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STANDARD

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Soil quality — Digestion of nitric acid soluble fractions of elements

Qualité du sol — Digestion des éléments solubles dans l'acide nitrique

Reference number
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Foreword

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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 WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

The committee responsible for this document is ISO/TC 190, *Soil quality*, Subcommittee SC 3, *Chemical methods and soil characteristics*.

Introduction

This method is intended to provide a multi-element digestion of sludge, treated biowaste and soil prior to analysis. It is known that the digestion of environmental samples with nitric acid will not necessarily lead to a complete element breakdown, and that the extract from a test sample may not reflect the total concentrations of the target analytes. However, for most environmental applications the result is fit for the purpose.

This International Standard is applicable and validated for several types of matrices as indicated in Table 1 (see also Annex A for the results of the validation).

Table 1 — Matrices for which this International Standard is applicable and validated

Matrix	Materials used for validation
Sludge	Municipal sludge
Biowaste	Compost
Soil	Sludge-amended soils

Soil quality — Digestion of nitric acid soluble fractions of elements

WARNING — Persons using this International Standard should be familiar with usual laboratory practice. The reagents used in this International Standard are strongly corrosive and partly very toxic. Safety precautions are absolutely necessary, not only due 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 shall 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 shall be performed in a fume 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.

IMPORTANT — It is absolutely essential that tests conducted according to this International Standard be carried out by suitably trained staff.

1 Scope

This International Standard specifies a method for microwave digestion of sludge, treated biowaste and soil using nitric acid.

This method is applicable for microwave-assisted nitric acid digestion of sludge, treated biowaste and soils for the following elements:

Aluminium (Al), antimony (Sb), arsenic (As), barium (Ba), beryllium (Be), bismuth (Bi), boron (B), cadmium (Cd), calcium (Ca), cerium (Ce), cesium (Cs), chromium (Cr), cobalt (Co), copper (Cu), dysprosium (Dy), erbium (Er), europium (Eu), gadolinium (Gd), gallium (Ga), germanium (Ge), gold (Au), hafnium (Hf), holmium (Ho), indium (In), iridium (Ir), iron (Fe), lanthanum (La), lead (Pb), lithium (Li), lutetium (Lu), magnesium (Mg), manganese (Mn), mercury (Hg), molybdenum (Mo), neodymium (Nd), nickel (Ni), palladium (Pd), phosphorus (P), platinum (Pt), potassium (K), praseodymium (Pr), rubidium (Rb), rhenium (Re), rhodium (Rh), ruthenium (Ru), samarium (Sm), scandium (Sc), selenium (Se), silicon (Si), sodium (Na), strontium (Sr), sulfur (S), tellurium (Te), terbium (Tb), thallium (Tl), thorium (Th), thulium (Tm), tin (Sn), titanium (Ti), tungsten (W), uranium (U), vanadium (V), ytterbium (Yb), yttrium (Y), zinc (Zn) and zirconium (Zr).

This International Standard may also be applicable for the digestion of other elements.

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.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. 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 11464, *Soil quality — Pretreatment of samples for physico-chemical analysis*

3 Principle

A test portion is digested in concentrated nitric acid by means of microwave heating with a suitable laboratory microwave unit. The samples and acid(s) are placed in a fluorocarbon polymer or 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 the clear solution is separated and diluted to volume and analysed by the appropriate measurement method.

4 Interferences and sources of errors

Due to the volatility of some compounds care shall be taken that the sample is not heated before the digestion and that any volatile reaction products formed during the digestion do not escape.

The container in which the sample is delivered and stored can be a source of errors. The 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 containing e.g. B, Na, K, Al.

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

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

Ensure that the complete test portion is brought into contact with the acid mixture in the digestion 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 a 0,1 g sample to begin with. If a vigorous reaction occurs upon addition of reagent(s), allow the sample to pre-digest in the uncapped digestion vessel until the reaction ceases. Heat may be added during this step for safety considerations (for example, the rapid release of carbon dioxide from carbonates, easily oxidized organic matter). Once the initial reaction has ceased, the sample may continue through the digestion procedure.

If the digested solution is filtrated, take care that the filtration procedure does not introduce contamination.

5 Reagents

Use only acids and reagents of recognized analytical grade to avoid high blank values for subsequent analytical measurements. Use a test blank solution throughout the procedure applying all steps with the same amount of acids, but without a sample.

5.1 Water, grade 2 as specified in ISO 3696 or better.

The water for preparation of reagents shall meet the requirements of the subsequent analysis. Verify the purity by performing a blank test.

5.2 Nitric acid, $c(\mathrm{HNO_3}) = 15$ mol/l, $\rho = 1{,}4$ kg/l.

Another grade may be used, provided the reagent is of sufficient purity to permit its use without decreasing the accuracy of the subsequent analysis.

5.3 Nitric acid, $c(\mathrm{HNO_3}) = 0{,}5$ mol/l; $\rho = 1{,}0$ kg/l.

6 Apparatus

Usual laboratory apparatus. All glassware and plastics ware shall be adequately cleaned and stored in order to avoid any contamination.

Depending on the concentration of the element of interest, a particular caution to the cleaning of the vessels shall be taken.

6.1 Microwave digestion system, corrosion resistant and well ventilated. All electronics shall be protected against corrosion for safe operation.

Use a laboratory-grade microwave oven with temperature feedback control mechanisms.

The microwave digestion system should be able to control the temperature with an accuracy of ± 5 °C and automatically adjust the microwave field output power within 2 s of sensing. Temperature sensors shall be accurate to ± 2 °C, including 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 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.

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

6.2 Rotating turntable, with a minimum speed of 3 min^{-1}.

6.3 Sample containers, plastics and glass containers are both suitable.

All containers shall be adequately acid cleaned and stored in order to avoid any contamination.

6.4 Digestion vessels of microwave transparent and reagent and temperature resistant materials, such as fluorocarbon (e.g. perfluoroalkoxylalkane (PFA), modified polytetrafluoroethene (PTFE)) or quartz.

The vessels may contain layers of different microwave transparent materials for strength, durability and safety. The internal volume shall be at least 45 ml, and the vessel shall be capable of withstanding pressures of at least 300 kPa and capable of controlled pressure relief.

NOTE 1 These specifications provide an appropriate, safe, and durable reaction vessel.

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.

Energy regulation of the microwave digestion system shall be based on the temperature in the digestion solutions. Depending on the construction of the unit used temperature is measured indirectly in every vessel, outside the vessels with optical systems or only in one vessel.

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

NOTE 2 Digestion vessels may be cleaned in e.g. 10 % nitric acid.

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

6.6 Filter funnel, glass, polypropene (PP) or other appropriate material.

6.7 Volumetric flask, usually of a nominal capacity of 50 ml or 100 ml.

6.8 Graduated pipettes or dispensers.

6.9 Analytical balance, with an accuracy of 0,1 mg or better.

7 Digestion procedure

Pretreat the test sample according to ISO 11464, if not otherwise specified.

Carry out a reagent blank test digestion in parallel with the determination, using the same procedure and the same quantities of all the reagents as in the determination but omitting the test portion.

NOTE 1 The measurement of a blank is introduced to determine the contribution of the extracting solution, glassware and filter paper used to the measured value.

Weigh an amount of no more than 2 g of the test portion (typically 0,5 g to 1 g of dry sample) containing not more than 0,5 g of organic carbon with an accuracy of 0,001 g and transfer it into the digestion vessel (6.4). Add (10 ± 0,1) ml of concentrated nitric acid (5.2) 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.

In the case of liquid sludge, either refer to ISO 15587-2 or perform a suitable drying procedure.

Cap the digestion vessel according to the manufacturer's instructions. Weigh the digestion vessel before digestion. Place in all positions of the microwave carrousel (usually 6, 12, 16 or 40 positions) sample vessels. If a lower number of samples are available compared to the vessel positions, place vessels filled with same amount of nitric acid without sample. This is to ascertain same microwave energy absorption during each digestion procedure. This method is an operationally defined method, designed to achieve consistent digestion of samples by specific reaction conditions. The temperature of the digestion mixture in each vessel shall be raised with a heating rate of approximately 10 °C/min to 15 °C/min to (175 ± 5) °C and remain at (175 ± 5) °C for (10 ± 1) min. Cool down to room temperature.

WARNING — Too high a temperature increase may cause a vigorous, exothermic reaction in the digestion solution with a high pressure increase and blow-off of the security valve. Losses of analytes are possible.

At the end of the microwave programme, allow the vessel to cool according to the manufacturer's instructions before removing it from the microwave system. Cooling of the vessel may be accelerated by internal or external cooling devices.

After reaching room temperature, check if the microwave vessels maintained their seals throughout the digestion. Due to the wide variety of vessel designs, a single procedure is not appropriate. Weigh the vessel after digestion to evaluate seal integrity. If the weight loss of the sample exceeds 10 % of the weight of the sample and reagents before the start of digestion, the sample is considered compromised.

Carefully uncap and vent each vessel in a well-ventilated fume hood according to the manufacturer's instructions. Add about 20 ml of water, filter the sample through an acid resistant membrane or filter paper (6.5) into a volumetric flask, and wash the residue with diluted nitric acid (6.4), and fill up to volume with water (typically 50 ml or 100 ml) or to the equivalent mass by weighing.

NOTE 2 Alternatively another procedure can be applied, such that the adjustment to volume with the solid residue still present will be carried out immediately after extraction, followed by filtration or centrifugation of a sample solution aliquot for final measurement.

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

If the measurement solution contains particles due to precipitation 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.

8 Test report

The test report shall contain at least the following information:

a) a reference to this International Standard (ISO 16729);

b) all information necessary for identification of the sample;

c) information about the pretreatment and digestion of the sample;

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

Annex A
(informative)

Repeatability and reproducibility data

A.1 Materials used in the interlaboratory comparison study

The interlaboratory comparison of microwave digestion for the extraction of nitric acid soluble fraction of trace elements in sludge, treated biowaste and soil was carried out with seven European laboratories on five materials. Detailed information can be found in the final report on the interlaboratory comparison study mentioned in Reference [7].

Table A.1 lists the types of materials tested.

Table A.1 — Materials tested and parameters analysed in the interlaboratory comparison of the microwave digestion of nitric acid soluble fractions of trace elements in sludge, treated biowaste and soil

Grain size	Sample	Material	Parameters
Sludge (< 0,5 mm)	Sludge 1	Mix 1 of municipal waste water treatment plant sludges from North Rhine Westphalia, Germany	Cd, Cr, Cu, Fe, Ni, Pb, Zn
	Sludge 2	Mix 2 of municipal waste water treatment plant sludges from North Rhine Westphalia, Germany	Cd, Cr, Cu, Fe, Ni, Pb, Zn
Fine grained (< 2,0 mm)	Compost 2	Compost from Germany	Cd, Cr, Cu, Fe, Ni, Pb, Zn
	Soil 1	A sludge-amended soil from Pavia, Italy	Cd, Cr, Cu, Fe, Ni, Pb, Zn
	Soil 2	A sludge-amended soil from Düsseldorf, Germany	Cd, Cr, Cu, Fe, Ni, Pb, Zn

A.2 Interlaboratory comparison results

The statistical evaluation was conducted according to ISO 5725-2 (see Table A.2).

Table A.2 — Results of the interlaboratory comparison study of the microwave digestion of nitric acid soluble fractions of trace elements

Matrix	l	n	o	$\bar{\bar{x}}$ mg/kg	s_R	$C_{V,R}$ %	s_r	$C_{V,r}$ %
Cd								
Sludge 1	6	29	2	2,2	0,09	4,1	0,14	6,2
Sludge 2	6	41	1	2,7	0,14	5,3	0,26	9,8
Compost 2	6	29	2	0,65	0,04	6,1	0,05	7,4
Soil 1	6	27	2	0,24	0,03	14	0,04	15,4
Soil 2	6	29	2	0,41	0,02	6,1	0,03	6,5
Cr								
Sludge 1	7	29	2	54,4	2,04	3,8	4,38	8,1
Sludge 2	7	43	2	46	1,24	2,7	12,49	27,1

Table A.2 *(continued)*

Matrix	l	n	o	$\bar{\bar{x}}$ mg/kg	s_R	$C_{V,R}$ %	s_r	$C_{V,r}$ %
Compost 2	8	35	2	20,7	1,72	8,3	5,09	24,6
Soil 1	6	37	2	43,9	2,32	5,3	9,21	21
Soil 2	6	51	0	17,7	1,77	10	6,6	37,3
Cu								
Sludge 1	7	35	2	376	31,9	8,5	42,3	11,2
Sludge 2	7	35	2	400	17,7	4,4	36,5	9,1
Compost 2	8	39	2	37,8	2,61	6,9	3,98	10,5
Soil 1	6	33	2	27,1	1,09	4	1,53	5,6
Soil 2	6	57	0	9	0,84	9,4	1,23	13,7
Fe								
Sludge 1	7	29	2	47492	1182	2,5	4514	9,5
Sludge 2	7	41	1	44532	1214	2,7	4475	10
Compost 2	8	51	0	9533	715	7,5	1734	18,2
Soil 1	6	27	2	24171	460	1,9	2998	12,4
Soil 2	6	39	1	7554	271	3,6	1288	17
Ni								
Sludge 1	7	29	2	44,5	1,15	2,6	4,05	9,1
Sludge 2	7	47	1	36,6	1,28	3,5	5,06	13,8
Compost 2	8	47	2	11,7	0,78	6,6	2,04	17,4
Soil 1	6	27	2	30,9	0,8	2,6	3,41	11
Soil 2	6	53	1	3,7	0,57	15,5	1,42	38,5
Pb								
Sludge 1	7	43	2	145,5	5,49	3,8	14,78	10,2
Sludge 2	7	53	0	80,2	4,4	5,5	10,18	12,7
Compost 2	8	35	2	39,7	2,42	6,1	6,96	17,5
Soil 1	6	51	0	25,3	1,97	7,8	4,15	16,4
Soil 2	6	51	0	28,3	2,26	8	3,69	13
Zn								
Sludge 1	7	29	2	1231,8	29,9	2,4	95,3	7,7
Sludge 2	7	29	2	737,4	15,9	2,2	113,7	15,4
Compost 2	8	51	1	184,9	10	5,4	25	13,5
Soil 1	6	57	0	74,4	5,5	7,4	7,7	10,4
Soil 2	6	57	0	52,3	3,6	7	4,4	8,4

l number of laboratories

o number of outliers

s_R reproducibility standard deviation

$C_{V,R}$ coefficient of variation of reproducibility

n number of analytical results after outlier rejection

$\bar{\bar{x}}$ total mean of analytical results (without outliers)

s_r repeatability standard deviation

$C_{V,r}$ coefficient of variation of repeatability

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