Appendix D : Waste Sampling
A supplement to
Hazardous waste : Interpretation of the definition and classification of hazardous waste (3rd Edition 2013)
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# Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Introduction</td>
<td>2</td>
</tr>
<tr>
<td>D1</td>
<td>Background</td>
<td>3</td>
</tr>
<tr>
<td>D1.1</td>
<td>Introduction</td>
<td>3</td>
</tr>
<tr>
<td>D1.2</td>
<td>Legal background</td>
<td>3</td>
</tr>
<tr>
<td>D1.3</td>
<td>The testing programme</td>
<td>3</td>
</tr>
<tr>
<td>D1.4</td>
<td>Application of this chapter</td>
<td>4</td>
</tr>
<tr>
<td>D2</td>
<td>Preparatory Steps</td>
<td>5</td>
</tr>
<tr>
<td>D2.1</td>
<td>Identify the involved parties</td>
<td>5</td>
</tr>
<tr>
<td>D2.2</td>
<td>Identify the objectives and technical goals</td>
<td>5</td>
</tr>
<tr>
<td>D2.3</td>
<td>Research background information</td>
<td>6</td>
</tr>
<tr>
<td>D2.4</td>
<td>Determine the level of testing required</td>
<td>7</td>
</tr>
<tr>
<td>D2.5</td>
<td>Identify constituents to be tested</td>
<td>7</td>
</tr>
<tr>
<td>D2.6</td>
<td>Identify health and safety precautions</td>
<td>8</td>
</tr>
<tr>
<td>D3</td>
<td>Develop the technical goals from the objectives</td>
<td>8</td>
</tr>
<tr>
<td>D3.1</td>
<td>Define the population to be sampled</td>
<td>8</td>
</tr>
<tr>
<td>D3.2</td>
<td>Assess variability</td>
<td>11</td>
</tr>
<tr>
<td>D3.3</td>
<td>Scale of sampling</td>
<td>12</td>
</tr>
<tr>
<td>D4</td>
<td>Determine the practical instructions</td>
<td>14</td>
</tr>
<tr>
<td>D4.1</td>
<td>Choose the statistical approach</td>
<td>14</td>
</tr>
<tr>
<td>D4.2</td>
<td>Select the sampling approach</td>
<td>21</td>
</tr>
<tr>
<td>D4.3</td>
<td>Determine the type, number and size of samples required</td>
<td>24</td>
</tr>
<tr>
<td>D4.4</td>
<td>Identify sampling techniques</td>
<td>28</td>
</tr>
<tr>
<td>D5</td>
<td>Define and document the sampling plan</td>
<td>30</td>
</tr>
<tr>
<td>D6</td>
<td>Subsequent steps</td>
<td>30</td>
</tr>
</tbody>
</table>
Introduction

What is this document about?
This document provides guidance on the sampling of waste.
This guidance is a supplement (Appendix D) to our Technical Guidance (WM2) on the assessment and classification of hazardous waste. It should be used in conjunction with WM2.

Who is it intended for?
This document is intended for anyone involved in the production, management and regulation of hazardous waste.
You only need to use this document if your assessment and classification includes, or is reliant on, results obtained from samples.
If you are inexperienced in waste sampling, or lack the necessary knowledge of hazardous waste, you should seek advice before using this document.

How is the information presented?
Technical Guidance WM2 is built around chapter 2: Hazardous Waste Assessment.
Each of the four Appendices A, B, C and D provide supporting information on a specific aspect of that assessment.
The diagram below illustrates how this document, Appendix D, relates to the other sections:

Chapter 2: Hazardous Waste Assessment
A flowchart and explanatory text to guide you through the assessment and classification of a waste.

Appendix A: Consolidated List of Waste
Guidance on how to use the list of waste, with numerous examples to illustrate common and specific aspects.

Appendix B: Data Sources
An explanation of where to find information on chemical classification and how to use it.

Appendix C: Hazardous Property Assessment
Each of the 15 hazardous properties and how to assess them is explained one at a time.

Appendix D: Waste Sampling (separate supplement)
If you are basing your assessment on analysis of samples you need to ensure that your sampling and interpretation is robust. This supplement explains what you need to consider.
Appendix D:

Waste Sampling

D1 Background

D1.1 Introduction

To obtain accurate and representative results, and a therefore a reliable assessment, it is essential that the sampling programme is properly planned and conducted.

The key principle is that a sampling plan should be prepared before the first sample is taken. This will help you ensure that relevant factors are considered, and sufficient representative samples are taken, to enable all parties to have confidence in the reliability of the results and their interpretation.

You should be prepared to provide a copy of your sampling plan to support any waste classifications and hazardous waste assessments you have made.

D1.2 Legal background

It is a legal requirement to correctly assess and classify your waste. For many wastes there may be sufficient information to do this without the need to sample. Where sampling is needed this appendix is guidance to help you do so properly.

This is based on the current European and British Standard, and supporting Technical Reports, on the Characterisation of waste – Sampling of waste materials:

- Framework for the preparation and application of a sampling plan (BS EN 14899:2005)
- Part 1: Guidance on selection and application of criteria for sampling under various conditions (PD CEN/TR 15310-1:2006)
- Part 3: Guidance on procedures for sub-sampling in the field (PD CEN/TR 15310-3:2006)
- Part 4: Guidance on procedures for sample packaging, storage, preservation, transport and delivery (CEN/TR 15310-4:2006)
- Part 5: Guidance on the process of defining the sampling plan (PD CEN/TR 15310-5:2006)

We will use these documents as the basis for assessing sampling procedures during our regulatory activities.

Alternative sampling procedures are acceptable if they have considered the relevant factors identified here and produce an equally reliable result.

Results should only be used, for waste classification or hazardous waste assessment purposes, if the sampling has considered the relevant factors.

D1.3: The testing programme

The testing programme can be broken down into key steps including:

- transporting and storing the sample
- preparing and Analysing the sample
- reporting and interpreting the results

The Figure D1.1 sets out the key steps involved in defining the sampling plan.
D1.4 Application of this chapter

This chapter provides guidance on how to assess a single waste using the results obtained by taking a number of samples of that waste.
Any waste (or individual batch/container thereof), or any waste in a mixed waste, that if sampled and assessed in isolation, would produce a classification or hazardous property different from others in that population, should be regarded as a discrete sub-population and assessed separately. This would include waste soil from ‘hotspots’ identified during site investigations. The sampling plan should be designed to enable reliable identification of such sub-populations.

**D2 Preparatory steps**

**D2.1 Identify the involved parties**

The sampling plan should be prepared under the direction of a nominated person, familiar with the requirements, in consultation with the appropriate involved parties.

The need to involve other parties will vary in each case, depending on the complexity, scale and purpose of the sampling. These parties may have additional or conflicting interests that should not undermine the objective.

<table>
<thead>
<tr>
<th>Example of Involved Parties</th>
<th>Typical Role</th>
</tr>
</thead>
<tbody>
<tr>
<td>Producer / Holder</td>
<td>Directly involved as responsible for the waste classification and assessment (and completion of waste documentation)</td>
</tr>
<tr>
<td>Laboratory / Sampler / Consultants engaged in sampling and analysis</td>
<td>Directly involved as responsible for conducting parts of the testing programme.</td>
</tr>
<tr>
<td>Carrier and Consignee</td>
<td>Directly involved, as the information is pertinent to carriage, subsequent management and completion of waste paperwork.</td>
</tr>
<tr>
<td>Regulator</td>
<td>Indirectly involved via provision of advice and guidance. May become directly involved through compliance checks.</td>
</tr>
</tbody>
</table>

**D2.2 Identify the objectives and technical goals**

A testing programme for hazardous waste assessment should normally have only one objective; to obtain sufficient information on the nature, composition and properties of the waste to determine if it is a hazardous waste, to assign hazardous properties, and to inform allocation the appropriate List of Waste (LoW) code.

If there is more than one objective, each should have a separate testing programme designed to deliver that objective.

