SLOVENSKI STANDARD
SIST EN 13656:2004

01-januar-2004

Karakterizacija odpadkov - Mikrovalovni razklop z zmesjo fluorovodikove (HF), klorovodikove (HCl) in duġikove(V) kisline (HNO3) za doloļ anje elementov

Characterization of waste - Microwave assisted digestion with hydrofluoric (HF), nitric (HNO3) and hydrochloric (HCl) acid mixture for subsequent determination of elements

Charakterisierung von Abfällen - Aufschluss mittels Mikrowellengerät mit einem Gemisch aus Fluorwasserstoffsäure (HF), Salpetersäure (HNO3) und Salzsäure (HCl) für die anschließende Bestimmung der Elemente im Abfall

Caractérisation des déchets - Digestion assistée par micro-ondes avec un mélange d'acides fluorhydrique (HF), nitrique (HNO3) et chlorhydrique (HCl) pour la détermination ultérieure d'éléments contenus dans les déchets

Ta slovenski standard je istoveten z: **EN 13656:2002**

ICS:

13.030.40	Naprave in oprema za odstranjevanje in obdelavo odpadkov	Installations and equipment for waste disposal and treatment

SIST EN 13656:2004 **en**

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 13656

October 2002

ICS 13.030.40

English version

Characterization of waste - Microwave assisted digestion with hydrofluoric (HF), nitric (HNO_3) and hydrochloric (HCl) acid mixture for subsequent determination of elements

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This European Standard was approved by CEN on 19 August 2002.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Management Centre or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Management Centre has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Malta, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and United Kingdom.

EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

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Ref. No. EN 13656:2002 E

Contents

Foreword

This document EN 13656:2002 has been prepared by Technical Committee CEN/TC 292 "Characterization of waste", the secretariat of which is held by NEN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by April 2003, and conflicting national standards shall be withdrawn at the latest by April 2003.

In this European Standard the annex A is normative and the annexe B is informative.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Malta, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

Introduction

The purpose of the method is to bring the elements to be determined in many types of waste into solution to provide a rapid digestion for analysis. Elements extractable by this procedure can in many instances be described as „total“. On another hand they cannot be regarded as available for leaching, as the extraction procedure is too vigorous to represent natural processes.

1 Scope

This European Standard specifies methods of microwave assisted digestion with hydrofluoric (HF), nitric (HNO_3) and hydrochloric (HCl) acid mixture. Solutions produced by the methods are suitable for analysis e.g. by atomic absorption spectrometry (FLAAS, HGAAS, CVAAS, GFAAS), inductively coupled plasma emission spectrometry (ICP-OES) and inductive coupled plasma mass spectrometry (ICP-MS).

The method is applicable to the microwave assisted acid digestion of waste for example for the following elements: Al, Sb, As, B, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Mo, Ni, P, K, Se, Ag, S, Na, Sr, Sn, Te, Ti, Tl, V, Zn.

2 Normative references

This European Standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text, and the publications are listed hereafter. 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).*

3 Terms and definitions

For the purposes of this European 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 completely, when reacted with a reagent mixture

3.2
sample
portion of material selected from a larger quantity of material

[ENV 12506:2001]

3.3
laboratory sample
sample or sub-sample(s) sent to or received by the laboratory

[ENV 12506:2001]

3.4
test sample; analytical sample
sample, prepared from the laboratory sample, from which test portions are removed for testing or analysis

[ENV 12506:2001]

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

[ENV 12506:2001]

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 residue
dry matter expressed as a percentage by mass after drying at 105 °C ± 5 °C to the constancy of weight

3.7
digestion vessel
special flask where the test portion and the acid mixture are filled in and the digestion is performed

3.8
microwave unit
whole microwave digestion system (oven and associated equipment)

3.9
microwave unit cavity
inner part of the microwave unit in which the digestion vessel is located and the microwave digestion is performed

3.10
focused microwave unit
microwave unit in which a precise control of the electric field is made by using a wave guide

NOTE Microwaves are focused at the bottom part of the digestion vessel.

4 Safety remarks

All this work has to be performed by skilled persons.

The reagents used within this European Standard are strongly corrosive and partly very toxic. Safety precautions are absolutely necessary due to strong corrosive reagents, high temperature and high pressure.

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 pressurised 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.

People performing the test shall be informed on the specific risk of HF.

5 Sample

5.1 Sample pre-treatment

The test portion should be transferred into the vessel as it is without any pre-treatment if possible.This is applicable only if the test portion is representative for the laboratory sample and the effectiveness of the digestion is proven.

If these conditions are not met a pre-treatment of the laboratory sample is necessary. This procedure shall not change the concentration of the elements of interest.

NOTE Pre-treatment may include drying or grain size reduction below a particle size of 250 µm for solid waste or homogenizing by use of a high speed mixer or sonification for liquid samples.

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

5.2 Mass of test portion

The mass of 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 manufacturer of the digestion unit.

NOTE If the representative test portion exceeds the manufacturers specifications the test portion should be devided into smaller quantities and digested seperately. The individual digests should be combined prior to analysis.

For representativity reason mass above 200 mg is to be preferred. Unless recommended by the manufacturer the amount of organic carbon shall not exceed 100 mg because of safety reasons in the case of closed digestion vessel.

6 Equipment

6.1 Closed vessel system

6.1.1 Microwave unit

The microwave unit shall provide programmable power which can be programmed to within ± 10 W of the required power. Typical units provide a nominal 600 W to 1 200 W of power. If necessary (referring to manufactures specifications) calibration of the microwave unit has to be performed (see annex A).

The microwave unit has to comply to European and national regulations relevant to microwave radiation.

The microwave unit cavity has to be well ventilated. It has to have an exhaust air tube which is connected to a corrosion resistant laboratory air outlet system or the instrument is provided for use in a laboratory hood.

All electronics are sufficiently protected against corrosion for safe operation. All parts which can have contact with acids or their vapours have to be corrosion resistant.

The microwave unit shall be designed in a way that guarantees homogeneous heating of the samples.

The microwave unit cavity has to be built in a way that even in case of leakage or explosion of the vessels the safety of the operators can be guaranteed. Household instruments are not suitable for laboratory use.

NOTE The microwave unit should include a temperature and/or pressure control system.

6.1.2 Digestion vessels

The vessels used in the microwave unit shall be equiped with a pressure relieve valve or another technical equipment which avoids the bursting of the vessels at suddenly occuring excess pressure. The material of the vessels has to be inert to the acids used for digestion. The digestion vessel shall withstand the pressure of at least 8 bar. If the amount of organic carbon exceeds 100 mg it has to be ensured that the digestion vessel is capable of withstanding higher pressures.

6.2 Semi-open vessel system

6.2.1 Microwave unit

The microwave unit shall be equiped with power control. Typical unit provides a nominal 200 W or 300 W of released power. If necessary, calibration of the microwave unit has to be performed by the manufacturer.

The microwave unit shall comply with European and national regulations relevant to microwave radiation.

The microwave unit shall be designed for use in a laboratory hood.

Fume extraction equipment, used to extract acid vapours from the reaction vessels during the digestion programme, shall have sufficient flow rate to prevent the release of dangerous vapours into the laboratory.

All electronics shall be sufficiently protected against corrosion for safe operation. All parts which can be in contact with acids or their vapours shall be corrosion resistant.

6.2.2 Digestion vessels

The vessel is working at atmospheric pressure and has to be connected with a reflux system to avoid losses of analytes. The vessel shall comply with the manufactures specifications and should have a minimum volume of 50 ml.

The material of the vessels has to be inert to the reagents used for digestion.

NOTE Quartz or borosilicated glass digestion vessels are not useable when hydrofluoric acid is used. For example polytetrafluorethylen (PTFE) digestion vessels can be used.

6.3 General equipment

The following equipment is used by both systems described in 6.1 and 6.2:

— volumetric graduated flasks and pipettes of adequate size;

— filter equipment of adequate chemical resistance and purity or centrifuge;

— analytical balance, with an error limit of ± 0,1 mg.

For the preparation of standards and the treatment and storage of samples for determination of boron, the use of borosilicate glass shall be avoided.

The use of glass ware shall be excluded when free hydrofluoric acid is present.

7 Reagents

Use reagents of analytical grade quality or better and water of grade 1 according to EN ISO 3696:1995.

— Hydrochloric acid (HCl): a mass fraction of 35 % to 37 %;

— Nitric acid (HNO_3): a mass fraction of 65 % to 70 %;

— Hydrofluoric acid (HF): a mass fraction of 40 % to 45 %;

— Boric acid ($B(OH)_3$): solid.

8 Interferences and sources of error

8.1 General informations

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 the volatile reaction products which might be formed during the digestion are not allowed to escape.

The container in which the sample is delivered and stored can be a source of errors. Its material shall be chosen according to the elements to be determined (e.g. elemental Hg can penetrate polyethylene walls very fast in both directions. Glass can contaminate samples with elements contained: e.g. B, Na, K, Al)

Grinding or milling samples includes a risk of contamination of the sample by the environment (air, dust, wear of milling equipment). Due to elevate temperature losses of volatile compounds are possible.

For the determination of elements forming volatile compounds (e.g. Hg, As, Pb) special care has to be taken at sample pre-treatment.

The use of the described digestion procedure may leave parts of the sample undissolved. This includes the risk of low recoveries and of bad repeatability. If required the residue can be analysed separately e.g. by alkaline fusion.

High acid and solute concentration in the digest solution can cause interferences at determination. Depending on the content of the digest solution some equipment for determination is not applicable.

Depending on the concentration of the element of interest and the wanted precision, a particular caution to the cleaning of the vessels shall be taken. It is recommended to clean the vessels with 10 % nitric acid.

Care shall be taken to ensure that all of the test portion is brought into contact with the acid mixture in the reaction vessel.

Some elements of interest can be lost because of precipitation with some ions of the solution. It is the case for insoluble chlorides, fluorides and sulphates for example. In this case the precipitate can be analysed separately.

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

8.2 Closed vessel system

The upper limits of mass of the test portion referring to the manufacturers specifications have to be taken into account.

Very reactive or volatile materials that may create high pressures when heated may cause a venting of the vessels with potential loss of sample and analytes. The complete decomposition of either carbonates, or carbon based samples, may cause enough pressure to vent the vessel.

After digestion, the vessel shall be cooled to room temperature before opening. If not, losses of certain elements, particulary volatile elements as mercury or arsenic can occur.

8.3 Semi-open vessel system

Depending on the volatility of some elements of interest, the reflux system can be inefficient to condense the vapours and losses of some elements of interest can happen.

9 Procedure

9.1 Blank test

To detect possible contaminations from vessels and/or reagents, blank tests shall be carried out in parallel by the same digestion procedure and filtration if appropriate, using the same quantities of all reagents but omitting the test portion.

9.2 Procedure for closed vessels

The following description have to be done step by step: