when and how the required samples are selected from the population. Three probabilistic sampling patterns and two options for judgemental sampling are illustrated in Figure 1.

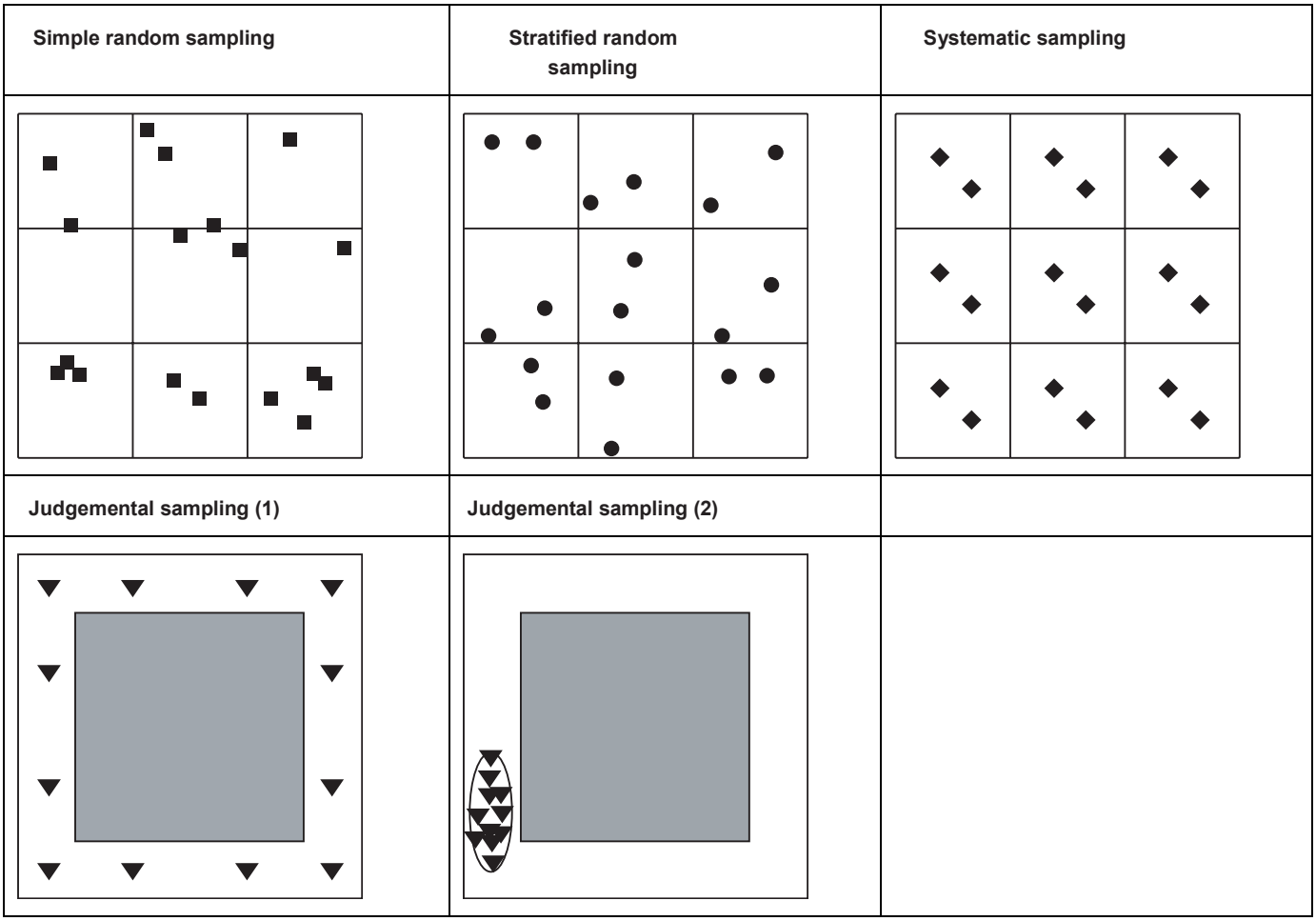


Figure 1 – Possible patterns of sampling

NOTE The figure illustrates the patterns for the context of a two-dimensional spatial area. However, the concepts apply as equally to temporal as they do to spatial components of variability.

5.2.2 Simple random sampling

With simple random sampling, every portion of the population has the same (small) chance of being selected as a sample. However, the resulting samples will not necessarily be very evenly spread across the population. Consequently other more structured forms of sampling are often preferred to simple random sampling.

5.2.3 Stratified random sampling

With stratified random sampling, specified numbers of samples are spread randomly over each of a number of strata that are predefined in the population. This preserves the advantages of random sampling (that is, every portion of the population has a known chance of being selected as a sample), whilst ensuring that each stratum is represented by a predetermined number of samples. Where the number of samples in each stratum is proportional to the proportion of the population falling into that stratum, the sampling is termed ‘self-weighting’. Often, however, there are advantages in having equal numbers of samples in each stratum, and subsequently weighting the results by the estimated stratum sizes in the population.

NOTE Suppose a tank contains a liquid that has stratified into three layers: top (20 %), middle (70 %) and bottom (10 %). Three samples taken from each layer give rise to mean concentrations of 8, 10 and 25 mg/l. The overall mean concentration would be estimated by (20×8 + 70×10 + 10×25) /100 = 11,1 mg/l. Note that the reliability of the estimated mean concentration very much depends on the accuracy of the estimated stratification.

5.2.4 Systematic sampling

With systematic sampling the samples are evenly spaced across the population, starting from a randomly chosen point (to ensure that each item in the population has an equal chance of being sampled, to fulfil the requirements of probabilistic sampling). This has obvious operational advantages. For the benefits of probabilistic sampling still to apply, however, the approach does rely on the assumption that there are no systematic components of variation within the population that 'run in step with' the chosen sampling frequency.

NOTE *Example 1:*
Suppose a sample is taken from a production process on the second Tuesday in every month. This would generate a systematic error in the results if the process happened to follow a regular weekly cycle. This could be avoided, however, by sampling on the second day in each month.

Example 2:
Suppose the plan were to sample every 20th bag of material from a conveyor belt. This would produce a systematic error in the results if the process generated a different level of contamination at a regular rate of one every five bags. The higher contamination category would either be permanently missed or be over-represented in the resulting samples, according to when the systematic programme happened to start.

Systematic sampling should therefore be applied with care when it is used in place of a random or stratified random sampling.

5.2.5 Judgemental sampling

Judgemental sampling can embrace a wide variety of sampling patterns that essentially differ in terms of how far they deviate from a truly probabilistic approach.

Option (1) in Figure 1 shows a form of judgemental sampling that is based on a probabilistic approach for part of the population. The sampled sub-population is the narrow strip around the shaded region. Within this, however, there is a systematic sampling pattern (chosen such that there is no risk of the samples running in step with any systematic pattern that may be present within the sub-population). As this is a form of probabilistic sampling, the statistical benefits associated with this approach may be exploited. That is, the methodology of Annex B can be used both to estimate the parameter of interest and also to calculate a confidence interval to quantify the uncertainty surrounding that estimate. Of course these calculations are only valid for the sampled sub-population; the wider relevance of the sampling results depends entirely on whether or not this sub-population is representative of the whole population.

In contrast, the pattern in Option (2) is fully judgemental. It provides no information about the waste except in the immediate vicinity of the samples, and so nothing can reliably be inferred about the quality of the sub-population. Conversely in some situations judgemental sampling can be the most appropriate form of sampling. For example, when the purpose of sampling is simply to investigate and estimate the characteristics of an atypical material that is unexpectedly present in the population.

5.3 Determine the increment and sample size (mass / volume)

5.3.1 General

An increment is the amount of material (mass or volume) that is obtained through one single sampling action. It is not analysed as an individual unit, but is combined with other increments to form a composite sample. Conversely a sample is an increment that does get analysed individually.

The degree to which we have to take account of the increment and sample size will very much depend on the type of waste material sampled. The minimum increment size is governed by the need for the sampling device to accommodate all particle sizes. Thus it has particular consequences for the sampling of particulate materials. In contrast, there is no practical requirement for a minimum increment size in the sampling of liquids, where the particle size goes down to the molecular scale.

A sample should be sufficiently large in order to minimise or exclude errors caused by the fundamental variability of the material that is determined by the differences between individual particles.

The terms fundamental variability (see A.2) and heterogeneity due to 'clustering' should not be confused. The latter relates to the preferential presence of a specific type of waste to be in a specific part of the population, and can be dealt with by the sampling pattern (see 5.2). Fundamental variability, however, should be overcome by putting a demand on the sample size and hence the number of particles in a sample.

The following clauses provide information on the determination of minimum increment and sample size for a range of material types.

5.3.2 Liquids

As previously stated, the minimum increment and sample size have no specific relevance to the Sampling Plan design for liquids as the potential differences are at a molecular scale when compared to the size of the samples. When taking composite samples, the sample size will be governed by the number of increments and the increment size. The increment size itself will be determined by the dimensions of the sampling equipment.

5.3.3 Powders and sludges

Powders and sludges are basically particulate materials with a (very) small particle size; sludges also contain a substantial amount of liquid. Provided the sample device allows the entry of all particles present in the material being sampled there are no additional requirements for the minimum increment size.

Similarly, given the small size of the particles in these types of material the differences between individual particles will not have a major affect on the characteristics of a sample, as in practice, the sample will be large enough to consist of a (very) high number of particles. There are therefore no practical requirements for the minimum sample size.

The sample size will therefore be governed by the quantity of material required by the laboratory for analysis, whilst the dimensions of the sampling device will determine the increment size. As with liquids, the size of any composite samples will primarily depend on the number of increments and the increment size.

NOTE Although the distinction between a powder and a granular material is not always obvious, the consequences on the minimum increment and sample size are potentially great. Care should be taken, therefore, that the aperture of the sampling device is suitable for the particle size distribution in the material to be sampled.

5.3.4 Particulate / granular materials

Where samples are to be taken from a particulate or granular material, account shall be taken of the *minimum* increment size. The size of the opening of the sampling device should be large enough to allow the entry of all particles present in the material. The aperture of the sampling device should also be large enough to allow the simultaneous entry of all particles within the material. In practice this means that the device opening should be at least three times the diameter of the largest particles. For a three dimensional sampling device the volume of the increment should be equal to $(3D)^3 = 27\ d^3$. For practical reasons, the diameter of the largest particles can be substituted by the size of the (estimated) 95-percentile of the particle size distribution.

More details on the minimum increment size are provided in D.1.2.

For particulate or granular materials the composition of individual particles could have a substantial influence on the composition of the sample, and the minimum sample size must be large enough to compensate for this. This is particularly important when the contaminant or characteristic of interest constitutes only a small proportion of the material. D.1.3. provides an expression for calculating the minimum sample size (by mass).

NOTE It is assumed that, in characterising the waste, we are interested not in the composition of the individual particles, but in the average composition of the waste (at the specified scale). To measure that average composition the sample should contain a sufficient number of particles to ensure that the effect of any individual particle within the sample does not have a disproportionate effect on the total composition of the sample.

The actual size of the increments and samples will depend not only on the minimum increment and sample size but also on:

– the quantity of material required by the laboratory for analysis;

– the number of increments in a composite sample (when increments are taken);

– the relation between the mass of the minimum increment size and the minimum sample size (in relation to the number of increments in a composite sample).

5.4 The use of composite versus individual samples

The objective of the Testing Programme, and in particular the choice of statistical parameter, will dictate whether individual or composite samples will generate the more appropriate type of data.

NOTE 1 There is an important distinction between an *increment* - which forms a part of a *composite sample* - and a *sample*, which is produced by a single sampling operation.

A number of basic scenarios are envisaged:

– When an approximate indication of the quality of a material is sufficient to meet the testing objective, as for example with on-site verification, this could be satisfied by the collection of one sample or at the most a small number of samples. In this example the costs of sampling and analysis would be low;

– Conversely a substantial number of *increments* should be taken if a reliable estimate of *mean* quality is required for one or a number of composite samples. Such an approach might provide a satisfactory approach for compliance testing (where that the compliance value is relevant to a mean concentration). In this example the cost of sampling could be relatively high, but costs of analysis would be low.

NOTE 2 Although the use of composite samples based on a (relatively) large number of increments is an attractive option for obtaining a good estimate of the mean concentration without substantial analysis costs, chemical or physical restrains to adding increments might need to be taken into account, as for example where the quantification of volatile components is of importance.

– When a substantial number of *samples* are taken in order to estimate a reliable estimate of a specific quality of the material and also provide information on the degree of heterogeneity within the material - as for example in basic characterisation - the costs of both sampling and analyses will be high.

5.5 Determine the required number of increments and samples

The required numbers of increments and samples should be determined using the methodology set out in Annex C.

6 Define the Sampling Plan

The previous clauses of this Technical Report all contribute to the definition of the Sampling Plan as specified in EN 14899. The various choices and decisions that have been made using the principles outlined in these clauses can now be drawn together to complete the "Sampling Methodology" section of the Sampling Plan as detailed in the example in Table A.1, Annex A of the Framework Standard, thereby developing a situation-specific Sampling Plan. In many cases an iterative process will be needed in reaching the finally agreed version of the Sampling Plan. This will ensure that a satisfactory compromise is reached between the objective as originally desired, and the objective that is practically achievable for the available resources in the light of any practical constraints of access and sampling.

The process steps that contribute to the definition of the Sampling Plan as specified in EN 14899 are:

Specify the objective of the Testing Programme **(3)**

- specify the objective of the Testing Programme (3)

Develop the Technical Goals from the objective **(4)**

- define the population to be sampled (4.2)
- assess variability (4.3)
- select the sampling approach (4.4)
- identify the scale (4.5)
- choose the required statistical approach (4.6)
- choose the desired reliability (4.7)

Determine the practical instructions **(5)**

- choose the sampling pattern (5.2)
- determine the increment/ sample size (5.3)
- determine the use of composite or individual samples (5.4)
- determine required number of samples (5.5)

Define the Sampling Plan **(6)**

- define the Sampling Plan (6)

NOTE Annex E provides a number of illustrative examples laid out in a standard tabular format. The examples cover three generic levels of sampling (basic characterisation, compliance testing and on-site verification), and include both probabilistic and judgemental sampling.

Annex A

The scale

A.1 Scale

NOTE This text is also part of CEN/TR 15310-5.

Scale is one of the essential issues of sampling. The scale defines the volume or mass of waste material that a sample directly represents. This implies that when the assessment of the waste is needed for example on one cubic metre, the sampling results should provide information on a cubic metre scale. Thus the analytical results should be representative for a cubic metre of waste.

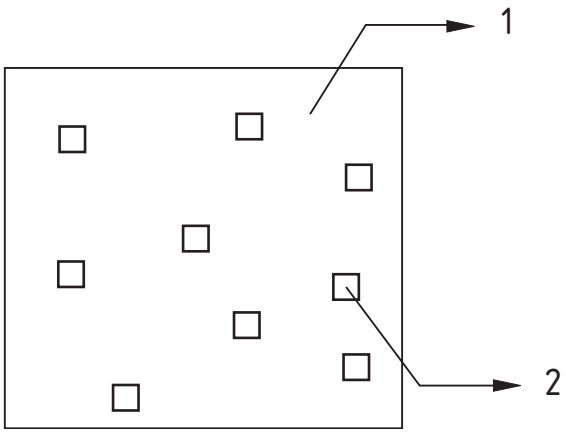
Depending on the objective of the testing programme, the scale of sampling may be equal to the size of individual particles of the waste (for particulate waste materials), the size of the sub-population or even the whole population.

Scale can also be defined in terms of time: if the population is the total amount of waste produced in one year, the scale may be one year (the whole population) but also one month, week or day, depending in the objective of the testing programme.

Defining the scale is important, as heterogeneity is a scale dependent characteristic. Let's assume a particulate waste material that consists of small particles that only vary in colour. The particles in the waste are fully mixed. In a series of samples, each with the size of an individual particle, each sample will have a different colour. Therefore the observed heterogeneity in colour between these samples will be high. However, the degree of heterogeneity on a scale of for example 1 kilogram, consisting of several thousands of particles, will be low. Each of these samples will have approximately the same mix of colours, and – looking from some distance (thus really on the scale of 1 kilogram) – the samples will have the same mixed colour. Thus the observed heterogeneity will now be low.

As a consequence of the direct relation between scale and heterogeneity, sampling results are only valid for the scale that is equal to the scale of sampling or higher scales. In general, the degree of heterogeneity will be higher for a smaller scale of sampling and will be lower for a larger scale of sampling.

Three specific examples for which the scale is defined are as follows:



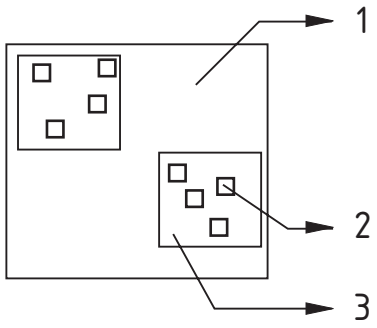
Key
1 Population 2.000 ton
2 Increment 200 gram (50 increments in a composite sample of 10 kg)

Figure A.1 – Scale situation 1

Situation 1 describes a population of 2.000 tons from which randomly 50 increments are taken. The resulting composite sample is 10 kg.

Assuming that the composite sample resulting from these 50 increments represents a good estimate of the mean concentration (but not of the variability) of the whole population, **the scale for the composite sample** in this example **is 2.000 tons**.

Note that the variability of the population (on the scale of the increments) is fully incorporated in the composite sample; the sampling method will however provide no information on the variability.

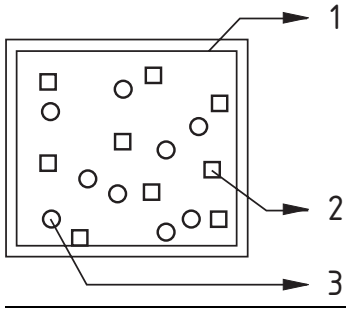


Key
1 Population 2.000 ton
2 Increment 200 gram (50 increments in a composite sample of 10 kg)
3 sub-population 50 ton

Figure A.2 – Scale situation 2

Situation 2 describes a population of 2.000 tons. Within this population – perhaps only for the purpose of sampling – sub-populations are defined of 50 tons each. From each sub-population 50 increments are taken. The resulting composite samples are 10 kg, each representing a sub-population.

The mass represented by each composite sample is now the mass of the individual sub-populations; thus 50 tons. **The scale for each composite sample** in this example **is 50 tons**. The mean value of all composite samples yields an estimate of the mean concentration of the whole population of 2.000 tons and the variability within the whole population is estimated on a scale of 50 tons.



Key
1 Population 2.000 ton
2 Increment 200 gram (50 increments in a composite sample of 10 kg)
3 Increment 200 gram (50 increments in a composite sample of 10 kg)

Figure A.3 – Scale situation 3

Situation 3 describes a population of 2.000 tons. More than one composite sample is taken. However, each composite sample (existing of 50 increments) is obtained by taking random

increments throughout the whole population. The mass represented by each composite sample is now equal to the mass of the whole population; thus 2.000 tons.

The scale for each composite sample in this example **is 2.000 tons**. The mean value of all composite samples yields an estimate of the mean concentration and the variability of the whole population of 2.000 tons is estimated on a scale of 200 grams (the mass of the increments).

The following example illustrates the effects of different definitions of the scale of sampling. Depending on the objective of the testing programme, the involved parties must make a choice.

Consider the three sub-populations as shown in Table A.1. Each sub-population consists of thirteen individual parts that have a 'quality' that is symbolised by a number between 0 and 99. Heterogeneity is quantified by the coefficient of variation: a high coefficient of variation indicates a high heterogeneity.

When the scale of sampling is equal to the size of the sub-population, the sampling result will only be an estimate of the mean concentration for each sub-population. Comparing the sub-populations in Table A.1 sub-population 1 and 2 are comparable while sub-population 3 has a higher mean.

When the scale of sampling is equal to the individual parts within each sub-population, we obtain not only an estimate for the mean concentration of the sub-population, but also an estimate for the heterogeneity within that sub-population. Comparing the sub-populations in Table A.1 now still gives the same result for the mean of the whole sub-population, but additionally we discover that sub-population 2 has a higher degree of variability than sub-populations 1 and 3.

Table A.1 – Example of three different sub-populations, characterised on the individual samples, the mean and coefficient of variation (CV). A high CV indicates a heterogeneous sample.

	Sub-pop. 1	Sub-pop. 2	Sub-pop. 3	
	20	15	32	
	30	14	36	
	20	22	3	
	30	72	37	
	40	9	38	
	20	23	36	
	30	64	37	
	30	46	30	
	40	5	40	
	20	16	41	
	10	2	17	
	20	17	39	
	30	35	36	
				Population
Mean	26,2	26,2	32,5	28,3
Coefficient of variation	33,3%	84,2%	33,2%	

Finally, when the scale of sampling is equal to the total population we obtain only an estimate of the mean for the whole population.

Different choices can now be made on the scale of sampling:

The scale of sampling is equal to the scale of the individual parts. It is not possible to define a smaller scale of sampling. The result of this definition of the scale is that information on the heterogeneity within the sub-populations can be obtained by calculating (for example) the coefficient of variation. Additionally, the heterogeneity between the sub-populations and within the population can be calculated. In this approach, the presumptions that led to identification of the sub-population

as a relatively homogeneous part of the population can be verified. For example, it may be argued that sub-population 2 in Table A.1 is so heterogeneous that at least a part of sub-population 2 will not comply with certain quality standards, although the mean value is within the quality range. Many sub-populations of high heterogeneity may lead to a re-evaluation of the Sampling Plan. Important disadvantage are the costs for measuring the individual parts, in this case thirteen per sub-population[1].

The scale of sampling is equal to the scale of the sub-populations. Therefore no information on individual parts within a sub-population is gathered. Characterisation of the sub-population is done by means of a composite sample per sub-population in which more than one of the individual items is put together prior to analysis. If this composite sample is taken and analysed correctly, the result of the composite sample will be a good estimate of the true mean of the sub-population. An important advantage of this approach is the low costs for measuring. Important disadvantage is the assumption that a composite sample can be obtained without a considerable sampling error. The analysis of a composite sample might pose problems as the amount of material in the sample will be (much) larger than the amount of material needed for the analysis and thus proper sample pre-treatment is necessary to obtain a representative analytical sample from a – potentially – highly heterogeneous composite sample. Additionally, there will be no information available on the heterogeneity within a sub-population.

The scale of sampling is equal to the scale of the population. In the example (Table A.1) the population is defined as the combination of the three sub-populations. Individual parts are gathered from the involved sub-populations and put together in a composite sample. Now there will be no information available on a smaller scale than the scale of the population. An important advantage are the (very) low costs for measuring, while, as long as it is technically possible to mix a large number of these parts, the result of the composite sample will still be representative for the true mean of the total population. But the population has to be treated as one entity. In case of a heterogeneous population (for example sub-population 2 in Table A.1) sampling on the scale of sub-populations or individual parts would have given the involved parties information that may have led to different choices for the destination of sub-populations of different quality.

Given the relation between scale and the encountered degree of heterogeneity, the applied scale of sampling might determine if a waste is considered homogeneous (i.e. there is little variation between individual sample results) or heterogeneous (i.e. high variation between sample results).

The type of information that is desired, the possible destination, the financial means available and the technical possibilities of working with composite samples determine the choice on the scale of sampling.

In addition to the more technical perspective from which the definition of scale was described in the previous text, the scale of sampling can also (or even should) be defined by policy considerations. In principle the scale of sampling should be equal to the amount of material that is considered relevant from a policy perspective. An example of a policy-defined scale of sampling might be as follows:

Based on the radius of action of small animals living in soil, the mean concentration of a soil volume of 25 m^3 is considered as relevant for assessing the seriousness of soil contamination. It is assumed that these animals throughout their whole life span are exposed to the mean concentration of the pollutants in this soil volume. Thus, when assessing the seriousness of polluted soil, we are interested in the mean concentration within this volume of 25 m^3. When acute exposure to (very) high concentrations is considered not to be relevant, there is no need to gather information on a smaller scale than 25 m^3. The scale of sampling is therefore 25 m^3 and is achieved by taking a number of increments within this volume; an estimate of the true mean concentration on the scale of 25 m^3 can thus be obtained.

For the definition of scale in time one should consider a production process that results in a continuous stream of waste. At t = 0 the production starts. Sampling takes place between t = 20 and t = 30. The sampling process results in a (good) estimate of the mean concentration between t = 20 en t = 30. Therefore, the scale of the obtained result is 10 (seconds, hours, …). Of course, knowing

[1] It should be noted that it is not necessary (nor practical) to measure each individual item within a sub-population. A sample survey within each sub-population might be sufficient.

the mass of material produced in for example 10 minutes, this time defined scale can be easily transferred into a mass defined scale.

A.2 Fundamental variability

Granular material will generally consist of different types and shapes of particles. As a consequence there is a degree of variability on the scale of the individual particles. This variability cannot be reduced without particle size reduction. This is called the 'fundamental variability'. It will be the cause of variability between samples whenever the characteristic of interest - e.g. the concentration of metals, or organic matter - is directly related to a specific portion or subset of the particles. Also when the concentration of the constituent of interest varies over the different particles, there is fundamental variability.

As the average number of particles per sample increases, so the effect of the fundamental variability becomes less dominant. Nevertheless, the effect can remain large even with a large number of particles in the sample if the constituent of interest (e.g. copper occurring incidentally within a material) arises in only a small proportion of particles but at very high concentrations. Annex D provides the details of a method that can be used to estimate the minimum size of samples to ensure that the error due to fundamental variability is as small as required.

Theoretically, the former also applies to liquids in which different substances are solved. However, as the particle size is on the molecular scale, the sample will always be large enough to contain a (very) large number of particles (molecules) and therefore fundamental variability is of no interest for liquids.

Annex B

Statistical methods for characterising a population

B.1 Terms and Definitions

B.1.1

binomial distribution

type of probability distribution that describes the statistical behaviour of 'presence/absence' data

NOTE If the presence or absence of some attribute (e.g. excedence of a limit) is noted for each of n random samples, and that attribute has an underlying probability of occurrence p, then the binomial distribution B(n,p) describes the variability to be expected in the observed number of samples showing the attribute.

B.1.2

composite sampling

process of taking composite samples

B.1.3

confidence level

value 100(1 - α) of the percentage probability associated with a confidence interval (after ISO 3534-1)

NOTE Where α is the significance level.

B.1.4

confidence limits

each of the limits, T1 and T2, of the two-sided confidence interval or the limit T of the one-sided confidence interval
[ISO 3534-1]

B.1.5

histogram

graphical representation of the frequency distribution of a quantitative characteristic, consisting of a set of contiguous rectangles, each with a base equal to the class width and an area proportional to the class frequency
[ISO 3534-1]

B.1.6

LogNormal Distribution

family of probability distributions characterised by right-handed skewness, and often a useful approximation to environmental variability. So called because the *logarithm* of such a constituent is *Normally* distributed

B.1.7

non-parametric method (distribution-free method)

any statistical method which makes no assumption about the probability distribution describing the variability of the sampled population, but is instead based on properties of the *ranked order* of the data

NOTE For example, given seven sample values {22, 28, 29, 33, 37, 41, 66}, the median (50%ile) can be estimated by the 4th ranked value, namely 33.

B.1.8

normal Distribution

probability distribution of a continuous random variable X, the probability density function of which is

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{1}{2}\left(\frac{x-\mu}{\sigma} \right)^2 \right]$$

for $-\infty < x < +\infty$ (ISO 3534-1).

NOTE 1 μ is the expectation and σ is the standard deviation of the Normal distribution.

NOTE 2 The Normal distribution is characterised by a symmetrical, bell-shaped curve, and is of fundamental importance in statistical theory.

B.1.9

parametric method

any statistical method which makes an assumption about the form of probability distribution describing the variability of the sampled population

NOTE For example, the method might assume that the distribution is logNormal.

B.1.10

skewness

measure of the asymmetry of a population - that is, the degree to which values extend further on one side of the median than the other

B.1.11

standard Normal deviate

values corresponding to specified cumulative proportions of a standard Normal distribution (that is, a Normal distribution with mean 0 and standard deviation 1)

NOTE Examples are:

Cumulative probability	Standard Normal deviate
0.05	-1.645
0.50	0.000
0.95	+1.645
0.975	+1.960

B.1.12

stratification

division of a population into mutually exclusive and exhaustive sub-populations (called strata), which are thought to be more homogeneous with respect to the characteristics investigated than the total population
[ISO 3534-1]

B.1.13

variance

measure of dispersion, which is the sum of the squared deviations of observations from their average divided by one less than the number of observations
[ISO 3534-1]

B.2 Probability distributions

B.2.1 General

The 'probability distribution' is a statistical term used to describe the relative frequencies with which different values arise in a given population. The reliability of a testing programme can be improved if the form of the underlying distribution is known (or can reasonably be assumed).

Three distributions of particular relevance to testing programmes are described in the following clauses. It is to be noted that in practice the actual distribution of measurements can be much more complex and as a result differ very much from the three distributions described here.

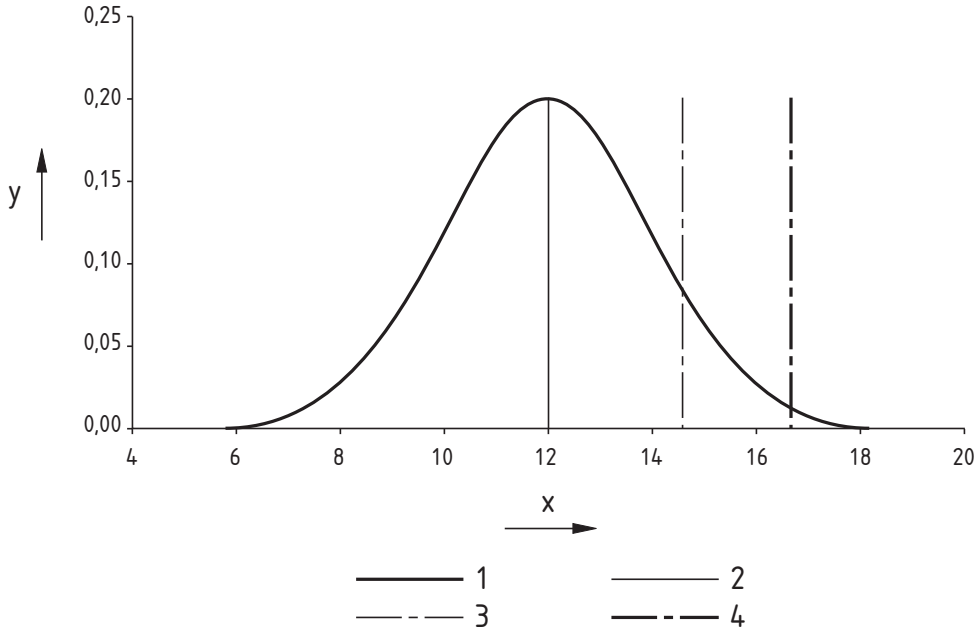
NOTE For example bimodal distributions are encountered often due to the fact that two mechanisms contribute to the measured characteristics.

B.2.2 Normal distribution

The probability distribution used most widely in statistics is the Normal distribution. This has a characteristic 'bell' shape, and is defined by two quantities or 'parameters': the mean (which fixes the centre of the distribution), and the standard deviation (which determines the degree of spread). These and other statistical parameters are discussed further in B.3.

Figure B.1 shows an example of a Normal distribution with mean 12 and standard deviation 2. A characteristic property of a Normally distributed population is that about 68% of its observations fall within a range of ± 1 standard deviation from the mean, and about 95% fall within ± 2 standard deviations. Here, therefore, most of the area under the curve lies in the range 12 ± 2×2, namely 8 to 16.

St.dev. = 2.0



Key

1 – Normal curve	2 – Mean, median
3 – 90 %ile	4 – 99 %ile
X - Concentration	Y – Probability density

Figure B.1 – Example of a Normal distribution

The Normal distribution is important for two main reasons. One is that many standard statistical test procedures (e.g. t-tests, F-tests) rest on the assumption that the sample values have been drawn from a Normal population.

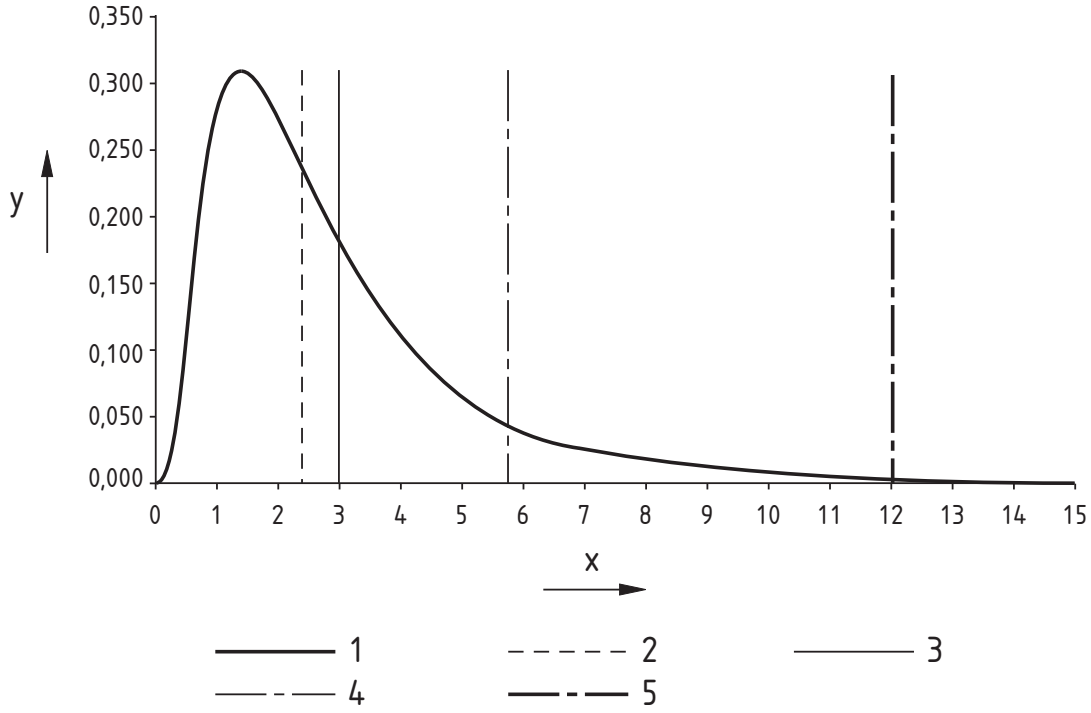
Normality is in general not applicable for the statistical distribution of observations on the composition of a heterogeneous material. It is more common to find a positively skewed distribution, whereby the majority of values are grouped relatively close to zero, but a minority of values form a tail of increasingly larger concentrations. It is easy to see how this can arise: concentrations (or other relevant characteristics of the material) can never be less than zero, but occasional high concentrations can occur.

Such populations are often better described by the logNormal distribution (see B.2.3).

B.2.3 LogNormal distribution

Figure B.2 shows an example of a logNormal distribution with mean 3,0 and standard deviation 2,4 (giving a *relative* standard deviation, or coefficient of variation, of 2,4 / 3,0 = 0,8). The right-hand skewness can clearly be seen: more than 90 percent of the population falls below 6 mg/l, whilst the greatest 1 percent of the population lies beyond 12 mg/l.

Relative st.dev = 0,8



Key

1 – LogNormal curve	2 – Median
3 – Mean	4 – 90 %ile
5 – 99%ile	
X – Concentration	Y – Probability density

Figure B.2 – Example of a logNormal distribution

The logNormal distribution is only a convenient approximation, and cannot always reflect the extreme skewness seen in some types of data. Nevertheless it often provides an acceptable assumption, especially where the purpose of the sampling is to estimate mean concentrations.

There is also a practical advantage in assuming a population to be logNormally distributed, in that after logarithmic transformation the values become Normally distributed. Although this makes statistical analysis more straightforward, and in particular allows methods based on standard Normal theory to be used, transposition of statistical characteristics calculated on the logarithmically transposed data is not in all cases allowed without loosing the statistical correctness of the estimate.

B.2.4 Tests for Normality and logNormality

Statistical techniques are available - known collectively as 'goodness-of-fit' methods - for testing whether a given data set could reasonably have come from a specified type of probability distribution, such as the Normal or the logNormal. Two fairly well known tests are the chi-squared goodness-of fit test and the Kolmogirov-Smirnov one-sample test. Although details of how these methods are applied go beyond the scope of this document, they can readily be found in most statistics textbooks and statistical software packages. Where there is sufficient data (say 50 or more sample values), it is certainly a good idea to examine the reliability of any distributional assumption that is made. However, even without formal statistical testing, a good indication of whether or not the Normality assumption is reasonable can be gained simply by examining a histogram of the data or – even better – looking at a 'normal probability plot'. A quick graphical check of the logNormal assumption can similarly be made by looking at a histogram of the logarithmically transposed values of the data.

B.2.5 Binomial distribution

Some cases will arise where the measurement of interest is not a continuous variable, but is instead an attribute or characteristic of the population that can be either 'present' or 'absent'. In such cases a widely applicable distribution is the 'binomial distribution'. This is defined by two parameters: the number of samples to be taken (n), and the proportion (p) of the population that has the attribute in question. The probability of observing a specific number of samples, r, exhibiting the attribute of interest is given by:

$$B(r;n,p) = \frac{n!}{(n-r)!r!} p^r (1-p)^{n-r} \qquad (B.1)$$

For small values of n, individual binomial probabilities can be evaluated by the straightforward application of this formula. However, it soon becomes a problem for larger values of n. Where binomial or cumulative binomial probabilities are needed, therefore, it is advisable that these are calculated using the statistical functions available in most popular spreadsheet packages.

NOTE Theoretical example:

If a fair coin is tossed 10 times, 'tails' will on average appear 5 times, but because of sampling error the actual number may well be less than or greater than 5. The binomial distribution B(r;10,0.5) determines the precise probabilities with which 0, 1, 2, …, 9, or 10 tails will be seen. For example, the probability of getting exactly 5 tails is 24,6%.

Practical application:

Suppose it has been agreed that not more than 50% of skips arising at a landfill site from a particular operator may contain a particular sort of (easily recognised) hazardous material - based on colour or smell, perhaps. From daily on-site verification over 30 days, 19 skips are identified as containing the material. The binomial distribution can quantify just how unusual it would be to get a proportion as high as 19 / 30 *through sampling error alone*, assuming that the process had truly been complying with the allowed rate of 50% (in this example the probability of getting a result at least as extreme as this is 8%, which is small but not unbelievably so).

B.3 Statistical parameters

B.3.1 General

A key step in planning a testing programme is to specify the statistical parameter that is to be estimated. This is important because the choice generally has a critical bearing on both the type of sampling and the number of samples needed.

NOTE For example, composite sampling is an effective method for estimating mean concentration, but is less appropriate for a percentile- or maximum-related objective.

Except for the expression for the estimation of the statistical parameter itself, a second expression is needed for calculating the statistical uncertainty associated with the estimate. The second of these is a critical piece of information, because it provides the quantitative link between the number of samples and the achievable reliability (i.e. precision and confidence). This is addressed in detail in Annex C.

The following clauses provide both expressions for each of a number of commonly used parameters.

B.3.2 Notation

B.3.2.1 General

The following terms are defined:

n is the total number of samples or observations

x_i is the i-th sample value (with i running from 1 to n)

$x(i)$ is the i-th ranked value - that is, the i-th value after sorting the n values into increasing order

μ is the population mean

$\overline{X}$ is the sample mean

σ is the population standard deviation

s is the estimated standard deviation

u_p is the standard Normal deviate corresponding to cumulative probability p

χ_p^2 is the chi-squared deviate corresponding to cumulative probability p

X_P is the population P-percentile

X_P is the estimated P-percentile

$SE(z)$ is the standard error of the statistic z

$B(r;n,p)$ is the Binomial probability that exactly r out of n random samples have a particular characteristic of interest, when the proportion of the entire population having this characteristic is p.

$CumB(r;n,p)$ is the Cumulative binomial probability that up to r out of n random samples have a particular characteristic of interest, when the proportion of the entire population having this characteristic is p.

B.3.2.2 Mean

The arithmetic mean - usually abbreviated to ‘mean’ - is the most commonly encountered parameter. It is a very useful measure of the ‘central tendency’ of a population. An unbiased estimate of the population mean is provided by the sample mean, given by:

$$\overline{x} = \frac{\sum x_i}{n} \qquad \text{(B.2)}$$

The uncertainty in $\bar{x}$ is given by:

$$SE(\bar{x}) = \frac{s}{\sqrt{n}} \quad \text{(B.3)}$$

B.3.2.3 Standard deviation

The standard deviation is a widely used measure of the variability of the population. It can be thought of as the root-mean-square of all the units in the population. A (nearly) unbiased estimate of the population standard deviation is calculated as:

$$s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{(n-1)}} \quad \text{(B.4)}$$

For Normal populations, the uncertainty in s can be assessed using the chi-squared distribution. A C% confidence interval for σ given s can be calculated as:

$$s\sqrt{\frac{(n-1)}{X_{1-p}^{\ 2}}} \text{ to } s\sqrt{\frac{(n-1)}{X_{p}^{\ 2}}}, \quad \text{(B.5)}$$

where p = (1 - C/100)/2.

The square of the standard deviation, s^2, is known as the 'variance'. The variance is of great importance in statistical theory, but is not a practically useful measure for reporting variability, as it is not defined in the same dimensions as the observed data.

NOTE Suppose a set of concentrations had a mean of 1,1 mg/l and a standard deviation of 0,3 mg/l. The variance would be 0,09 mg^2/l^2.