The testing programme for hazardous waste assessment should be broken down into specific technical goals which may include, for example:

- identifying if the waste is mixture of two or more wastes or subpopulations
- identifying which dangerous substances are present
- determining the concentration of dangerous substance present
- testing directly for certain hazardous properties for which that is appropriate, for example H3-A and H3-B Flammable

In the sampling plan each of these technical goals should be further broken down into detailed instructions and technical specifications that should address, for example:

- define the population to be sampled
- assess variability
- select the sampling approach
- select constituents to be studied
D2.3 Determine level of testing required

The Testing Level is the type(s) and frequency of investigation required to meet the technical goals and deliver the objective. This is largely determined by how much information you already have, and how much is unknown, and may for example encompass each of the following:

**Basic (comprehensive) characterisation**: a thorough initial investigation of a waste, considering the key aspects in this chapter, to support development of a compliance testing programme. These are normally required:

- initially, or periodically, where a process or activity regularly produces waste, (for example the outputs of a waste treatment process), and/or
- where many of the relevant factors (e.g. nature and causes of variability) are unknown

**Compliance testing**: the routine sampling and assessment of a waste or wastes, for example to compare the concentrations of dangerous substances to hazardous waste thresholds. This is likely to be appropriate:

- for processes or activities that regularly produce waste where basic characterisation has already provided sufficient information on the relevant factors (for example, to identify sub-populations), or
- for one-off wastes of a type that is well characterised

**On-site verification**: checks at any point in the waste chain, using ‘quick check’ methods to confirm specific information obtained from compliance testing or included on the waste paperwork. These are confirmatory checks only, not a stand alone hazardous waste assessment and might for example include:

- identification of visually non-conforming wastes in bulk containers
- a check of key relevant characteristic, e.g. pH or a metal concentration

<table>
<thead>
<tr>
<th>An Example of how levels of testing are applied:</th>
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<tbody>
<tr>
<td>A waste treatment process receives and processes waste of variable quality after robust pre-acceptance and waste acceptance checks. The composition and potential contaminants, or non-conforming elements, of the input materials are known or reasonably predictable. The waste is received from 10 different producers via a number of intermediary carriers and transfer stations.</td>
</tr>
</tbody>
</table>

A **comprehensive basic characterisation** study is undertaken to provide evidence of the impact of the various factors identified in this chapter (from differences in input materials from different producers, to heterogeneity of treated residues and identification of sub-populations)

From this a routine **compliance testing programme** is designed that involves identification and regular assessment of the output sub-populations from the treatment plant for a range of relevant parameters, excluding those proven unnecessary by the basic characterisation tests.

In addition each batch of treated residues is **verified on site** specifically for pH and nickel contamination, as basic characterisation identified the potential for individual batches to be hazardous as a result of these two criteria.
D2.4 Research background information

Site details
The sampling plan should identify the details of the sampling location and restrictions to access. Any additional access problems encountered during sampling must be recorded in the sampling record so any impacts on the quality of the collected samples can be considered.

Process or nature of arising
The sampling plan should include a general description of the circumstances that resulted in the waste being produced. This could be based on following:

- direct knowledge of the primary process
- the nature of arising, or
- inspection of the process / nature of arising

Material type and dimensions
The sampling plan should identify the physical nature and dimensions of the sub-population to be sampled. For example, this might include:

- solids, liquid or gas
- moving stream (e.g. conveyor or pipeline) or static
- if static, is it contained or in heaps
- if contained, what type and size of container; plastic 25 litre drum, silo etc.
- number of containers, and quantity, i.e. kilos, tonnes, etc
- physical and chemical characteristics

The sampling plan must list all known physical and chemical characteristics of the material including all known potential hazards, and any operational procedures that could affect the chemical, biological and physical properties.

D2.5: Identify constituents to be tested

For waste classification there are three key points to consider here:

- the regulations require that the composition of the waste, concentration of the components, and hazardous properties are recorded on the consignment note. This is not restricted to dangerous substances
- many ‘mirror’ entries in the LoW consider all dangerous substances
- some LoW entries may identify the relevance of specific items, articles, components, properties or substances to determining the classification

In many instances it will be possible to reduce the number of constituents to be tested to a much smaller number of key constituents. For example, the possible constituents of waste from a manufacturing process may be extrapolated from the raw materials and process itself. Substances that are known not to be present, used, or produced by the process can often be excluded.

In other circumstance a basic (comprehensive) characterisation exercise might be undertaken, considering a wide range of dangerous substances, to identify those of potential relevance. Compliance testing can subsequently focus on those substances.

Clearly, however, if the inputs to a process are variable, poorly characterised, or subject to more limited checks, then the uncertainty over the constituents would require more expansive testing.

The constituents considered, and the basis for any potentially relevant exclusions, should be specified in the sampling plan.
D2.6: **Identify health and safety precautions**

A full exploration of this issue is beyond the scope of this document. Advice should always be sought from a qualified health and safety professional.

The sampling plan should ensure that all relevant health and safety issues, and necessary precautions, are identified to those involved in the testing programmes. This might include, for example, risks arising from:

- the nature of the waste
- how it is contained or stored
- access
- site operations, plant or activities, or
- sampling equipment or tools

**D3 Develop the technical goals from the objectives**

**D3.1 Define the population to be sampled**

The sampling plan should contain a description of the population or subpopulations to be sampled to avoid ambiguity.

**D3.1.1 Population**

The ‘population’ is the total amount of waste that you want to obtain information on by sampling. Examples might include:

- a single container of waste
- a batch of waste from a process, or
- a continuous stream of waste produced by a production process in a specific period of time (e.g. a day, a week, a month)

It is important to note that the population must always be defined explicitly with reference to spatial or temporal factors, otherwise it is impossible to determine if sampling of that population is representative or not. The choice of population relies on experience and judgement, rather than statistics.

Key point: If the population is defined as the waste from a process produced over a period of one month, then the testing programme will not be completed until that one month of production has been sampled. None of the waste produced can be assessed, classified and disposed of before then.

**D3.1.2 Overall population**

The term overall population is sometimes used to indicate a wider population, of which the sampled population(s) is itself a subset. For example the entire lifetimes operational output of a process would be an ‘overall population’. From within this overall population one or more populations might be defined for sampling and assessment purposes.

In some instances it may be possible to apply the results of sampling a population to an overall population, however to do so the onus in on the producer to demonstrate during the testing programme that the overall population does not differ from the population. This is most likely to be applicable where a manufacturing process generates a continuous stream of homogenous waste from raw materials of a defined composition.

**D3.1.3 Sub-populations**

Depending on the circumstances it is sometimes necessary to divide a population into sub-populations, a portion of the material that needs to be sampled and the results considered separately. For example a process might generate 24 batches of waste (the population), however each batch is a sub-population that is sampled and assessed separately.
The division into subpopulations is normally required where the samples from one portion of the population may generate a different classification when considered separately from another portion. Conversely, if the producer wishes to consider all the wastes to be part of a single population, with no sub-populations, the testing programme would need to demonstrate that this is a reasonable assumption and that no sub-populations exist.

The nature of the waste production process is the principal factor that determines the need for subpopulations. The more consistent, controlled and characterised the process, its outputs, and its raw materials/feedstock, the fewer sub-populations are likely to be generated.

Sub-populations may also be generated:

- where access restrictions inhibit or prevent access to the population as a whole, or
- by characteristics such as non-conforming or deviating parts in the waste

Due consideration needs to be given to ‘scale’ when defining the subpopulation.

The samples taken from a sub-population can only be considered representative of that sub-population. The relevance of these results to the population is entirely dependent on the validity of the assumptions made in generating the sampling plan.

D3.1.4 One-off production waste

The simplest form of waste production is a one-off production of a single waste stored in a single container, stockpile, lorry or other container. The ‘population’ can easily be defined as the material in the specific container or location. There is no need to divide this into subpopulations.

The next level of complexity is where a one-off production of a waste is stored in more than one container. Although sampling would normally include multiple containers, the need to divide this into subpopulations would be dependent on whether other factors differentiate the containers (for example different storage conditions or methods).

