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Soil quality — Dissolution for the determination of total element content —

Part 3:
Dissolution with hydrofluoric, hydrochloric and nitric acids using pressurised microwave technique

Qualité du sol — Mise en solution pour la détermination des teneurs élémentaires totales —

Partie 3: Mise en solution par l'acide fluorhydrique, l'acide chlorhydrique et l'acide nitrique à l'aide de la technique de micro-ondes pressurisées

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ISO copyright office
Ch. de Blandonnet 8 • CP 401
CH-1214 Vernier, Geneva, Switzerland
Tel. +41 22 749 01 11
Fax +41 22 749 09 47
copyright@iso.org
www.iso.org

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 190, *Soil quality*, Subcommittee SC 3, *Chemical methods and soil characteristics*.

A list of all parts in the ISO 14869 series can be found on the ISO website.

Introduction

This document is a module for analysis of inorganic parameters in soil and soil material. This document concerns the complete dissolution for the subsequent analysis of elements.

An acid mixture based on nitric acid, hydrofluoric acid and hydrochloric acid will be used to totally dissolve most soils and similar materials. The resulting solutions can be determined separately or after combination with atomic absorption spectrometry (AAS) techniques, inductively coupled plasma optical emission spectrometry (ICP-OES) or inductively coupled plasma mass spectrometry (ICP-MS) determination methods.

Soil quality — Dissolution for the determination of total element content —

Part 3:
Dissolution with hydrofluoric, hydrochloric and nitric acids using pressurised microwave technique

1 Scope

This document specifies a method for microwave-assisted dissolution of soil samples for determination of total element contents of

Al, As, Ba, Ca, Cd, Co, Cr, Cs, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, P, Pb, S, Se, Sb, Sr, Tl, V, Zn

using an acid mixture of nitric acid (HNO_3), hydrofluoric acid (HF) and hydrochloric acid (HCl). This method is applicable to all types of soil and soil material.

The main field of application is geological and pedological survey.

The acid mixture is suitable for total dissolution of element contents in soil (major, minor and trace), but some refractory compounds such as SiO_2, TiO_2, spinel, Al_2O_3 or other compounds may remain as a residue. In such a case, the use of alkaline fusion, following ISO 14869-2, is recommended to determine the true total element content.

NOTE 1 In environmental studies, usually, aqua regia extraction is applied using ISO 12914 or ISO 11466.

Solutions produced by the microwave method are suitable for analysis, for example, by using atomic absorption spectrometry (FAAS, HGAAS, CVAAS, GFAAS), inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS).

NOTE 2 Due to the presence of chloride in the digestion solution, limitations for the application of some analytical techniques can occur.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 11074, *Soil quality — Vocabulary*

ISO 11464, *Soil quality — Pretreatment of samples for physico-chemical analysis*

ISO 11465, *Soil quality — Determination of dry matter and water content on a mass basis — Gravimetric method*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 11074, ISO 11464 and ISO 11465 apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at http://www.electropedia.org/
- ISO Online browsing platform: available at http://www.iso.org/obp

4 Safety remarks

All this work has to be performed by trained persons.

The reagents used within this document are strongly corrosive and potentially very harmful. 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.

DANGER — Hydrofluoric acid is dangerous if inhaled as vapour or by direct contact with skin and mucosa. It should be noted that the effects of exposure to HF may not be apparent for several hours, particularly for skin, after which effective treatment can be difficult. Users of this document should familiarize themselves with the necessary precautions, taking professional and medical advice where appropriate. The use of an efficient exhaust hood, rubber gloves, glasses or face protection and protected pipetting devices is essential. Observe safety precaution for handling hydrofluoric acid.

WARNING — Several stages of the procedure are potentially hazardous, especially those involving concentrated acids under pressurized conditions. Users of this document should familiarize themselves with the necessary safety precautions and, where appropriate, any legal requirements for their use. If in doubt, seek professional advice.

5 Principle

The laboratory sample shall be treated in accordance with the principles of ISO 11464 in order to produce a homogeneous test sample from which a representative test portion can be sub-sampled and completely dissolved in an acid mixture by microwave-assisted heating.

6 Interferences and sources of errors

During trace element determinations, contaminations shall be avoided. The container in which the sample is delivered and stored can be a source of errors. The container's material shall be chosen such that it does not absorb the elements to be determined (e.g. elemental Hg can penetrate polyethylene walls very fast in both directions).

Grinding or milling samples includes a risk of contamination of the sample by the environment (e.g. air, dust, wear of milling equipment). Due to the volatility of some compounds, it is important to take care that the sample is not heated before the dissolution and that the volatile reaction products which might be formed during the dissolution are not allowed to escape.

For the determination of elements forming volatile compounds (e.g. Hg, As, Cr, Se), special care shall be taken during sample pre-treatment and pressurized digestions.

High acid and high dissolved matrix element concentrations in the dissolution solution may cause interferences in the analytical method.

Depending on the concentration of the elements of interest, particular attention needs to be paid to the cleaning of the laboratory equipment. It is recommended to thoroughly clean all laboratory equipment and as a minimum, leave the equipment standing over night in 5 % nitric acid.

Some elements of interest can be lost due to precipitation with ions present in the digestion solution, e.g. low-solubility chloride, fluoride or sulfate compounds. Before starting filtration, boric acid should be added to bind excess hydrofluoric acid and re-dissolve insoluble fluorides. During filtration, avoid introduction of contaminants.

7 Reagents

Use only reagents of recognized analytical grade.

7.1 Water.

Deionised or distilled water used shall conform at least to grade 2 of ISO 3696.

It is recommended that the same batch of water be used throughout a given batch of determinations. Blank tests are carried out in each series of sample determination.

7.2 Hydrochloric acid, $c(HCl)$ = 12 mol/l; ρ = 1,18 g/ml; $w(HCl)$ = 36 %.

7.3 Nitric acid, $c(HNO_3)$ = 14,3 mol/l; ρ = 1,4 g/ml; not less than $w(HNO_3)$ = 65 %.

7.4 Nitric acid, diluted, $c(HNO_3)$ = 0,5 mol/l, dilute 35 ml nitric acid (7.3) to 1 l with water (7.1).

7.5 Hydrofluoric acid, $c(HF)$ = 22,6 mol/l, ρ = 1,13 g/ml, $w(HF)$ = 40 %.

7.6 Antifoaming agent.

For example, *n*-dodecane ($C_{12}H_{26}$) or polyethyleneglycol *p*-(1,1,3,3-tetramethylbutyl)-phenyl ether ($C_{14}H_{22}O(C_2H_4O)_n$) is suitable.

7.7 Boric acid solution, $w(H_3BO_3)$ approximately 4 %.

Dissolve 20 g boric acid (H_3BO_3) in 450 ml of water and dilute to 500 ml with water. Store in a polyethylene bottle. Solubility limit of H_3BO_3 is 49 g in 1 000 ml of water.

8 Apparatus

All glassware and plasticware shall be adequately cleaned and stored in order to avoid any contamination.

8.1 Microwave-assisted dissolution system.

8.1.1 Microwave apparatus requirements, microwave apparatus for pressurised digestions — preferably a temperature-regulated device, in combination with pressure measurement for laboratory use only.

A laboratory-grade microwave unit cavity shall be well ventilated and corrosion resistant. All electronics shall be protected against corrosion for safe operation. The temperature performance requirements necessitate that the microwave decomposition system is able to sense the temperature with an accuracy of ±2,5 °C and automatically adjust the microwave field output power within 2 s of sensing. Temperature sensors should be accurate to ±2 °C [including at the final reaction temperature of (175 ± 5) °C]. Temperature feedback control provides the primary performance mechanism for the method. Due to the variability in sample matrices and microwave equipment (i.e. different vessel types and microwave designs), control of the temperature during the dissolution process is important for ensuring reproducible microwave heating for different units.

The accuracy of the temperature measurement system shall be periodically tested at an elevated temperature according to the manufacturer's instructions. If the temperature deviates by more than 2,5 °C from the temperature measured by an external calibrated temperature measurement system, the microwave temperature measurement system should be calibrated.

8.1.2 Rotating turntable.

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

8.1.3 Microwave dissolution vessels.

Digestion vessels shall be made of materials that are microwave transparent and resistant to reagents and temperature, such as fluorocarbon (e.g. PTA or TFM). The vessels may be placed in different microwave-transparent containers for stability, durability and safety. The internal volume of dissolution vessels should preferably be 100 ml. 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, capable of withstanding pressures of at least 20 bar and capable of controlled pressure relief. 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.

8.2 Filter papers.

Use cellulose-based filter paper, hardened and resistant to acid mixture or suitable membrane filters with 0,45 µm pore size. Filtration should be done in a glass device only after boric acid addition. Otherwise, use an all-plastic membrane filtration device and a polypropylene volumetric flask.

8.3 Volumetric flasks, capacity 100 ml or higher made of borosilicate glass or polypropylene.

8.4 Balance, accuracy of 0,1 mg.

9 Sampling and sample pre-treatment

9.1 Sample pre-treatment

Pre-treat samples according to ISO 11464.

9.2 Pre-treatment of test portion

The test sample shall be a representative part of the laboratory sample for the elements of interest with sufficient homogeneity for analysis.

Pre-treatment should include drying and grain size reduction to a particle size less than of 250 µm, preferably 125 µm. The mass of test samples shall be sufficient for multiple digestion procedures and determination of the dry matter. The dry matter content determination according to ISO 11465 shall be carried out using a separate portion of the test sample.

10 Procedure

10.1 Blank test

Carry out a blank test in parallel with the determination by using the same procedure, the same quantities of reagents but omitting the test portion (10.2).

10.2 Test portion

Weigh the empty digestion vessel with the cap. Weigh approximately 0,5 g (based on dry weight) of the test sample, accurately to 0,1 mg. Sample weights from 0,2 g to 0,5 g can be used, if the volume of digestion vessel and maximum pressure resistance are sufficient. Assure that the test portion amount selected is a representative of the test sample and the laboratory sample.

Referring to the manufacturer's specifications, the upper limits of the test portion mass should be taken into account.

10.3 Dissolution

Moisten the test portion in the digestion vessel with a few drops of water (7.1). Add separately (6 ± 0,1) ml of hydrochloric acid (7.2), (2 ± 0,1) ml of nitric acid (7.3) and (2 ± 0,1) ml HF (7.5) to the digestion vessel (8.1.3) and mix well.

If a vigorous reaction occurs, allow the reaction to subside before capping the vessel. If excessive foaming occurs, add a drop of anti-foaming agent (7.6).

The amount of nitric acid is sufficient to oxidize approximately 250 mg of organic carbon in the sample. If the organic carbon content is higher, add an extra 0,5 ml nitric acid (7.3) for every 50 mg of organic carbon.

Cap the digestion vessel (8.1.3) and weigh it. Connect the digestion vessel to the microwave equipment and place it into the carrousel. Always fill all positions of the microwave equipment (usually 6, 12, 16 or 40 positions). If not all positions are occupied by test portions, fill the remaining digestion vessels with the same amount of acid mixture as in the sample vessels to make sure that the energy is evenly absorbed.

Increase the temperature with a rate of not more than 15 °C/min. Select the temperature programme carefully to avoid pressure increase rates higher than 0,2 bar/s to 0,3 bar/s. The temperature programme in Table 1 is given as an example.

Table 1 — Example of a temperature schedule during the dissolution of soil sample

Step	**Temperature** °C	**Ramp** min:s	**Hold** min:s	**Fan**
1	90	15:00	5:00	1
2	140	5:00	10:00	1
3	175	5:00	10:00	1
4	room temperature (20 to 25)	00:00	20:00	2

NOTE 1 Too fast increase of the temperature may lead to exothermic reactions which can result in opening of the pressure safety valve and loss of analytes.

NOTE 2 Instead of a mixture HCl, HNO_3, HF and H_3BO_3, a mixture of HCl, HNO_3, HBF_4 can be used if internal validation data for all relevant soil matrices are provided by the laboratory.

Allow the digestion vessel to fully cool to room temperature before opening. Otherwise, volatile fluoride or chloride compounds may escape.

Weigh each digestion vessel again and record the mass. The difference before and after digestion of the vessel content (test portion and acid) can be considered acceptable if the mass loss is less than 10 % to 15 %. If losses are higher, an unacceptable release of fumes has occurred and the sample shall be discarded.

Uncap and vent the digestion vessel in a fume hood. Complex the hydrofluoric acid in excess boric acid by adding 20 ml of a 4 % m/v boric acid solution (7.7). Close the digestion vessels and heat for an additional 15 min at 130 °C in the microwave device. The temperature programme in Table 2 is given as an example.

Table 2 — Example of a temperature schedule during the boric acid addition step

Step	Temperature °C	Ramp min:s	Hold min:s	Fan
5	130	10:00	5:00	1
6	room temperature (20 to 25)	00:00	10:00	2

Allow the digestion vessel to fully cool to room temperature before opening. Uncap and vent the digestion vessel in a fume hood. Filter the digestion solution through a filter (8.2) or a suitable membrane filtration device with a 0,45 µm pore size into a 100 ml volumetric flask. Then, wash the container and the residue (if any) with warm nitric acid (7.4) and then water and quantitatively transfer to the 100 ml volumetric flask. Fill up the volumetric flask to the mark with water (7.1). If a hydrofluoric-resistant analytical instrument is available (HF-resistant torches for ICP-OES or ICP-MS), addition of boric acid can be avoided. Use a plastic filter equipment and a plastic volumetric flask if the sample solution contains hydrofluoric acid. The test portion solution can be measured directly.

NOTE 3 If the digestion solution contains undissolved particles, centrifugation at 2 000 min^{-1} to 3 000 min^{-1} for 10 min before the filtration step can be helpful.

The digestion solution is now ready for analysis using appropriate elemental analysis techniques for elements of interest.

11 Quality control

A control sample should be processed with each operating cycle of the microwave oven. This can be a suitable in-house reference material or commercial reference material.

12 Test report

The test report shall include at least the following information:

a) a reference to this document, i.e. ISO 14869-3;

b) complete identification of the sample;

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

d) any detail not specified in this document, or which are optional, as well as any factor which may have affected the results.

13 Performance characteristics

Performance data in terms of reproducibility are given in Annex A.