B.3.2.4 Coefficient of variation

The variability of a population can also be defined in a non-dimensional manner by the coefficient of variation, CV. An approximately unbiased estimate of the coefficient of variation is given by:

$$CV = \frac{s}{\bar{x}} \quad \text{(B.6)}$$

The uncertainty in CV can be quantified for Normal populations, but this information is not required for the present applications.

The coefficient of variation is particularly useful when the variability of different populations is to be compared. For many types of material, it is found that the standard deviation of a constituent tends to increase in proportion with its mean. Thus the *relative* standard deviation - i.e. the CV - is approximately constant, and so this forms a good basis for comparison.

B.3.2.5 Percentiles

B.3.2.5.1 General

The P-percentile of a population is that value below which P % of the population lays.

NOTE Example:

In Figure B.1, the 90-percentile has a value of about 14,6 mg/l. This means that 90 % of the population is less than or equal to 14,6 mg/l. Equivalently, 10% of the population lies above 14,6 mg/l.

Depending on what information is available about the underlying probability distribution, percentiles can be estimated in a variety of different ways, which will result in different estimates for the same percentile. Three methods to estimate a percentile are described below. Given the variety of methods to estimate the percentiles and the differences between these estimates, it is important to specify how percentiles are calculated.

B.3.2.5.2 Percentiles assuming Normality

The P-percentile is defined as $\mu + u_p \sigma$,

where p = P/100.

NOTE Standard Normal deviates u_p for various values of p are as follows:

P	1	5	10	50	75	90	95	97.5
p	0.01	0.050	0.1	0.5	0.75	0.9	0.95	0.975
u_p	-2.326	-1.645	-1.282	0.000	0.675	1.282	1.645	1.960

For example, the 95-percentile is $\mu + 1.645\sigma$, and the 1-percentile is $\mu - 2.326\sigma$.

An (almost) unbiased estimate of the P-percentile is given by:

$$X_P = \overline{x} + u_p s \quad \text{(B.7)}$$

where p = P/100.

An approximate expression for the uncertainty in X_P is:

$$SE(X_P) = s\sqrt{\frac{1}{n} + \frac{u_p^{\,2}}{2(n-1)}} \quad \text{(B.8)}$$

B.3.2.5.3 Percentiles assuming logNormality

B.3.2.5.2 apply equally to the case of logNormally distributed data, with the following adjustments:

a) the standard deviation s refers to the log-transformed data (it being immaterial whether base-10 or base-e is used);

b) at the end of the calculation X_P, the estimate of the P-percentile, should finally be antilogged to return to the unlogged domain.

B.3.2.5.4 Percentiles - non-parametric approach

If nothing can reliably be assumed about the probability distribution, a 'non-parametric' method is suggested. This is somewhat less precise than a parametric method - such as those in the preceding clauses - but is clearly a safer option when the parametric approach cannot be relied upon.

There are numerous slight variants of the non-parametric approach. The one proposed here is the so-called 'Weibull' convention, whereby the P-percentile is estimated as follows:

$$X_P = X(r), \text{ where } r = (P/100)(n+1) \quad \text{(B.9)}$$

If r is not an exact integer, linear interpolation should be used as follows:

$$X_P = (1-d)X(s) + dX(s+1) \quad \text{(B.10)}$$

where:

s = integer part of r, and

d = r - s

The concept of standard error is less appropriate for non-parametric methods. Instead, the uncertainty in X_P can be quantified by a conservative confidence interval {$X(r_1)$ to $X(r_2)$}, where r_1 and r_2 are defined by the following cumulative binomial expressions:

r_1 is the largest integer satisfying the condition $CumB(r_1-1; n,p) \leq (1 - C/100)/2$, and

r_2 is the smallest integer satisfying the condition $CumB(r_2-1; n,p) \geq 1 - (1 - C/100)/2$.

NOTE The resulting interval will in general have a confidence coefficient rather larger than C% because of the discrete nature of binomial probabilities.

Example: Suppose it is required to estimate the 80-percentile cadmium concentration from 39 random samples taken from a waste stream, together with a 90% confidence interval.

(1) By the Weibull method, $X_{80} = X(r)$, where r = (80/100)(39+1) = 32. Thus X_{80} is estimated by X(32), the ordered sample value with rank 32 (or, equivalently, the 8th largest value).

(2) C = 90 %, and so the conditions for r1 and r2 are:
$CumB(r_1-1; 39,0.8) \leq 0.05$, and $CumB(r_2-1; 39,0.8) \geq 0.95$.

Using appropriate software, we find by experimentation that:
CumB(26; 39,0.8) = 0.0355 and CumB(35; 39,0.8) = 0.9668.

Thus the interval X(27) to X(36) - that is, the interval from the 13th biggest to the 4th biggest sample value - provides a conservative 90% confidence interval for the true 80-percentile cadmium concentration (the actual confidence coefficient is 0.9668 - 0.0355 = 0.931, or 93.1 %).

B.3.2.6 Maximum

The population maximum should never be used as the desired statistical parameter (except in the unlikely event of the sampling being of very high frequency). This is because no reliable estimate of the maximum can ever be obtained from a set of sample values. The sample maximum will always be an under-estimate of the population maximum, and furthermore there is no straightforward method available for quantifying the extent of that bias.

Where the primary objective is concerned with ‘worst case’ values, the suggested approach is to recast the objective in terms of a suitably high percentile - say the 99-percentile. The methods described in B.2.1.4 can then be applied.

B.3.2.7 Percentage compliance with a given limit

B.3.2.7.1 General

The primary sampling objective often relates to the percentage of a population that complies with a specific limit (e.g. a target or intervention value). This is especially true for compliance testing and on-site verification.

As with percentile-type objectives, both parametric and non-parametric approaches can be taken. To contrast the two approaches, imagine that the limit L must be complied with for P% of the time or better.

B.3.2.7.2 Percentage compliance - parametric approach

Using the parametric approach, the P-percentile would be estimated assuming a particular distribution (e.g. Normal), and the resulting estimate X_P would be compared with L. The statistical uncertainty in the compliance result would then be assessed using the quantity $SE(X_P)$.

The parametric approach is not, however, generally suggested unless there is reliable information about the nature of the underlying distribution, because of the confusion that can be caused whenever the parametric estimate differs markedly from the non-parametric compliance figure - that is, the simple pass rate calculated directly from the data. Moreover, the details of the statistical method go beyond the scope of this document (even in the case where Normality can be assumed), and so specialist statistical advice should be sought for its application.

B.3.2.7.3 Percentage compliance - non-parametric approach

By the non-parametric approach, the quantity r - the number of sample values $\leq$ L - is first calculated. The sample compliance 100(r/n)% can then be determined. The advantage now is that 100(r/n) is binomially distributed (irrespective of the distribution followed by the original samples), and so the statistical uncertainty in the compliance result can be assessed without the need for any distributional assumptions about the population. Specifically, a C% confidence interval for the true population compliance is given by [$100p_{LO}$ to $100p_{UP}$], where:
p_{LO} is chosen so that $1 - CumB(r-1; p_{LO},n) = (1 - C/100)/2$,

and p_{UP} is chosen so that $CumB(r; p_{UP},n) = (100 - C)/2$.

NOTE Although the definition of the limit with which the observations are to be compared falls outside the scope of this Technical Report, it is important to realise that the (often implicit) statement that 'no observation may exceed the limit' is statistically unusable. It implies that not even one single unit of the population (at the investigated scale, see also Annex A) might have a concentration above that limit. In order to test this hypothesis, it would be necessary to test the entire population at the predefined scale!

However, an almost equivalent but statistically 'coherent' level of protection can be obtained by requiring that 99 % (or even 99,9 %) of the population at the defined scale, rather than 100 %, should comply with the limit.

Example:

Suppose that drums entering a reprocessing plant are required to have pH < 5. It is decided routinely to submit half of the incoming drums to on-site verification. After several months, 300 out of the 600 drums received have been checked, and all are satisfactory. Even from evidence as strong as this, it is impossible to say with any confidence that all 600 drums were satisfactory. However, what can be said with 95 % confidence is that at least 99 % of the drums will comply because $Cum\ P(0; 0.99,300) = 0.049$

Annex C

Calculating the required numbers of increments and samples

C.1 Notation

The following terms are defined:

n is the total number of samples or observations

m is the number of increments per composite sample

μ is the population mean

u_p is the standard Normal deviate corresponding to cumulative probability p

χ_p^2 is the chi-squared deviate corresponding to cumulative probability p

X_P is the population P-percentile

$SE(z)$ is the standard error of the statistic z

σ_w is the standard deviation of local (i.e. within-composite) spatial variation

σ_b is the standard deviation of between-composites spatial and/or temporal variation

σ_s is the standard deviation of total spatial and/or temporal variation ($= \sqrt{[\sigma_w^2 + \sigma_b^2]}$)

NOTE In cases where composite sampling is not being considered, spot samples can be thought of as composite samples with just a single increment, and so the 'within-composite' standard deviation becomes zero, and the 'between-composites' standard deviation becomes the 'between-spots' standard deviation.

σ_e is the standard deviation of analytical error

C is the desired confidence level (%)

a is the cumulative probability related to the desired confidence level

d is the desired precision

C.2 Estimating a mean concentration

C.2.1 Using composite samples

The standard error of the mean is given by:

$$SE(mean) = \sqrt{[(\sigma_w^2/m + \sigma_b^2 + \sigma_e^2)/n]} \quad (C.1)$$

Thus for a given value of m, and assuming Normality, the number of composites required to achieve the desired precision (d) and confidence (C), as specified by the user, is given approximately by:

$$n = (u_a/d)^2(\sigma_w^2/m + \sigma_b^2 + \sigma_e^2) \quad (C.2)$$

where a = 1 - (1 - C/100)/2. Alternatively, Equation C.2 can be re-written to determine the number of increments (m) needed per composite sample if n, the total number of composite samples, has been set in advance. Thus:

$$m = \sigma_w^2/[\, n(d/u_a)^2 - \sigma_b^2 - \sigma_e^2\,] \,. \qquad \text{(C.3)}$$

NOTE 1 It may be desirable - especially for on-site verification - to plan to take only a single composite sample. Provided $\sigma_b^2 + \sigma_e^2$ is sufficiently small, this can be achieved by setting n equal to 1 in Equation C.3.

In practice, the true standard deviations are unknown and so estimates must be used. In some cases it may be appropriate to use the values obtained from the past analysis of sample data from similar investigations. Otherwise the estimates should, where possible, be obtained from a preliminary pilot study.

NOTE 2 Suppose that:

- estimates of σ_w, σ_b and σ_e are 4, 2 and 0,5 mg/l;
- 10 increments are to be taken per composite (i.e. m = 10); and
- the mean is required to be estimated to a precision of d = 1 mg/l with 90 % confidence.

For C = 90, a = 1 - (1 - 90/100)/2 = 0,95, and so u_a = 1,65.

From Equation C.2, $n = (1,65)^2(16/10 + 4 + 0,25) = 15,9$.

Thus about 16 composite samples would be needed to produce a mean to the required reliability.

To decide on the most appropriate value of m it is necessary to consider the relative costs of sampling and analysis. Suppose that the sampling cost per increment is A, and the analysis cost per sample is B. The total cost TC is accordingly given by:

$$TC = (Am + B)n \qquad \text{(C.4)}$$

Thus, using Equation C.2 with various trial values of m it is possible to find the combination of m and n which minimises TC.

NOTE 3 Continuing with the earlier example, suppose that:

- values of m ranging from 1 to 20 are considered; and
- B/A = 30 - that is, a sample analysis is 30 times more expensive than the cost of sampling an increment.

The upper panel of C.2 shows the n value given by Equation C.2 for each trial value of m. The lower panel then shows the corresponding values of the total sampling cost TC (in arbitrary units). It is apparent that the optimum number of increments per composite sample is about 6.

C.2.2 Using individual samples

The standard error of the mean is given by:

$$SE(mean) = \sqrt{[(\sigma_s^2 + \sigma_e^2)/n]} \qquad \text{(C.5)}$$

Thus the number of samples required to achieve the desired precision (d) and confidence (C), as specified by the user, is given approximately by:

$$n = (u_a/d)^2(\sigma_s^2 + \sigma_e^2) , \qquad \text{(C.6)}$$

where a = 1 - (1 - C/100)/2.

NOTE 1 Individual sampling can be thought of as composite sampling with just one increment per composite. Thus the results of the previous section apply to the case of spot sampling by substituting m = 1 and replacing

$\sigma_w^2 + \sigma_b^2$ by σ_s^2 .

In practice, the true standard deviations are unknown and so estimates must be used. In some cases it may be appropriate to use the values obtained from the past analysis of sample data from similar investigations. Otherwise the estimates should where possible be obtained from a preliminary pilot study.

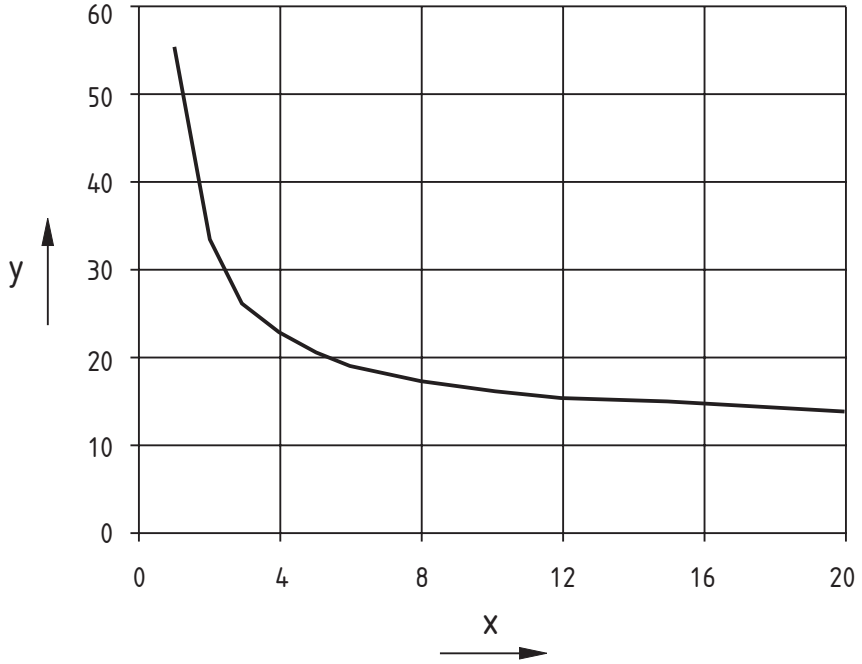
NOTE 2 Suppose that:

- estimates of σ_s and σ_e are 4,5 and 0,5 mg/l; and
- the mean is required to be estimated to a precision of d = 2 mg/l with 90 % confidence.

For C = 90, a = 1 - (1 - 90/100)/2 = 0,95, and so u_a = 1,65.

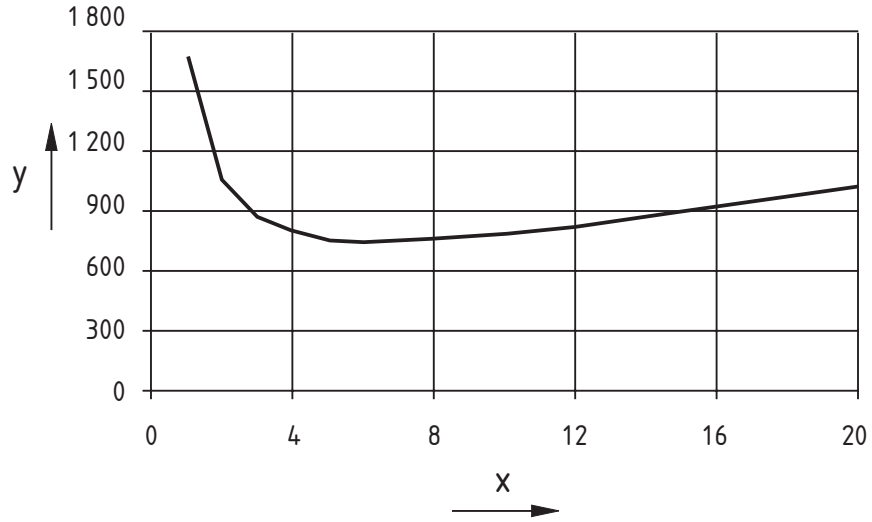
From Equation C.6, $n = (0,825)^2(20,25 + 0,25) = 13,9$.

Thus about 14 individual samples would be needed to produce a mean to the required reliability.



Key
X No of increments, m
Y Required no of composites, n

Figure C.1 – Illustration of the relationships between m, n and TC (see text for details) – Samples needed to achieve specified precision and confidence



Key
X No of increments, m
Y Total cost of sampling

Figure C.2 – Illustration of the relationships between m, n and TC (see text for details) – Cost of sampling in relation to no of increments per composite sample

C.3 Estimating a standard deviation

The following approach is applicable when the population can be assumed to be Normally distributed. Even for non-Normal populations, however, the method is useful as a rough approximation.

Confidence intervals for σ can be calculated using the expression given in B.3.2.3. For a given choice of confidence C, this can be evaluated for a range of trial n values, and this will identify the number of samples that provides the required precision.

NOTE Suppose it is required to estimate the standard deviation to a precision of 20 % with 90 % confidence. For 90 % confidence, the lower and upper p values are = $(1 \pm C/100)/2 = 0,05$ and 0,95. With the help of statistical tables of the χ^2 distribution at the p = 0,05 and 0,95 points, the following table can be constructed:

Table C.1 – 90% confidence limits for σ/s for various numbers of samples

Number of samples	Lower 90 % confidence limit for σ/s	Upper 90 % confidence limit for σ/s
N	$\sqrt{[(n-1)/\chi^2]}$ (p = 0,05)	$\sqrt{[(n-1)/\chi^2]}$ (p = 0,95)
20	0,79	1,37
30	0,83	1,28
40	0,85	1,23
50	0,86	1,20
60	0,87	1,18
70	0,88	1,16
80	0,89	1,15
90	0,89	1,14
100	0,90	1,13
120	0,90	1,12
150	0,91	1,11
200	0,92	1,09

By inspection it can be seen that with 50 samples, the lower and upper confidence limits are 0,86 and 1,20. That is, the population standard deviation σ may be 14 % below or 20 % above s, the observed standard deviation. Note that the interval is not symmetrical. Thus, at the 90 % confidence level, a precision of 20 % or better will be achieved by a standard deviation calculated from 50 random samples.

C.4 Estimating a percentile

C.4.1 Assuming Normality

The standard error of the P-percentile X_P is given by:

$$SE(X_P) = \sigma\sqrt{\frac{1}{n} + \frac{{u_p}^2}{2(n-1)}} \qquad \text{(C.7)}$$

where p = P/100, and $\sigma = \sqrt{(\sigma_s^2 + \sigma_e^2)}$. Thus the number of samples required to achieve the desired precision and confidence is given approximately by:

$n = (u_a s/d)^2(1 + u_p^2/2),$ (C.8)

where a = 1 - (1 - C/100)/2, and s is an estimate of σ.

NOTE Suppose that:

- σ is estimated by s = 3,5 mg/l; and
- the 95-percentile is required to be estimated to a precision of d = 1,46 mg/l with 90% confidence.

For the 95-percentile, p = 0,95 and so u_p = 1,65.
For C = 90, a = 1 - (1 - 90/100)/2 = 0,95, and so u_a = 1,65.
Thus from Equation C.8, $n = (1,65 \times 3,5/1,46)^2(1 + 1,65^2/2) = 36,9$.

Thus about 37 samples would be needed for the 90-percentile to the estimated to the required reliability.

C.4.2 Non-parametric approach

For determining the precision achievable by a non-parametric approach, there is no direct expression available corresponding to the one given above for the Normal case. As a rough approximation, however, the equation given in C.4.1 can still be used, but with an additional multiplicative factor of 1,3 applied to represent the poorer precision typically attained by the non-parametric rather than the Normal-based approach.

Alternatively, exact results can be obtained using the following more time-consuming approach. The first step is to select a trial number of samples and desired confidence level, C. The methodology described in B.3.2.5.4 for calculating C % confidence intervals around non-parametric percentile estimates is then applied. This should be repeated for different trial sample numbers. The various confidence intervals will be expressed as ranked values, but these can be converted into equivalent actual measurements as long as a suitable historical data set is available. These trial calculations will give an indication of the precision that can typically be achieved at C % confidence for various numbers of samples; and from this an appropriate choice can be made.

NOTE Suppose that the 80-percentile cadmium concentration from a particular waste stream is required to be estimated to a precision of d = 15 mg/l with 90 % confidence.

Select n = 39 as the trial number of samples.

From B.3.1.4.3, a conservative 90 % confidence interval is provided by the interval X(27) to X(36).

Past cadmium data is available for this waste stream. From a set of 39 values taken at random from this data, the 15 highest values are:

12, 12, 13, 15, 17, 20, 20, 25, 26, 31, 31, 35, 36, 40, 55 mg/l.

Thus the 27th and 36th ranked values are 13 and 35 mg/l and so the expected precision is (35 - 13)/2 = 11 mg/l. This is better than required, and so a lower trial value of n is selected.

Select n = 29 as the new trial number of samples.

From B.3.2.5.4, a conservative 90 % confidence interval is provided by the interval X(20) to X(28).

From a set of 29 values taken at random from the historical data, the 12 highest values are:

10, 12, 12, 15, 20, 20, 25, 26, 31, 35, 40, 55 mg/l.

Thus the 20th and 28th ranked values are 12 and 40 mg/l and so the expected precision is (40 - 12)/2 = 14 mg/l. This is adequately close to the required precision.

About 29 samples would therefore be needed for the 80-percentile to be estimated to the required reliability.

C.5 Estimating a percentage compliance with a given limit

The approach here is similar to that described in C.4.2. First the desired confidence level, C, is chosen. Then, for each of a range of trial sample numbers, the C % confidence interval for the true percent compliance is calculated using the methodology described in B.3.2.7. The resulting set of confidence intervals shows the quantitative link between achievable precision and samples taken, and hence provides a rational basis for arriving at an acceptable compromise.

NOTE Suppose that:

- the percentage of waste meeting a particular cadmium concentration limit is thought to be about 80 %;

- this percentage must be estimated to a precision of 10 % with 90 % confidence; and nothing is known about the statistical nature of the cadmium distribution

Select a trial number of samples of n = 20, and suppose that 16 samples meet the required cadmium limit (that is, the observed compliance rate is 80 %).

Using the non-parametric binomial method described in B.3.2.7.3, calculate a 90 % confidence interval for the true compliance percentage. This is 71,7% - 98,2 %, giving a precision of about 13 %. Thus a greater number of samples is needed.

Select a trial number of samples of n = 40, and suppose that 32 samples meet the required cadmium limit (to keep the observed compliance rate at 80 %).

Using B.3.2.7.3., calculate a 90 % confidence interval for the true compliance percentage. This is 78,6 % - 96,5 %, giving a precision of about 9% . This is adequately close to the required precision.

About 40 samples would therefore be needed for the compliance percentage to be estimated to the required reliability.

Annex D

Minimum increment and sample size (mass / volume)

The sampling plan must contain specific instructions on the type of samples to be taken, the size of increments and/or samples, the number of increments and/or samples to be taken and, when relevant, the number of increments that should be put together in a composite sample.

D.1 Estimation of increment and sample size

D.1.1 General

As mentioned in 4.4, a key feature of probabilistic sampling is that all parts of the population have the chance of being part of the sample. For the sampling of granular material, this has an effect on the scale (volume or mass) of both increments and samples. This paragraph and subsequent sub-paragraphs show how the increment and sample size should be determined according to the following steps:

1) determination of the minimum increment size;

2) determination of the minimum sample size;

3) determination of the number of increments and/or samples;

4) calculation of the actual increment and/or sample size.

D.1.2 Determination of the minimum increment size

The minimum increment size when sampling from a sub-population should meet the following requirements:

- the actual width, height and length of the sampling equipment must be at least equal to three times the 'maximum' particle size (D_{95}) of the material to be sampled in the case of materials with a maximum particle size (D_{95}) of at least 3 mm;
- the actual width, height and length of the sampling equipment must be at least equal to 10 mm in the case of materials with a maximum particle size (D_{95}) of less than 3 mm.

NOTE $D_{95} \geq 3$mm If the maximum particle size is at least 3 mm and the width, height and length of the increment are chosen to be equal to three times the maximum particle size (D_{95}), then the following formula applies to the mass of the minimum increment size:

$$M_{inc} = 10^{-9}\rho(3D_{95})^3 = 2{,}7\times10^{-8}\rho D_{95}^3. \qquad (1)$$

where:

M_{inc} mass of minimum increment size, in kg,

D_{95} the 95-percentile particle size, in mm, and

ρ the bulk density of the material, in kg/m^3.

Moreover, the mass of the maximum particle is $(4/3)\pi\rho10^{-9}(D_{95}/2)^3 = 5{,}2\times10^{-10}\rho D_{95}^3$.

Thus the quantity (mass of increment)/(mass of maximum particle) = 270/5,2 = 51,6. In other words, the mass of the minimum increment should be about 50 times that of a maximum particle (95-percentile of the particle size distribution).

D_{95} <3mm

In the case of materials with a maximum particle size (D_{95}) of less than 3 mm, the following formula applies to the mass of the minimum increment size:

$M_{inc} = 1 \times 10^{-6} \rho$

where:

M_{inc} = the mass of the minimum increment size, in kg, and

ρ = the bulk density of the material, in kg/m^3.

D.1.3 Determination of the minimum sample size

The minimum sample size to be applied to the material in question is given by:

$$M_{sam} = \frac{1}{6}\pi \times (D_{95})^3 \times \rho \times g \times \frac{(1-p)}{CV^2 \times p} \qquad \text{(D.1)}$$

where:

M_{sam} is the mass of the sample in g;

D_{95} is the 'maximum' particle size (defined as the 95-percentile), in cm;

ρ is the specific mass of the particles in the material, in g/cm^3;

g is the correction factor for the particle size distribution of the material to be sampled;

p is the fraction of the particles with a specific characteristic (m/m);

CV is the desired coefficient of variation caused by the fundamental error.

Note that this calculation results only in a rough estimate of the minimum sample size. The estimate however is precise enough to know the order of magnitude of the sample size. Two, partly related, aspects determine the correctness of the estimate: the quality of the assumptions made for the parameters in the formula (thus how correct are the estimates) and the correctness of the formula itself for non-spherical particles. As the aim is to obtain a (rough) estimate of the minimum sample size, the formula can also be used for non-spherical (e.g. irregularly shaped materials) or even non-granular materials.

NOTE 1) The variables in the formula for the estimation of the minimum sample size are expressed in CGS units for practical reasons.

2) The minimum sample size is directly related to the desired coefficient of variation of the fundamental error (CV) and to the size of fraction of the particles with the characteristic to be determined (p). The result is derived from binomial sampling theory as follows. Suppose n samples are taken from the material. The standard error of the observed proportion of particles with the characteristic of interest is $\sqrt{[p(1-p)/n]}$, and so the coefficient of variation CV is given by:

$CV^2 = (1-p)/(pn)$.

Thus to achieve an adequately small value of CV, the value of n must be:

$n = (1-p)/[CV^2 p]$ - which is the final term in the expression for M_{sam}.

3) As the influence of the fundamental variability (see A.2) should be low, a well accepted value for the coefficient of variation due to the fundamental variability is 0,1.

4) The actual value of p, the fraction of particles with a certain characteristic, depends on the waste to be sampled and the substances in it to be determined. Knowledge of the waste consistency is required in order to determine this value.

5) The formula for estimating the minimum sample size is derived for spherical particles of diameter d, and so is only an approximation for non-spherical particles.

6) The following applies for the correction factor for the particle size distribution (g):

Broad particle size distribution: $D_{95}/D_{05} > 4$ g = 0,25

Medium particle size distribution: $2 < D_{95}/D_{05} \leq 4$ g = 0,50

Narrow particle size distribution: $1 < D_{95}/D_{05} \leq 2$ g = 0,75

Uniform particles: $D_{95}/D_{05} = 1$ g = 1,00

where D_{05} = the 'minimum' particle size (defined as the 5-percentile of the particle size distribution).

7) For the sampling of fine granular material with a broad particle size distribution (for example soils), the following default values can be used for the factors in the formula:

ρ = 2,6 g/cm^3

g = 0,25

p = 0,02

D.2 Determination of the number of increments and/or samples

The number of increments and/or samples is directly related to the objective of the testing programme (Clause 3), the variability of the material to be sampled (4.3), and the desired precision and confidence (4.7). Reliable information in variability is commonly unavailable - in which case it is not possible to fulfil the exact requirements for precision and confidence without carrying out a preliminary sampling investigation.

From these specified inputs, the number of increments (where relevant) and samples can be calculated using the expressions given in Annex C.

D.3 Calculation of the actual increment and/or sample size

D.3.1 General

On the basis of the relationship between the minimum increment size (D.1.2), the minimum sample size (D.1.3) and the number of increments to be included per composite sample (D.2), the actual increment size and the actual sample size should be determined according to the following rules.

D.3.2 Taking individual samples

Where composite sampling is not being considered, the question of increment size will in most cases be irrelevant as the mass of the minimum sample size (D.1.3) will exceed the mass of the minimum increment size. When the amount of material necessary for the analysis exceeds the mass of the minimum sample size, the actual sample size should of course be sufficient for the analysis.

D.3.3 Composite sampling

Where composite sampling is to be undertaken, there is a possible conflict between:

a) the previously calculated minimum values for increment size (D.1.2) and sample size (D.1.3);

b) the planned number of increments, m (Annex C).

Such conflict should be resolved as follows:

– if m increments of minimum size amount to *less than* the required minimum sample size, then the increment size must be increased accordingly so that m *actual* increments will produce an adequately large composite sample;

– conversely, if m increments of minimum size amount to *more than* the required minimum sample size, then this larger quantity defines the actual sample size.

Annex E

Example sampling scenarios

E.1 Sampling scenarios

A number of sampling scenarios have been developed for a single waste stream to illustrate the range of approaches that may be required for basic characterisation, compliance testing and on-site verification from different sampling points, as summarised in the numbered positions ' ' in Figure E.1 and as Examples 1-14 the list below and subsequent sections E2 to E15.

NOTE A two-phase waste has been selected for the example, which also allows sampling scenarios to be developed for both sludge and liquid wastes. The examples also cover a range of sampling situations (e.g. lagoon, drum, tanker).

A chrome processing plant generates a liquid sludge waste, which can potentially be disposed in one of three ways:

1) transportation by pipe to an on-site hazardous waste lagoon;

2) temporary storage within drums prior to off-site treatment and disposal at an off-site landfill;

3) discharge directly to a liquid tanker for off-site treatment and disposal at an off-site landfill.

On standing, the liquid sludge tends to separate into a heavy metal-rich sludge and a supernatant liquid. Opportunities for sampling from a moving stream are provided at a valve on the discharge pipe work from the plant and on discharge from the tanker at the treatment plant. Static samples can be retrieved from the lagoon, the top hatch of the tanker or the drums.

Example sampling scenarios address sampling that may be carried out by the waste producer, the waste treatment plant operator and the landfill operators. The objectives of the testing programme in the different scenarios are as follows:

Example 1 (section E.2) waste producer to carry out a basic characterisation on the concentration of Cr^{6+} in a waste liquid during discharge to the on-site lagoon;

Example 2 (section E.3) waste producer to undertake a regular compliance testing programme to check conformance with data obtained from the basic characterisation;

Example 3 (section E.4) regulator to undertake an on-site verification of supernatant liquid in the hazardous waste lagoon;

Example 4 (section E.5) waste producer to carry out a basic characterisation on the concentration of Cr^{6+} in a waste liquid held in drum storage at the factory, for disposal purposes;

Example 5 (section E.6) waste producer to carry out a compliance testing of the Cr^{6+} concentration of waste liquid held in drums prior to disposal, against a permitted mean limit of 100 mg/l;

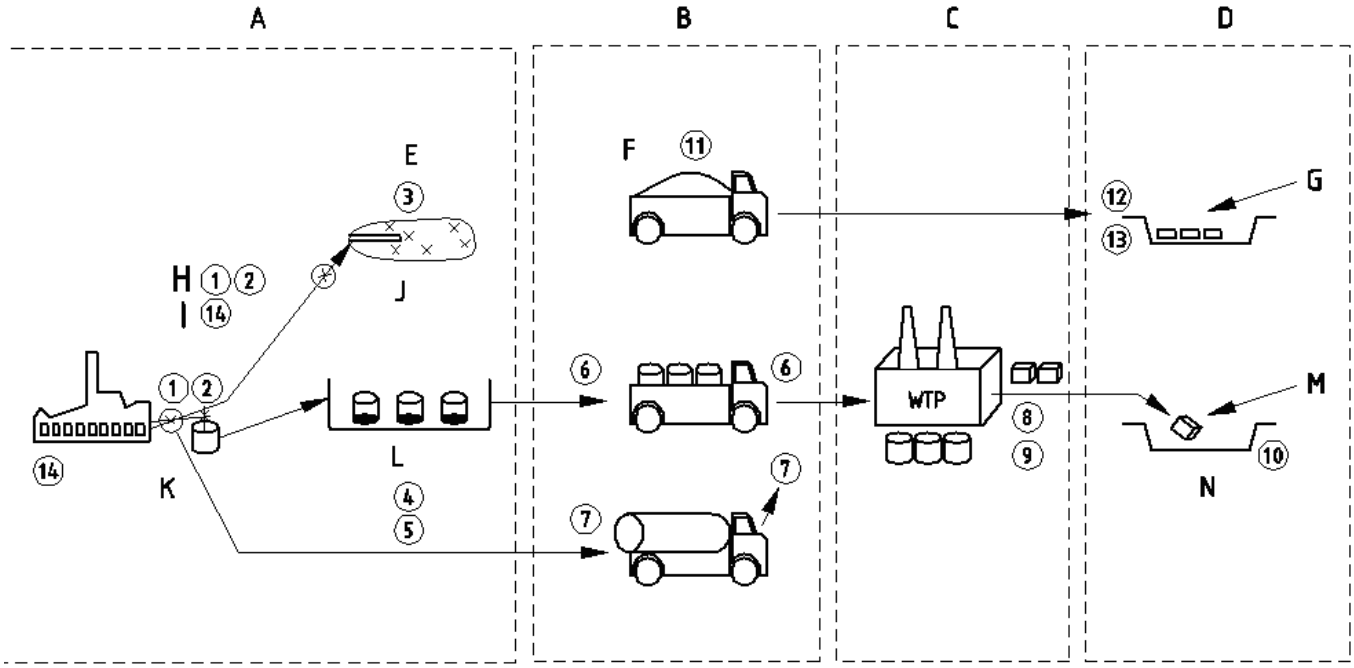
Example 6 (section E.7) carrier or Disposal Company to carry out an on-site verification of drums containing Cr-contaminated liquid sludge prior to treatment;

Example 7 (section E.8) carrier or Disposal Company to carry out an on-site verification of the contents of *tankers* containing Cr^{6+} contaminated liquid sludge prior to treatment;

Example 8 (section E.9) treatment plant operator applying basic characterisation to identify variability of Cr^{6+} in a treated waste using a two-step leaching test at LS 2 and LS 8 (EN 12457-3);

Example 9 (section E.10) treatment plant operator to perform compliance testing to determine whether the treated hazardous waste complies with a limit determined on the basis of the basic characterisation, using a combined one-step leaching test at LS10 (EN 12457-2).

In addition, example scenarios 10-14 are outlined which can be developed in full from some of the earlier examples.



Key

Identifier	Caption	Identifier	Caption
A	Waste Producer	H	Normal operations
B	Waste Carrier	I	Decommissioning
C	Waste Treatment Plant	J	Hazardous waste lagoon
D	Landfill Operator	K	Valve
E	*Regulatory Testing*	L	Temporary drum storage
F	Sludge/ soil from decommissioning of lagoon	M	Solidified/treated hazardous waste in non-hazardous landfill (part of waste treatment complex)
G	"off-specification" treated waste sent to third party hazardous landfill	N	*Regulatory Testing*

Examples of possible sampling scenarios and different levels of testing for a single waste stream

Example No.	Persons undertaking testing	Level of Testing	Example No.	Persons undertaking Testing	Level of Testing
1	Waste Producer – point of discharge to lagoon	1	2	Waste Producer – point of discharge to lagoon	2
3	Regulator - point of discharge to lagoon	3	4	Waste Producer – drummed storage	1
5	Waste Producer – drummed storage	2	6	Waste Carrier/Disposal contractor – drummed waste prior to off-site treatment	3
7	Waste Carrier/Disposal contractor – tankered waste prior to off-site treatment	3	8	Treatment Plant – treated waste	1
9	Treatment Plant – treated waste	2	10	Regulator – treated waste prior to disposal	3
11	Waste Producer – a comparison of aged and fresh sludge	2	12	Landfill Operator – verify aged sludge matches basic characterization data	3
13	Landfill Operator - verify treated load matches basic characterization data	3	14	Site Developer – contaminated site investigation	1

NOTE Level 1 – basic characterization, Level 2 – compliance testing Level 3 – on-site verification

Figure E.1 – Examples of sampling scenarios for liquid, sludge and solid wastes from a chrome processing plant

E.2 Example 1: Waste producer to carry out a basic characterisation on the concentration of Cr^{6+} in a waste liquid during discharge to the on-site lagoon

An assessment is required of worst-case concentrations of relevant waste contaminants. Samples are to be collected from the discharge pipe work between the plant and the on-site lagoon for basic characterisation. In practice a full range of parameters would need to be assessed at this level, but to simplify this example the calculations will be undertaken for just one parameter – Cr^{6+}. This represents only one part of the complete characterisation programme for this waste material that could be required by the Regulator. Other tests might include an assessment of leaching behaviour in the short- and long-term under simulated landfill disposal conditions.

Specify the objective of the testing programme		
1	**Specify the objective in terms of the overall population**	Waste producer to carry out a basic characterisation of Cr^{6+} in a waste liquid during discharge to the on-site lagoon for the entire volume of liquid sludge discharged over the lifetime of the plant.
Develop the Technical Goals from the objective		
2	**Define the population to be sampled**	Population: The entire volume of liquid sludge discharged over one year. Sub-population: The entire volume of liquid sludge discharged over a particular Mon-Fri period. NOTE For the stated objective sampling should be carried out over a period when maximum contaminant levels are expected.
3	**Assess variability**	Spatial variability not relevant. Substantial temporal variation due to spasmodic changes in plant operating conditions. The plant is only operational between Monday to Friday and is shut down at the weekend. Re-starting the plant on a Monday leads to differences in the waste stream between the start and end of the week. Variability on a week-by-week basis is therefore likely to be small in comparison to variability within a week. The selection of a period of one week for sampling is therefore a valid approach to meet the overall sampling objective and provides a microcosm of the expected variability. Analytical error known from AQC records. Some past data available, for which mean = 8,8 mg/l and standard deviation = 3,5 mg/l. Thus historical 90-percentile is approximately mean + 1,28 st.dev = 13,3 mg/l.
4	**Select the sampling approach**	Probabilistic sampling is feasible because of good access to discharge pipe. Individual samples are needed rather than composites because the required parameter is not mean concentration.
5	**Identify the scale**	Not relevant.
6	**Identify the required statistical approach**	Time-based 90-percentile Cr^{6+} concentration. NOTE Unnecessary to consider loads, as flow rate is fairly regular.

7	**Choose the desired reliability**	Required parameter (i.e. 90-percentile) to be estimated to a precision of 20 % with 95 % confidence
Determine the practical instructions		
8	**Choose the sampling pattern**	Sample at fixed time intervals over the 5 days.
9	**Determine increment /sample size**	Sludge adequately mixed at well below the scale of the intended sampling method. Thus sample size selected to meet requirements for analysis. NOTE The lab specifies that 500 ml samples are needed.
10	**Determine the use of composite or individual samples**	Analyse each sample separately.
11	**Determine required number of samples**	Past data suggests assumption of Normality is reasonable. Approximate number of samples needed is therefore 12. NOTE From Annex C, approx formula for n is: n = [ua×s/d]2×(1 + up2/2) = [1,96×3,5/(0,2×13,3)]2×(1 + 1,282/2) = [6,86/2,66]2×1,82 = 12,1.
12	**Define statistical elements of the Sampling Plan**	Select a random starting point within three hours of the start of the assessment period, and then take individual samples every 10 hrs thereafter until the required 12 samples have been collected. NOTE 12 samples over 5 days requires samples to be taken at intervals of 10 h.

E.3 Example 2: Waste producer to undertake a regular compliance testing programme to check conformance with data obtained from the basic characterisation

Following the basic characterisation programme to determine potential worst-case concentrations of Cr^{6+} in the liquid waste (see Example 1), the producer now needs to undertake regular compliance checks to provide evidence that the waste stream is within the previously determined worst case concentration. As the 90-percentile concentration was used for the basic characterisation, an appropriate criterion now is to test for 90 % compliance with this value.

Specify the objective of the testing programme		
1	**Specify the objective in terms of the overall population**	Waste Producer to undertake a regular compliance testing programme to check conformance with set compliance level for the entire volume of liquid sludge discharged over the lifetime of the plant.
Develop the Technical Goals from the objective		
2	**Define the population to be sampled**	Population: The entire volume of liquid sludge discharged over one year. Sub-population: The entire volume of liquid sludge discharged on Mondays though the year.
3	**Assess variability**	The five-day basic characterisation exercise indicated maximum concentrations in the waste can be expected on a Monday when the plant is re-opened after weekend shut-down.
4	**Select the sampling approach**	Probabilistic - individual samples.
5	**Identify the scale**	Not relevant.
6	**Identify the required statistical approach**	Proportion of liquid exceeding the set compliance level.
7	**Choose the desired reliability**	If liquid is truly complying with Cr^{6+} limit for 90 % of the time, The risk of declaring non-compliance should be no worse than 5 %. Failure should be declared if fewer than 75 % of samples comply with the limit.
Determine the practical instructions		
8	**Choose the sampling pattern**	Samples taken on selected Mondays at a randomly chosen time.
9	**Determine increment /sample size**	Not relevant.
10	**Determine the use of composite or individual samples**	Each sample should be analysed separately.

11	**Determine required number of samples**	From the methodology described in Annex C, the minimum number of samples required is 19, with the control rule: declare the system non-compliant if 5 or more samples exceed the limit. NOTE The probability of getting ≤4 high values is CumB(4; 19,01) = 0,965, or 96,5 % Thus the probability of getting 5 or more values above the limit is only 3,5 %. This is just less than the required risk of 5 %, and so 5 high values can trigger a non-compliance decision. Moreover, 4 high values is equivalent to 100(15/19) = 79 % sample compliance, whilst 5 high values is equivalent to 100(14/19) = 74 % sample compliance. The compliance rule therefore achieves the required precision.
12	**Define statistical elements of the Sampling Plan**	Sample the waste liquid sludge at a random time of day on a randomly chosen Monday during the first 3 weeks, and then sample at intervals of 3, 3, 2 and 3 weeks thereafter. NOTE For 19 samples to be taken over 52 weeks, the average time between samples is 52/19 = 2,74 weeks. This is achieved by taking 4 samples every 11 weeks (3 + 3 + 2 + 3). If the Cr^{6+} concentrations of 5 or more of the 19 samples exceed the limit, declare the process non-compliant.

E.4 Example 3: Regulator to undertake an on-site verification of supernatant liquid in the hazardous waste lagoon

For this example a regulatory body wishes to collect samples of the supernatant liquid at the on-site lagoon in order to verify that it is comparable with data the producer has supplied to the regulator. A secondary purpose of the check is to check that waste from other sources has not been directed to the lagoon, i.e. that analysis shows the supernatant to be a single-source term waste. A full analysis is required at the laboratory, but sampling will only be undertaken on one occasion. The regulator will ask the producer to provide summary data (produced during basic characterisation) for a full range of parameters in order to assess with specified precision and confidence whether the estimated on-site verification mean is consistent with the basic characterisation. For the purpose of this example the Regulator will assess levels of Cr^{6+} to establish that the sample is compliant with information provided by the waste producer -i.e that levels fall within the range of values previously reported.

Specify the objective of the testing programme		
1	**Specify the objective in terms of the overall population**	Regulator to undertake an on-site verification of supernatant liquid in the on-site hazardous waste lagoon for the entire supernatant contents of the lagoon.
Develop the Technical Goals from the objective		
2	**Define the population to be sampled**	Supernatant liquid that can be accessed from the bank of the lagoon using a liquid tube sampler.
3	**Assess variability**	The spatial variability in supernatant concentrations is assumed to be approximately equal to the temporal variability seen during the basic characterisation. This was characterised by a standard deviation of 11 mg/l. The mean concentration of Cr^{6+} was 40 mg/l, and the analytical error standard deviation was 3 mg/l.
4	**Select the sampling approach**	Judgemental sampling. Individual samples will be taken around the perimeter of the lagoon and bulked to form a single composite sample.
5	**Identify the scale**	Not relevant.
6	**Identify the required statistical approach**	Mean concentration of Cr^{6+} in supernatant.
7	**Choose the desired reliability**	The estimated supernatant mean concentration should be estimated to a precision of 20 % with 95 % confidence.
Determine the practical instructions		
8	**Choose the sampling pattern**	Around edge lagoon
9	**Determine increment /sample size**	Not relevant
10	**Determine the use of composite or individual samples**	A single composite sample of 16 increments is needed (see step 11).

11	**Determine required number of samples**	From Annex C, formula for number of increments composite samples is: m = σw2/[n(d/ua)2 - σb2 - σe2] , where a = 1 - (1 - C/100)/2. Here, d = 20 % of 40 = 8 mg/l, n = 1, and estimates of σw and σe are 11 and 3 mg/l. Also, σb can be set to zero as the composite sample is being drawn from the entire sub-population. Finally, 95 % confidence is required: thus a = 0,975, and ua = 1,96. This gives m = 121/[(8/1,96)2 - 9] = 121/7,66 = 15,8. Thus a single composite sample comprising 16 increments will provide the required precision.
12	**Define statistical elements of the Sampling Plan**	From plan of lagoon, select 16 locations roughly equi-spaced around the perimeter. The location of the first sampling spot is chosen randomly. Mix the 16 increments into a single composite sample.

E.5 Example 4: Waste producer to carry out a basic characterisation on the concentration of Cr6+ in a waste liquid held in drum storage at the factory, for disposal purposes

For this example it is assumed that there are problems with the distribution system to the on-site lagoon, or that it is full and it is necessary to send the waste sludge for treatment and subsequent disposal as a non-hazardous material via interim drum storage. Assuming there is no access to the waste stream from the plant prior to drum filling, it would be necessary to complete a basic characterisation to obtain a measure of drum-to-drum variability. This will enable the waste producer subsequently to set up a statistically sound compliance assessment system that will operate during routine disposal of the drums.

Specify the objective of the testing programme		
1	**Specify the objective in terms of the overall population**	Waste producer to carry out basic characterisation of the Cr^{6+} concentration in a waste liquid held in drum storage at the factory, for disposal purposes over the lifetime of the plant.
Develop the Technical Goals from the objective		
2	**Define the population to be sampled**	Population: The entire volume of liquid sludge contained in all drums in the storage area both now *and* potentially arising over the coming 12 months. Sub-population: The entire volume of liquid contained in all drums *at present* in the storage area NOTE It is judged that the drums presently in store are typical of the full range of variation produced by the factory. Furthermore, all of the drums are readily accessible.
3	**Assess variability**	Temporal variability was originally present in the liquid sludge due to spasmodic changes in plant operating conditions, and this has resulted in substantial *spatial* variation between drums. Pronounced stratification expected, with a supernatant liquid layer above a Cr-rich sludge layer. Test sampling of a few drums indicates that within-drum variability is small in relation to between-drum variability.
4	**Select the sampling approach**	Probabilistic sampling is feasible because of good access to drums. For each drum sampled, composite samples taken from both liquid and sludge strata and analysed separately, and liquid : sludge ratio measured. NOTE If Health and Safety requirements allow, each selected drum could be mixed and a single sample submitted for analysis. The number of drums to be sampled would still be 50, but the total number of analyses would be reduced from 100 to 50.
5	**Identify the scale**	The mean concentration for a drum should be determined; the scale is the volume of a drum

6	**Identify the required statistical approach**	Standard deviation of mean Cr^{6+} concentration from drum to drum. Average Cr^{6+} for each drum should be calculated as weighted average of supernatant and sludge concentrations, with weights equal to stratum depths. NOTE As the contents of each drum will be well mixed by the point of disposal, within-drum variation is unimportant. All that is of concern is the variation from drum to drum in its average contents.
7	**Choose the desired reliability**	Required parameter (i.e. standard deviation) to be estimated to a precision of 20 % with 90 % confidence.
Determine the practical instructions		
8	**Choose the sampling pattern**	Select drums at random from the storage area.
9	**Determine increment /sample size**	Supernatant and sludge both adequately mixed, so increment size is adequate. Sample volumes selected to meet requirements for analysis. NOTE With the sampling implement used, three increments provide sufficiently large samples for analysis.
10	**Determine the use of composite or individual samples**	Composite sampling
11	**Determine required number of samples**	Assumption of Normality is reasonable because each drum mean is estimated using composite sampling. Approximate number of drums to be sampled is therefore 50. NOTE Number of samples obtained by picking out an appropriate value from the trial calculations tabulated in Annex C. Note that if fewer than 50 drums are presently available in store, these should be supplemented with incoming drums until the required number is reached.
12	**Define statistical elements of the Sampling Plan**	Prepare a list of all drums in storage area using an unambiguous labelling system. Use random number tables to select the required number of drums.

E.6 Example 5: Waste producer to carry out a compliance testing of the Cr6+ concentration of waste liquid held in drums prior to disposal, against a permitted mean limit of 100 mg/l

The waste producer has previously carried out a basic characterisation to determine the extent of drum-to-drum variation in mean Cr concentration: this was characterised by the standard deviation s. Now he wishes to implement a compliance testing scheme. For this he sets an upper 99 % control limit defined by: U = L + 2,33s, where L is the permitted long-run mean Cr^{6+} concentration. About once a week a drum is to be selected at random, and the mean Cr^{6+} determined. If this falls below U, the process is judged to be 'in control'. But if a value exceeds U, this sounds a warning that the process may have slipped out of control. Two exceedances of U within, say, 10 consecutive samples would trigger a full investigation.

Specify the objective of the testing programme		
1	**Specify the objective**	Waste producer to carry out compliance testing of Cr^{6+} content of waste liquid held in drums prior to disposal, against a permitted mean limit of 100 mg/l.
Develop the Technical Goals from the objective		
2	**Define the population to be sampled**	The liquid in all drums to be disposed of over a 12-month period. NOTE All drums through the year will be equally accessible, and so available for sampling.
3	**Assess variability**	From previous basic characterisation, drum-to-drum variation in mean Cr^{6+} has an estimated standard deviation of 20 mg/l.
4	**Select the sampling approach**	Probabilistic sampling feasible because of good access to drums. For each sampled drum, a composite sample is appropriate because mean concentration is required.
5	**Identify the scale**	Information is required on the between-drum scale; the scale is the volume of a drum
6	**Identify the required statistical approach**	Mean Cr^{6+} concentration for each sampled drum.
7	**Choose the desired reliability**	Precision not relevant for a control-chart-type compliance scheme. Confidence to be 99 % that a non-compliant drum represents a genuine increase in long-term mean Cr. For 99 % confidence, corresponding standard Normal deviate is 2,33. Thus control limit is set at L + 2,33s, namely 100 + 2,33×20 = 146,6. In practice, convenient to round this up to 150 mg/l as a convenient pass/fail criterion.
Determine the practical instructions		
8	**Choose the sampling pattern**	Select drums at systematic frequency of 1 in 20 from the disposal stream. NOTE Drums for disposal are produced at about 20 per week. There is no reason to suspect every 20th drum of having any recurring feature that will bias the assessment.

9	**Determine increment /sample size**	Liquid sludge adequately mixed, so increment size is adequate. Check made that sample volumes meet requirements for analysis. NOTE With the sampling implement used, six increments provide sufficiently large samples for analysis.
10	**Determine the use of composite or individual samples**	Experience indicates that six increments taken at progressive depths will provide a satisfactory composite sample.
11	**Determine required number of samples**	Not relevant for an on-going compliance scheme based on control chart principles. NOTE With control charts, the main factor determining the sampling frequency is the number of samples needed to sound the alarm at a specified degree of non-compliance. The statistical details for determining this fall beyond the scope of the present document.
12	**Define statistical elements of the Sampling Plan**	Starting with a randomly chosen drum, select every 20th drum thereafter. For each sampled drum, take a composite sample as specified above and determine the average Cr^{6+} concentration for that drum. Compare with control limit U.

E.7 Example 6: Carrier or Disposal company to carry out an on-site verification of drums containing Cr-contaminated liquid sludge prior to treatment

In this example of on-site verification, either the waste carrier or chemical waste treatment plant operator wishes to carry out on-site verification of a proportion of incoming drums containing a Cr-contaminated liquid sludge. The previous basic characterisation undertaken by the producer has shown that a drum with mean pH between 3 and 4 provides a reliable indication that the Cr in the liquid sludge is of the correct form.

Specify the objective of the testing programme		
1	**Specify the objective**	Carrier or Disposal company to carry out an on-going, on-site verification of drums containing Cr-contaminated liquid sludge prior to treatment
Develop the Technical Goals from the objective		
2	**Define the population to be sampled**	All drums to be treated over a 12-month period. NOTE All drums through the year will be equally accessible, and so available for checking.
3	**Assess variability**	It can be assumed that the contents of a drum are adequately mixed.
4	**Select the sampling approach**	Probabilistic sampling feasible because of good access to drums. For each selected drum, a single in situ pH analysis is judged adequate (see 3 above).
5	**Identify the scale**	Information is required on the between-drum scale; the scale is the volume of a drum.
6	**Identify the required statistical approach**	Proportion of 'failing' drums, i.e. those with mean pH < 3 or > 4.
7	**Choose the desired reliability**	Precision not relevant for a pass/fail form of compliance scheme. If true proportion of failing drums is as high as 2 %, this must be detected with 95 % confidence.
Determine the practical instructions		
8	**Choose the sampling pattern**	Select one in every 10 incoming drums for assessment. NOTE At the expected throughput, this proportion amounts to about one sample every two days, which is a manageable frequency.
9	**Determine increment /sample size**	Not relevant.
10	**Determine the use of composite or individual samples**	Individual sample.
11	**Determine required number of samples**	Using the method in Annex B shows that about 150 samples are sufficient to provide 95 % confidence of detecting a situation where the true proportion of failing drums is 2 % or worse.
12	**Define statistical elements of the Sampling Plan**	Test every tenth drum as specified above, and keep track of the number of drums with pH < 3 or > 4.

13		If 150 results accumulate with no failures, conclude that the failure rate is satisfactorily low. If appropriate, reduce frequency of verification sampling. If one or more failed drums are found within the first 150 sampled, conclude that the failure rate is unacceptably high, and if appropriate mount an investigation.

E.8 Example 7: Carrier or Disposal Company to carry out an on-site verification of the contents of tankers containing Cr6+ contaminated liquid sludge prior to treatment

In this on-site verification example the chromium sludge is being transported to the treatment facility using a road tanker. The tanker is filled from a pipeline valve at the factory. Either the waste carrier or the chemical waste treatment plant operator wishes to carry out on-site verification of the contents of the tanker. As in Example 6 it is reasonable to assume that a mean pH between 3 and 4 is adequate evidence that the contents are acceptable. Samples can be taken (a) during discharge to a holding tank, or, when the holding tank is full, (b) from the static load via an inspection hatch located in the top of the tanker.

Specify the objective of the testing programme		
1	**Specify the objective in terms of the overall population**	Carrier or Disposal Company to carry out on-going, on-site verification of the contents of tankers containing Cr^{6+} contaminated liquid sludge prior to treatment.
Develop the Technical Goals from the objective		
2	**Define the population to be sampled**	NOTE The requirement is to reach an accept/reject decision about each individual tanker. The scheme described here therefore relates to the contents of any one tanker. Scenario (a) A specific tanker delivery requiring treatment. Scenario (b) Portion of tanker contents accessible from inspection hatch.
3	**Assess variability**	A previous basic characterisation determined that pH concentrations within a tanker were roughly Normally distributed with standard deviation s = 0,3 pH units. Analytical error has standard deviation 0,05 pH units.
4	**Select the sampling approach**	Scenario (a): Probabilistic - composite sampling over the period of discharge. Scenario (b): judgemental sampling - composite sampling.
5	**Identify the scale**	Information is required on the scale of a tanker.
6	**Identify the required statistical approach**	Mean pH
7	**Choose the desired reliability**	Mean pH should be estimated to a precision of 5 % with 90 % confidence.
Determine the practical instructions		

8	**Choose the sampling pattern**	Scenario (a): Take stipulated number of samples over the period of discharge and bulk for a single analysis. Scenario (b): Take a full depth sample from the hatch of the liquid sludge and pour the full sample into a bottle for a single analysis.
9	**Determine increment /sample size**	Not relevant.
10	**Determine the use of composite or individual samples**	Composite samples
11	**Determine required number of samples**	For Scenario (a) a single composite sample of 8 increments is needed. NOTE From Annex C, formula for number of increments composite samples is: $m = \sigma w2/[n(d/ua)2 - \sigma b2 - \sigma e2]$, where a = 1 - (1 - C/100)/2. Here, d = 5% of 4 = .2 pH units, n = 1, and estimates of σw and σe are 0,3 and 0,05 pH units. Also, σb can be set to zero as the composite sample is being drawn from the entire sub-population. Finally, 90% confidence is required: thus a = 0,95, and ua = 1,65. This gives m = 0,09/[(.2/1,65)2 - .0025] = 0,09/.0122 = 7,4. Thus a single composite sample comprising 8 increments will provide the required precision. For Scenario (b) a single full-depth sample will be taken.
12	**Define statistical elements of the Sampling Plan**	Scenario (a): Take 8 increments spaced evenly over the period of discharge. Mix increments in one sample and determine pH. Accept tanker if pH is within 3 - 4 pH units, and 'reject' (i.e. subject to more detailed scrutiny) if pH is <2,8 or > 4,2 pH units. Scenario (b): Take full-depth sample. Produce composite sample over full depth for single analysis. Determine pH. Accept tanker if pH is within 3 - 4 pH units; otherwise 'reject'.

E.9 Example 8: Treatment plant operator applying basic characterisation to identify variability of Cr6+ in a treated waste using a two-step leaching test at LS 2 and LS 8

The hazardous liquid sludge is delivered to the treatment facility for processing into a non-hazardous solid block. Each load of drums or delivery of waste in the tanker is treated as a separate sub-population. Following solidification of the hazardous waste sludge from the Cr^{6+} plant, the treatment plant operator needs to undertake a basic characterisation of the now purportedly non-hazardous material to ascertain the basic properties of the material prior to disposal in an on-site landfill. A range of physical tests and chemical leaching tests may be required to complete this characterisation programme to show that the treated waste meets limit criteria for non-hazardous material in both the short and longer term, and to assess variability and mean concentrations of key components in the material. One example from the range of anticipated tests, relating to concentrations of Cr^{6+} in leaching test eluates, is used in the example below.

Specify the objective of the testing programme		
1	**Specify the objective**	Treatment plant operator applying basic characterisation to identify variability of Cr^{6+} in a treated Cr^{6+} waste using a two-step leaching test at LS 2 and LS 8 (EN 12457-3).
Develop the Technical Goals from the objective		
2	**Define the population to be sampled**	Population: Volume of solidified blocks produced in a six-month period. Sub-population: Accessible outer region of the volume of blocks produced during the six months. NOTE Access on site is only available to outer edge of block - i.e. samples can be cut off with mechanical cutting equipment or chipped off with a hammer.
3	**Assess variability**	Variability of source waste is known, but not of treated material. The material arises in weekly sub-populations of about 20 blocks.
4	**Select the sampling approach**	Judgemental sampling, systematic sampling for a selected number of sub-populations within the sub-population.
5	**Identify the scale**	Within-sub-population and between-sub-population levels
6	**Identify the required statistical approach**	Mean and standard deviation of Cr6+ for each of a number of randomly selected sub-populations as well as the standard deviation of mean Cr6+ between sub-populations. NOTE A further objective might be to obtain separate estimates of the within-block and between-block variability in Cr^{6+}, but this is assumed not to be relevant in the present example.
7	**Choose the desired reliability**	Within-sub-population standard deviations to be estimated to a precision of 30 % with 90 % confidence.
Determine the practical instructions		

8	**Choose the sampling pattern**	Systematic sampling of blocks within each selected sub-population. NOTE Suppose 30 samples were to be taken from each selected sub-population of 20 blocks. An appropriate pattern would be to take one sample at a random location from each of 10 blocks (selected at random) and two samples at random from each of the other 10 blocks.
9	**Determine increment /sample size**	It is assumed that the blocks are adequately homogenous at the scale of sampling. If this is not the case and the material was badly mixed prior to solidification, then the issues of increment and sample size (see Annex D) come into play.
10	**Determine the use of composite or individual samples**	Individual samples.
11	**Determine required number of samples**	Making assumption of Normality, approximate number of samples to be taken per sub-population is 28. NOTE Number of samples obtained by picking out an appropriate value from the trial calculations tabulated in Annex C. Number of sub-populations to be sampled cannot be determined statistically because nothing is known at this stage about the size of the within-sub-population standard deviation. A minimum of four sub-populations should be sampled if possible - or more if the sampling resources are available.
12	**Define statistical elements of the Sampling Plan**	Select the agreed number of sub-populations at random times during the six-month period. For each sub-population, take 28 samples at regular intervals from the accessible block volumes. Analyse each sample separately. Calculate mean and standard deviation separately for each sub-population. NOTE The statistical methods needed (a) to test whether within-sub-population variability is consistent from one sub-population to another, and (b) to estimate the size of the sub-population-to-sub-population variability, go beyond the scope of this document. For further details the reader would need to seek the help of a statistician.

E.10 Example 9: Treatment plant operator to perform compliance testing to determine whether the treated hazardous waste complies with a limit determined on the basis of the basic characterisation, using a combined one-step leaching test at LS10

Following completion of a basic characterisation, the waste treatment plant operator is now required to complete a programme of regular compliance testing to show compliance with the site operating licence. Compliance can be judged on the basis of a one-step granular leaching test at LS 10. The basic characterisation will have identified a range of key parameters that must be checked during compliance testing. The example below illustrates an appropriate approach for looking at Cr^{6+} concentrations. The compliance scheme would need to be constructed similarly for the other parameters.

Specify the objective of the testing programme		
1	**Specify the objective in terms of the overall population**	Treatment plant operator undertake on-going testing regime to determine whether the treated hazardous Cr^{6+} waste complies with a limit determined on the basis of the basic characterisation, using a combined one-step leaching test at LS10 (EN 12457-2).
Develop the Technical Goals from the objective		
2	**Define the population to be sampled**	Population: Volume of solidified blocks produced in a 12-month period. Sub-population: Accessible outer region of the volume of blocks produced during the 12 months. NOTE Access on site is only available to outer edge of block - i.e. samples can be cut off with mechanical cutting equipment or chipped off with a hammer.
3	**Assess variability**	Basic characterisation showed little within-sub-population variation but substantial between-sub-population variation. The 95-percentile concentration of Cr^{6+} in the eluates was estimated to be 13 mg/l.
4	**Select the sampling approach**	Judgemental sampling
5	**Identify the scale**	Between-sub-population.
6	**Identify the required statistical approach**	Proportion of blocks for which mean value of Cr^{6+} in eluates exceeds the 95-percentile standard (13 mg/l).
7	**Choose the desired reliability**	If 95 % of blocks are truly complying, the 'false alarm' or risk of declaring non-compliance should be no worse than 5 %. Sufficient samples should be taken to ensure that non-compliance can be declared if 85 % or fewer of the sampled blocks comply.
Determine the practical instructions		
8	**Choose the sampling pattern**	Take a single sample at random from each of a number of systematically selected sub-populations.
9	**Determine increment /sample size**	It is assumed that the blocks are adequately homogenous at the scale of sampling. If this is not the case and the material was badly mixed prior to solidification, then the issues of increment and sample size (see Annex D) come into play.

10	**Determine the use of composite or individual samples**	Systematic individual sampling.
11	**Determine required number of samples**	From the methodology described in Annex C, the minimum number of samples required is 27, with the control rule: declare the process non-compliant if 4 or more samples exceed the limit (13 mg/l). NOTE The probability of getting ≤ 3 high values from 27 random samples is CumB(3; 27,0,05) = .956, or 95,6% Thus the probability of getting 4 or more values above the limit is only 4,4%. This is just less than the required risk of 5 %, and so 4 high values can trigger a non-compliance decision. Moreover, 3 high values is equivalent to 100(24/27) = 89 % sample compliance, whilst 4 high values is equivalent to 100(13/27) = 85 % sample compliance. The compliance rule therefore achieves the required precision.
12	**Define statistical elements of the Sampling Plan**	Select a block at random some time during the first two weeks and take a random sample from this. Sample similarly once every two weeks thereafter. Sample on one further randomly chosen week to bring the total number of samples in the year up to 27. Each sample should be analysed separately. If the Cr^{6+} concentrations of 4 or more of the 27 samples exceed the limit, declare the process non-compliant.

E.11 Example 10: On-site verification

An on-site verification of the treated material is carried out by the Regulator on an ad hoc timescale. Off-site analyses for pH, total Cr^{6+} and physical stability tests will be undertaken. This example requires essentially the same approach as for Example 3, except that samples need to be taken from the outside of a block instead of around the perimeter of a lagoon.

E.12 Example 11: Compliance testing

The regulator has identified contamination of a key public supply borehole and linked it to the disposal lagoon at the Cr^{6+} processing plant. The on-site sludge lagoon at the waste production facility must be emptied and the waste despatched to an off-site hazardous landfill. During routine disposal of the Cr^{6+} sludge at the lagoon, the supernatant liquid is returned to the production facility following a suitable period to allow separation of the solid/liquid constituents of the sludge. Prior to excavation all supernatant is pumped back to the factory.

The producer to show that the aged sludge has comparable chemical characteristics of key components to the mixed fresh non-aged sludge originally disposed to the lagoon - that is, the sludge characteristics are to be compared with the results of the previous basic characterisation must carry out a compliance test. It is estimated that the contents of the lagoon represent a period of disposal of twenty years. Analysis of total chromium and Cr^{6+} levels will provide the necessary data for such a comparison. This represents a series of sub-populations or consignments of a one-off waste. Samples will be taken during the excavation and loading into an open road truck, prior to transport to an off-site hazardous waste landfill. Good access to all the material is available during loading.

If the required objective is to ascertain worst-case concentrations of chromium and Cr^{6+} in the sludge, the approach identified in Example 2 could be used. Alternatively if the requirement is to check whether the variability of the material conforms with previous data, the approach detailed in Example 9 would be appropriate.

There may be a need to undertake a further basic characterisation of the aged sludge if the compliance check indicates that the material no longer conforms with the data of the basic characterisation of the fresh material. The methodologies outlined in Examples 1 and 8 could provide an appropriate approach.

E.13 Example 12: On-site verification

The hazardous waste landfill operator requires an on-site verification test of incoming loads of aged sludge from the processing plant lagoon on arrival at the landfill site. A single sample is required from the open truck prior to tipping to ascertain whether the material pH is within the range established in the basic characterisation analysis of between pH 3 and 4.

Despite the limited approach outlined in this example and that of Example 13, it is still possible to make some statement about the load utilising prior knowledge about the material. For example, it might have previously been established that pH could vary by as much as $\pm$ 1 pH unit around the mean. It would then be reasonable to say that if a single sample is tested and has a pH of < 2 or > 5, the mean of the load in the lorry is unlikely to be between pH 3 and 4.

Even if time or funds are minimal, it is preferable to take a number of increments and analyse a bulked composite sample (as per Example 3) in order to improve the precision in the result of the test and to increase the likelihood that the result is representative of the sub-population being tested. For a continuous waste stream the approach identified in Example 6 is additionally advantageous.

E.14 Example 13: On-site verification

A compliance check by the operator of the waste treatment plant has shown that a particular sub-population of the treated hazardous waste falls outside acceptable limit criteria for the on-site landfill. This sub-population must therefore be sent to the hazardous waste landfill operator. The latter wants to do an on-site verification test to show that the waste conforms to characterisation data supplied by the Waste treatment plant operator. A single block will be selected to determine physical integrity. The block will be struck with a hammer and should remain intact. The limitations of this proposed approach are as discussed in Example 12.

E.15 Example 14: Basic characterisation

Following closure of the Plant and redevelopment of the site, contaminated soil must be removed for disposal. Using the approaches detailed in Examples 2 and 8 a sampling programme for basic characterisation can be devised taking samples from the mechanical excavator to establish worst-case concentrations, for example, or a measure of the variability of the soil. It is preferable to sample the material, as it is being excavated and therefore mixed to some extent, rather than undertake an *in situ* sampling programme, which would need to involve depth sampling and a grid pattern of sampling. It may be important to consider the relevant scale of sampling in this example and potential implications for the minimum increment size.

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