D3.1.5 Continuous production of a homogenous stream of waste

Where a continuous process produces a stream of waste that is homogenous the population can be defined in time. For example, all the waste produced in one month or one year.

The waste classification and assessment delivered by the sampling plan can be applied to that entire time period. However the sampling plan would have to demonstrate that the material is homogenous. We would look for two key factors to underpin this:

- a process with demonstrably consistent, well characterised, and controlled inputs/raw materials that do not vary in composition or quantity, and
- the results from the sampling demonstrate that no statistical difference exists between samples taken over the time period (i.e. one batch is the same as any other)

This is more likely to be applicable to manufacturing processes using quality raw materials, than waste disposal or recovery processes where that level of input control is not achievable.

D3.1.6 Continuous production of a heterogeneous stream of waste

Continuous production processes can often result in a stream of heterogeneous (variable quality) waste. This is particularly true of waste disposal or recovery processes where the nature, composition, consistency of quantity of input materials is potentially more variable than the higher quality raw materials used in production processes.

The consequence is that one portion of the waste stream may differ from another. Specifically, they may have different compositions, properties and/or classifications.

For the purposes of hazardous waste assessment and waste classification the sampling plan should be organised specifically to identify the proportion of the waste stream that:

- is hazardous, and/or
- is classified under a different LoW code
To sample a waste of this nature, and gain and insight into the heterogeneity of the population, the waste will need to be divided into sub-populations. These sub-populations should be physically separated until the results of the testing programme are obtained to allow separate actions to be taken as a consequence of different classifications etc.

The standard and technical reports identify three different perspectives generally applicable to waste characterisation:

<table>
<thead>
<tr>
<th>Perspective</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production</td>
<td>Potentially a clear relation between the sub-population and the production process results in relatively lower costs for the testing programme</td>
<td>Production process must be known and samples must be taken during or directly after production</td>
</tr>
<tr>
<td>Transport</td>
<td>Practical from the perspective of sampling</td>
<td>Might result in high costs when there are lots of sub-populations</td>
</tr>
<tr>
<td>Destination</td>
<td>Potentially a direct link can be defined between the quantities of material that are considered relevant, for example from a toxicological perspective</td>
<td>Variations caused by production, transport and/or mixing of quantities can no longer be identified</td>
</tr>
</tbody>
</table>

The legal requirements for waste classification and assessment relate principally to the production of hazardous waste and prevention of its subsequent mixing. This is entirely independent of subsequent transport to a destination. Production therefore becomes the primary mechanism for defining sub-populations for hazardous waste assessment. Any differences in the production process that might cause variation in the waste produced should be considered, for example:

- different producer, department or activity
- variations in quality raw materials or feedstock
- waste produced by more than one device, unit or plant
- where the production process is not uniform (for example production of one batch differs from the next)

Once production subpopulations have been determined further subdivisions relating to transport and destination can also be considered if necessary.

As each load of hazardous waste, when transported, is accompanied by a consignment note, variations between loads also have the potential to generate subpopulations. There are several options, depending on the circumstances, including regarding:

- each load as an entirely separate population
- each load as a separate sub-population

Where several loads are transported to the same destination, it may also be appropriate to define the sub-population by destination, grouping those loads together.

**D3.1.7 Mixed waste**

Where the waste is a mixture of two or more wastes then the testing programme each would normally need to classify and assess each waste separately.

The sole exception would be where the LoW specifically provides a code for mixed waste of that nature. In this instance the testing programme would normally need to determine the relative proportions and composition of each waste in the mix.

Where the list of wastes provides a single code for a mixed waste, it should be noted that the scope of the single code would not include a waste(s) that the law would prohibit from being
combined with the other waste(s). Such a waste would need to be coded and assessed separately.

Typical examples of mixed waste that has to be assessed as separate wastes include:

- **Waste disposal / recovery process residues** - A waste treatment process generates five batches of filtercake. Due to the variation and nature of the waste inputs processed the last batch is actually hazardous. The hazardous batch would need to be identified, assessed and coded separately (as a sub-population) from the non-hazardous batches. The five batches should not be assessed as a single waste.

- **Asbestos materials in construction and demolition waste** - The LoW contains specific codes for construction or insulation materials containing asbestos. This asbestos should normally be assessed and classified separately from other wastes. Therefore a skip containing a mixture of construction and demolition waste and asbestos containing insulation board, tiles, coatings, etc (or fragments thereof) should be classified as mixed, and the asbestos materials classified and assessed separately.

- **Laboratory chemicals**, consisting of or containing dangerous substances, including mixtures of laboratory chemicals - A crate containing bottles of three different laboratory chemicals, each would need to be assessed as a separate waste.

Typical examples of mixed waste that can be assessed as a single waste include:

- **Mixed municipal waste** from domestic premises
- Mixtures of waste from **grit chambers** and **oil water separator contents**
- Mixtures of, or separate fractions of **concrete, bricks, tiles and ceramics** ‘containing dangerous substances’, or ‘other than those mentioned’ Noting that any construction and demolition waste for which separate codes are specifically provided (e.g. asbestos containing materials, gypsum, etc) would need to be classified and assessed separately.

### D3.2 Assess variability

#### D3.2.1 General

Variability is normally a characteristic of a waste that cannot be changed without intensive manipulation.

Understanding the main components of variability in the population being sampled is required to design the testing programme.

Investigating and understanding the types of spatial and temporal variability is important as it allows that knowledge to be used to design the sampling plan to match the characteristics of the population. This increases the reliability of the results. For example:

- where variability is temporal, perhaps related to different feedstock, the waste could be divided into subpopulations on that basis, and/or
- where day to day variation in production differs more than variation within a single day, then sampling effort should focus on taking samples over many days rather than many samples on a single day

#### D3.2.2 Spatial variability

Spatial variability is where one part of a waste differs from another. Most materials are heterogeneous in this way when considered in bulk. The spatial variability might arise from:

- the waste arising in physically different locations, e.g. three different containers
- temporal variation in the producing process, for example three different batches of filter cake in a single skip may differ due to the feedstock used
- a separation within in the waste, for example solids settling out in a container of liquid
The spatial variability is an inherent characteristic that will not change without manipulation (e.g. mixing a fluid that has separated into phases)

D3.2.3 Within-stratum variability
This defines variability seen between samples taken from the same sub-population or strata, for example, the variation between samples taken from a single batch of filter cake.

D3.2.4 Between-stratum variability
This defines the variability seen between samples taken from different sub-populations or strata, for example, the variation between samples taken from three different batches of filter cake placed in a single skip or liquids that have separated into different layers. The distinction between within-stratum and between-stratum is most obviously relevant when the strata are in physically separate parts. However they are of equal relevance and importance to sequentially accumulated or arising material.

D3.2.5 Temporal variability
Temporal variability can be considered in three main types, cyclic, driven and random.

Cyclic
The material exhibits a regular temporal pattern dependent on the time of day, day of week or time of year. For example municipal waste composition may include more packaging materials after Christmas and Easter.

Driven
The variability is ‘driven’ by known factors. For example, the composition of the output from a waste disposal process is dependent on the composition of the input waste received from each producer.

Random
This typically describes the net effect of a large number of smaller unknown factors that generate temporal variability that often cannot be accounted for. One of the technical goals of the sampling plan should be to identify the significant causes of temporal variability where they are unknown.

D3.3 Scale of sampling
The ‘scale’ is the amount of waste which a sample directly represents. For example, a sample taken from a drum may directly represent the material in that drum.

Depending on the circumstances the scale might be defined by:

- particle size in the waste
- the size of the population or sub-population, or
- in terms of time (a day, a month, a week, or a year)

There is a strong relationship between heterogeneity and scale. The heterogeneity is normally larger if the scale is smaller.

The scale defines the minimum quantity of material below which variations are judged to be unimportant. For that reason the scale chosen should be based on knowledge of potential heterogeneity in the waste, and care should be taken not to ensure that a large scale does not mask relevant smaller subpopulations. So for example if the scale of sampling of a skip of construction and demolition waste was ‘a skip’, then the skip should not contain any heterogeneity below that (e.g. coal tar or asbestos containing fragments in a skip of soil)

The results from sampling are only valid for a scale equal to or greater than the scale of sampling.

The following example illustrates this:
Example: A waste treatment process produces 10 x 1 tonne batches of filter cake that are placed in a skip:

- 5 batches of filter cake were produced from treatment of waste acid A, containing higher levels of heavy metals, and
- 5 from treatment of waste acid B containing lower levels of heavy metals

Basic (comprehensive) characterisation has already demonstrated that variation within any single batch of filter cake from the process is unimportant, and that waste acid is the only significant source of variation.

There are three different approaches that might be applied here:

1. sample the skip (scale = 10 tonnes, the population)
2. sample the filter cake from the treatment of waste acid A separately from waste acid B (scale = 5 tonnes, 2 sub-populations identified)
3. sample each separate batch of filter cake (scale = 1 tonne)

Option (i) provides information on the population, not on sub-populations. It assumes that there is no variation between batches of filter cake. In this instance the filter cake from acid A and acid B may be different. These should be viewed as different sub-populations, and a smaller scale used, until proven otherwise.

Option (ii) provides information on the population, and on the heterogeneity introduced by the two identified sub-populations. The scale is equal to the sub-population. This relies on the basic characterisation to confirm that source acid is the only significant source of heterogeneity.

Option (iii) is appropriate where the waste acid is not only variable, for example where a number of waste materials of varying quality are treated. It may be possible to focus and increase the scale of compliance check sampling later, if basic characterisation sampling provides more detailed information on heterogeneity that supports that approach.

The key point here is that scale and heterogeneity interact. The choice of scale must not make any assumptions about heterogeneity, and therefore mask sub-populations.
D4  Determine the practical instructions

The technical goals must be translated into practical instructions for those involved. This should include:

- choosing the statistical approach
- selecting the sampling approach
- determining the number type and size of samples
- identify sampling techniques.

D4.1  Choose the statistical approach

This section discusses the statistical approaches applicable to, and the interpretation of results obtained from, sampling a waste.

The approach provided here is based primarily on:

- determining the mean concentration (or 50th percentile)
- calculating confidence intervals around that mean. and
- comparing the confidence intervals to hazardous waste thresholds.

The confidence intervals are used to determine the reliability of the interpretation, and will generate three possible answers:

- The waste is reliably known to be hazardous
- The waste is reliably known to be non-hazardous, or
- The sampling has not provided a reliable answer and either the waste is classified as hazardous on a precautionary basis, or additional sampling is undertaken to provide a reliable answer

Four statistical approaches are provided to suit different circumstances as set out in Figure D4.1. These include:

- A parametric method (where the data is normally distributed or approximates a normal distribution), and
- Non-parametric methods (for use where this is unknown or is not the case)

Statistical tests may be used to determine if the data has, or approximates, a normal distribution.

As an alternative to using the statistics presented here the producer or holder may assume that a waste possesses a hazardous property if:

- any individual sample has exceeded the threshold for that hazardous property, or
- such a sample could reasonably be taken by another party, for example the regulator.
D4.1.2 Parametric method - The mean and its confidence intervals

For simple, and particularly one-off, waste sampling scenarios the objective is to determine whether the concentration of dangerous substance in the waste is above or below the threshold.

Waste can be heterogeneous so the concentration may vary from one part of the waste to another. The mean concentration in the waste (\(\mu\)) is therefore the key criteria against which thresholds are considered.

Sampling generates a sampling mean (\(\bar{x}\)) which is an estimate of the actual population mean (\(\mu\)). Like any estimate, there is a degree of uncertainty. This uncertainty is represented by the confidence intervals of the mean. This is the range in which the results suggest that additional estimates of the mean, from further sampling of the same waste, might reasonably fall. Or to put it another way, the range within which (\(\mu\)) can be confidently be predicted to lie.
For hazardous waste purposes we need to be confident that the uncertainty associated with sampling mean ($\bar{x}$) does not span the threshold concentration. This would mean that $\mu$ could lie either side of the threshold, rendering the assessment inconclusive. Figure D4.2 illustrates this, and shows the sampling mean in relation to a hazardous waste threshold for four wastes (A to D):

- Waste A does not possess the hazardous property because the upper confidence interval for the sampling mean ($\bar{x}$) is below the threshold. We can therefore have confidence that $\mu$ is below the threshold.
- Similarly Waste D does possess the hazardous property because the lower confidence interval for the sampling mean ($\bar{x}$) is above the threshold. We can therefore have confidence that $\mu$ is above the threshold.
- For Wastes B and C the uncertainty spans the threshold. The results are inconclusive and we cannot reliably determine whether the waste possesses the hazardous property or not. Further sampling of the same waste may reasonably produce sampling means on either side of the hazardous waste threshold.

![Figure D4.2: Statistical reliability of the sampling mean](image)

The uncertainty of the mean is derived from the standard error (SE) of the mean calculated from the number of samples (n) and the standard deviation (s);

$$\frac{s}{\sqrt{n}}$$

Therefore, to reduce the uncertainty, it is essential that the minimum number of samples (n) required to obtain a reliable estimate of the mean for a particular waste is determined prior to sampling.

The upper and lower confidence intervals for the mean are calculated from:

$$\text{Sample Mean} \pm \text{Margin of error (ME)}$$

$$\text{ME} = \text{SE} \times \text{critical value of the t-distribution}$$
The critical values of the t-distribution are determined using a one-tailed t-test using:

- (n-1) degrees of freedom
- probability = 0.95 / 0.05

This generates a 90% confidence interval (allowing for 5% above and 5% below the interval) around the sampling mean.

Where the upper 90% confidence interval is below the hazardous waste threshold we can be 95% confident that further sampling would not generate a sampling mean at or above the threshold, and that $\mu$ also lies below the threshold.

---

**For example**

A batch of filtercake produced by a waste treatment process has been sampled. The filtercake contains metal compounds A and B, both of which are classified as R50-53.

The producer has calculated that a minimum of 6 samples are required to give a reliable estimate of the mean.

The relevant hazardous waste threshold is 2500mg/kg for H14 Ecotoxic.

The results for the total concentration of metal compounds (A+B) are:

- 2600 mg/kg, 1600 mg/kg, 900 mg/kg,
- 1300 mg/kg, 1200 mg/kg, 1400 mg/kg

The sampling mean concentration ($\bar{x}$) = 1500 mg/kg

The standard deviation = 587 mg/kg

n = 6

Standard error = 587 / $\sqrt{6}$ = 239

t-distribution criteria = (p=0.05), (n-1=5) = 2.015

Confidence interval of the mean

- $1500 \pm (2.015 \times 239)$
- 1018 to 1982 mg/kg

The upper confidence interval of the mean (1982) is below the threshold (2500), so we can be confident that the estimate of the mean is reliable enough for us to conclude that the waste does not possess the hazardous property H14 Ecotoxic.

---

**D4.1.3 Non-parametric method - The mean and its confidence intervals**

Non-parametric methods are used when the nature of the statistical distribution is uncertain. They make no assumptions about the distribution and are consequently less precise.

Rather than the sample mean used in the parametric method, this approach is based on the 50th percentile and its confidence intervals.

Sample results are ranked, with the lowest result assigned the rank (r) of 1, the second lowest the rank of 2 etc.

The 50th percentile ($X_{50}$) is estimated as follows:

$X_{50} = X(r)$ where $r = (50/100)(n+1) = (n+1)/2$

For example where n= 11:

$X_{50} = X(r)$ where $r = (11+1)/2 = 6$

$X_{50}$ is therefore estimated by the sample with the rank of 6
If ‘n’ is an even number, r will not be an exact integer, and the following should be used.

\[ X_{50} = \frac{X(r-0.5) + X(r+0.5)}{2} \]

For example where n = 12

where \( r = \frac{(12+1)}{2} = 6.5 \)

\[ X_{50} = \frac{X(6.5-0.5) + X(6.5+0.5)}{2} = \frac{X_6 + X_7}{2} \]

\( X_{50} \) is therefore estimated by the average of the two samples ranked of 6th and 7th.

The 90% confidence intervals for the estimate of \( X_{50} \) are defined by the following cumulative binomial expression:

- \( r_1 \) is the largest integer satisfying the condition \( \text{CumB}(r_1-1; n, 0.5) \leq 0.05 \)
- \( r_2 \) is the smallest integer satisfying the \( \text{CumB}(r_2-1; n, 0.5) \geq 0.95 \)

These can be calculated easily on readily available spreadsheet software.

For example, where n = 11

<table>
<thead>
<tr>
<th>r (column A)</th>
<th>r-1 (column B)</th>
<th>CumB (Binomdist (column B,11,0.5,True))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0.0005</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>0.0059</td>
</tr>
<tr>
<td>3 (r_1)</td>
<td>2</td>
<td>0.0327 (r_1)</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>0.1133</td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>0.2744</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>0.5000</td>
</tr>
<tr>
<td>7</td>
<td>6</td>
<td>0.7256</td>
</tr>
<tr>
<td>8</td>
<td>7</td>
<td>0.8867</td>
</tr>
<tr>
<td>9 (r_2)</td>
<td>8</td>
<td>0.9673 (r_2)</td>
</tr>
<tr>
<td>10</td>
<td>9</td>
<td>0.9941</td>
</tr>
<tr>
<td>11</td>
<td>10</td>
<td>0.9995</td>
</tr>
</tbody>
</table>

From the distribution of CumB,

- The 3\textsuperscript{rd} ranked sample is largest integer \( \leq 0.05 \), and
- The 9\textsuperscript{th} ranked sample is smallest integer \( \geq 0.95 \)
- The upper 90% confidence interval is set by the 9\textsuperscript{th} sample
- The lower 90% confidence interval is set by the 3\textsuperscript{rd} sample

These confidence intervals should be interpreted as set out above for the parametric approach. Where the upper 90% confidence interval is below the hazardous waste threshold we can be 95% confident that the 50\textsuperscript{th} percentile is below the hazardous waste threshold.

**D4.1.4 Further application of the non-parametric approach to compliance assessment**

This section provides an alternative method for assessing the continuous homogenous output of a manufacturing process, or a homogenous waste divided into numerous containers. It is not applicable where different subpopulations may exist.

In these circumstances it is often reasonable to take few samples from many batches. The significance and reliability of any individual sample is then limited, however the information gathered on the population is significant.

Each sample is considered against the threshold criteria and noted simply as

- satisfactory (below threshold), or
- unsatisfactory (at or above threshold)
The overall population is then assessed on the number of satisfactory and unsatisfactory batches. Provided that 'n' is large enough (typically at least 20), this can be assessed using the cumulative binomial approach, considering whether we can be 95% confident that 10% or more of samples exceed the threshold.

For example if $n = 20$

<table>
<thead>
<tr>
<th>No. samples satisfactory (Column A)</th>
<th>CumB (Binomdist(col.A,20,0.9,True))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-12</td>
<td>0.0004</td>
</tr>
<tr>
<td>13</td>
<td>0.0023</td>
</tr>
<tr>
<td>14</td>
<td>0.0112</td>
</tr>
<tr>
<td>15</td>
<td>0.0432</td>
</tr>
<tr>
<td>16</td>
<td>0.1329</td>
</tr>
<tr>
<td>17</td>
<td>0.3230</td>
</tr>
<tr>
<td>18</td>
<td>0.6083</td>
</tr>
<tr>
<td>19</td>
<td>0.8784</td>
</tr>
<tr>
<td>20</td>
<td>1.0000</td>
</tr>
</tbody>
</table>

In this instance 15 or fewer samples, out of 20 samples, would need to be satisfactory before we could conclude with 95% certainty that at least 10% of samples exceed the threshold.

Where it is known with 95% certainty that 10% of the samples exceed the threshold, then the population is either:

- heterogeneous
- is too close to the threshold to be differentiated from it by this test, or
- is hazardous

In any event further investigation to determine which, and where relevant to identify hazardous sub-populations, would be necessary. A non-hazardous classification could not reliably be assigned.

If 'n' is small the statistical power of the test will be insufficient for assessment purposes and the non-parametric approach using 50th percentiles should be used instead.

This approach would not normally be applicable to outputs from waste management processes due to the variation in input quality and composition.

**D4.1.5 Application of the non-parametric approach to on-site verification checks**

Statistically the reliability that can be attached to on-site verification checks at any point in the waste chain, for example at the producer or consignee, can be calculated.

This approach is most applicable to presence/absence or pass/fail type criteria, for example whether containers hold non-conforming or conforming waste.

Permitted sites typically have permit conditions, for example relating to permitted waste types that are absolute. They are either allowed to treat a waste or they are not.

In addition on a consignment note they are required to legally certify the nature and quantity of the waste received, how they intend to manage it, and that they are authorised to do so.

The 100% ‘absolute’ can be assessed statistically, with a virtually equivalent level of protection, using a 99% as the compliance level.

For example, to achieve a 95% confidence that 99% of the containers received do not have characteristic X, the number of containers that would have to be checked can be derived using a cumulative binomial calculation.

The lower 90% confidence interval for true population compliance is given by:

- $P_{LO}$ is chosen so that $1 - CumB(r-1; 0.99, n) = 0.05$
Where:

- \( r = \) number of satisfactory containers
- \( n = \) number of containers checked.

In practice this means that as long as all containers checked are satisfactory, 299 containers is the value of \( n \) required to give 95% confidence that 99% compliance has been achieved. So:

- where the number of containers received is <299, all would need to be checked, or
- where the number of containers received is \( \geq 299 \), then no more than 299 would need to be checked

This number changes significantly however if checks identify any non-conforming waste, as this affects the value of \( r \).

This number can only be applied to a single population (or sub-population where one exists) of waste, which might for example be all drums of a specific waste received from a single producer in a year, rather than all the different inputs to a site over that period.

### D4.1.6 Dangerous substances and hazardous properties

Each sample should be assessed to determine the concentration of dangerous substances relevant to each hazardous property.

Some hazardous properties may add the concentrations of relevant dangerous substances together (e.g. H4 and H8, H5 and H6, and H14). The same must be done for each sample prior to the results being interpreted using the statistical tests given here. So a sample that contains 500 mg/kg of chemical A and 1,500 mg/kg of chemical B would be interpreted as containing 2000 mg/kg for an additive hazardous property.

Other hazardous properties consider the concentration of each dangerous substance in isolation (e.g. H7, H10 and H11). However where a waste contains more than one relevant dangerous substance you may get the situation where:

- sample 1 contains 1500 mg/kg of chemical A and 500 mg/kg of chemical B with the same risk phrase, and
- sample 2 contains 500 mg/kg of chemical B and 1500 mg/kg of chemical B

In this instance the results for that hazardous property are interpreted using the highest concentration of chemical with that risk phrase e.g. chemical A for sample 1, and chemical B for sample 2.

### D4.1.7 The reliability of sampling results

The objective of designing the sampling plan is to ensure that the results identify, with a high degree of statistical confidence (reliability), that a waste is a hazardous waste or not.

The closer the levels of dangerous substances in the waste are to hazardous waste thresholds, and the more variable they are the greater the need for reliability. Conversely reliability is perhaps less important where the composition is consistently well above or below thresholds.

To achieve reliable conclusions:

- sufficient samples have to be taken to address heterogeneity
- the sampling plan will need to be more robust where the range of dangerous substance concentration in the samples spans a threshold
- subpopulations need to be identified and sampled separately

If it is not possible to prove with a high degree of statistical reliability that a waste is non-hazardous, then either

- further sampling should be undertaken to increase the statistical reliability of the conclusion, or
- the material should be classified as a hazardous waste to provide the greatest degree of protection of human health and the environment.

The sampling plan often has to balance achievable reliability and the cost of sampling. An initial basic characterisation exercise may inform this balance.

