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**Soil quality — Microwave-assisted
extraction of the aqua regia soluble
fraction for the determination of elements**

*Qualité du sol — Extraction assistée par micro-ondes de la fraction
soluble dans l'eau régale pour la détermination des éléments*



Reference number
ISO 12914:2012(E)

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Foreword

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The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 12914 was prepared by Technical Committee ISO/TC 190, *Soil quality*, Subcommittee SC 3, *Chemical methods and soil characteristics*.

Introduction

This International Standard is a module for analysis of inorganic parameters in soil and soil material. This International Standard concerns the extraction with *aqua regia* for the subsequent analysis of elements.

Aqua regia will not totally dissolve most soils and similar materials, and the efficiency of the extraction for particular elements differs from element to element. Such efficiency might also differ for the same element in different matrices. Users of this International Standard should carry out a program of analysis using reference materials to ensure that the method given here is appropriate for their needs. Elements extractable in *aqua regia* cannot, therefore, be regarded as 'totals'; conversely, they cannot be regarded as the 'bio available' fraction, as the extraction procedure is too vigorous to represent any biological process.

Soil quality — Microwave-assisted extraction of the aqua regia soluble fraction for the determination of elements

1 Scope

This International Standard specifies a method for microwave-assisted extraction of elements from samples using *aqua regia* as the extraction solution for the determination of elements. This method is applicable to all types of soil and soil material.

Aqua regia extraction is suitable for the release of trace and major element fractions in soil. *Aqua regia* is not suitable for the extraction of elements from refractory compounds, such as SiO₂, TiO₂ and Al₂O₃.

The extraction with *aqua regia* is operationally defined and will not necessarily release all elements completely.

The microwave method is generic and can be implemented using a wide variety of equipment, provided:

- a) the extraction mixture ratio is unchanged;
- b) the extraction temperature is known.

Solutions produced by the microwave method are suitable for analysis, for example, by using atomic absorption spectrometry (flame: FAAS, hydride generation: HGAAS, cold vapour: CVAAS, graphite furnace; GFAAS), inductively coupled plasma emission spectrometry (ICP/OES) and inductively coupled plasma mass spectrometry (ICP/MS).

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

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 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 10381-1, *Soil quality — Sampling — Part 1: Guidance on the design of sampling programmes*

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

ISO 11465:1993, *Soil quality — Determination of dry matter and water content on a mass base — Gravimetric method*

ISO 18512, *Soil quality — Guidance on long and short term storage of soil samples*

3 Terms and definitions

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

3.1

aqua regia

extraction solution obtained by mixing 1 volume of nitric acid, $w(\text{HNO}_3) = 65\% \text{ to } 70\%$, and 3 volumes of hydrochloric acid, $w(\text{HCl}) = 35\% \text{ to } 37\%$

3.2

extraction

mineralization of the organic matter of a sample and dissolution of its mineral part, more or less completely, when reacting with the reagent mixture

3.3

sample

portion of soil material selected from a larger quantity of material

[ISO 11074:2005]

3.4

laboratory sample

sample intended for laboratory inspection of testing

[ISO 11074:2005]

3.5

test sample

portion of material resulting from the laboratory sample by means of an appropriate method of sample pretreatment and having the size (volume/mass) necessary for the desired testing or analysis

[ISO 11074:2005]

3.6

**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 11074:2005]

3.7

dry matter

mass fraction of a sample weight after the specified drying process and the weight of the moist sample

NOTE It is expressed in percent.

[ISO 11465:1993]

4 Safety remarks

All of the work has to be performed by trained persons.

The reagents used within this International Standard are strongly corrosive and potentially very harmful. Safety precautions are absolutely necessary due to toxic fumes and 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 oxidizing 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.

5 Principle

The laboratory sample should be treated in accordance with the principles of ISO 11464, in order to produce a homogeneous test sample from which a test portion can be subsampled and digested by *aqua regia* to the following heating procedure.

Microwave extraction at $175\text{ °C} \pm 5\text{ °C}$ for $10\text{ min} \pm 1\text{ min}$ in a closed vessel, followed by filtration and adjustment of the volume in a volumetric flask.

6 Interferences and sources of errors

Due to the volatility of some compounds, it is important to take care that the sample is not heated before the extraction, and that the volatile reaction products which might be formed during the extraction are not allowed to escape. Grinding or milling samples includes a risk of contamination of the sample by the environment (e. g. air, dust, wear of milling equipment). Losses of volatile compounds are possible due to elevated temperatures (e.g. a drying temperature over 40 °C may result in losses of mercury).

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 and glass can contaminate samples with its constituent elements such as B, Na, K, Al).

For the determination of elements forming volatile compounds (e.g. Hg, As), special care has to be taken during sample pretreatment.

The use of the described extraction procedures may leave large parts of the sample undissolved.

High-acid and high-dissolved-matrix concentrations in the extract may cause interferences in measurement steps.

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 overnight in 1 % to 5 % nitric acid.

Care shall be taken to ensure that the test portion is in contact with the acid mixture in the reaction vessel. Boiling aids like glass beads should be used, provided they do not contain constituents contaminating the sample.

Some elements of interest can be lost due to precipitation with ions present in the extract solution, e. g. low soluble compounds of chlorides. During filtration of the extracted solution, it is necessary that the filtration procedure does not introduce contaminants.

7 Reagents

Use only reagents of recognized analytical grade.

7.1 Water: deionized or distilled water used shall conform at least to grade 2 of ISO 3696.

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

7.2 Hydrochloric acid, $c(\text{HCl}) = 12\text{ mol/l}$; $\rho = 1,18\text{ g/ml}$; $w(\text{HCl}) = 36\text{ %}$.

7.3 Nitric acid, $c(\text{HNO}_3) = 14,3\text{ mol/l}$; $\rho = 1,4\text{ g/ml}$; not less than $w(\text{HNO}_3) = 65\text{ %}$.

7.4 Nitric acid, diluted, $c(\text{HNO}_3) = 0,5\text{ mol/l}$, dilute 35 ml of nitric acid (7.3) to 1 l with water (7.1).

7.5 Anti-foaming agent, for example, *n*-dodecane ($\text{C}_{12}\text{H}_{26}$) or polyethyleneglycol *p*-(1,1,2,3-tetramethylbutyl)-phenyl ether [$\text{C}_{14}\text{H}_{22}\text{O}(\text{C}_2\text{H}_4\text{O})_n$] is suitable.

8 Apparatus

8.1 General

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

8.2 Microwave-assisted extraction system

8.2.1 Microwave apparatus requirements

The microwave extraction apparatus shall be either temperature regulated or power controlled, in combination with temperature calibration and pressure measurement. The microwave unit shall ensure equal distribution of energy over the samples. These devices shall be calibrated to establish the temperature and time relation as described in 10.3.

The microwave unit cavity shall be well ventilated and corrosion resistant. In addition, ventilation in power-controlled units shall be sufficient to maintain room temperature inside the cavity.

All electronics shall be protected against corrosion for safe operation. A laboratory-grade microwave oven with temperature-feedback control mechanisms is preferred. The temperature performance requirements necessitate that the microwave decomposition system be able to sense the temperature with an accuracy of $\pm 2,5$ °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 °C ± 5 °C). Temperature feedback control provides the primary performance mechanism for this method. Due to the variability in sample matrices and microwave extraction equipment (i.e. different vessel types and microwave designs), control of the temperature during extraction is important for ensuring reproducible microwave heating and comparable data between different apparatuses.

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.

8.2.2 Rotating turntable

The speed of the turntable should be a minimum of 3 min^{-1} . Other types of equipment used to assist in achieving uniformity of the microwave field may also be appropriate.

8.2.3 Microwave extraction vessels

Extraction vessels shall be made of materials that are microwave-transparent, and resistant to reagents and temperature, such as fluorocarbon (e.g. PTA or TFM) or quartz. The vessels may be placed in different microwave-transparent containers for stability, durability and safety. The internal volume of extraction vessels should preferably be 50 ml or 100 ml. The inner wall of the vessel shall be inert and shall not release substances to the extract 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 30 bar (435 psi) 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.

8.3 Filter papers, cellulose-based, hardened and resistant to *aqua regia*.

Membrane filtration ($0,45 \mu\text{m}$) may also be used.

8.4 Volumetric flasks, of capacity 50 ml or 100 ml.

8.5 Balance, with an accuracy of 1 mg or better.

9 Sampling and sample pretreatment

9.1 Sampling

Sampling should be carried out in accordance with ISO 10381-1, as appropriate.

Laboratory samples should be stored in accordance with ISO 18512.

9.2 Sample pretreatment

Pretreat samples according to ISO 11464.

9.3 Pretreatment 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.

Pretreatment should include drying and grain size reduction to below a particle size of 250 µm. The mass of test samples shall be sufficient for the multiple extraction 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 at least 0,5 g to 1,0 g (based on dry mass) of the test sample, accurate to 1 mg, prepared according to 9.3 and transfer to the microwave extraction vessel (8.2.3).

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

10.3 Extraction

Moisten the test portion with a few drops of water (7.1). Add separately 6 ml ± 0,1 ml of hydrochloric acid (7.2) and then 2 ml ± 0,1 ml of nitric acid (7.3) to the extraction vessel (8.2.3) 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 (7.5).

The amount of nitric acid is sufficient for approximately 0,1 g of organic carbon in the sample. If the organic carbon percentage is higher, then add an extra 0,5 ml of nitric acid (7.3) for every 0,05 g of organic carbon, up to a maximum of 4 ml of extra nitric acid for a sample with 0,5 g of organic carbon. Do not add >5 ml of nitric acid. Allow any reaction to subside before proceeding further.

Cap the extraction vessel (8.2.3) and weigh it. Connect the extraction vessel to the microwave equipment or place it into the carousel. 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 extraction vessels with the same amount of *aqua regia* as in the sample vessels, to make sure that the energy is evenly absorbed.

Increase the temperature of the extraction mixture with a rate of approximately 10 °C/min to a temperature of (175 ± 5) °C.

NOTE 1 Too fast an increase in the temperature might lead to exothermic reactions which can result in a release through the pressure safety valve and loss of analytes.

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Maintain the extraction at 175 °C for 10 min ± 1 min. Then allow the extraction vessel to cool to room temperature. Weigh the extraction vessel again and record the mass. The mass loss can be considered consistent when it differs by less than 5 % of the mass loss of a well known reference material. If the loss is higher than 5 %, a release of fumes has occurred and possibly some volatile analytes may be lost.

Uncap and vent the extraction vessel in a fume hood.

Transfer the extract quantitatively into a clean volumetric flask by rinsing the vessel with nitric acid (7.4) and fill up with water to the mark. If appropriate, add releasing agents or internal standards solution necessary for the determination method before filling up to the mark. Filtrate the extract using a filter paper (8.3) before subsequent measurement.

NOTE 2 Alternatively, centrifugation at 2 000 min⁻¹ to 3 000 min⁻¹ for 10 min can be sufficient to clear the supernatant.

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

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 a spiked sample material.

12 Test report

The test report shall include at least the following information:

- a) a reference to this International Standard;
- b) complete identification of the sample;
- c) information about the pretreatment and extraction of the sample;
- d) any details not specified in this International Standard, or which are optional.

13 Performance characteristics

Performance data in terms of repeatability and reproducibility will be available after validation by a round-robin test.

Bibliography

- [1] ISO 10694, *Soil quality — Determination of organic and total carbon after dry combustion (elementary analysis)*
- [2] ISO 11074:2005, *Soil quality — Vocabulary*
- [3] NEN 6961:2005, *Milieu – Ontsluiting met salpeterzuur en zoutzuur (koningswater) voor de bepaling van geselecteerde elementen in water, waterbodem, slib, slibhoudend water, luchtstof, grond en bouwstoffen*
- [4] EPA Method 3015:1990, *Microwave assisted acid digestion of aqueous samples and extracts*
- [5] EPA Method 3051:1994, *Microwave assisted acid digestion of sediments, sludges, soils and oils*
- [6] EPA Method 3052:1995, *Microwave assisted acid digestion of siliceous and organically based materials*

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