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Soil, sludge and treated biowaste — Guidance for sample pretreatment

Boden, Schlamm und behandelter Bioabfall — Anleitung zur Probenvorbehandlung

Élément introductif — Élément central

ICS:

Descriptors:

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Foreword

This document (BT/TF151 WI CSs99034:2007) has been prepared by Technical Committee CEN/TC BT/TF 151 “Horizontal”, the secretariat of which is held by DS.

This document is a working document.

Introduction

This European standard specifies the pretreatment required for sludges, treated biowastes and soils (including soil materials), that are to be subjected to analysis of organic as well as inorganic chemical and physico-chemical parameters.

This document has been developed upon existing International Standards for the pretreatment of soils of specified particle fractions.

Historically this has been the case for analysing organic compounds after pretreatment according to e. g. ISO 14507. Standards describing pretreatment for chemical and physico-chemical parameters, e.g. ISO 11464, historically have divided the samples into fractions < 2mm and > 2mm where the fraction < 2 mm was taken for testing. By this the concentrations reported for organic compounds could be related to another part of the sample that those of the chemical and physico-chemical parameters. This European standard stems on the assumption that the same part of the original sample is used for all parameters to be analysed.

The pretreatment procedures described in this European standard are not applicable if they affect the results of the determinations to be made. For example the properties of the parameters to be analysed may differ greatly according to chemical species:

— they can range from non volatile to very volatile compounds (low to high vapour pressure);

— they may be labile or reactive at ambient or elevated temperatures;

— they may be biodegradable or U.V. degradable;

— they may have considerable different solubility's in water;

— they need different analytical procedures.

Because of these differences it is not possible to specify one general pretreatment procedure to fit all materials and goals of investigation. The aim of a pretreatment procedure is to prepare a test sample of which the content of a substance or a characteristic is equal to original material providedthat the applied pretreatment procedure does not considerably alter the chemical nature of the substance to be analysed or of the characteristic. It should be noted that every type of pretreatment will have an influence on several material properties.

For environmental investigation it is assumed that generally the whole sample is of interest and has to be pre-treated. Only extraneous materials May need to be removed under specific circumstances (and usually then has to be reported accordingly).

pretreatmentpretreatmentpretreatment

Important for both sampling and pretreatment are the particle size distribution and form and the degree of chemical heterogeneity of the sample in relation to the minimum required mass of the sample. In general it can be stated that the smaller the particle size and form, and the smaller the chemical heterogeneity of the original material, the less sample mass is required for a reliable test or – the other way around – the less material is (or can) used for a test the more the material has to be ground for a reliable result. ((This is not the other way round but a different approach. A small mass of material as is required for some micro-methods may need an extra grinding to give the necessary fineness of material. In my point of view the other way round would be)) – the other way around – the coarser the particle size or the greater the range of particle size and forms, and the greater the chemical heterogeneity might be, the bigger the sample mass needs to be for a reliable test. Clause 5 and 8.3 deal with this subject.

This European standard describes the following procedures for sample pretreatment:

- Sample pretreatment in the field (clause 8)

- Sample pretreatment in the laboratory:

  - for chemical and physico-chemical parameters (10.2)
  - for organic parameters (10.3)

In a situation in which accurate results are needed the best available pretreatment procedures have to be used. The procedures described in this European standard have proven in practice to lead to reliable results. A laboratory using different procedures than described here may need to prove the suitability, see clause 10 for requirements.

If it is necessary to establish whether the content of a substance is above a certain limit and it is already known that the material is heavily polluted, a simpler pretreatment procedure may meet the needs. In that case the result may not be presented as a representative value for the whole sample.

1 Scope

This European standard specifies the pretreatment required for sludges, treated biowastes and soils (including soil materials), that are to be subjected to analysis of organic as well as inorganic chemical and physico-chemical parameters.

pretreatmentThe pretreatment of samples aims at preparing a (small) test sample which is representative for the original sample.

PretreatmentThis European standard describes the pretreatment which could be performed under field conditions if necessary (see clause 8) and the sample pretreatment under laboratory conditions (clause 10).

For determining inorganic chemical and physico-chemical parameters this European standard describes procedures to achieve:

- subsamples for tests under field moist conditions;
- subsamples for testing after drying, crushing, grinding, sieving etc.;
- subsamples of liquid sludge

For determination of organic compounds three pretreatment methods are specified:

— A method pretreatmentif volatile organic compounds are to be measured (10.3.2).

— A method pretreatmentif moderately volatile to non-volatile organic compounds are to be measured and the result of the following analysis must be accurate and reproducible. The sample contains particles larger than 2 mm and/or the contaminant is heterogeneously distributed (10.3.3).

— A method pretreatmentif non volatile organic compounds are to be measured and the extraction procedure prescribes a field moist sample or if the largest particles of the sample are smaller than 2 mm and the contaminant is homogeneously distributed. This procedure may also be used if reduced accuracy and repeatability are acceptable (10.3.4).

The choice depends above all on the volatility of the organic compounds under analysis. It also depends on the particle size distribution of the material (see 5 and 8.3), the heterogeneity of the sample and the following analytical procedure.

This European Standard is applicable for samples of which the following compounds and/or characteristics may need to be determined:

- polycyclic aromatic hydrocarbons (PAH),

- polychlorinated biphenyles (PCB),
- organochlorine pesticides (OCP),
- phenols and chlorophenols,
- phthalates,
- nonylphenol-Polyethoxylates (NPnE),
- linear alkylbenzenesulfonates (LAS),
- mineral Oil,
- polychlorinated dibenzo-*p*-dioxins/furans (PCDD/F),
- polybrominated diphenylethers,
- volatile organic compounds,
- AOX,
- trace elements, e.g. As, Ba, Cd, Cr, Co, Cu, Hg, Ni, Pb, Sb, Se, V, Zn,
- anions (chloride, bromide, fluoride, sulfate, phosphate, nitrate, nitrite),
- ammonium,
- total Kjeldahl-nitrogen,
- total nitrogen (Dumas),
- physico-chemical parameters: dry matter, organic matter, particle size distribution, TOC, LOI, pH / electric conductivity (EC)

If the procedures are used for other parameters or matrices the suitability has to be proven.

2 Normative references

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

ISO 565	Test sieves – Metal wire cloth, perforated metal plate and electroformed sheet – Nominal sizes of openings.
ISO/FDIS 10381-8	Soil quality – Sampling — Part 8: Guidance on sampling of stockpiles
ISO 11465	Soil quality – Determination of dry matter and water content on a mass basis – Gravimetric method
EN 12880	Characterization of sludge's – Determination of dry residue and water content

ISO 16720 Soil quality – Pretreatment of samples by freeze-drying for subsequent analysis

Move 11465 and 12880 to Bibliography (are not obligatory part of this pretreatment standard)?

Add:

EN 12457-1 to –4

EN 12579

EN 13040

CSS99031 Sludge, treated biowaste, and soils in the landscape – Sampling – Framework for the preparation and application of a sampling plan

CSS99058 Sludge, treated biowaste, and soils in the landscape – Sampling – Part 1: Guidance on selection and application of criteria for sampling under various conditions

CSS99057 Sludge, treated biowaste, and soils in the landscape – Sampling – Part 2: Guidance on sampling techniques

CSS99032 Sludge, treated biowaste, and soils in the landscape – Sampling - Part 3: Guidance on sub-sampling in the field

CSS99059 Sludge, treated biowaste, and soils in the landscape – Sampling – Part 4: Guidance on procedures for sample packaging, storage, preservation, transport and delivery

CSS99060 Sludge, treated biowaste, and soils in the landscape – Sampling – Part 5: Guidance on the process of defining the sampling plan

3 Terms and definitions

For the purposes of this document, the following definitions apply.

3.1
field sample
the quantity (mass or volume) of material obtained through sampling without any sub-sampling

[EN 14899]

3.2
composite sample
average sample
aggregated sample
two or more increments/subsamples 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 11074:2006]

3.3
extraneous material
materials not belonging to the matrix or particle fraction to be analysed.

3.4
increment
sampling unit collected by a single operation of a sampling device and being used in a composite sample

[ISO 11074:2006]

NOTE When an individual portion of material is collected in a single operation of a sampling device and this portion is analysed as an individual unit, it is by definition a sample.

3.5
laboratory sample
sample intended for laboratory inspection or testing

NOTE 1 When the laboratory sample is further prepared (reduced) by subdividing, mixing, grinding or by combinations of these operations, the result is the test sample. When no preparation of the laboratory sample is required, the laboratory sample is the test sample. A test portion is removed from the test sample for the performance of the test or analysis.

NOTE 2 The laboratory sample is the final sample from the point of view of sample collection but it is the initial sample from the point of view of the laboratory.

NOTE 3 Several laboratory samples may be prepared and sent to different laboratories or to the same laboratory for different purposes.

[ISO 11074:2006]

3.6
maximum particle size (D_{95})
particle size that concurs with the mesh width of a sieve on which a maximum of 5 % (m/m) of the material remains

pretreatment3.7
particle size reduction
grinding or crushing the sample in order to reduce the particle size of the whole (sub)sample without reducing the sample size (mass)

[ISO 11074:2006]

3.8
sample
portion of material selected from a larger quantity of material

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

((obvious according to title and scope of this document))

[modified after ISO 11074:2006]

3.9
subsampling
sample division
process of selecting one or more subsamples from a sample of a population

[ISO 11074:2006]

3.10
sampling plan
pretreatmentpredetermined procedure for the selection, withdrawal, on-site pretreatment, preservation, transportation and preparation of the portions to be removed from a population as a sample

[ISO 11074:2006]

3.11
sample pretreatment
collective noun for all procedures used for conditioning a sample to a defined state which allows subsequent examination or analysis or long-term storage

NOTE Sample pretreatment includes, e.g. mixing, splitting, drying, crushing, stabilization.

3.12
subsample
sample taken from a sample of a population

NOTE 1 A subsample may be:

a) portion of the sample obtained by selection or division;

b) an individual unit of the lot taken as part of the sample;

c) The final unit of multistage sampling.

NOTE 2 The term 'subsample' is used either in the sense of a 'sample of a sample' or as synonym for 'unit'. In practice, the meaning is usually apparent from the context or is defined.

[ISO 11074:2006]

3.13
test portion
analytical portion
quantity of material, of proper size, for measurement of the concentration or other property of interest, removed from the test sample

NOTE 1 The test portion may be taken from the primary sample or from the laboratory sample directly if no preparation of sample is required (e. g. with liquids), but usually it is taken from the prepared test sample.

NOTE 2 A unit or increment of proper homogeneity, size, and fineness, needing no further preparation, may be a test portion.

[ISO 11074:2006]

3.14
test sample
analytical sample
sample, prepared from the laboratory sample, from which test portions are removed for testing or for analysis

[modified after ISO 11074:2006]

4 Safety remarks

Special precautions should usually be taken for samples from contaminated material. It is important to avoid any contact with the skin and special measures should be taken when drying such samples (ventilation, air removal, etc.). Samples may be hazardous because of the presence of chemical contaminants, fungal spores, or pathogens such as leptospirosis.

Appropriate national safety precautions shall be followed.

5 Principle

5.1 General

Pretreatment in this European standard is the process of sub-sampling and considers the treatment of a sample from soon after sampling until the production of a homogeneous test sample under laboratory conditions. The operations and treatment steps are divided into pretreatment procedures suitable in the field (clause 8) and pretreatment procedures that are restricted to be performed in the laboratory (clause 10).

pretreatmentIt is important that the methods and instruments described are meant as examples for suitable routine procedures. A laboratory may decide to use other procedures and/or instruments as long as the requirements of the client are met (see clause 10).

Another important item concerns the part of the sample delivered to the laboratory which has to be taken for the determinations and the part of the sample which is removed before starting the tests. This European standard states that for environmental testing usually the whole sample should be taken into account. Only extraneous materials (3.3) are removed.

Beside the requirements given in this European standard the subsequently applied analytical standards shall be regarded for particular requirements to be observed. The determination of some parameters requires sample pretreatment soon after sampling as specified in the respective methods.

If several parameters have to be investigated, the sample pretreatment shall be designed in such manner that the parameters of major importance are determining the pretreatment. If this is not possible, e. g. the required precision for each parameter can not be achieved, separate pretreatment shall be set up for each group of parameters.

Whenever volatile compounds are to be determined, the process of sample pretreatment can result in a substantial loss of these compounds. Sample pretreatment shall be omitted in these cases by taking specific samples for the determination of volatile components. These samples shall be pre-treated in accordance with the appropriate analytical standard and analysed as soon as possible after sampling.

When preparing composite samples regard should be paid to analytical requirements. For example, composite samples are not appropriate if volatile compounds are to be determined.

Figures 1, 2 and 3 show flow diagrams for:

- Pretreatment for inorganic chemical and physico-chemical parameters in sludge (solid), treated biowaste and soil (figure 1),
- Pretreatment for chemical, physico-chemical and organic parameters in liquid sludge (figure 2),
- Pretreatment for organic parameters sludge (solid), treated biowaste and soil (figure 3).

The procedure to be applied depends besides the parameter to be determined also on the required minimum size of the sample to be used in relation to the maximum particle size D_{95} of the sample. For this the relationship described in ISO 10381-8 is used. 8.3 gives more information on the minimum size of the sample depending on the particle size and the particle size to which grinding is required depending on the size of the subsample being taken.

NOTE 3 For some parameters the tables in 8.3 are not followed exactly as generally the homogeneity of the samples is enough for getting adequate results. Examples are: dry matter, organic matter, pH, EC.

Table 1 Required maximum particle size (D_{95}) for several parameters.

Parameter	Matrix	Sample size	D_{95} required, rem
Ammonium- and nitrate-nitrogen	Solid Liquid	> 15 g ??	No D_{95} requirements, sample as received, n No D_{95} requirements, direct measurement in
Anions (Cl, F, Br, PO_4, SO_4)			
Adsorbable organic halogens (AOX)	All	5 mg to 100 mg	< 250 µm, after drying at 105 °C
Cyanide (CN)			
Dry matter (DM)	Solid Solid, air dried Liquid	30 g to 50 g 10 g to 15 g > 0,5 g on DM basis	No D_{95} requirements. No D_{95} requirements. No D_{95} requirements.
Electrical conductivity (EC)	Solid Treated biowaste Liquid	20 g ??? 	No D_{95} requirements. Drying?? ?? No grinding, direct measurement in liquid ph
Loss on ignition (LOI) at 550 °C	All	< 0,2 g 0,2 g to 2 g after drying > 2 g after drying	< 250 µm < 500 µm No D_{95} requirements, dried sample for deter
Organic matter: see LOI			
Particle size distribution			No pretreatment allowed
pH	Solid Treated biowaste Liquid	5 ml ??? 	No D_{95} requirements, drying at 40 °C No D_{95} requirements, after drying at 40 °C (No D_{95} requirements, direct measurement in
Phosphorus (total): see trace elements			
Total organic carbon (TOC)	All	< 0,2 g 0,2 g to 2 g after drying > 2 g after drying	< 250 µm < 500 µm < 1 mm
Total Kjeldahl nitrogen	Solid Liquid	< 0,2 g 0,2 g to 2 g after drying > 2 g after drying 0,1 g to 1 g on DM basis	< 250 µm < 500 µm < 1 mm No grinding, sample as received
Total nitrogen (Dumas),	All	< 0,2 g 0,2 g to 2 g after drying > 2 g after drying	< 250 µm < 500 µm < 1 mm
Trace elements (As, Ba, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, Se, V, Zn, etc.) Extraction with aqua egia	Solid Dried sludge	< 0.2 g 0,2 g to 2 g after drying > 2 g after drying ??	< 250 µm < 500 µm < 1 mm No D_{95} requirements, homogenisation by ha soil???)

Parameter	Matrix	Sample size	D_{95} required, remarks
	Liquid ??		No D_{95} requirements, homogenisation with high speed sonification, than direct digestion
Trace elements (As, Ba, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, Se, V, Zn, etc.), Extraction with nitric acid (HNO_3)	Solid Dried sludge Liquid	< 0,2 g 0,2 g to- 2 g after drying > 2 g after drying ?? ??	< 250 µm < 500 µm < 1 mm No D_{95} requirements, homogenisation by hand.??? (w soil???) No D_{95} requirements, homogenisation with high speed sonification, than direct digestion
Organic compounds, volatile (e.g. volatile aromatic and halogenated compounds)	All	See analytical standard	No D_{95} requirements and homogenisation allowed
Organic compounds, moderately volatile (e.g.: PAH, mineral oil, OCP, PCB, phenols, chlorophenols, phthalates, NpnE, LAS, PCDD/F, polybrominated diphenylethers)	Solid Liquid	< 2 g 2 g to 15 g > 15 g ??	< 500 µm < 1 mm < 2 mm No D_{95} requirements, sample as received
Matrix: "Solid" = sludge (solid), treated biowaste, soil; "Liquid" = liquid sludge Procedure: figure + option in that figure			

5.2 Sampling

Sampling shall be carried out in accordance with sampling standards CSS99031-32 and 99057-60.

The samples shall be kept cool and processed as soon as possible (see ISO 18512 for preservation and storage of soil samples). pretreatment

5.3 Pretreatment in the field

NOTE When possible, the sample pretreatment will take place in the laboratory, as sample integrity can be best guaranteed under laboratory conditions. Sub-sampling by methods given in 8.5 can be performed in the field as well in the laboratory.

In the field sample pretreatment is restricted to the process of sub-sampling by sample division. It will be necessary

– if field samples are too large to take to the laboratory

or

– if the amount of material sampled is larger than the amount of material necessary for the test or analysis.

pretreatmentWhen sub-sampling is necessary the relation between the minimum size of the subsamples and the maximum size of the particles (D_{95}) in the original field sample has to be taken into account (see 8.3).

Samples are divided into subsamples either mechanically or manually. Sub-sampling methods are described in 8.4.2.

In some cases the soil is strongly aggregated. Such macro aggregates can be reduced by hand (see 8.4.1) otherwise they should be seen as individual "particles".

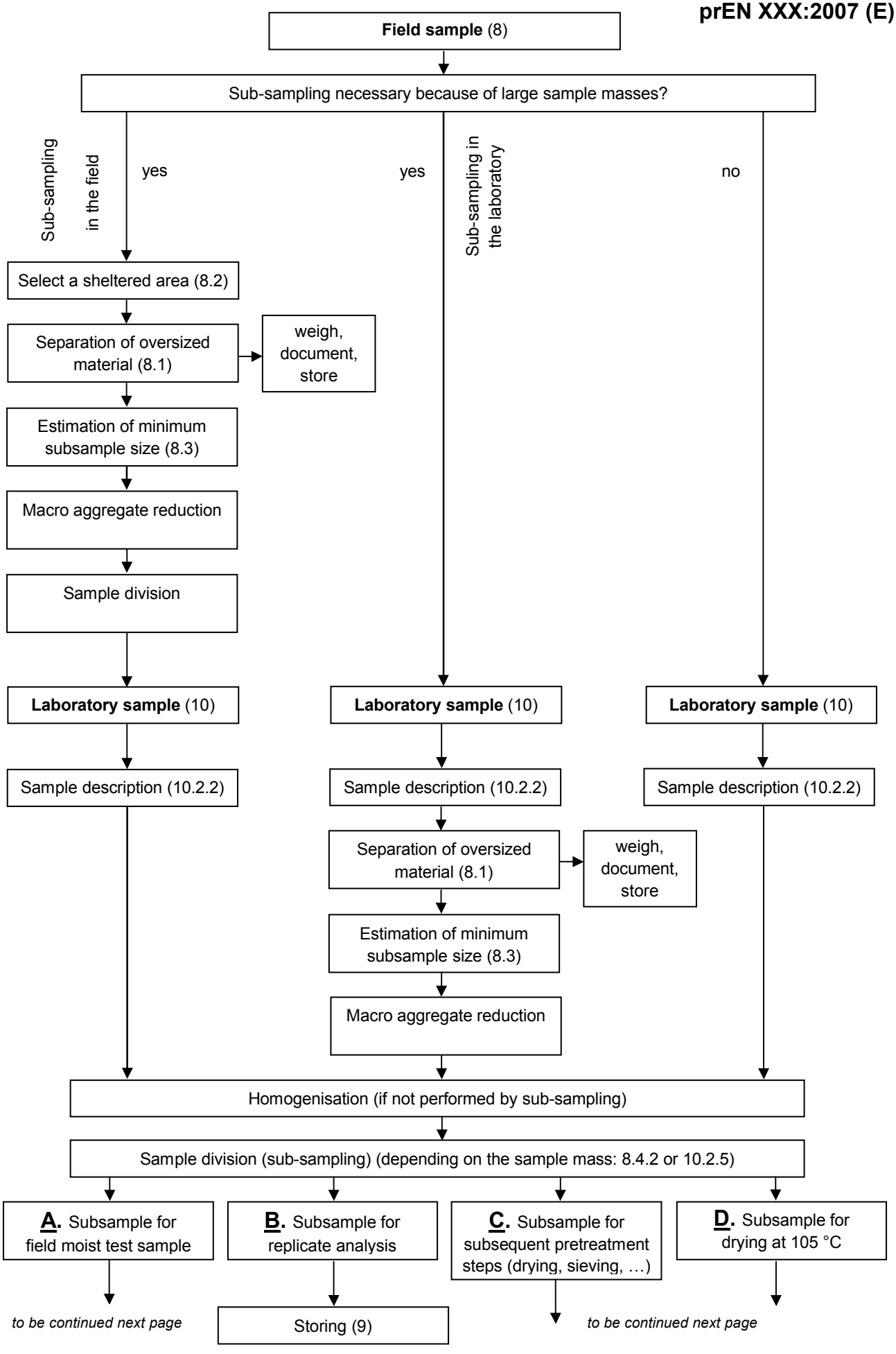

Figure 1 – Diagram for pretreatment of soil, sludge (solid), sediment, inorganic parameters

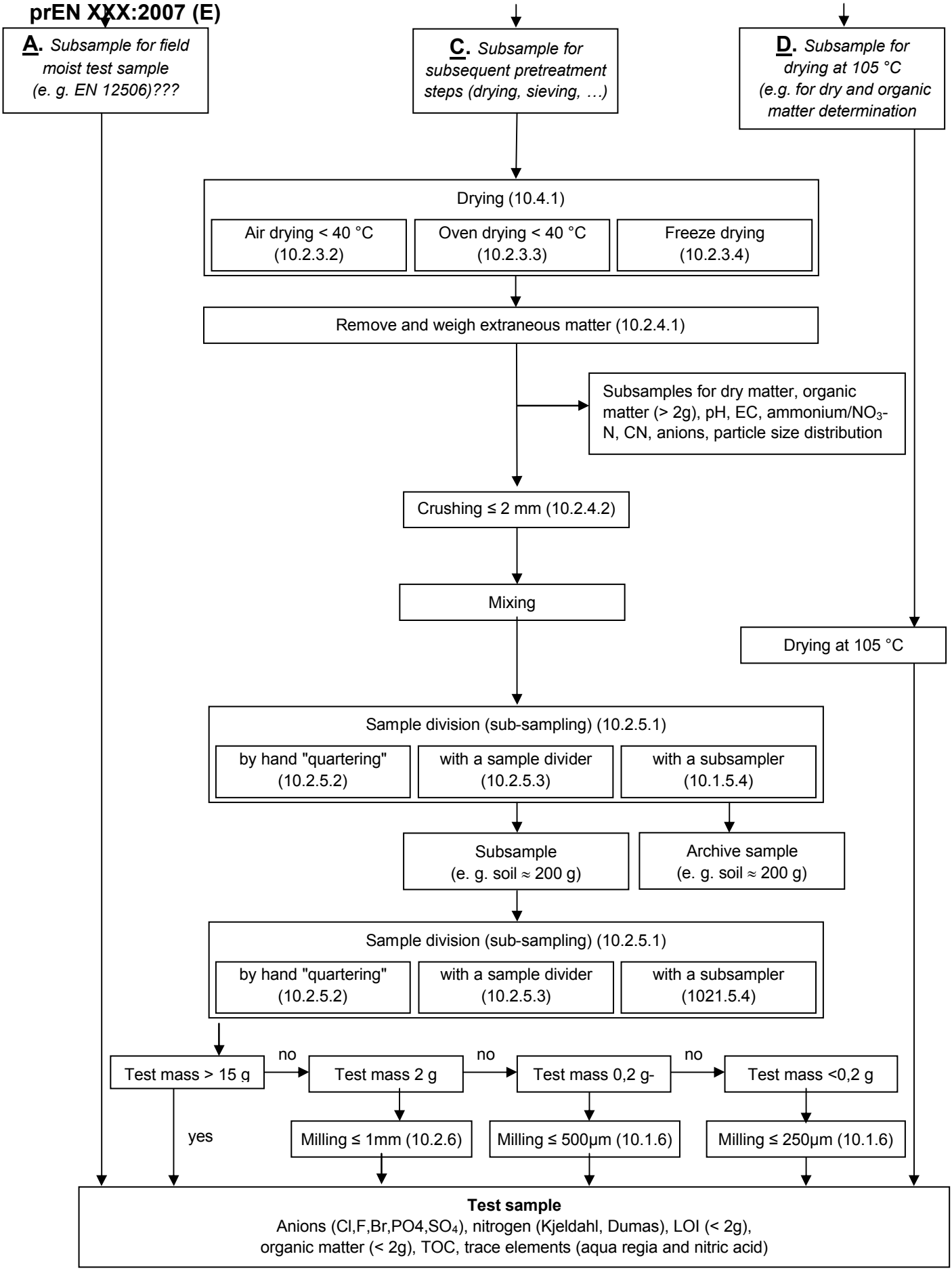

Figure 1 – Diagram for pretreatment of soil, sludge (solid), sediment, inorganic parameters

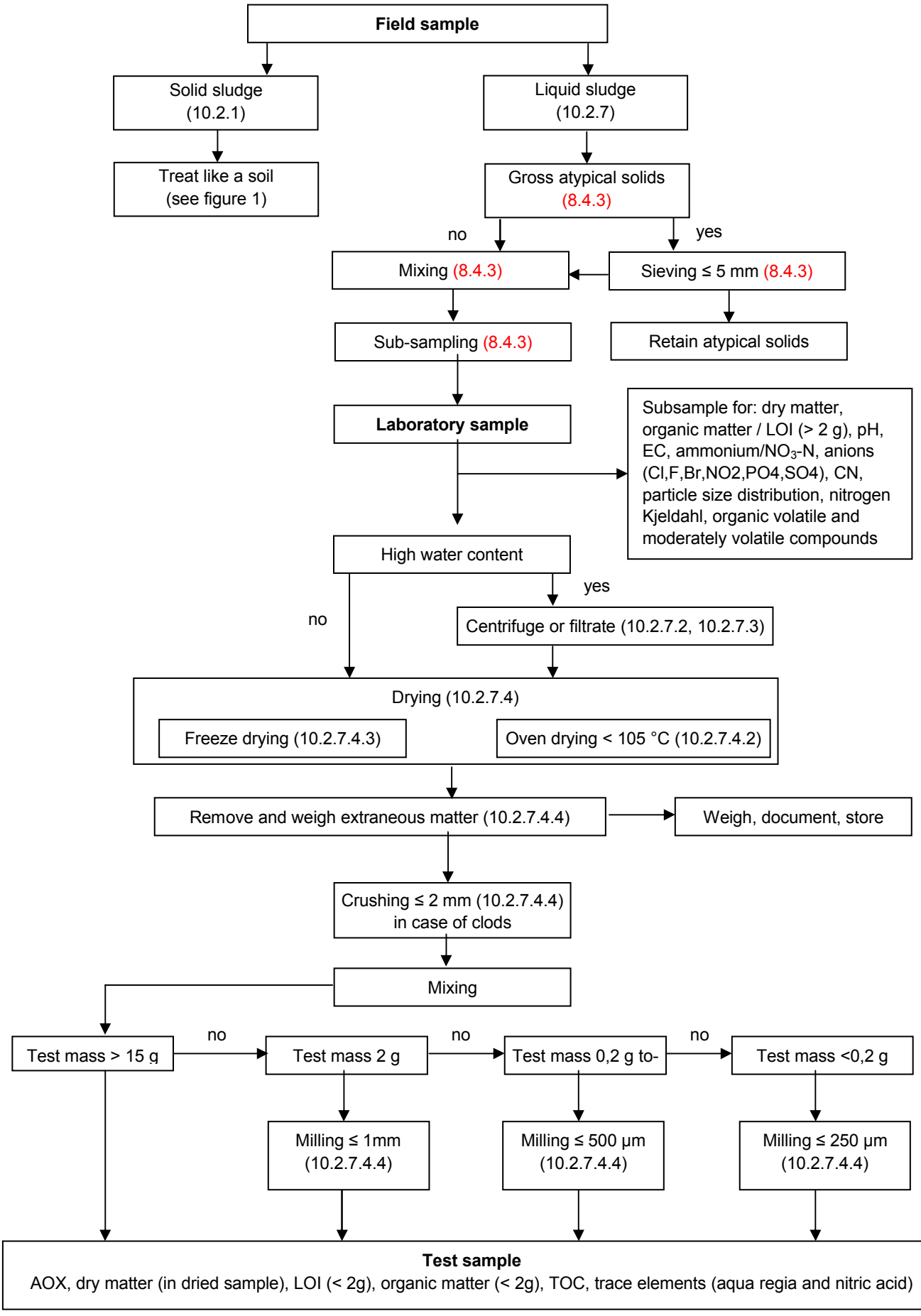

Figure 2 – Diagram for pretreatment of liquid sludge, inorganic and organic parameters

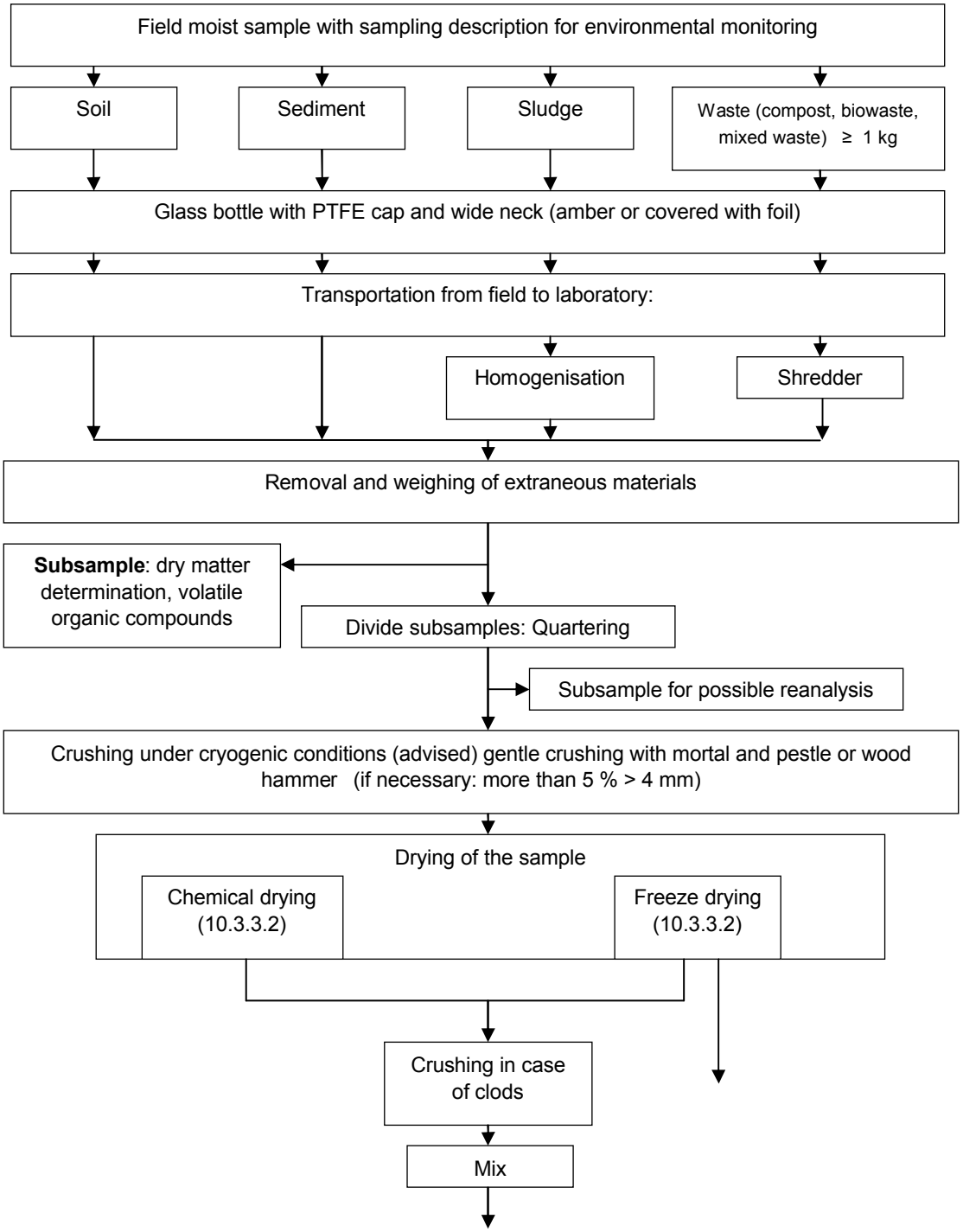

Figure 3 – Diagram for pretreatment of sludge (solid), treated biowaste and soil, organic parameters (to be continued)

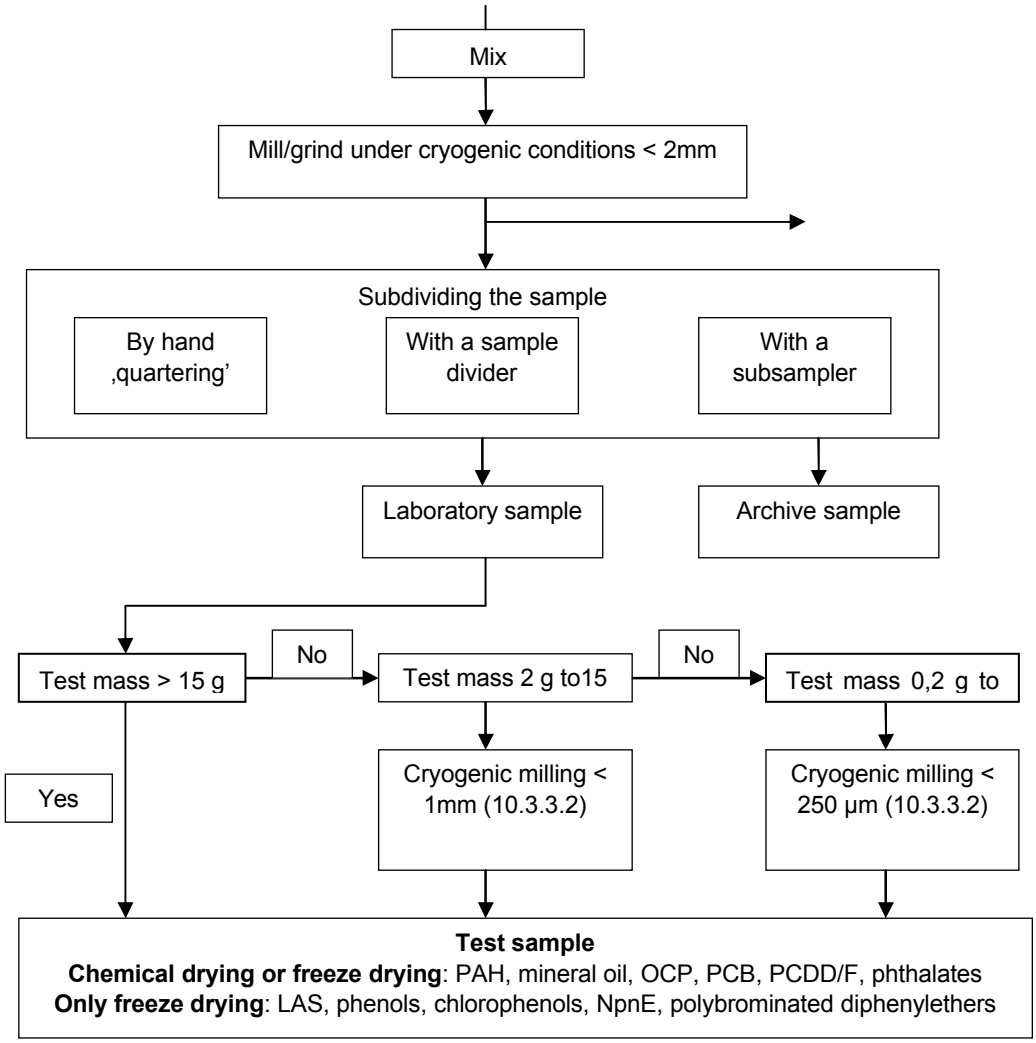

Figure 3 – Diagram for sample pretreatment of sludge (solid), treated biowaste and soil, organic parameters

Sample division in the field shall be carried out only if a sheltered area is available (see 8.2).

Soon after sampling until pretreatment in the laboratory samples should be stored in such a way that the characteristics of the sample are preserved (e. g. cool and light protected, see clause 9).

5.4 Pretreatment in the laboratory for determination of inorganic and physico-chemical parameters

This clause describes the principles of pretreatment in the laboratory for determining inorganic parameters (e.g. elements, anions) as well as physico-chemical parameters (e.g. dry matter, organic matter, particle size distribution). For details see 10.2.

Large sample masses which are not subsampled in the field are divided prior to further treatment (see 10.2).

The laboratory samples are dried in air, or in an oven at temperature not exceeding 40 °C, or freeze-dried (see 10.2.3). If necessary, the soil sample is crushed while still damp and friable and again after drying (see 10.2.4). The sample is sieved (see 10.2.4) and the fraction smaller than 2 mm is divided into portions mechanically or by hand, to enable representative sub-sampling for analysis (see 10.2.5). The size of the particles of the fraction smaller than 2 mm is further decreased (see 10.2.6), e. g. if small subsamples (< 2 g) are required for analysis or trace elements soluble in *aqua regia* should be extracted. For liquid sludge see clause 10.2.7.

When replicate analyses are required, it shall be clarified in the overall investigation plan at which stage of sub-sampling replicates shall be separated. The most representative stage would be a very early one, e. g. the laboratory sample.

NOTE 1 A drying temperature of 40 °C in an oven is preferable to air drying at room temperature because the increased speed of the drying limits changes due to microbial activity.

NOTE 2 The sieve aperture size of 2 mm is generally used. However, before the pretreatment is started, it should be checked if any of the analytical methods to be applied later require other sieve sizes.

NOTE 3 Storing soil samples, including samples that are as received, air dried, refrigerated or stored in the absence of light, for a long time may have an influence on a number of soil parameters, especially solubility of both inorganic and organic fractions.

NOTE 4 Keeping an archive sample (see figure 1) is optional and should be clearly stated in the overall description of the investigation programme.

5.5 Pretreatment in the laboratory for determination of organic volatile compounds

The method of pretreatment depends on the volatility of the compound(s) or group(s) of compounds to be determined.

NOTE The selection of the categories for volatile and moderately volatile compounds can be related in principle to the vapour pressure. However, as the vapour pressure of only a small number of compounds is known, and in view of the relationship between vapour pressure and boiling point, the boiling point has been chosen as the criterion for distinction. See Annex C.

For determination of volatile organic compounds, core test samples are taken from the sample and extracted according to the specific analytical procedure. If composite samples are required extracts of individual samples are mixed. It is not possible to obtain composite samples without severe losses of volatiles. The procedure is described in 10.3.2.

5.6 Pretreatment in the laboratory for determination of organic moderately volatile compounds

Samples are either chemically dried at a low temperature (-196 °C, liquid nitrogen) or freeze dried. The dried samples are cooled with liquid nitrogen and cryogenically ground.. After grinding suitable test portions are processed according to the specific analytical procedures. Composite samples can be prepared by mixing of the ground samples. This procedure is described in 10.3.3.

If the extraction procedure prescribes a field moist sample, drying and grinding is not possible.

If the original samples only contains a small fraction of particles greater than 2 mm and the distribution of contaminants is likely to be homogeneous grinding may be omitted. In these two cases suitable test portions are directly taken after mixing of the sample. This procedure is described in 10.3.4. If hand mixing is used this has to be stated clearly in the report; a remark has to be made that the results are indicative.

NOTE 1 To distinguish the volatile organic compounds from the moderately volatile organic compounds, boiling points are used instead of the vapour pressure at ambient temperature. This is explained in Annex c. Annex c also gives boiling points and vapour pressures of compounds regularly determined in soil investigations.

NOTE 2 For some specific components in the group of moderately volatile organic compounds freeze-drying may give good results. In this European Standard freeze-drying is not described. For freeze drying see EN ISO 16720.

NOTE 3 For practical reasons the pretreatment for moderately volatile compounds should be prescribed for the determination of mineral oil. As a result of cryogenic crushing, an improvement in the extraction yield occurs for compounds with a boiling point above 300 °C. The possible losses for the lower boiling hydrocarbons (C_{10} to C_{16}) are assumed to be low due to the retaining effect of the higher boiling hydrocarbons present in mineral oil and to be compensated by the higher extraction yield of the other hydrocarbons present. As the total yield is used to determine the mineral oil as a group parameter, it is assumed that pretreatment using the method for moderately volatile compounds gives the best results at present. It is important to realise that some mineral oils (gasoline, petroleum) have high fractions

of compounds with boiling points below C_{10}. Losses of these fractions will be severe with the method described in this European standard for moderately volatile compounds.

6 Reagents

6.1 General

Use only reagents of recognised analytical quality. Check samples of each batch of the reagents for the presence of contaminating compounds.

6.2 Sodium sulfate, anhydrous

Heat the sodium sulfate before use for at least 6 h at about 550 °C to remove crystalline water and organic materials. After heating, allow to cool in a desiccator and store in a closed container

NOTE Heating of the Sodium sulfate at 550 °C may be necessary in order to be sure that it contains no organic compounds. Heating at a lower temperature, e.g. 150 °C during at least 16 h may be also enough to dry the sodium sulfate. It has to be shown that the sodium sulfate is clean enough (see blank test in clause 10.3.5).

6.3 Magnesium silicate (talcum powder)

6.4 Sand or gravel

Before use, wash the sand or gravel at least twice with an equivalent quantity (same mass) of demineralised water. If the sand or gravel used shows to be not clean enough (blank test, see 10.3.5)) it may be required to heat the material before use; heating for 6 h at about 550 °C to remove organic materials may be necessary. See also the NOTE under 6.2.

6.5 Liquid nitrogen

WARNING —

1) **When handling liquid nitrogen and samples cooled to -196 °C, suitable gloves and face protection shall be used.**

2) **Polyethylene containers are fragile at a temperature of -196 °C. ((and what about – 195 °C ?))**

((I assume this warning note needs to be much more open as just be limited to – 196 °C. Sincere "burnings" etc. can occur at less deep temperatures))

7 Apparatus

7.1 General

It is essential that the apparatus and tools used for the pretreatment do not add or remove any of the substances under investigation. If the use of certain equipment and/or materials is not permitted in pretreatment of samples required for particular physico-chemical analysis, this shall be mentioned in the relevant horizontal modules on analysis.

NOTE The apparatus to be used are not specified in detail. Most comparable European standards and national contain detailed equipment specifications and these may be used, provided they meet the basic performance requirements indicated in this document.

((Although I remember being the person who introduced the figures of the annex in the very first edition of ISO 11464, I have the idea that these are not really making a usefull contribution to our standards anymore. I would like to see them vanishing in the archives))

7.2 Balance, readable and accurate to 1 g.

7.3 Balances, readable and accurate to 0,1 g.

7.4 Analytical balance, readable and accurate to 0,0001 g.

7.5 Centrifuge, optional.

7.6 Crusher(s), e. g. jaw crusher or cutting device.

Due to crushing, contamination of the sample can occur to an extent which affects the leaching of some constituents of concern e.g. cobalt and tungsten from tungsten carbide equipment or chromium, nickel and molybdenum from stainless steel equipment. The laboratory has to show that the equipment used does not significantly contribute to increase of the compound determined. As a rule the equipment may be assumed to be fit for purpose in this regard if the increase in concentration is not more 30% of the concentration level of interest (e.g. the lowest target limit for a certain environmental legislation).

7.7 Drying oven, thermostatically controlled, with forced ventilation and capable of maintaining a temperature not exceeding 40 °C, optional.

7.8 Drying oven, thermostatically controlled and capable of maintaining a temperature not exceeding 105 °C, optional.

7.9 Freeze-drier, optional.

7.10 Grinding mill, capable of grinding dried materials to a size in accordance with EN XXXXX(digestion standards HORIZONTAL) without contamination by the elements to be determined. For requirements, see above under crushers.

7.11 Cross beater mill or mill with comparable qualities, with a sieve of mesh size 1 mm and accessories. A cross beater mill as used in most soil laboratories is suitable for milling of soil samples cooled with liquid nitrogen.

The cross beater mill shall be placed in a well-ventilated area. At all times, a dust mask shall be used in the case of the release of dust and inhalable quartz. Also, contaminated matter can escape in the form of dust; the personal protection should be designed for this.
For requirements, see above under crushers.

If other equipment is used it should be proven that D_{95} is < 1 mm of the ground material.
Disc mills have also proven to be suitable for reaching a particle size of < 1mm or < 500um.

7.12 Large heavy-duty plastic sheeting, optional.

7.13 Mechanical mixer(s), optional.

7.14 Mechanical shovel, optional.

7.15 Mechanical sieve shaker, optional.

7.16 Mechanised turntable/Rotating dividers, optional.

7.17 Mesh sieves, complying with ISO 565, with apertures of 150 µm, 100 µm or of the size specified in the relevant test method.

7.18 Pestle and mortar, made of porcelain or sintered corundum.

7.19 Porcelain dish, diameter 30 cm, or bigger.

7.20 Riffle box, optional.

7.21 Sample splitter or utensils for cone and quartering for subsampling of test samples (optional).

7.22 Screens, having a mesh size of 2 mm for air-dried samples and of 5 mm to 8 mm for freshly collected samples and which do not cause contamination by elements to be determined.

NOTE Due to sieving, contamination of the sample can occur to an extent which affects the leaching of some constituents of concern e. g. cobalt and tungsten from tungsten carbide equipment or chromium, nickel and molybdenum from stainless steel equipment.

7.23 Sledge hammer, optional.

7.24 Spade, optional.

7.25 Spoon, metal and porcelain, optional.

7.26 Tyler divider, optional.

7.27 Wooden or other soft-faced hammer, optional.

7.28 Glass containers, with a volume of 750 ml to 1000 ml, with a wide neck and screw cap with a polytetrafluoroethylene (PTFE) inlay.

7.29 Polyethylene containers, with a volume of 750 ml to 1000 ml, with a wide neck and screw cap. Do not use larger containers to prevent a significant headspace being formed.

7.30 Refrigerator, capable to maintain a temperature of 1 °C to 5 °C (for special requirements see ENxxxx for storage of samples).

7.31 Dewar vessel(s), capable of holding at least one polyethylene container of about 750 ml.

7.32 Gloves, suitable for working at low temperatures.

7.33 Oven, suitable for heating to about 550 °C.

7.34 Core cutter or similar instrument, for example apple corer.

When taking a subsample, the quantity of soil should be removed from the container in such a way that this quantity:

a) is a subsample over the full depth of the sample, and

b) can be taken quickly.

Depending on the type of soil (sand, clay), different instruments can be used.

8 Sampling and pretreatment procedures in the field (from field to laboratory sample)

8.1 General

Sample pretreatment (in the field or laboratory) is the process of sub-sampling, necessary to obtain a representative subsample for further measures which have to be carried out under laboratory conditions. A selection of pretreatment techniques suitable for sample division in the field as well as in the laboratory is given in 8.4.

Regarding sample pretreatment in the field the next remarks can be made:

- The requirements for sample pretreatment in the field are the same as for sample pretreatment in the laboratory. In general, the sample pretreatment shall not affect subsequent examinations – i. e. contamination of the sample and/or involuntary loss of material or components have to be avoided.
- The type of sample pretreatment that is allowed in the field is limited to sample division, as the circumstances are in most situations not at all comparable to laboratory conditions. Particle size reduction – for example by grinding or crushing – has to be avoided since that process requires good defined conditions which can not be achieved in the field. Particle size reduction is restricted to being a laboratory operation.

- One should realise that the quality of sample division (sub-sampling) in the field is less than the quality of sample division in the laboratory, due to both the (environmental) circumstances for sample division as to the inability to use the best possible division method. When transfer of the sample(s) to the laboratory is possible, this should be considered as a preferable option. The measures for sample division described in 8.4 are suitable for pretreatment in the field as well as in the laboratory.

NOTE 1 Only when laboratory conditions are available on site (there is a sample pretreatment laboratory/facility present) the full range of sample pretreatment activities – thus also including particle size reduction – can be carried out directly after sampling.

NOTE 2 If the sample has a dust-like consistency, part of it may be lost and this may alter its physico-chemical properties.

If the sampling involves the separation of oversized material (i. e. mineral grains, sand, pebble and all other materials) due to very coarse grained or heterogeneous conditions, the material removed shall be weighed or estimated and recorded and described to enable the analytical results to be given with reference to the composition of the original sample.

The compounds to be analysed in the sample(s), or the test to be carried out, will in some cases affect the possibilities or methods of sub-sampling. Therefore the requirements for e. g. pretreatment, preservation and transportation have to be described in the sampling plan and/or communicated by the laboratory.

The methods applied (e. g. sample size reduction) shall be documented and recorded in the test report.

NOTE 1 In most guidelines on sampling for agricultural or similar investigations it is recommended that composite samples are collected by taking a number of increments (e. g. according to ISO 10381-4 at least 25 increments should be obtained) and combining them to form a composite sample.

NOTE 2 When preparing composite samples regard should be paid to analytical requirements. For example, composite samples should never be used if volatile compounds are to be determined.

8.2 Selection of workplace

The division of the field sample as received into a number of representative subsamples shall be carried out only when the integrity of the sample and subsamples can be assured. To assure this effectively a sheltered area is necessary in most situations. Without adequate shelter, weather conditions like wind and rain can pose a serious threat to the quality of the samples. The area should be preferably flat and large enough to allow ease of access around the whole sample when spread evenly on the surface.

It is recommended to protect the sample from contamination by the surface by a clean protective floor covering, preferable heavy-duty plastic sheeting.

NOTE Nevertheless, also sample division can result in significant changes in the composition of the material when no or inadequate precautions are taken. Examples include loss of moisture or volatile components due to evaporation and loss of fine particles due to air entrainment.

8.3 Estimation of minimum subsample size

The minimum size of the subsample is determined by the maximum size of the particles (D_{95}) that are present in the sample. When the sample contains macro aggregates, the maximum size of the macro aggregates determines the minimum size of the subsamples whenever the macro aggregates behave like individual particles during sample pretreatment (that is when macro aggregates will not be cut in pieces by the (sub-) sampling equipment used). See also 8.4.1 for macro aggregate size reduction.

The relation between the minimum size of the subsample and the maximum size of the particles (D_{95}) in the original sample is given in table 2. The relation is based on the equation for the minimum sample size as given in the ISO 10831-8. The table shows that for small particle sizes the minimum size of the subsample can be very small. For sub-sampling in the field a minimum amount of 500 g has to be obtained. Further sub-sampling will then take place in the laboratory.

NOTE 1 The relationship between particle size and sample size given in ISO 10831-8 was developed for sampling in the field. In this standard this relationship however is also used for sub-sampling in the laboratory.

NOTE 2 Some soils (partly) contain (very) large boulders. When these boulders should be considered as part of the sample, this would result in extremely large samples, both in the field as well as for the material to be transported to the laboratory. pretreatmentWhenever such a situation is encountered, the sampling plan should clearly define the material that is to be sampled/subsampled.

Table 2 – Minimum size of subsamples as a function of the maximum size (D_{95}) of macro aggregates or particles present in the sample (taken from: ISO 10381-8)

Maximum size (D_{95}) of macro aggregates or particles in the sample mm	Minimum size of subsample(s) g
0,2	0,01
0,4	0,1
0,6	0,4
0,8	0,8
1	2
2	15
4	110
6	360
8	850
10	1 600
12	2 900
14	4 600
16	6 800
18	9 700
20	13 000
22	18 000
24	23 000
26	29 000

The minimum size of the subsample(s) as given in table 2 does not necessarily mean that this is the actual size to be used. Larger sizes of subsamples might be needed for analysis, and therefore the size of the subsample(s) shall be checked with the laboratory.

In order to avoid large sample masses, the size of the laboratory sample required should be specified in the sampling plan and/or communicated by the laboratory.

For practical reasons, the maximum size of the samples to be sent to the laboratory should be not larger than approximately 20 kg to 30 kg. When larger subsamples are needed because of the large particle size, the particle size should be reduced adjacent to sampling in order to be able to send a representative subsample of an acceptable size to the laboratory. When grinding or crushing for particle size reduction 'in the field' is necessary, it is only allowed under laboratory conditions, see clause 10. For these situations either a mobile laboratory or on site laboratory is needed.

Based on table 2 it is possible to establish to which size a sample has to be ground if a certain sample size is taken. Table 3 gives this relationship.

NOTE 3 For pragmatic reasons here it was chosen to give a maximum particle size for ranges of the sample size.

Table 3 Maximum particle size to which a sample has to be ground related to the size of the subsample to be taken

Minimum size of subsample(s) g	Maximum size (D_{95}) of macro aggregates or particles in the sample

	mm
< 0,2	0,25
0,2 to 2	0,5
2 to 15	1
15 to 100	2
> 100	4

8.4 Pretreatment methods

8.4.1 Procedure for macro aggregate reduction by hand

In some cases a sample – especially soil samples – can be strongly aggregated. Macro aggregates should be seen as individual "particles" when the method of sampling and sample pretreatment is not able to sample part of a macro aggregate. For sample pretreatment this happens for instance when a riffle box is used for dividing a moist or clay-like soil. As the particle size determines the minimum size of the subsample(s), it will be preferable when the size of macro aggregates can be reduced during or prior to sub-sampling.

As reduction of macro aggregates by hand will result in a relative long and intense contact of the sample with the air, this method may only be applied when sample integrity is not influenced during this period.

- Identify the maximum size of the macro aggregates, using the minimum size of the subsample as a starting point as given in table 2 and 3. When the desired size of the subsample is smaller than a given minimum size of the subsample, further reduction of the macro aggregate size is necessary.

- Identify an area of hard surface sheltered from the effects of wind and rain, preferably flat and large enough to allow ease of access around the whole sample when spread evenly on the surface.

- Place a clean protective floor covering, preferable heavy-duty plastic sheeting, to protect the sample from contamination by the surface.

- Place the sample on the covering/plastic sheeting and spread evenly to identify all macro aggregates within the sample.

- Using the base of a spade or the head of a sledge hammer gently reduce the size of the macro aggregates until all oversized material is less than or equal to the required particle size.

8.4.2 Sub-sampling methods

A sample can be divided into subsamples either mechanically or manually. Potentially it is preferable to use a mechanical system for sub-sampling, since this results in more representative subsamples. Especially for soil this is however only true when the material is dry and particles can move through a stream of particles on an individual basis.

NOTE 1 This situation can be realised in the laboratory, but is not possible for sub-sampling in the field directly after sampling (see clause 10).

NOTE 2 If the particles in the sample behave cohesively, mechanical division is often impossible due to cohesion of soil in the system and subsequent blockage of the divider. And even when the mechanical division is still possible, mechanical sub-sampling devices will probably function incorrectly, and therefore will result in biased subsamples. As a consequence, the manual sub-sampling methods are often to be preferred for sub-sampling in the field.

In Annex A the following sub-sampling methods are described:

- Long pile and alternate shovel method, see A.1

- Coning and quartering, see A.2

- Riffling, see A.3

– Application of Tyler divider, see A.4

– Application of mechanised turntable (rotating divider), see A.5.

NOTE The sub-sampling methods in Annex A are also suitable for sample division in the laboratory.

To obtain a representative sample of sludge cake, the mass accumulated will always be too large for laboratory manipulation at the bench. Sample size reduction is, therefore, best carried out in the field by coning and quartering as described in Annex A.2 for sub-sampling of soil

Sludges that have a gelatinous appearance and behave more like a jelly than a mineral solid like gravel, are unlikely to be suitably homogenized by coning and quartering. Mixing, such as that employed for the hand or mechanical preparation of cement mortar, may be more appropriate. Division into subsamples can still be achieved by the combination of diametrically opposed quarters. ((How shall this work with jelly sludge?))

8.4.3 Liquid sludge handling

For some types of liquid sludge, particularly raw sewage sludge, gross atypical solids, such as rags, may be removed by passing the sample through a stainless steel or plastics screen of aperture size not less than 5 mm.

NOTE It should be remembered that stainless steel contains chromium and nickel. Neither would be expected to be a significant problem in terms of release to the sample, but awareness of the presence of these metals would be prudent when extremes of pH are encountered. With plastics screens, the plasticizer used in manufacture may interfere with biocide analysis.

Atypical solids may be needed for further examination and should be retained. Some samples may change significantly because of biological activity and it is therefore important that such samples be analysed as soon as possible after collection.

Large volumes of liquid sludges accrued by the combination of representative samples will need to be homogenized before sub-sampling. The mixing process should preferably be tested to ensure efficiency of mixing. In the event of there being any risk of demixing, the subsample shall be taken during the mixing process. The homogenisation can be achieved in a container such as a plastics dustbin using a suitable paddle to prevent settlement.

9 Storing and preservation

9.1 General

Storage begins when the sample is taken. Soil samples are liable to change in the basic characteristics as a result of various causes. To ensure the integrity and identity of the sample methods, materials and requirements are described for:

– Storing the sample(s) prior to transport;

– Preserving the sample(s);

Storage of the sample as described in this European standard deals only with the short-term storage of the sample between sampling and, when relevant, sample pretreatment in the field, during transport to the laboratory were it is delivered for further treatment (analysis) and with storage in the laboratory before the tests are started.

In most cases the suitable method of preservation will only be storing the sample in a dark and cool environment.

In this European standard on sample pretreatment general requirements on storing are given which are necessary to guarantee the integrity of the sample when transporting to the laboratory. Further precautions recommended to minimise chemical/physical and biological changes while the sample is stored within a container from the point of sampling to the time of analysis are given in prENxxxx and [22]

Suitable packing, preservation, storage, transportation and delivery of soil samples are given in prENxxxx, ISO 10381-8, ISO 18512 and ISO 5667-15.

Storage and preservation can affect the integrity of the sample. Therefore the requirements for the storage and preservation have to be in accordance with the analytical method(s) and have to be described in the sampling plan and/or communicated by the laboratory.

The methods applied shall be documented and recorded in the test report.

9.2 Appropriate sample container

The purpose of the sample container is to protect the sample during transport and storage until it is further treated or analysed. The type and size of the container shall prevent changes in the sample.

Suitable sample containers have to be selected before the beginning of the sampling. Requirements have to be incorporated in the sampling plan. The same containment materials shall be used for samples taken in the field and subsamples of these.

9.3 Preservation

Time between sampling and analysis has to be kept to a minimum to avoid sample alteration – ideally, soil samples should be analysed immediately after collection.

The method of preservation will influence the acceptable time between sampling and analysis. It depends on the components to be determined and the length of time for which the sample must be kept prior to analysis.

NOTE 1 The chosen method of preservation will often be the same from sampling over the whole period before analysis.

NOTE 2 An interruption is acceptable if pretreatment in the field is necessary.

A number of preservation methods are available for sludge, treated biowaste and soil samples:

- air tight storage;
- dark storage;
- cooled storage at 1 °C to 5 °C

Refrigeration at 1 °C to 5 °C is the recommended basic preservation method for samples.

The storage durations depends on the sample material and the storage conditions:

- soil and soil related samples can be stored unlimited without cooling, if they are dried prior to storage

  If the sample is not dried but cooled at 1 °C to 5 °C the storage duration depends on the parameter of interest.

- reducing soils (when reducing characteristics are to be maintained): air tight storage, maximum period of storage < 4 d
- sludge and sediments: usually the storage condition is 1 °C to 5 °C; however, container and particularly storage duration depend on the parameters measured.

The maximum storage time for a sample kept in the dark at low temperatures depends on the parameters to be determined. For further information see [22].

Other preservation methods are also available, like drying or freezing, but can only be applied under laboratory conditions.

The addition of chemical preservatives or stabilizing agents is not a common practice for solid material samples. This is because a single sample is usually used for a large number of different determinations, and moreover has to undergo preparation (drying, milling etc.) during which unwanted and unquantifiable reactions of the preservatives may occur.

The use of liquid nitrogen for immediate deep freezing of soil sample in vapour phase is effective, the use of containers made of stainless steel (not chromium or nickel plated) is recommended.

Freezing of sludge or addition of chemicals to sludge samples is recommended for determining organic constituents. All means of preservation, if practical, should be carried out in the field prior to transportation.

If final preservation methods are not possible in the field, the sludge sample should be transported in coolers filled with ice or in a car with an active cooling system to retain the integrity of the collected material. To avoid loss of volatile species, samples should be collected in a completely filled container, overfilling it before capping or sealing. Temperature is the most important factor affecting the samples, from the time of sample collection through handling to the final analyses. Samples that are to be frozen may simply be placed in a cooler with dry ice. Any deviation should be recorded in a sampling protocol.

More detailed guidance on specific sample preservation methods for sludges and sediments are given in prENxxxx, ISO 5667-13 and ISO 5667-15.

10 Pretreatment procedures in the laboratory (from laboratory sample to test sample)

10.1 General

This clause contains two sections: sample pretreatment in the laboratory for inorganic chemical and physico-chemical parameters (10.2) and for organic compounds (10.3). Basic requirements for the several tests and the flow charts for the pretreatment processes are given in clause 5, see especially table 1 and figures 1 to 3.

For organic parameters the procedure is based on direct starting with the analysis (volatile compounds) or chemical/freeze drying and grinding (moderately volatile compounds). For chemical and physico-chemical parameters the procedure is based on direct starting with the analysis (e.g. dry mater, organic matter, particle size distribution) or drying and grinding (e.g. elements). Instruments and processes described in this standard have to be seen as examples. A laboratory may decide to use instruments not mentioned in this standard (e.g. milling equipment) and to develop it's own pretreatment procedure as long as the next requirements are met:

- The procedure has to lead to significant improvement of the homogeneity of the sample processed.
- the instruments used may not lead to an increase of the parameter to be analysed (contamination by the material of which the instrument is made. Examples: material of the discs of a disc mill, material of the balls of a ball mill).
- The procedure may not lead to loss of the parameter to be analysed; the requirements regarding recovery in the analytical standards have to be met.
- The procedure may not lead to loss of sample material: at least 95% of the material has to be retained during each sieving, sub-dividing and grinding step.
- The relationship between particle size and sample size as described in 5.1 and 8.3 has to be met.
- If the analytical standard describes specific requirements regarding the pretreatment this may not be changed (example: the standard for determining the pH states that the soil sample has to be dried prior to the test. A procedure in which the sample is not dried is in this case not acceptable as this may lead to different results).

10.2 Pretreatment for determination of chemical and physico-chemical parameters

10.2.1 General

In case of large sample masses sub-sampling methods prior to further treatment according to 8.4 should be achieved in the laboratory to reduce the initial sample size. The relation between the minimum size of the

subsample and the maximum size of the particles that are present in the sample have to be taken into account (see 8.3).

Archive and replicate samples should be taken at this stage.

The procedures for drying, fraction separation and size reduction are set out in 10.2.3 to 10.2.6. At several stages in the procedure, the laboratory will be required to make decisions, referring in particular to whether size fractions are to be combined or treated separately: this will depend on the nature of the material and the objectives of the analytical programme.

The sample shall be re-homogenised after any separation, sieving, crushing or milling operation (that may have resulted in segregation of different sized particles) has been carried out.

Care should be taken to avoid contamination of the sample via the air or by dust (e. g. from the ambient laboratory atmosphere or between samples stored or processed close to one another).

Pretreatments should always be performed in a room used only for this purpose and remote from locations where analytical measurements are made.

If the sample has a dust-like consistency, part of it may be lost and this may alter its physico-chemical properties.

pretreatmentAs long as a sludge sample is not solid it is treated like a liquid sludge sample (see 10.2.7) otherwise like a soil sample (see 10.2.3 to 10.2.6) because in the analysis of sludges, various and high water contents of the sludge may cause difficulties.

NOTE Depending on the parameter liquid sludge samples are analysed with or without drying. Drying is not required if $N\text{-}NH_3$, $o\text{-}PO_4$, SO_4, Cl^-, NO_3 or NO_2 are determined, see clause 5.

10.2.2 Laboratory sample description

Examine the sample as received and record the description including details of extraneous matter, remains of vegetation, and other noticeable or relevant features.

10.2.3 Drying of soil and waste samples

10.2.3.1 General

The laboratory samples are dried in air, or in an oven at temperature not exceeding 40 °C. Dry the complete laboratory sample in air or in a ventilated drying oven from which the moist air is removed or in a freeze dryer. Depending on the chosen method of drying, follow the procedure set out in 10.2.3.2, 10.2.3.3 or 10.2.3.4. The aim of drying is to produce a material which can be ground with the equipment used. Drying to complete dryness is not necessary for all equipment. After the drying process has been completed, determine and record the total mass of the dried sample. The dry matter of the dried sample has to be used in calculating the concentration of the parameters determined in the dried sample.

To accelerate the drying process, break down the size of larger aggregates (larger than 15 mm) during the process. When samples are dried in air, crush them lightly by hand using a wooden hammer or a mortar and pestle, taking great care to avoid contamination. When samples are dried in an oven, remove them temporarily from the oven and treat them in the same way. This procedure also makes it easier to separate the extraneous materials.

Freeze-drying has the advantage that the sample to be dried rarely dries into clods; it usually breaks up into parts.

For the determination of the pH of soil samples according to prENxxxx the drying temperature has to be 40°C. For the extraction of trace elements soluble in *aqua regia* according prENxxxx and the determination of trace

elements according prENxxxx air-drying or drying at a temperature not higher than 40°C is recommended. Drying of the sample is not suitable if volatile elements have to be analysed like volatile mercury. If the sample is dried only non-volatile mercury can be analysed.

NOTE 1 Drying can influence the pH of the soil. In some soil samples, particularly those containing sulphides, drying can lower the pH substantially, see prENxxxxx

NOTE 2 The drying time depends on the type of material, the thickness of the layer, the initial moisture content of the material and of the air, and on the rate of ventilation. In a drying oven, the drying time for sandy soils is usually not more than 24 h and for clay soils more than 48 h. For soils containing a large proportion of fresh organic matter (e. g. plant roots etc.), 72 h to 96 h may be required.

NOTE 3 Ammonia nitrogen is lost during freeze-drying of sludges. Therefore determination of ammonia nitrogen content should be avoided after freeze-drying, at least for liquid sludges.

.((Anybody is free to switch to different temperatures on his own responsibilities. We should avoid to tell at several places not to exceed 40 °C and then open the floor by NOTE 4. I do not doubt that the Dutch figures are ok, there is similar experience also from trials in Germany. But it cannot be either or at this place.))

10.2.3.2 Air drying

Spread all the material, in a layer not thicker than 5 cm, on a tray which does not absorb any moisture from the soil and which does not cause contamination.

It is essential that direct sunlight is avoided and the temperature does not exceed 40 °C.

NOTE Direct sunlight could create large temperature differences in the sample, especially between the partly or completely dried top layer and the lower layers.

10.2.3.3 Oven drying

Spread all the material, in a layer not thicker than 5 cm, on a tray made of material which does not absorb any moisture from the soil and which does not cause contamination. Put the tray in the drying oven (7.7) and dry at a temperature that is not higher than 40 °C.

10.2.3.4 Freeze drying

Perform freeze-drying according to EN ISO 16720.

10.2.4 Crushing and removal of extraneous materials

10.2.4.1 Separation of extraneous materials, etc.

Before crushing the sample, which will be necessary if samples, especially soil, have dried into large aggregates, extraneous matters should be removed from the dried sample (3.3). Care should be taken to minimise the amount of fine material adhering to the extraneous matter removed.

The mass of the extraneous matters shall be weighed and documented and the removed material has to be kept for any further research that may be performed.

10.2.4.2 Crushing

After separation of the extraneous materials the sample has to be crushed if it contains large dried particles. For suitable instruments see 7.6.

10.2.5 Sub-sampling

10.2.5.1 General

Sub-sampling is necessary when the sample cannot be stored (laboratory sample and archive sample) or used (test sample) completely, because of its size. Divide the dried and crushed laboratory sample into representative portions of 200 g to 300 g according to 10.2.5.2 or 10.2.5.3**.** For the preparation of a test sample, split up the laboratory sample into representative portions until the required sizes of samples are obtained. Avoid the production of dust as much as possible.

NOTE 1 It could be of advantage to divide large laboratory samples according 8.4 prior to further sub-sampling.

NOTE 2 It may be necessary to mill the material (10.2.6) between sub-sampling stages, to ensure homogeneity as the mass of the subsample is decreased. The procedures described in 10.2.5.2, 10.2.5.3 and 10.2.5.4 may be used to produce subsamples/test portions of the materials less than 2 mm and not less than 2 g in mass.

Select the method of sub-sampling (10.2.5.2, 10.2.5.3 or 10.2.5.4) according to the nature of the sample, the requirements of the subsequent determinations and the equipment available.

10.2.5.2 Sub-sampling by hand (quartering)

Mix the soil sample thoroughly using a suitable mechanical mixer (7.13) and spread it into a thin layer on a tray of a type which will not influence the composition of the sample. Separate the soil into four equal portions (quadrants). Combine two of the four portions diagonally, rejecting the other two. Repeat this procedure until the desired amount of soil is obtained.

10.2.5.3 Use of the sample divider

A suitable example of a sample divider of the multiple-slot type (riffle box) is shown in Annex C, figure C.2. This splits the sample into two equal parts.

NOTE The dimensions of the equipment should be chosen in such a way as to suit the amount and particle size of the materials to be divided (see Annex C, figure C.2 and table C.1).

10.2.5.4 Mechanical sub-sampling

A variety of appropriate equipment for sub-sampling is available, often manufactured according to national standards. These may be used for sub-sampling in accordance with the appropriate national standard and the manufacturer's instructions.

An example of mechanical sub-sampling equipment is illustrated in Annex C, figure C.3. This operates according to the following procedure.

Pour the soil sample into the funnel of the subsampler (Annex C, figure C.3) and screw the sample bottles into place. Start the subsampler. After sub-sampling, pour the contents of the bottles into other sample containers. Repeat this procedure, if necessary, with the contents of one of the containers until the desired amount of soil is obtained. The material should be rehomogenized between each stage of sub-sampling. The contents of more than one container may be thoroughly mixed and used for subsequent phases of the sub-sampling routine.

10.2.6 Milling

Depending on the size of the subsample to be taken the sample has to be ground, see 8.3 for the maximum particle size related to the size of the subsample. The mill to be used depends on the particle size to be reached. Ball mills e.g. are suitable for very small particle sizes (< 250 µm), cross beater mills for particle sizes < 1 mm and disc mills for < 500 µm. See 7.10 and 7.11.

NOTE grinding is designed to
- give a more homogenous sample from which a subsample (test-sample) is taken;
- increase the efficiency of acid attack by increasing the surface area of the particles in case of analysing trace elements.

For some soils, experience has shown that there is little difference between the results before and after such grinding. However, it is difficult to predict, with certainty, which soils will behave in this way.
Therefore, the user should verify that the use of ground or ungrounded soil yields results suitable for the purpose of the investigation. Whether ground or ungrounded soil has been used shall be stated in the test report.

Mill a representative subsample (see 10.2.5) of the dried, crushed and sieved soil.

On a regular basis the laboratory has to prove that the required maximum particle size (D_{95}) really is reached, i.e. that > 95% of the ground material passes the corresponding sieve.

If more than one analysis is to be made, sufficient material shall be ground to the smallest particle size specified, to enable all the analysis to be made on this one subsample.

10.2.7 Liquid sludge samples

10.2.7.1 General

For sub-sampling of liquid sludge see 8.4.3.

Depending on the parameter liquid sludge samples are analysed with or without drying. Liquid sludge samples are dried in an oven at a temperature not exceeding 105°C or freeze dried (see 10.2.7.4.2, 10.2.7.4.3). After drying the sludge sample can be sieved (see 10.2.7.5).

NOTE The original material is used if N-NH_3, o-PO_4, SO_4, Cl^-, NO_3 or NO_2 are determined.

Depending on the kind of subsequent pretreatment, use spoons (7.25) for homogenisation. In the case that heavy metals shall be analysed use a porcelain spoon (7.25).

If the sludge sample shall be dried by freeze drying or in the oven and the particles are sedimented remove the supernatant.

10.2.7.2 Centrifugation

Sludge can be centrifuged (7.5) according to the procedures recommended by the manufacturers of the centrifuge to achieve a lower water content. After centrifugation the remaining water can be removed. It has to be stored if a balance of the total contaminant content inclusive water soluble contaminants is required.

NOTE Depending on the sludge material, especially sewage sludge with a high water content, centrifugation doesn't make sense, because even after 12 h centrifugation particles can still swim on the surface, or are still in sedimentation.

10.2.7.3 Filtration

To obtain a sample with a lower water content the samples can also be filtrated through a suction filter. The filter cake can be dried in the oven or by freeze drying afterwards. Some of the inorganic parameters can be analysed directly out of the remaining water.

Depending of the parameter to be analysed, glass fibre filters can be applied. In the case that organic parameters shall be analysed use glass filters.

NOTE Organic solvents may be components of the glass fibre filters, which may solve organic parameters from the particles. Therefore use glass filters if organic compounds shall be analysed.

10.2.7.4 Drying

10.2.7.4.1 General

Dry the sample in a drying oven or in a freeze drier. Depending on the chosen method of drying, follow the procedures set out in 10.2.7.4.2 or 10.2.7.4.3.

10.2.7.4.2 Drying oven

Spread the sludge sample in a porcelain dish (6.18). Put the porcelain dish in the drying oven (7.7) and dry at a temperature < 105°C until the mass is constant.

NOTE Losses of some parameters cannot be avoided (example: volatile Hg). ((How to do this, if you do not know what is in the sample before analysis? We are not going to write riddles, aren't we?))

10.2.7.4.3 Freeze Drying

Perform freeze-drying according to EN ISO 16720.

If heavy metals shall be analysed, fill the sample into porcelain dishes and carry out the freeze drying.

Freeze-drying must be performed in such a way that evaporation losses of the substances to be analysed are avoided. In particular, it shall be ensured that the sample is unable to thaw during the freeze-drying process. Sewage sludge with high water content should be partially dewatered by centrifuge prior to freeze-drying. The separated centrifugate shall not contain particles.

NOTE 1 Freeze dried material is hygroscopic, therefore dry the freeze dried material before analysis with Na_2SO_4, if the storage time of the material is longer than 2 h. ((Unclear to me: who is freeze-drying materials for a time less thn 2 h in practice?))

NOTE 2 The drying time depends on the type of sludge and the water content. Drying time between 36 h to 96 h may be required. ((I had always bad feelings reading these figures, since these are reflecting working hours instead of really robust figures. Why not just saying: "Considerably long drying times should be expected with these samples." And that's it!))

10.2.7.4.4 Removal of extraneous materials / crushing / milling

Remove extraneous materials (3.3).

Mill a representative subsample (see 7.10, 7.11) to the required particle size. Use the relationship between maximum particle size and sample size given in 8.3. ((Why?))

10.3 Pretreatment for determination of organic compounds

10.3.1 General

The pretreatment method depends on the volatility of the substance(s) or group(s) of substances to be determined. Two categories are distinguished here:

a) Volatile compounds: boiling point < 300 °C, see 10.3.2.

b) Moderately volatile organic compounds: boiling point > 300 °C.

   1) grinding necessary, see 10.3.3

   2) grinding not possible or not necessary, see 10.3.4.

If the pretreatment methods differ for various parameters to be determined, divide the sample before pretreatment into subsamples which are as large as possible.

If it is known in advance that both volatile organic compounds and other parameters are to be determined in a sample, it is essential that a separate sample is taken in the field in accordance with the appropriate standard.

For the purposes of calculation of the content of volatile and moderately volatile organic compounds on the basis of dry matter, the content of dry matter shall be determined in accordance with ENYYYYY in a subsample of the original (moist) sample.

10.3.2 Volatile compounds (boiling point < 300 °C)

10.3.2.1 General

For samples in which volatile compounds are to be determined, no sample pretreatment is carried out. Take test samples from the sample as soon as possible to avoid losses after removal of extraneous materials (3.3).

NOTE Test samples may be taken and extracted in the field. Precautions should be taken to prevent contamination of the extraction liquid. This should be verified using field blanks, which are subject to the same procedures as the samples. Otherwise the sample should be covered with the extraction solution, the container tightly closed and transported to the laboratory under cool conditions, to perform the extraction.

10.3.2.2 Individual samples

Using a corer (7.34) take at least 3 cores from different points in the container such that the combined mass of the cores corresponds to the required size of the test sample (see clause 5 and 8.3 for details).

10.3.2.3 Composite samples

It is not possible to form composite samples for the analysis of volatile organic compounds. If the analysis method involves a liquid extract, a composite extract can be prepared by mixing equivalent volumes of the extracts from the different samples.

10.3.3 Moderately volatile organic compounds (boiling point > 300 °C) - Grinding necessary

10.3.3.1 General

Remove extraneous materials (3.3) from the sample.

A note shall be made to this effect in the analytical report.

10.3.3.2 Drying

Either dry the sample by freeze drying or by chemical drying. Perform freeze drying according to EN ISO 16720. Chemical drying is described below.

Chemical drying can be carried out for solid samples like solid sludge, treated biowaste and soil. Liquid sludges cannot be chemically dried as they contain too much water. The use of chemical drying has been proven to be suitable for non-polar compounds. Examples are PAH, mineral oil, OCP, PCB.

NOTE For polar compounds the suitability has not been shown yet and should be shown by the laboratory wishing to use this procedure.

For each sample to be analysed, add approximately 200 g of sodium sulfate (6.1) and approximately 50 g of magnesium silicate (6.2) to a glass container (7.28) or polyethylene container (7.29). Determine the total mass of these substances with an accuracy of 0,1 g. After sealing the container mix the two substances by shaking and cool to a temperature of below 10 °C.

For each sample, add approximately 250 g of soil (weighed to 1 decimal point) to the glass container with the sodium sulfate and magnesium sulfide.

Close the container and mix the soil and the additives by shaking. Place the container in a refrigerator (7.30). Shake the container vigorously every hour for the first 4 h to avoid clod formation. Leave the containers to stand cold for 12 h to 16 h.

NOTE 1 If the moisture content is greater than 60 %, extra sodium sulfate is added instead of reducing the amount of sample.

NOTE 2 This section of this European Standard is less suitable for the determination of moderately volatile organic compounds in sludges or sediments with a high water content. Chemical drying of such a sample before crushing can cause problems due to insufficient drying and clod formation(only soil and treated biowaste).

NOTE 3 The sample should be kept in a cool environment as long as possible, not only before, but also after weighing.

NOTE 4 If the soil is not properly mixed with the additives in the initial phase, large clods can form which do not dry further.

NOTE 5 If large clods are formed in the initial phase e,g. larger than 3 cm, these can be crushed manually by cutting with a spatula in the container. This may particularly be necessary with heavy clay soil.

NOTE 6 If a sample has a low moisture content and no clods are formed, it is possible to dry for less than 12 h. An adequate drying time should be ensured.

NOTE 7 If a sample is not completely dry before the cryogenic crushing, considerable contamination of the grinding instrument can occur. In particular, clods (which may not be fully dry on the inside after too short a drying time) may have a relatively long retention in the grinding instrument. This results in the heating of the clod and the moist matter is spread over the inside of the crusher. This contamination is very difficult to remove and can lead to serious contamination of subsequent samples.

Before the end of the drying time, the samples are again shaken vigorously.

Fill the Dewar vessels (7.31) to be used with sufficient liquid nitrogen for the polyethylene containers (7.29) to be fully covered by the liquid nitrogen when placed in the Dewar vessels. Quickly transfer the content of each glass container with soil and additives into a polyethylene container. Seal the polyethylene container and immerse completely in the liquid nitrogen. Allow the container to stand until the liquid nitrogen no longer boils vigorously. Cool for approximately 10 min. After complete cooling, retrieve the container from the liquid nitrogen and transfer the content to the mill (7.11).

10.3.3.3 Grinding

Grind the sample to the required maximum particle size (see chapter 5 and 8.4) and take the necessary test samples from the ground soil. The test sample shall be carefully taken from the collection tray. Samples shall be taken both in depth and over the (entire) surface so as to ensure as representative as possible a test sample. While taking the test sample, the sample should not be shaken as this can cause (further) separation on the basis of particle size and mass.

Start the prescribed extraction procedure immediately after weighing.

NOTE 1 Usually, it takes about half an hour for the sample to be fully cooled in the liquid nitrogen. This cooling period can be lengthened slightly to guarantee complete cooling in the container.

NOTE 2 When removing the collection tray, take into account the release of fine dust. For this reason, do not remove the tray until a few minutes after the motor has stopped. However, do not wait too long so as to avoid heating the sample.

NOTE 3 After each sample, the equipment should be cleaned to avoid contamination of the following samples. This can be done efficiently by grinding a quantity of clean (uncontaminated) gravel (6.4) and then cleaning the cross beater mill with a vacuum cleaner.

NOTE 4 As a result of the better accessibility of the soil due to cryogenic grinding, the analysis result after cryogenic grinding may be found higher than in the untreated sample.

NOTE 5 Chemically dried and ground samples are generally stable for longer periods if stored cool and in the dark. Freezing samples can also extend the useful storage time. Dried samples are assumed to be stable for at least 4 weeks.

After analysis correct the calculation of contents for the dry weight and the additives. Carry out the latter correction by multiplying the measured content by the additive factor f_t:

$$Q_m = Q \cdot f_t \quad (1)$$

where:

Q_m is the content present in the sample;

Q is the content measured in the test sample;

f_t is the additive factor.

With:

$$f_t = \frac{[mass\ (sample + sodiumsulfate + magnesium\ silicate)]}{mass\ sample} \quad (2)$$

As the water present in the sample is not removed correct the content in the sample calculated in this way for the dry weight as specified in ENYYYYY.

10.3.3.4 Composite samples

It is not possible to make composite samples from unpre-treated samples as part of the compounds may get lost. If a composite sample has to be made either mix the cryogenically ground samples before extraction or combine the extracts of the samples to be mixed equivalently into a composite extract. Here too, the content shall be corrected for the dry weight and additives. The latter correction can be carried out by multiplying the measured content by the additive factor f_t (see 10.3.3.3).

With composite samples f_t is the average of the additive factors of the individual samples:

$$f_t = \frac{\sum_{i=1}^{n} [mass_i\ (sample + sodiumsulfate + magenesium\ silicate)]}{\sum_{i=1}^{n} mass_i\ sample} \quad (3)$$

where n is the number of samples combined.

10.3.4 Moderately volatile organic compounds (boiling point > 300 °C) - Grinding not possible or not necessary

10.3.4.1 General

For this method mixing by hand is the only pretreatment procedure. This method may also be used as indicative measurement for moderate volatile organic compounds; procedure 10.3.3 is necessary for accurate results.

If hand mixing is applied a note shall be made in the analytical report that hand mixing has been applied and that results are only indicative..

10.3.4.2 Individual samples

Mix the sample in the container or in a separate vessel. Remove the extraneous materials (3.3) from the sample. If required reduce the particle size by moderate grinding by hand (for instance mortar and pestle) e.g. if the sample contains aggregates composed of more or less weakly cohesive materials and plant residues. Take a representative test sample with a spoon or corer. The accuracy and reproducibility will be better if larger test samples are taken (further information may be obtained from the specific analytical procedure).

NOTE In contradiction to the test sample prepared according to 10.3.3 the sample from this method contains free water. This may have an effect on the analytical procedure used after the pretreatment and should be mentioned in the test report.

10.3.4.3 Composite samples

If this method is used as an indicative method, preparing composite samples will further reduce the value of the results. Composite samples are preferably not prepared by mixing the samples but by equivalent mixing of the extracts from the different soil samples.

10.4 Blank measurements

To determine whether the pretreatment process causes contamination in the samples a blank measurement shall be carried out. This blank measurement shall be carried out each time a new compound (or compounds group) is to be determined following a pretreatment method specified in this European Standard, and then as often as required for the purposes of quality control of the analytical results of the laboratory.

To carry out the blank measurement follow procedure 10.2 and/or 10.3 using all described chemicals without the soil sample.

11 Test report

The test report shall at least contain the following information:

a) a reference to this European standard;

b) the date and time of sampling (or, if the time of taking the sample is not known, the time of receipt of the sample by the laboratory);

c) a complete identification and description of the sample;

d) the presence and mass of extraneous material that might have been removed from the sample;

e) sub-sampling, drying, crushing, grinding and milling procedures and apparatus applied;

f) preservation measures applied;

g) any storage measure apllied;

h) ((this is subject of analysis not of pretreatment)), including

i) any details not specified in this European Standard or which are optional, as well as any factor which may have affected the results.

Annex A
(informative)

Sub-sampling methods

A.1 Long pile and alternate shovel method

This sub-sampling method is suitable for samples in excess of approximately 100 kg.

Identify the maximum particle size of the sample and determine the minimum size of the subsample(s) according to table 1. When the minimum size of the subsamples is larger than desired and the maximum particle size is related to the size of macro aggregates, the macro aggregate size can be reduced according to 8.4.1. The sub-sampling process shall be stopped when the size of the subsample is equal to or larger than the minimum size of the subsample as derived from table 1.

- Identify an area of hard surface sheltered from the effects of wind and rain, preferably flat and large enough to allow ease of access around the whole sample when spread on the surface.
- Place a clean protective floor covering, preferable heavy duty plastic sheeting, to protect the sample from contamination by the surface.
- Shovel the soil sample into a conical pile on the protective floor covering, placing each shovelful on the top of the preceding one. For samples in excess of approximately 500 kg, the use of a mechanical shovel is to be preferred above the use of a (manually handled) spade.
- When the entire soil sample is on the floor, circumvent the cone systematically depositing shovelfuls from the base to the apex of the cone so that the centre of the cone is not displaced. Repeat the process twice.
- Form the cone into a long pile as follows:
  - Taking a shovelful from the base of the cone spread the material into a ribbon having an initial width equal to that of a shovel and a length of 1,5 m to 3,0 m.
  - Take the next shovelful from a different point at the base of the cone and spread directly over the previous shovelful, but in the opposite direction.
  - Repeat the above step until one long pile is formed.
- Discard half the soil sample in the following manner:
  - Take a shovelful from the bottom of one end of the pile and set aside.
  - Take the next shovelful immediately adjacent to the first by advancing along the side of a pile a distance equal to the width of the shovel and discard.
  - Again, advancing in the same direction a distance of one shovel width, take the third shovelful and add to the first.
  - Continue along the pile following the above procedure, discarding alternate shovelfuls so that the pile is decreased gradually and uniformly.
  - Repeat the above procedure (from forming the coning to halving the pile) until the retained amount of material is equal to the desired size of the subsample (but no less than the minimum size of the subsample in accordance table 1).
- Transfer the subsample to an appropriate sample container in accordance to clause 10.

A.2 Coning and Quartering

This procedure is suitable for all samples down to approximately 1 kg.

- Identify the maximum particle size of the sample and determine the minimum size of the subsample(s) according to table 1. When the minimum size of the subsamples is larger than desired and the maximum particle size is related to the size of macro aggregates, the macro aggregate size can be reduced according to 8.4 or 10.2.4.2. The sub-sampling process shall be stopped when the size of the subsample is equal to or larger than the minimum size of the subsample as derived from table 1.

- Identify an area of hard surface sheltered from the effects of wind and rain, preferably flat and large enough to allow ease of access around the whole sample when spread on the surface.

- Place a clean protective floor covering, preferable heavy-duty plastic sheeting, to protect the sample from contamination by the surface.

- Shovel the soil sample into a conical pile on the protective floor covering, placing each shovelful on the top of the preceding one. For samples in excess of approximately 500 kg, the use of a mechanical shovel is to be preferred above the use of a (manually handled) spade. Manual handling is preferred for samples smaller than 100 kg.

- When the entire soil sample is on the floor circumvent the cone systematically taking shovelfuls from the base and forming a second cone with all the material from the first cone transferred to the apex of the second cone. Repeat the process twice.

- Flatten the cone so that the height is less than or equal to the height of the shovel or spade used.

- Divide the pile into quarters along two lines intersecting at 90° to each other, using one of the following methods:

  - Method 1:

    - Place the centre of a sheet metal cross, made with four blades joined together at the centre at 90° to each other, at the centre of the flattened cone and press the lower edges of the metal cross through the soil sample. The height and length of the blades forming the cross should be greater than that of the flattened cone.

    - With the metal cross left in position discard opposite diagonal quarters and brush clean the space they occupied.

    - Remove the metal cross and mix together the remaining two quarters.

    - Cone and quarter again using the previous stages until the volume of remaining soil is equal to the desired size of the subsample (but no less than the minimum size of the subsample in accordance with table 1).

  - Method 2:

    - Quarter the flattened cone along two diagonals intersecting at right angles, using a shovel inserted vertically into the soil.

    - Discard one pair of opposite quarters and shovel the remainder into a stockpile.

    - Check if the mass of the discarded material is equal to half the mass of the (sub-) sample before subdivision, allowing a variation of ± 10 % (m/m). When this condition is not met, the discarded material should be added and mixed again, where after the subdivision can continue.

    - Repeat the process of mixing and quartering until the volume of remaining soil is equal to the desired size of the subsample (but no less than the minimum size of the subsample in accordance with table 1).

– Transfer the subsample to an appropriate sample container in accordance to clause 9.

NOTE Coning and quartering are known to be subject to bias. This bias is partly caused by the tendency of larger particles to roll down the side of the cone and to collect at the base. This results in segregation of particles from the top to the bottom of the cone. The same problem arises when taking subsamples when the areas to be subsampled are not previously separated (for instance by the metal cross as described in the first method of quartering).

A.3 Riffling

The use of a riffle box is possible when the soil is dry enough to allow free flow of the soil particles through the riffle box. Division of the sample with a riffle box is most often only practical for samples less than approximately 100 kg (but depending on the size of the riffle box).

Division of the sample with a riffle box will result in a reduction to one half or one quarter (depending on the riffle) at each operation.

– Identify the maximum particle size of the sample and determine the minimum size of the subsample(s) according to table 1. When the minimum size of the subsamples is larger than desired and the maximum particle size is related to the size of macro aggregates, the macro aggregate size can be reduced according to 8.5. The sub-sampling process shall be stopped when the size of the subsample is equal to or larger than the minimum size of the subsample as derived from table 1.

– Identify an area of hard surface sheltered from the effects of wind and rain, preferably flat and large enough to allow ease of access around the whole sample when spread on the surface.

– Place a clean protective floor covering, preferable heavy-duty plastic sheeting, to protect the sample from contamination by the surface.

– Shovel the soil sample into a conical pile on the protective floor covering, placing each shovelful on the top of the preceding one. Manual handling is preferred for samples smaller than 100 kg.

– When the entire soil sample is on the floor circumvent the cone systematically taking shovelfuls from the base and forming a second cone with all the material from the first cone transferred to the apex of the second cone. Repeat the process twice.

– Check that the slot widths of the riffle box are at least three times larger than the maximum particle size of the soil to be subsampled.

– Using a shovel or container, pour the material into the riffle box. It is essential that the soil is poured evenly over the whole riffle in order to prohibit biased sub-sampling.

– Remove one subsample as the reduced sample, discarding the remaining material.

– Check if the mass of the discarded material is equal to half (or three quarters of) the mass of the (sub-) sample before subdivision, allowing a variation of ± 10 % (m/m). When this condition is not met, the discarded material should be added and mixed again, where after the subdivision can continue.

– Repeat the process of riffling until the volume of remaining soil is equal to the desired size of the subsample (but no less than the minimum size of the subsample in accordance with table 1).

– Transfer the subsample to an appropriate sample container in accordance to clause 10.

A.4 Application of Tyler divider

The sloping plate of the Tyler divider provides a reduction ratio of 16:1. Material flows over the plate and is reduced successively in steps at each station down the plate by means of slots or holes placed in the plate. Each reduction is to one half the amount passing the station and a means for re-mixing after each stage is incorporated in the plate. An essential requirement in applying a Tyler divider is that the soil is dry enough to allow free flow of the soil particles.

The mechanical feed should be set at a constant rate suitable for the material being sampled and as identified in the sampling plan. This implies the requirement for the hopper width to be equal to that of the sloping plate and a gate of variable height.

- Identify the maximum particle size of the sample.
- Check that the slot width of the Tyler divider is at least three times larger than the maximum particle size.
- Determine the minimum size of the subsample(s) according to table 1 and calculate if the reduction ratio of the divider will result in a subsample that is equal to or larger than the minimum size of the subsample. If not, this type of divider shall not be used.
- Start the division process by pouring the sample into the divider with a constant rate and catch the subsamples(s) in (an) appropriate sample container(s).
- When necessary repeat the process of sub-sampling be using one or more of the resulting subsamples until a subsample of the required size is obtained (but is no less than the minimum size of the subsample in accordance with table 1).
- Transfer the subsample to an appropriate sample container in accordance to clause 10.

A.5 Application of mechanised turntable (rotating divider)

The mechanised turntable comprises a of a number of prismatic containers, of equal size, mounted round the periphery of a circle which pass under the falling stream of the sample fed from a hopper mounted above the turntable, and off-set from the centre.

The turntable should operate at a constant speed of rotation that should not change (significantly) while sample material is coming into the turntable.

- Check that the slot width of the turntable is at least three times larger than the maximum particle size.
- Transfer the soil with a constant speed into the turntable. The speed should be relatively low in order to allow all particles to fall freely into the slot of the turntable and it will take a large number of rotations of the turntable before the full amount of soil is transferred into the slot.
- After completion of the division process, one or more of the subsamples is (are) collected.
- Check the mass of one of the subsamples. If the mass is not equal to the product of the total mass and the inverse number of subsamples in the rotating divider, allowing a variation of ± 10 % (m/m), all subsamples shall be added and the sub-sampling step shall be repeated.
- The subsamples obtained are (if necessary) divided again, until a subsample of the required size is obtained, or until the minimum sample size is achieved, see Table 1.
- Transfer the subsample to an appropriate sample container in accordance to clause 10

Annex B

(informative)

Homogenisation, initial sample mass and extraction(for extraction of trace elements in soils using ammonium nitrate solution)

B.1 Homogenization of freshly collected samples

Depending on their cohesion, freshly collected samples should be forced by hand through a 2 mm, 5 mm or 8 mm screen using gloves. For samples of mineral soils, particles exceeding about 2 mm in diameter can be picked out by hand. If homogenisation is inadequate, larger sample masses may be extracted (e. g. 100 g of soil with 250 ml of ammonium nitrate solution), but the ratio of air-dried or freshly collected soil to solution shall be kept constant in order to obtain reproducible results.

B.2 Extraction of organic horizons

Samples from organic horizons shall be weighed out in the freshly collected state since dried samples are frequently hydrophobic or absorb only some of the ammonium nitrate solution. The mixing of the sample can be improved by increasing the amounts extracted (e. g. 40 g of soil with 100 l of ammonium nitrate solution) and adding glass beads (e.g. 20 g of beads with a diameter of 3 mm). The ratio of air-dried or freshly collected soil to solution shall be kept constant in order to obtain reproducible results.

B.3 Extraction of reductomorphic horizons

Samples from reductomorphic horizons shall be processed with oxygen excluded from the beginning of sampling to the extraction. Extraction should be carried out as soon as possible after sample preparation (in particular the reduction in size of large aggregates).

Annex C
(Informative)

Information concerning vapour pressure, boiling and melting points of volatile organic compounds

This Annex C gives an overview of the volatile organic compounds with associated vapour pressure, boiling and melting points.

The compounds are arranged in tables C.1 and C.2 by increasing boiling point.

Compounds, which are regularly determined in soil investigations, have been listed. The vapour pressure at 20 °C is an approximation. The Handbook of Chemistry and Physics gives the associated temperatures for a number of substances for fixed vapour pressures (1 mm, 10 mm, 40 mm, 100 mm, 400 mm and 760 mm Hg). In the case where the vapour pressures are given for temperatures above and below 20 °C, linear interpolation is used to determine the vapour pressure in kPa at 20 °C, which is given in table C.1 with the boiling and melting points of the compounds concerned. When carrying out the interpolation, a linear relationship has been assumed between the temperature and the vapour pressure over the period around 20 °C. In view of the fact that only the trend in vapour pressure in relation to the boiling and melting points is of interest, the error in this approximation is not important. If the lowest vapour pressure given (1 mm Hg (= 0,13 kPa)) lies above 20 °C, the temperature at which this vapour pressure occurs and the boiling and melting point of the compound concerned are given in table C.2 as interpolation is not possible in these cases.

Tables C.1 and C.2 show a clear relation between vapour pressure and boiling point. In contrast, there is no relation between vapour pressure and melting point. As the vapour pressure decreases, the boiling point increases. As the vapour pressure is known only for a limited number of compounds, classification on the basis of volatility is, for practical reasons, better related to the boiling point than to the vapour pressure.

For cryogenic crushing, losses are observed for substances with boiling points below or close to that of hexadecane (see [20] in Bibliography). Hexadecane is one of the last compounds to be clearly indicated in gas chromatographic analysis of volatile hydrocarbons.

This results in the limit in boiling point between compounds in the volatile group and the moderately volatile group lying around 300 °C. Thus in this European Standard distinction is made between the following two categories:

a) volatile organic compounds: boiling point < 300 °C

b) moderately volatile organic compounds: boiling point > 300 °C

Table C.1 — Volatile compounds with associated vapour pressure at 20 °C, boiling and melting points

Compound	Vapour pressure at 20°C kPa	Boiling point °C	Melting point°C
pentane	57,3	36	-130
dichloromethane	47,8	40	97
1,1-dichloroethane	29,0	57	-97
trichloromethane	24,9	61	-64
hexane	18,2	69	-95
1,1,1-trichloroethane	13,3	74	-31
tetrachloromethane	12,0	77	-23
benzene	10,6	80	6
1,2-dichloroethane	9,4	84	-35
2-methylhexane	7,4	90	-118
3-methylhexane	6,8	92	-119
heptane	4,9	98	-91
toluene	3,5	111	-95
1,1,2-trichloroethane	3,1	113	-37
3-methylheptane	2,4	115	-121
2-methylheptane	2,5	118	-110
octane	1,5	125	-57
chlorobenzene	1,2	132	-45
ethylbenzene	1,13	136	-95
p-xylene	1,08	138	13
m-xylene	1,05	139	-48
o-xylene	0,93	144	-25
nonane	0,75	151	-54
1,3,5-trimethylbenzene	0,47	165	-45
1,2,4-trimethylbenzene	0,36	170	-44
decane	0,24	174	-30
2-chlorophenol	0,40	175	7
1,2,3-trimethylbenzene	0,56	176	-26

Table C.2 — Volatile compounds with the temperature associated with 0,13 kPa vapour pressure, and boiling and melting points

Compound	Temperature°C	Boiling point°C	Melting point°C
benzaldehyde	26	178	-56
phenol	40	182	41
butylbenzene	23	183	-88
undecane	33	195	-26
2,4-dichlorophenol	53	206	45
naphthalene	53	211	80
3-chlorophenol	44	213	33
dodecane	48	216	-10
2,6-dichlorophenol	60	219	68
4-chlorophenol	50	220	42
tridecane	59	234	-6
tetradecane	75	253	6
pentadecane	92	270	10
2-chlorobiphenyl	89	274	34
hexadecane	105	287	19
4-chlorobiphenyl	96	291	76
heptadecane	115	303	23
octadecane	120	316	28
nonadecane	133	330	32
anthracene	145	340	218
phenanthrene	118	340	100

Bibliography

[1] ISO 5667-3 Water quality – Sampling – Part 3: Guidance on the preservation and handling of water samples water

[2] ISO 5667-10 Water quality – Sampling – Part 10: Guidance on sampling of waste waters

[3] ISO 5667-13 Water quality – Sampling – Part 13: Guidance on sampling of sludges from sewage and water-treatment works

[4] ISO 5667-15 Water quality – Sampling – Part 15: Guidance on preservation and handling of sludge and sediment samples

[5] ISO 10381-4 Soil quality – Sampling – Part 4: Guidance on the procedure for investigation of natural, near-natural and cultivated sites

[6] ISO 10390 Soil quality – Determination of pH

[7] ISO 11074-2 Soil quality – Vocabulary – Part 2: Terms and definitions relating to sampling

[8] ISO 11277 Soil quality – Determination of particle size distribution in mineral soil material – Method by sieving and sedimentation

[9] ISO 11466 Soil quality – Extraction of trace elements soluble in *aqua regia*

[10] EN 12457-1 Characterisation of waste – Leaching – Compliance test for leaching of granular waste materials and sludges – Part 1: One stage batch test at a liquid to solid ratio of 2 l/kg for materials with high solid content and with particle size below 4 mm (without or with size reduction)

[11] EN 12457-2 Characterisation of waste – Leaching – Compliance test for leaching of granular waste materials and sludges – Part 2: One stage batch test at a liquid to solid ratio of 10 l/kg for materials with particle size below 4 mm (without or with size reduction)

[12] EN 12457-3 Characterisation of waste – Leaching – Compliance test for leaching of granular waste materials and sludges – Part 3: Two stage batch test at a liquid to solid ratio of 2 l/kg and 8 l/kg for materials with high solid content and with particle size below 4 mm (without or with size reduction)

[13] EN 12457-4 Characterisation of waste – Leaching – Compliance test for leaching of granular waste materials and sludges – Part 4: One stage batch test at a liquid to solid ratio of 10 l/kg for materials with particle size below 10 mm (without or with size reduction)

[14] EN 12579 Soll improvers and growing media – Sampling

[15] EN 13040 Soil improvers and growing media – Sample preparation for chemical and physical tests, determination of dry matter content, moisture content and laboratory compacted bulk densitiy

[16] ISO 14869-1 Soil quality – Dissolution for the determination of total element content – Part 1: Dissolution with hydrofluoric and perchloric acids

[17] ISO 14869-2 Soil quality – Dissolution for the determination of total element content – Part 2: Dissolution by alkaline fusion

[18] ISO 14870 Soil quality – Extraction of trace elements by buffered DTPA solution

[19] EN 14899 Characterization of waste – Sampling of waste materials – Framework for the preparation and application of a Sampling Plan

[20] Horizontal standardisation for soil, sludge, sediment and bio-waste – report of the desk-study “Pretreatment for organic parameters” for the European project HORIZONTAL.

[21] Horizontal standards on organic micro-pollutants for implementation of EU-Directives on sludge, soil and treated bio-waste – D 2.2 – part B. Sampling of sewage sludge and treated bio-wastes – Technical Report on Sampling – Guidance on selection and application of criteria for sampling under various conditions.

[22] Horizontal standards on organic micro-pollutants for implementation of EU-Directives on sludge, soil and treated bio-waste – D 2.2 – part C. Sampling of sewage sludge and treated bio-wastes – Technical Report on Sampling – Guidance on procedures for sample packaging, storage, preservation, transport and delivery.

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Parameter	D_{95} (mm) required	Standard
Dry matter	No D_{95} requirements are given.	
Organic matter	See LOI	
Particle size distribution	No pretreatment allowed	
TOC	< 200um after drying • at maximum 105 °C (if contents of volatile compounds is negligible) • with Aluminiumoxide • by freeze drying	
LOI (loss on ignition) at 550 °C	No D_{95} requirements are given. However 0.1 g to 5 gr can be taken as sample amount. (a remark has been made that co-ordination with HOR pretreatment has to be made)	
Total Kjeldahl Nitrogen	No D_{95} requirements are given. It is stated that normally samples are dried and homogenised. 0.1 – 2 gram is taken as sample (kjeldahl).	
Total Nitrogen (Dumas),	< 2mm after drying at 40 °C as fast as possible in order to avoid loss of Nitrogen.	
Ammonium- and Nitrate-Nitrogen	Moist: no grinding Dry: < 250 um?? (Drying should be avoided it is stated, so how can samples be dried??)	
Total Phosphorus	2mm, 500um or better (…)	
pH	Soil: 2mm after drying < 40 °C (5ml of sample) Treated biowaste: 20-40mm, EN 13040 ?????????????? (60 ml of sample) liquid sludge's: direct measurement	
EC	Soil: 2mm (20 g sample is taken) Treated biowaste: 20-40mm, EN 13040 ?????????????? liquid sludge's: direct measurement	
Trace elements (As,Ba,Cd,Co, Cr,Cu,Hg,Ni,Pb,Sb,Se,V,Zn, etc.), Extraction with Aqua Regia	Dried sludge's: pestle and mortar Liquid samples: high speed mixer or sonification Dried soil: < 250um (sample mass > 200mg) (remark: this is confusing in the standard; in a NOTE also < 2mm is mentioned with the remark that decreasing the particles may influence the recovery rate of the digestion)	
Trace elements (As,Ba,Cd,Co, Cr,Cu,Hg,Ni,Pb,Sb,Se,V,Zn, etc.), Extraction with Nitric Acid (HNO_3)	No D_{95} requirements are given. Remark that the text is to be coordinated with the standard on pretreatment.	
AOX	< 0.1mm after drying at 105 °C (Only 5 – 100 mg of sample is taken)	
Volatile organic compounds	No grinding and homogenisation allowed	
Moderately volatile organic compounds (e.g.: PAH, mineral oil, OCP, PCB, phenols, chlorophenols, phtalates, NpnE, LAS, PCDD/F, polybrominated diphenylethers)	PAH: no D_{95} requirements PCB: ditto LAS: no D_{95} requirements, drying at max. 60 °C, by – preferably – by freeze drying (➔ concerning to the standard drying is obliged!!!??) Phtalates: no D_{95} requirements, drying with Na_2SO_4 or by freeze drying (if Dry Matter < 50%). PCDD/F: no D_{95} requirements. polybrominated diphenylethers: no D_{95} requirements	