**Confidence Intervals** - Probabilistic sampling (see D4.2) allows a confidence interval (or error band) to be calculated. This identifies the range around the estimate, with a certain degree of confidence, within which the true value of the waste falls. The narrower the confidence interval the better the sampling estimates the true value of the population. The size of the confidence interval depends upon:

- the heterogeneity of the population or sub-population sampled
- the number of samples taken, and
- the desired confidence interval

The more confidence needed, the wider the confidence interval.

**Precision** is the semi-width of the confidence interval, and depends on the desired degree of confidence, variability in the population or subpopulation, sampling pattern, chosen number of samples, and assumed probability distribution of the population.

The key benefit of being able to estimate the achievable confidence and precision associated with a proposed testing programme is that it forms the link with the number of samples taken and the reliability of the answers they produce.

**Systemic error (Bias):** a persistent tendency to either under-estimate or over-estimate the parameter due to the approach adopted. A risk where a sub-population is sampled and assumed to be representative of the population, for example where:

- only the surface of a waste is sampled, or
- sampling is restricted to daytime, when a process operates at night as well

**Random error:** The sample differs from the population as it is a small fraction of the population, and its composition being determined to varying degrees by chance.

**Statistical sampling error:** The difference between the answer obtained by sampling a proportion of the waste and the one that would have been obtained if the entire population had been sampled. This may result from systemic and/or random error.

**Physical sampling error:** The sampling method introduces a systemic or random error, for example if it favours the inclusion or exclusion of large or small particles.

**Analytical error:** Errors that arise during laboratory analysis. An accredited laboratory should be able to provide a reliable estimate of the random component of analytical error, and an upper limit of the possible systemic error or bias. A systemic error might be introduced where preparation and analysis of the sample resulted in loss of (or failure to detect) some of the dangerous substance, leading to an underestimate unless corrected.

Analytical results reported by an accredited laboratory, in accordance with their quality control systems, should not be excluded as outliers. If the result is in any doubt additional sampling should be undertaken to investigate it.

**D4.2 Select the sampling approach**

**D4.2.1 Types of sampling**

There are two approaches to sampling are **Probabilistic and Judgemental.**

**Probabilistic sampling** has an equal chance of sampling any individual part of a waste, and implies that the entire population is accessible for sampling. The approach enables the reliability of the resulting conclusions to be quantified statistically. For that reason the sampling plan for waste classification and hazardous waste assessment should be based wherever possible on probabilistic sampling.
Judgemental sampling is where part of the waste is excluded from sampling (non-probabilistic) or has a reduced chance of being sampled (partially probabilistic). Examples of where judgemental sampling might need to be considered are:

- to target a specific item or component of the waste, or
- where probabilistic sampling of the entire population is practically impossible given time, resources or money

The consequence of judgemental sampling is that it generates information a sub-population that cannot be relied upon to be representative of the population or as reliable as probabilistic sampling.

These uncertainties mean that the usefulness of results from judgemental sampling is dependent on the reliability of the waste material background information on which any expert judgement and ultimately the sampling plan is based. The limitations are particularly significant in a new sampling situation where background information is weak or where basic characterisation has not been performed.

Where judgemental sampling is used the technical arguments for doing so, instead of probabilistic sampling, must be set out in the sampling plan and such sampling should approximate probabilistic sampling as much as possible. Any assumptions relating to unsampled sub-populations should be supported by evidence to justify this approach.

D4.2.2 Sampling pattern

The sampling pattern defines when, where and how the samples of the population are taken. Various types of sampling patterns are, discussed below and illustrated in Figure D4.3 and D4.4:

- **Simple random sampling (Probabilistic):** In ‘simple random sampling’ the samples are taken at random from the population. Every part of the population has an equal chance of being sampled, but the spread across the population may not be even. This method of sampling may not be appropriate where the population can be divided into sub-populations or strata.

- **Stratified random sampling (Probabilistic):** In ‘stratified random sampling’ the population is divided into sub-populations or strata, and a specified number of samples taken randomly from each. If each stratum is the same size, or the number of samples is weighted relative to strata size, every part of the population has an equal chance of being sampled and sampling is spread evenly across the population. In some instances it may be appropriate to take equal numbers of samples from each stratum, regardless of size, and then weight the results.

- **Systemic sampling (Probabilistic):** In ‘systematic sampling’ the samples are evenly spread across the population, starting from a randomly chosen point for example sampling every Tuesday. Although this does ensure that each part of the population has an equal chance of being sampled, it assumes that there are no systemic components of variation within the population that interact with the sampling frequency. If this assumption is incorrect the approach is not valid. For example the outputs from a waste disposal process may vary depending on the feedstock that is collected on a regular schedule. For that reason this approach should be applied with considerable caution, and such assumptions tested.
**Figure D4.3:** An illustration of probabilistic and sampling patterns

<table>
<thead>
<tr>
<th>Simple random sampling</th>
<th>Stratified random sampling</th>
<th>Systemic sampling</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Simple random sampling" /></td>
<td><img src="image" alt="Stratified random sampling" /></td>
<td><img src="image" alt="Systemic sampling" /></td>
</tr>
</tbody>
</table>

**Judgemental Sampling**

A wide variety of sampling patterns can be generated by judgemental sampling, differing in how far they are from a probabilistic approach.

**Figure D4.4:** An illustration of judgemental sampling patterns

<table>
<thead>
<tr>
<th>Judgemental sampling A</th>
<th>Judgemental sampling B</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Judgemental sampling A" /></td>
<td><img src="image" alt="Judgemental sampling B" /></td>
</tr>
</tbody>
</table>
Example A shows systemic sampling from the edge or surface of the population, which becomes a subpopulation. This allows statistical parameters and confidence to be determined for the subpopulation. Application to the population depends on whether the subpopulation has been proven to be representative or not.

Example B shows sampling from a specific place, for example an access point. It provides no information about either the population or the sub-population, except in the vicinity of where samples were taken. Nothing can be reliably concluded about the hazardous waste assessment of the population. This approach might be valid in some situations, for example to specifically investigate an atypical material identified in that location.

D4.3 Determine the type, number and size of samples required

A sample is a quantity of waste obtained from a single sampling action that is analysed as a single unit.

A composite sample is a collection of increments, each obtained from a single sampling action, that are combined to form a single unit for analysis.

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/samples and the number of increments in any composite sample.

D4.3.1 Determination of the number of increments and/or samples

The number of increments and samples is dependent on the:

- Objective
- Variability of the material, and
- Desired precision and confidence

A preliminary sampling exercise will often be needed to provide a reliable estimate of variability to fulfil the requirements for precision and confidence.

D4.3.2 The use of composite versus individual samples

Using many samples gives you:

- A estimate of the mean, and
- Information on the variability/heterogeneity of the material

Using a composite sample, generated from taking multiple increments, gives you:

- an estimate of the mean, but
- not the variability

Taking a small number of samples provides only an approximate indication of the quality of the material.

The two approaches can be combined in some circumstances.

D4.3.3 Determine the required number of increments and samples

This section considers how many samples and increments are required to reliably estimate a mean concentration and confidence intervals for the purposes of hazardous waste assessment.

These calculations require that a number of parameters are estimated in advance. In some cases it may be appropriate to use values from past analysis of sample data from similar investigations. The alternative would be to conduct and initial investigative study to generate the estimates.

Underestimating these parameters can increase the risk of an unreliable result from the sampling exercise.
D4.3.4 Number of individual samples

The number of individual samples \( n \) required to estimate the mean with the necessary confidence and precision are calculated as follows:

\[
n = \left( \frac{u_a}{d} \right)^2 \left( \sigma_s^2 + \sigma_e^2 \right)
\]

where,
- \( u_a \) = the standard normal deviate corresponding a confidence of 95% (1.96)

and where, in mg/kg
- \( d \) = the desired precision
- \( \sigma_s \) = standard deviation of total spatial and/or temporal variation \( (= \sqrt{\sigma_w^2 + \sigma_b^2}) \)
- \( \sigma_w \) = standard deviation of local spatial variation
- \( \sigma_b \) = standard deviation of spatial or temporal variation
- \( \sigma_e \) = standard deviation of the analytical error

The desired precision \( (d) \) is affected by how close the level of dangerous substances is to a relevant threshold concentration. The closer it is, the greater the level of precision that will be needed to distinguish the two. The desired precision should always be less than the distance between the level of dangerous substance(s) and the relevant threshold.

Example:

A manufacturing process generates ten batches of granular waste containing a single dangerous substance X, a category 1 carcinogen, with a threshold of 1000 mg/kg.

Due to the process controls and consistent quality specification of raw materials used this is considered to be a single population.

Analysis of previous batches allows the following estimates to be made
- Previous levels of dangerous substance X have been 500-800 mg/kg
- \( \sigma_s \) is estimated to be 50 mg/kg
- \( \sigma_e \) is estimated to be 25 mg/kg
- precision is selected as 50 mg/kg since the mean may be close to the threshold.

\[ u_a = 1.96 \text{ for 95% confidence} \]

\[ n = \left( \frac{1.96}{50} \right)^2 (50^2 + 25^2) = 4.8 \]

So a minimum of five samples are needed.

The operator decides to adopt a probabilistic stratified random sampling approach, using the ten batches as the stratification, and takes a single sample randomly from each batch. Ten samples in total.

Using this approach the operator can expect to be at least 95% confident that the mean concentration of dangerous substance X in the waste is within 50mg/kg of that measured by the ten samples.

This also enables them to check their estimates of standard deviation for use in future assessments.

D4.3.5 Number of composite samples and increments

A single composite sample, made up of several increments, can provide a more reliable estimate of the mean than an individual sample. However it cannot provide an estimate of the confidence interval around that mean that are needed for hazardous waste assessment. More than one such sample will normally be needed.
Multiple composite samples can serve the same purpose as several individual samples to provide an estimate of this. For example, in the preceding example a single composite sample could have been taken from each of the ten batches.

The number of composite samples and increments required to estimate the mean concentration of a dangerous substance(s) in a waste to a specific precision and confidence can be calculated.

The level of confidence should be at least 95%.

The level of precision required will depend on how close the mean is believed to be the threshold. The closer the mean value is to the threshold the greater the need for precision.

In general, the precision should be less than the distance between the mean and the threshold to be confident that the population mean is below the threshold.

For example if the estimate of the mean concentration is 950 mg/kg, against a threshold of 1000 mg/kg, then a precision of no more than 49 mg/kg is required.

The number of composite samples (n) is calculated as follows:

\[ n = \left( \frac{\upsilon_a}{d} \right)^2 \left( \sigma_w^2 + \sigma_b^2 + \sigma_e^2 \right) \]

Where:
- \( \upsilon_a \) = the standard normal deviate corresponding a confidence of 95% (1.96)

and where, in mg/kg:
- \( d \) = the desired precision
- \( \sigma_w \) = standard deviation of local spatial variation (within the composite sample)
- \( \sigma_b \) = standard deviation of spatial or temporal variation (between composite samples)
- \( \sigma_e \) = standard deviation of the analytical error

The number of increments (m) in each composite sample is calculated as follows:

\[ m = \frac{\sigma_w^2}{\left[ n \left( \frac{d}{\upsilon_a} \right)^2 - \sigma_b^2 - \sigma_e^2 \right]} \]

The relative cost of sampling per increment and analysis per sample can be used to consider the various combinations of n and m that deliver the necessary confidence and precision.

Total cost = (Am + B)n

Where:
- A = cost of sampling per increment, and
- B = cost of analysis per composite sample

**D4.3.6 Estimating the 50\(^{th}\) percentile for non-parametric tests**

The number of samples determines the precision with which percentiles can be estimated.

The number of samples required to estimate the 50\(^{th}\) percentile with 95% confidence can be calculated from:

\[ n = 1.3 \times \left[ \left( \upsilon_a s/d \right)^2 \left( 1 + \upsilon_p^2 / 2 \right) \right] \]

Where:
- \( \upsilon_a \) = the standard normal deviate corresponding to a confidence of 90% (1.65)
- \( \upsilon_p \) = the standard normal deviate corresponding to the cumulative probability \( p = 50\% \) (0.88).
• \( s \) = an estimate of the standard deviation.
and where, in mg/kg:

• \( d \) = the desired precision

\[
n = 1.3 \times \left[ \frac{(1.65s/d)^2(1+0.68^2/2)}{} \right] = 1.3 \times 1.2312 \times (1.65 \times s/d)^2
\]

\[
n = 4.4 \times (s/d)^2
\]

In practice this means that a waste with a standard deviation that is relatively large, compared to the precision, will need more samples taken to determine the 50\(^{th}\) percentile with precision.

**D4.3.7 Estimating a percentage compliance with a given limit**

The number of samples required to determine (non-parametrically) percentage compliance with a given limit can be calculated in a manner similar to D4.3.6

**D4.3.8 Determine the increment and sample size (mass/volume)**

The relationship between minimum sample size, minimum increment size and the number of increments per composite sample allows the actual increment or sample size to be calculated.

The actual size of an individual sample must exceed the minimum sample size and provide enough material for analysis.

For each composite sample:

• the size of each increment must equal or exceed the minimum increment size, and
• the sum of increments must equal or exceed the minimum sample size. The increment size may need to be increased to achieve this.

The size of increments and samples will depend on:

• the quantity of material required by the laboratory for analysis
• the number of increments in the composite samples
• the relation between minimum increment size and minimum sample size, and
• the nature of the material

Probabilistic sampling relies on all parts of the population having an equal chance of being sampled. The sample must therefore be big enough to exclude errors caused by the fundamental variability (rather than heterogeneity) in the material generated by differences between individual particles within the waste.

The sample/increment must be big enough to accommodate all particle sizes.

For liquids, where differences are at a molecular level, the minimum sample and increment size is not normally affected by the nature of the material.

For powders and sludges, as the particulates are small and as long as sampling allows entry at all particulates present and captures any liquid, the same is true. The large number of particles makes the difference between them of minimal significance.

For particulate and granular material the nature of the material means that individual particles can have a substantial effect on sample composition. The minimum sample and increment size need further consideration:

• the diameter \( (d) \) of the largest particle should be determined
• the aperture of the sampling device must be at least \( 3 \times d \) to allow simultaneous entry of all particles or granules in the material
• the volume of the sample or increment should be at least \( 27d^3 \)
D4.3.9 Determination of minimum increment size

Maximum particle size can be based on the upper 95th percentile of particle diameter ($D_{95}$).

Where the maximum particle size is < 3mm, the actual width, height and length of the sampling equipment must be ≥ 10mm. The minimum mass of the increment is then given by:

$$\text{Mass (kg)} = 1 \times 10^{-6} \times \rho$$

Where $\rho$ = the density of the waste in kg/m$^3$

Where the maximum particle size in the waste is ≥ 3mm. The actual width, height and length of the sampling equipment must be at least three times the maximum particle size. Where this is the case then the minimum mass of the increment is given by:

$$\text{Mass (Kg)} = 10^{-3} \times \rho \times (3D_{95})^3 = 2.7 \times 10^{-8} \times \rho \times D_{95}^3.$$

Where $D_{95}$ = maximum particle size in mm.

D4.3.10 Determination of minimum sample size

Although dependent on the quality of assumptions made and the approximation required to apply this to non-spherical particles, the minimum sample size can be estimated from:

$$\text{Mass (g)} = \frac{1}{6} \pi \times (D_{95})^3 \times \rho \times g \times (1 - P) \times \frac{1}{CV^2 \times P}$$

Where:
- $\rho$ = the specific mass of the particles in the material in g/cm$^3$
- $D_{95}$ = maximum particle size in cm
- $g$ = the correction factor for particle size distribution based on $D_{95}/D_{05}$
  - (broad particle size distribution - $D_{95}/D_{05}$ is > 4 cm, $g = 0.25$)
  - (medium particle size distribution - $D_{95}/D_{05}$ is >2 but ≤ 4, $g = 0.50$)
  - (narrow particle size distribution - $D_{95}/D_{05}$ is >1 but ≤ 2 cm, $g=0.75$)
  - (uniform particle size distribution - $D_{95}/D_{05} = 1$, $g =1$)
- $P$ = is the fraction of the particles with a specific characteristic
- $CV$ = desired coefficient of variation cause by the fundamental error and is calculated from $CV^2 = (1-p)/(pn)$ (where $n$=number of samples). (0.1 is an accepted value of CV where the fundamental variability in the waste is low)

For sampling a fine granular material, where the influence of fundamental variability is low, and with a broad particle size distribution, the following default equation can be used.

$$\text{Mass (g)} = \frac{1}{6} \pi \times (D_{95})^3 \times 2.6 \times 0.25 \times 0.1^2 x 0.02 = 1668 \times (D_{95})^3$$

D4.4 Identify sampling techniques

D4.4.1 Identifying the most appropriate sampling technique

Provision of full guidance on this aspect is beyond the scope of this document.

The sampling plan should identify:
- the techniques and equipment to be used to take the sample, and the consequences of deviating from this
- any requirement to produce composite samples from incremental samples and for sub-sampling in the field to produce the laboratory sample, and the methods to be used to do so
### D4.4.2 Guidance on sampling techniques (PD CEN/TR 15310-2:2006)

This report provides detailed advice on the sampling of different waste materials in different circumstances. This includes, for example, the following materials:

- mobile or viscous liquids
- sludges or paste-like substances
- powders granules and small crystals
- coarse or lumpy solids

In the following circumstances:

- drums, bags, kegs, blocks, cask or small or flexible walled containers
- vertical uniform or irregular, or horizontal cylindrical tanks
- moving liquids in a pipeline
- lagoons or pits
- hoppers, heaps, stockpiles and silos, falling streams and band or screw conveyors, and
- massive or large pieces.

### D4.4.3 Guidance on procedures for sub-sampling in the field (PD CEN/TR 15310-3:2006)

This report provides guidance on procedures to reduce the overall size of a sample, in the field, primarily to aid transport to the laboratory.

### D4.4.4 Guidance on procedures for sample packaging, storage, preservation, transport and delivery (PD CEN/TR 15310-4: 2006)

Sample integrity may be compromised if the sample is incorrectly packaged, stored, preserved or transported. The results obtained may not be representative of the waste.

The procedures required are likely to dependent on the nature of the waste in questions, the properties of the dangerous substances of concern, and the analytical requirements of the laboratory.

Those involved in the transport of samples should be aware of any waste documentation (transfer notes or consignment notes) that may be required by legislation.

Samples should be transported in a manner that does not cause deterioration. It is advisable to check with the chosen analytical laboratory that the packaging, transportation and storage procedures are appropriate to protect the integrity of the sample. CEN/TR 15310-4 provides guidance on sample packaging, storage, preservation, transport and delivery. Requirements for these should be documented in the sampling plan.

### Packaging and labels

The sample container opening should be of the appropriate size for the material to be packaged. The samples must be packed such that they are protected from potential reactions with the packaging or light, deterioration (perhaps through moisture loss or gain) or contamination.

The packaging should be of suitable size for transportation and reception by the analytical laboratory. Consideration should be given to health and safety restrictions that could influence the size of the packaging.

Analytical laboratories should be able to provide advice on requirements recommended for designated tests.
All sample containers should be marked with a unique identifier that is recognisable to the sampler and the laboratory. This should be done in the manner identified in the sampling plan. A chain of custody form (see example in Figure B.5.3) should be completed for each sample and sent with the sample to the analytical laboratory.

**Preservation**

Depending on the nature of the material, the time between sampling and analysis should be minimised to avoid deterioration or contamination of the sample. It is advisable to discuss and agree the requirements with the analytical laboratory prior to sampling.

**D5 Define and Document the Sampling Plan**

The preceding steps should be considered and documented in the sampling plan. An example sampling plan is provided as Figure D.5.1. The size and content of each information field should be adapted and expanded to incorporate any relevant information as necessary. The size of a field in the example should not be taken as an indication of the level detail required.

**D6 Subsequent Steps**

**D6.1 Taking the sample**

Sampling should be taken in accordance with the sampling plan. Any deviations from the sampling plan should be documented on the Sampling Record. Observations made during sampling should also be recorded. These can be useful when interpreting the results.

**D6.2 Analytical methods**

The approach must be consistent with that set out in Appendix C of technical guidance WM2. The analytical laboratory (whether in-house or external provision) should, wherever possible, be accredited by the United Kingdom Accreditation Service (UKAS) (or equivalent) to BS EN ISO/IEC 17025 ‘General requirements for the competence of testing and calibration laboratories’ for the scope of the work. A competent laboratory will be able to give advice on which analytical and test methods should be chosen to meet the sampling objective.

**D6.3 Sample records**

To have traceability there must be records and documentation. All documentation must be traceable to the sampling plan. BS EN 14899:2005 lists the following documents, examples of which are given in Annexes A and B of the Standard:

- **Sampling Plan** – The instructions on how to take the sample. Completed by the waste producer in consultation with relevant parties
- **Sampling Record** – A record of changes to the agreed sampling plan. Completed by the sampler
- **Chain of Custody form** – A record completed by the sampler, carrier and analytical laboratory
- **Sample analysis request form** - Completed by the sampler

Analytical test methods often have specific record and reporting requirements. For example Test Method Regulation 440/2008 indicates the requirements for some test methods used for hazardous waste assessment. Test reports must contain details of sample preparation as well as the reference to the sampling plan.

In addition to test results, the test report should include at the following information as a minimum:
• description and identification of the laboratory sample
• which processes, procedures and apparatus were used
• results of the determination expressed in the appropriate units
• any details not specified in the Standard or which are optional, and any other factors which may have affected the results
• date of receipt of laboratory sample and dates(s) when the test was carried out
• reference to the standard or procedure followed.
### Figure D5.1: Example Sampling Plan (adjust field size to suit information)

**Sampling Plan for Waste Classification and Assessment**

<table>
<thead>
<tr>
<th>Sampling Plan Name / Ref.</th>
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<tbody>
<tr>
<td>Date prepared:</td>
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<tr>
<td>Prepared by:</td>
</tr>
<tr>
<td>Prepared for:</td>
</tr>
</tbody>
</table>

#### Preparatory Steps

**Involved parties:**

#### Objectives:

**Technical goals:**

#### Background information researched:

- Site details
- Process or nature of arising
- Type, form and amount of material
- Known physical, biological or chemical characteristics
- Operational procedures that may affect characteristics
- Previous investigations or analysis

#### Determine level of testing required:

#### Constituents to be tested:

#### Health and Safety Precautions, and Access Restrictions:

### Technical Goals

**Define**

- Populations and subpopulations

**Variability and causes:**

- Spatial
- Temporal

**Scale of sampling**
<table>
<thead>
<tr>
<th>Practical Instructions and Sampling Methodology (CEN/TR 15310-1&amp;2)</th>
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</thead>
<tbody>
<tr>
<td>Name and Organisation of sampler</td>
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<td></td>
</tr>
<tr>
<td>Other parties present during sampling (name and organisation)</td>
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<td></td>
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<tr>
<td>Statistical approach to be used</td>
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<td></td>
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<tr>
<td>Sampling approach and pattern (including justification)</td>
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<td></td>
</tr>
<tr>
<td>Identify sampling place and points</td>
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<td>Requirements for sample reduction</td>
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<td>Requirements for on-site determinations</td>
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<td></td>
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<tr>
<td>Anticipated restrictions or limitations that may impact on data reliability</td>
</tr>
</tbody>
</table>

**Sub-Sampling (CEN/TR 15310-3)**

Detail procedure used (if applicable)

**Packaging, Preservation, Storage, and Transport Requirements (CEN/TR 15310-4)**

Packaging (type, size, material considering risk of adsorption/reaction, cleaning etc.)

Preservation (samples shall be packed and transported in such a way that their condition at the time of sampling is preserved)

Storage

Transport Method

Transport Company details:

Contact: Delivery date:

**Analytical laboratory**

Company details: Contact name: