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2nd consultation

Solid materials – Microwave digestion of sediment, sludge, soil and biowaste for the extraction of nitric acid soluble fraction of trace elements

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Foreword

This document is a working document.

This document has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association, and supports essential requirements of EU Directive(s).

[table to be filled and amended by the standards writer]

Material	**Validated for** **(type of sample, e.g. municipal sludge, compost)**	**Document**
Sludge		
Soil and sediment		
Sediment		
Soil improvers (to be specified)		

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Introduction

This document has been prepared as part of the project 'Horizontal'. It is the result of a desk study "Digestion of Solid Matrices – Desk study – Horizontal" and aims at evaluating the latest developments in the assessment of digestion methods for the determination of trace elements and other elements in sludge, soil, treated biowaste and neighbouring fields. After discussion with all parties concerned in CEN and selection of a number of test methods described in this study, the standard has been developed further as an modular horizontal method and has been validated within in the project 'Horizontal'.

A horizontal modular approach is being investigated and developed in the project 'Horizontal'. 'Horizontal' means that the methods can be used for a wide range of materials and products with certain properties. 'Modular' means that a test standard developed in this approach concerns a specific step in a test procedure and not the whole test procedure (from sampling to analysis).

The use of modular horizontal standards implies the drawing of test schemes, as well. Before executing a test on a certain material or product to determine certain characteristics, it is necessary to draw up a protocol in which the adequate modules are selected and together form the basis for the test procedure.

This standard is a module for the analysis of inorganic parameters in solid matrices. The module concerns the digestion in microwave oven with nitric acid for the subsequent analysis of elements.

The other horizontal modules that will be available in due time are to be found in the informative annex [*xxx*], which contains a brief overview of the modules that will be worked out in the project 'Horizontal.'

The texts of chapters 1 to 13 are normative; annexes are normative or informative, as stated in the top lines of the annexes.

1 Scope

This Part of EN XXXXX specifies a method for microwave digestion of biowaste, sediment, sludge and soil by the use of nitric acid.

Digestion with nitric acid will not necessarily accomplish total decomposition of the sample; the extracted analyte concentrations may not necessarily reflect the total content in the sample. However, for most environmental applications the result is fit for the purpose. This method is applicable to microwave-assisted acid digestion of biowaste, sediment, sludge and soils for the following elements: Aluminium (Al), antimony (Sb), arsenic (As), barium (Ba), boron (B), cadmium (Cd), calcium (Ca), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), magnesium (Mg), manganese (Mn), mercury (Hg), molybdenum (Mo), nickel (Ni), potassium (K), selenium (Se), sodium (Na), strontium (Sr), tallium (Tl), vanadium (V) and zinc (Zn).

The method is intended to provide a rapid multi-element acid digestion prior to analysis. Solutions produced by the method are suitable for analysis by e.g. atomic absorption spectrometry (FAAS, HGAAS, CVAAS, and GFAAS), inductively coupled plasma emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). However, the addition of HCl may limit the methods of detection, or increase the difficulties of detection with some techniques.

NOTE The degree to which analytes are brought into solution suitable for subsequent analysis may depend on the principle of the subsequent analysis. Some analytical methods require the element in solution independent of its chemical state, others require a specific valence or a specific ionic species, for instance hydride atomic spectrometry, photometry and electrochemical methods.

2 Normative references

This European Standard incorporates, by dated or undated reference, provisions from other publications. These normative references are cited at appropriate places in the text and the publications are listed below. For dated references, subsequent amendments to, or revisions of, any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references, the latest edition of the publication referred to applies (including amendments).

EN ISO 3696:1995	Water for analytical laboratory use - Specification and test methods (ISO 3696:1987)
EN XXXX	Solid materials. Determination of dry matter and water content on a mass basis - gravimetric method
EN XXXX	Pre-treatment …(Horizontal)
EN XXXX	Sampling of soil,sludge…… (Horizontal)

3 Definitions

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

3.1 digestion

mineralization of the organic matter of a sample and dissolution of its mineral part, more or less complete, when reacted with a reagent.

3.2 sample

portion of material selected from a larger quantity of material.

3.3 laboratory sample

sample or subsample(s) sent to or received by the laboratory.

3.4 test sample, analytical sample

sample prepared from the laboratory sample from which test portions are removed for testing or analysis.

3.5 test portion, analytical portion

quantity of material of proper size for measurement of the concentration, or other properties of interest, removed from the test sample.

NOTE 1: The test portion may be taken 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.

3.6 dry matter

the remaining mass fraction of a sample after the specified drying process. It is expressed in percentage or as grams per kilogram.

3.7 digestion vessel

special flask that fits into the microwave oven and into which the test portion and acid are filled and the digestion is performed.

3.8 microwave unit

is the whole microwave digestion system (oven and associated equipment).

4 Safety remarks

All this work has to be performed by skilled persons. The reagents used within this EN are strongly corrosive and partly very toxic. Safety precautions are absolutely necessary due not only to the strong corrosive reagents, but also to high temperature and high pressure.

The use of laboratory-grade microwave equipment with isolated and corrosion resistant safety devices is required. Domestic (kitchen) type microwave ovens should not be used, as corrosion by acid vapours may compromise the function of the safety devices and prevent the microwave magnetron from shutting off when the door is open, which could result in operator exposure to microwave energy.

All procedures have to be performed in a hood or in closed force-ventilated equipment. By the use of strong oxidising reagents, the formation of explosive organic intermediates is possible, especially when dealing with samples with a high organic content. Do not open pressurized vessels before they have cooled down. Avoid contact with the chemicals and the gaseous reaction products. Samples and solutions have to be disposed of according to regulations.

Toxic nitrogen oxide(s) and chlorine fumes are usually produced during digestion. Therefore, all steps involving open or the opening of microwave vessels must be performed in a proper fume ventilation system. The analyst should use protective gloves and face protection.

5 Principle

The test portion of up to 0.5 g is digested in 10 mL concentrated nitric acid for 10 minutes by means of microwave heating with a suitable laboratory microwave unit. The samples and acid(s) are placed in a fluorocarbon polymer of quartz microwave vessel or vessel liner. The vessel is sealed and heated in the microwave unit. After cooling, the vessel contents are filtered, centrifuged or allowed to settle and then diluted to volume and analysed by the appropriate determinative method.

6 Interferences and sources of error

Due to the volatility of some compounds, it is of great importance to take care that the sample is not heated before the digestion and that any volatile reaction products formed during the digestion are not allowed to escape.

Grinding or milling of samples includes a risk of contamination of the sample from the environment (air, dust, wear of milling equipment). Due to elevated temperature, loss of volatile compounds is possible. For the determination of elements forming volatile compounds (e.g. Hg, As, Pb), take special care at the sample pre-treatment.

A few refractory sample matrix compounds, such as quartz, silicates, titanium dioxid, alumina and other oxids may not be dissolved. These bound elements are considered non-mobile in the environment and are excluded from most aquous transport mechanisms of pollusion.

High acid and solute concentrations in the digest cause interferences need to be properly addressed during determination.

Be careful to ensure that all of the test portion is brought into contact with the acid mixture in the reaction vessel.

There is a potential for vigorous reaction, especially with samples containing volatile or easily oxidized species. When digesting a matrix of this type, use no more than 0,100 g sample to begin with. If a vigorous reaction occur upon addition of reagents(s), allow the sample to predigest in the uncapped digestion vessel until the reaction ceases. Heat may be added in this step for safety considerations (for example, the rapid release of carbon dioxid from carbonates, easily oxidiced organic matter etc.) Once the initial reaction has ceased, the sample may continue through the digestion procedure.

In the case of filtration of the digested solution, it is necessary to take care that the filtration procedure does not introduce contamination.

7 Reagents

All reagents used shall be of recognized quality. During analysis, use only reagents of recognized analytical grade that meet the purity requirements of the subsequent analysis.

7.1 Water

Comply with grade 2 of EN ISO 3696 or better. The water for preparation of reagent shall meet the requirement of the subsequent analysis. Verify their purity by performing a blank test.

7.2 Nitric acid

$c(HN0_3) = 15$ mol/L, $p = 1{,}4$ kg/L

Sub-boiling distilled. Other grade may be used provided it is ascertained that the reagent is of sufficient purity to permit its use without decreasing the accuracy of the subsequent analysis.

8 Apparatus

All digestion vessels and volumetric ware shall be adequately acid cleaned and stored in order to avoid any contamination.

8.1 Digestion vessel

Temperature- and pressure-resistant and having a nominal volume of 100 mL.

Only fluorocarbon or quartz containers with pressure-relief mechanisms or containers with fluorocarbon or quartz liners and pressure-relief mechanisms are considered acceptable.

The inner wall of the vessel shall be inert and shall not release substances to the digest in excess of the purity requirements of the subsequent analysis. The vessel shall be suitable for the safe application in the temperature and pressure range applied.

NOTE Digestion vessels may be cleaned in e.g. 10% nitric acid.

8.2 Microwave oven

8.2.1 Microwave apparatus requirements

Corrosion resistant and well ventilated. All electronics must be protected against corrosion for safe operation.

A laboratory-grade microwave oven with temperature feedback control mechanisms is preferred. The temperature performance requirements necessitate the microwave decomposition system to sense the temperature with an accuracy of ± 2,5ºC and automatically adjust the microwave field output power within 2 seconds of sensing. Temperature sensors should be accurate to ± 2ºC (including the final reaction time of 175 ± 5ºC). Temperature feedback control provides the primary performance mechanism for the method. Due to the variability in sample matrix types and microwave digestion equipment (i.e. different vessel types and microwave designs), control of the temperature during digestion is important for reproducible microwave heating and comparable data.

Alternatively, for specific vessel types, specific sample types and specific sets of reagent(s) a calibration control mechanism could be developed that would allow the use of microwave systems with power programmable to within ± 12 W of the required power. Typical systems provide a nominal 600 W to 1200 W of power. Calibration control provides a backward comparability with older laboratory microwave systems, which may not be equipped for temperature monitoring or feedback control. See clause 10.1 for calibration.

Note. The accuracy of the temperature measurement system shall be periodically controlled at an elevated temperature according to the manufactures instructions. If the temperature deviates by more than 1 to 2 ºC from the temperature measured by an external, calibrated temperature measurement system, the microwave temperature measurement system should be calibrated.

8.2.2 Rotating turntable

The speed of the turntable should be a minimum of 3 rpm. Other types of equipment used to assist in achieving uniformity of the microwave field may also be appropriate.

8.2.3 Sample containers

- plastic and glass containers are both suitable.

8.2.4 Digestion vessels

Digestion vessels of microwave transparent and reagent resistant materials, such as fluorocarbon (e.g. PTA or TFM) or quartz. The vessels may be contained within layers of different microwave transparent materials for strength, durability and safety. The internal volume should be at least 45 mL, and the vessel must be capable of withstanding pressures of at least 30 atm (435 psi) and capable of controlled pressure relief. These specifications are to provide an appropriate, safe, and durable reaction vessel.

Temperature control of closed vessel microwave instruments provides the main feedback performance mechanism for the method. Method control requires a temperature sensor in one or more vessels during the entire decomposition.

8.3 Filter paper

cellulose-based ashless type, hardened and resistant to nitric acid.

8.4 Filter funnel

glass, polypropylene or other appropriate material.

8.5 Volumetric flask

usually of a nominal capacity of 50 mL or 100 mL.

8.6 Graduated pipettes or dispensers

8.7 Analytical balance

with an accuracy of 0,1 mg or better.

9 Sampling and sample pre-treatment

9.1 Sampling

Sampling should be carried out in accordance with EN yyyy:2003 (Horizontal standard module(s) for sampling of sludge, soil and waste).

Samples should be stored in suitable plastic or glass containers with an appropriate closure material.

Samples should be kept cold (< 4°C).

9.2 Pre-treatment of test portion

The test portion should be transferred into the digestion vessel after a pre-treatment of the laboratory sample that result in homogeneous and representative test portions out of the laboratory sample. This procedure shall not change the concentration of the elements of interest.

If the laboratory sample cannot be well mixed and homogenized as received, then air or oven dry at 60ºC or less, crush, sieve, grind and mix as necessary or homogenize the sample until the subsampling variance is less than the data quality objectives of the analysis. Be aware that in certain circumstances a loss of volatile metals (e.g. Hg, organometallics) could occur during sample preparation.

NOTE: For soil samples it is common to use the fraction < 2mm.

The mass of laboratory samples shall be sufficient for the multiple digestion procedures and the determination of the dry matter.

9.3 Mass of test portion

The mass of the test portion for a single digestion has to be selected in a way, that:

- it is representative for the laboratory sample

- it complies with the specifications of manufactures of the digestion unit

10 Procedure

10.1 Calibration of microwave equipment

If the microwave unit uses temperature feedback to control the performance specifications of the method, then performing the calibration procedure is not necessary.

Calibration is the normalization and reproduction of microwave field strength to permit reagent and energy coupling in a predictable and reproducible manner. It balances reagent heating and heat loss from the vessels and is equipment dependent due to the heat retention and loss characteristics of the specific vessel. The available power is evaluated to permit the microwave field output in watts to be transferred from one microwave system to another.

Use of calibration to control this reaction requires balancing output power, coupled energy and heat loss to reproduce the temperature heating profile as described by the procedure. The conditions for each acid mixture and each batch containing the same specified number of vessels must be determined individually. Only identical acid mixtures and vessel models and specified numbers of vessels may be used in a given batch.

For cavity type microwave equipment, calibration is accomplished by measuring the temperature rise in 1 kg of water exposed to microwave radiation for a fixed period of time. The analyst can relate power in watts to the partial power setting of the system. The calibration format required for laboratory microwave systems depends on the type of electronic system used by the manufacturer to provide partial microwave power. Few systems have an accurate and precise linear relationship between percent power settings and absorbed power. The calibration curve can be determined by a three-point calibration method or by the multiple point calibration.

In calibrating the microwave unit, the power absorbed (for each power setting) by 1 kg of reagent water exposed to 120 seconds of microwave energy is determined by the expression

$$\text{Power (in watts)} = (T_1 - T_2)\ (34.86)$$

where: T_1 = Initial temperature of water (between 21 and 25ºC to nearest 0.1ºC)

T_2 = Final temperature of water (to nearest 0.1ºC)

Plot the power settings against the absorbed power to obtain a calibration relationship. Alternatively, use a microwave calibration program to analyse the calibration data. Interpolate the data to obtain the instrument settings needed to provide the wattage levels.

Equilibrate a large volume of water to room temperature (22 ± 3ºC). One kg of reagent water is weighed (1 000,0 ± 0,1 g) into a fluorocarbon beaker or a beaker made of some other material that does not significantly absorb microwave energy (glass adsorbs microwave energy and is not recommended). The initial temperature of the water should be 22 ± 3ºC measured to ± 0,05ºC. The covered beaker is circulated continuously (in the normal sample path) through the microwave field for 2 minutes at the desired partial power setting with the system’s exhaust fan on maximum (as it will be during normal operation). The beaker is removed and the water vigorously stirred. Use a magnetic stirring bar inserted immediately after microwave irradiation (irradiation with the stirring bar inserted could cause electrical arcing). Record the maximum temperature within the first 30 seconds to ± 0,05ºC. Three measurements at each power setting should be made.

The absorbed power is determined by the following relationship:

$$P = \frac{(K)(C_p)(m)(\Delta T)}{t} \tag{1}$$

where

P = the apparent power absorbed by the sample in watts (W) (joule/sec)

K = the conversion factor for thermochemical calories sec^{-1} to watts (K=4,184)

C_p = the heat capacity, thermal capacity, or specific heat [cal/g ºC)] of water

m = the mass of the water sample in grams (g)

ΔT = the final temperature minus the initial temperature (ºC)

t = the time in seconds (s)

Using the experimental conditions of 2 minutes (120 sec) and 1 kg (1000 g) of distilled water [heat capacity at 25ºC is 0.9997 cal/(g ºC)] the calibration equation simplifies to:

$$P = (\Delta T)(34.86)$$

The multiple point calibration involves the measurement of absorbed power over a large range of power settings. Typically, for a 600 W unit, the following power settings are measured: 100, 99, 98, 97, 95, 90, 80, 70, 60, 50, and 40%. This data is clustered about the customary working power ranges. Non-linearity has been encountered at the upper end of the calibration. If the system's electronics are known to have non-linear deviations in any region of proportional power control, is will be necessary to make a set of measurements that bracket the power to be used. The final calibration point should be at the partial power setting that will be used in the test. This setting should be checked periodically to evaluate the integrity of the calibration. If a significant change is detected (± 10 W), then the entire calibration should be re-evaluated.

The three-point calibration involves the measurement of absorbed power at three different power settings. Measure the power at 100% and 50%. From this 2-point line, determine the partial power setting that corresponds to the power, in watts, specified in the procedure to reproduce the heating profiles specified in Section 10.2. Measure the absorbed power at that partial power setting. If the measured absorbed power does not correspond to the specified power within ± 10 W, use the multiple point calibration. This point should also be used to periodically verify the integrity of the calibration.

10.2 Digestion

Weigh into the digestion vessel an amount equal to 0,25 – 0,5 g dried sample accurately at 0,001 g, prepared according to clause 9 and transfer it into the digestion vessel (7.2.4). Add 10 mL ± 0,1 mL of concentrated nitric acid (6.2) to the digestion vessel with test portion in a fume hood (or fume exhausted enclosure). Swirl and allow the mixture to stand until any visible reaction has stopped.

Cap the digestion vessel according to the manufacturer's directions. Place the vessel in the microwave system according to the manufacturer's recommended specifications and, when applicable, connect appropriate temperature and pressure sensors to vessles according to the manufacturer's specifications.

This method is a performance based method, designed to achieve or approach consistent leaching of the sample by achieving specific reaction conditions. The temperature of each sample should rise to 175 ± 0,5ºC in approximately 5,5 ± 0,25 minutes and remain at 175 ± 0,5ºC for 4,5 minutes, or for the remainder of ten minute digestion period.

At the end of the microwave programme, allow the vessels to cool for a minimum of 5 minutes before removing them from the microwave system. Cooling of the vessels may be accelerated by internal or external cooling devices. When the vessels have cooled to near room temperature, determine if the microwave vessels have maintained their seal throughout the digestion. Due to the wide variety of vessel designs, a single procedure is not appropriate. The vessel may be weighed before and after digstion to evaluate seal integrity. If the weight loss of the sample exceeds 1% of the weight of the sample and reagents, then the sample is considered compromised.

Carefully uncap and vent each vessel in a chemical in a well-ventilated fume hood using the procedure recommended by the manufacturer. Quantitatively transfer the sample to an acid-cleaned bottle. If the digested sample contains particles which may clog nebulizers or interfere with an injection of the sample into the instrument, the sample may be centrifuged, allowed to settle, or filtered.

Note. Centrifugation at 2,000 – 3,000 rpm for ten minutes is usually sufficient to clear the supernatant.

Note. Settling: If undissolved material, such as SiO_2, TiO_2, or other refractory oxides, remains, allow the sample to stand until the supernatant is clear. Allowing a sample to stand overnight will usually accomplish this. If it does not, centrifuge or filter the sample.

Note. Filtering: If necessary, the filtering apparatus must be throughly cleaned and pre-rinsed with dilute (approximately 10 % V/V) nitric acid. Filter the sample through qualitative filter paper into a second acid-cleaned container.

Note. The final solution typically requires nitric acid to maintain appropriate sample solution acidity and stability of the elements. Commonly, a 2% (V/V) nitric acid concentration is desirable.

Transfer or decant the sample into volumetric ware and dilute the digest to a known volume. The digest is now ready for analysis for elements of interest using appropriate elemental analysis techniques.

11 Quality control

11.1 Control charts

Data from quality control should be recorded for each control sample in control charts.

11.2 Duplicate samples

Duplicate samples should be processed on a routine basis. A duplicate sample is a sample brought through the whole sample preparation and analysis process a second time. A duplicate sample should be processed with each analytical batch or every 20 samples, whichever is the greater number. A duplicate should be prepared for each matrix type (i.e. soil, sludge, etc.).

Spiked samples or standard reference materials should be included with each group of samples processed, or every 20 samples, whichever is the greater number. A spiked sample should also be included whenever a new sample matrix is being analysed.

11.3 Blank test

Blank samples, reflecting blank values for the sampling bottles, reagents, digestion vessels and any contamination during the whole procedure, shall be prepared and digested in parallel with the batch of samples, by the same procedure, by the use of the same quantities of all the reagents as in the determination but omitting the test portion.

12 Test report

The work carried out by the testing laboratory shall be covered by a report that accurately, clearly and unambiguously presents the test results and all other relevant information. The test report shall be issued separately or in conjunction with the report from the subsequent analytical method. Either of these shall include the following information:

a) a reference to this European Standard;

b) complete identification of the sample;

c) information about the pre-treatment and digestion of the sample;

d) any detail not specified in this European Standard, or which are optional;

e) any other information pertinent to the quality of the analytical data.

The test report may include the following information:

a) information about the sampling and sample pre-treatment;

b) results of the analytical determinations carried out according to other methods on the same samples, if any.

NOTE: The final report should include all results and relevant information on the sampling, the digestion method and the analytical methods used.

Where the test is not carried out in accordance with this standard, reference may only be made to EN xxxx:2003 in the report in case all deviations from the procedures prescribed in this standard are indicated in the report stating the reasons for the deviations.

13 Performance characteristics

Performance data in terms of repeatability and reproducibility…………..

Annex A

(informative)

Validation of methods

Annex B
(informative)

The modular horizontal system

Annex C
(informative)

Information on WP xx and the project Horizontal

Bibliography

[1] US EPA Method 3051A. Microwave assisted acid digestion of sediments, sludges, soils, and oils. Rev. 1. January 1998.