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Water quality — Digestion for the determination of selected elements in water —

Part 2:
Nitric acid digestion

Qualité de l'eau — Digestion pour la détermination de certains éléments dans l'eau —

Partie 2: Digestion à l'acide nitrique

Reference number
ISO 15587-2:2002(E)

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Contents

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

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 part of ISO 15587 may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 15587-2 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical method*.

ISO 15587 consists of the following parts, under the general title *Water quality — Digestion for the determination of selected elements in water*:

- *Part 1:* Aqua regia *digestion*
- *Part 2: Nitric acid digestion*

Annexes A to E of this part of ISO 15587 are for information only.

Water quality — Digestion for the determination of selected elements in water —

Part 2:
Nitric acid digestion

WARNING — Persons using this part of ISO 15587 should be familiar with normal laboratory practice. This part of ISO 15587 does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

1 Scope

This part of ISO 15587 specifies a method for extracting trace elements from a water sample using nitric acid as a digestion agent. The method is applicable to all types of waters with a suspended solids concentration of less than 20 g/l and a total organic carbon (TOC) concentration expressed as carbon of less than 5 g/l.

The nitric acid digestion method is empirical and it might not necessarily release elements completely. However, for most environmental applications the result is fit for purpose.

Nitric acid digestion is suitable for the release of: Al*, As, B, Ba*, Be*, Ca, Cd, Co, Cr*, Cu, Fe*, Hg, K, Mg*, Mn, Mo, Na, Ni, P, Pb, Se, Sr, Tl, V*, Zn (asterisk indicates a possible lower recovery compared to *aqua regia* digestion method specified in ISO 15587-1, see reference [1]). It is suitable for the release of Ag only if the sample is stabilized immediately after digestion. Nitric acid digestion is not suitable for Sb, Sn and for the digestion of refractory compounds such as SiO_2, TiO_2 and Al_2O_3.

The method is generic and may be implemented using a wide variety of equipment provided

- the digestion composition is unchanged,
- the digestion temperature is known, and
- the digestion duration is in accordance with this temperature.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this part of ISO 15587. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this part of ISO 15587 are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*

ISO 5667-3:1994; *Water quality — Sampling — Part 3: Guidance on the preservation and handling of samples*

3 Term and definition

For the purposes of this part of ISO 15587, the following term and definition applies.

3.1
wet digestion
treatment with reactive liquid chemicals with the aim of bringing analytes into solution so as to be suitable for subsequent analysis

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. For the latter, special attention should be paid to the presence of chemically stable organometals [4].

4 Principle

The test portion is digested with nitric acid at a defined temperature. The temperature is at least the boiling point (103 °C at 101,3 kPa) and at most 175 °C. At the boiling point (101,3 kPa), the minimum duration to release the digestible fraction is 120 min. The maximum duration is set at four times the minimum duration. By convention, both the required minimum and maximum duration are assumed to halve with every 15 °C increase in temperature above the boiling point (see Figure 1).

After digestion the digest is clarified, if necessary.

5 Reagents

During analysis, use only reagents of recognized analytical grade that meet the purity requirements of the subsequent analysis. Verify their purity by performing a blank test.

5.1 Water, complying with grade 1 of ISO 3696. Grade 2 may be used if it meets the purity requirements for the subsequent analysis.

5.2 Nitric acid, $c(\mathrm{HNO_3}) = 15{,}8$ mol/l, $\rho = 1{,}4$ kg/l.

Nitric acid is available both as $\rho(\mathrm{HNO_3}) = 1{,}40$ kg/l, approximately 65 % by mass and $\rho(\mathrm{HNO_3}) = 1{,}42$ kg/l, approximately 69 % by mass. Both are suitable.

5.3 Antifoaming agent, for instance *n*-dodecane ($C_{12}H_{26}$).

5.4 Ammonia solution, approximately 25 % by mass.

6 Apparatus

6.1 Digestion vessel, temperature- and pressure-resistant and capable of containing the mixture of sample and digest solution.

If a closed vessel is applied, its inner wall shall be inert and shall not release substances to the digest in excess of the purity requirements of the subsequent analysis.

6.2 Vapour recovery system, capable of recovering the evaporated digest during open digestion (e.g. reflux condenser) and designed to minimize losses.

Materials in contact with the vapour shall be inert and shall meet the purity requirements of the subsequent analysis.

6.3 Volatile species trap, in an open digestion system capable of trapping one or more volatile measurement species which may pass through the vapour recovery system (6.2).

This trap may comprise condensation equipment or equipment to absorb these species in nitric acid or *aqua regia*. Materials in contact with the vapour shall be inert and shall meet the purity requirements of the subsequent analysis.

6.4 Heating device, capable of maintaining the target temperature for the required time period.

6.5 Filter paper, cellulose-based ashless type, with a median pore size adapted to the apparatus used for analysis.

It shall not be able to release substances to the digest in excess of the purity requirements of the subsequent analysis and shall not absorb substances from the digest beyond the level of negligible impact on trueness of the analytical result.

6.6 Anti-bumping granules or **roughened glass beads**, having a diameter of 2 mm to 3 mm and acid-washed [for instance with warm nitric acid (5.2) diluted to 10 % by volume with water (5.1)].

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

6.8 Graduated pipettes or **dispensers**.

7 Sampling

Handle and preserve the water sample in accordance with ISO 5667-3.

The digestion procedure (see clause 8) is based on a test portion of 25,0 ml ± 0,1 ml taken from a well-shaken homogeneous water sample. Any test portion larger than 20 ml is allowed, provided that the volume of nitric acid is modified proportionally.

If suspended solids make it impossible to deliver a representative test portion of a known volume, deliver the test portion otherwise, for instance by weighing. Calculate the volume from the determination of its mass, possibly corrected for the mass and density of solids. Report the uncertainty of the volume if it is higher than 0,1 ml for a volume of 25 ml.

8 Procedure

8.1 Preparation

Carefully acid-wash digestion equipment in contact with the digestion solution and volumetric ware [for instance with warm nitric acid (5.2) diluted to 10 % by volume with water (5.1)] and rinse with water (5.1).

Add a test portion of 25,0 ml ± 0,1 ml to the digestion vessel (6.1).

Add 6,25 ml ± 0,1 ml of nitric acid (5.2). The boiling point of this mixture is equal to 103 °C.

If excessive foaming occurs, add one or more drops of antifoaming agent (5.3).

Swirl and allow the mixture to stand until any visible reaction has stopped.

If the digestion vessel is of the open type, proceed with 8.2. If not, proceed with 8.3.

Examples of digestion in an open system are given in annexes A and B.

8.2 Digestion in an open system

Connect the digestion vessel (6.1) to the vapour recovery system (6.2).

Connect the volatile species trap (6.3), so as to prevent volatile measurement species from passing through the vapour recovery system.

Place the digestion vessel in the heating device (6.4).

Increase the temperature to the boiling point.

Maintain boiling for at least 120 min. As the boiling point decreases with altitude add 20 min to the minimum duration for every 1 000 m above sea level. The maximum allowed duration equals four times the minimum duration.

Once the digestion period is completed, allow the digestion vessel to cool. If silver is an analyte, add 30 ml of ammonia solution (5.4) to the digestion vessel immediately after cooling.

If the volatile species trap (6.3) is used, add the contents to the digestion vessel.

Rinse the trap and/or the condenser with water (5.1), for instance 10 ml, and decant. Collect the water in the digestion vessel.

Dismount the digestion vessel from the digestion system.

Examples of digestion in an open system are given in annexes A and B.

8.3 Digestion in a closed system

Cap the digestion vessel (6.1) and weigh it.

Connect the digestion vessel to or place it in the heating device (6.4).

Increase the temperature of the digestion mixture slowly to temperature T_d between the boiling point (103 °C at 101,3 kPa) and 175 °C.

Maintain digestion for a period Δt of at least 10 min and at most 480 min (101,3 kPa).

Given the digestion period Δt, expressed in minutes, the digestion temperature T_d, expressed in degrees Celsius, shall meet the following condition:

$$206{,}6 - 21{,}64 \times \ln(\Delta t) < T_\mathrm{d} < 236{,}6 - 21{,}64 \times \ln(\Delta t) \qquad (1)$$

NOTE 1 Boundary conditions in equation (1) reflect the assumption of clause 4 on release kinetics and duration time.

The permitted domain of digestion temperature and duration is shown in Figure 1.

Once the digestion period is completed, allow the digestion vessel to cool. Weigh the digestion vessel and accept the digest if the mass loss is consistent with the mass loss of a well documented reference material known to lead to acceptable results.

Uncap and vent the digestion vessel in a fume hood.

If silver is an analyte, add 30 ml of ammonia solution (5.4) to the digestion vessel immediately after cooling.

Examples of digestion in a closed system are given in annexes C and D.

NOTE 2 Several microwave units control power rather than temperature. A procedure to establish the relationship between microwave power and temperature is given in C.6.

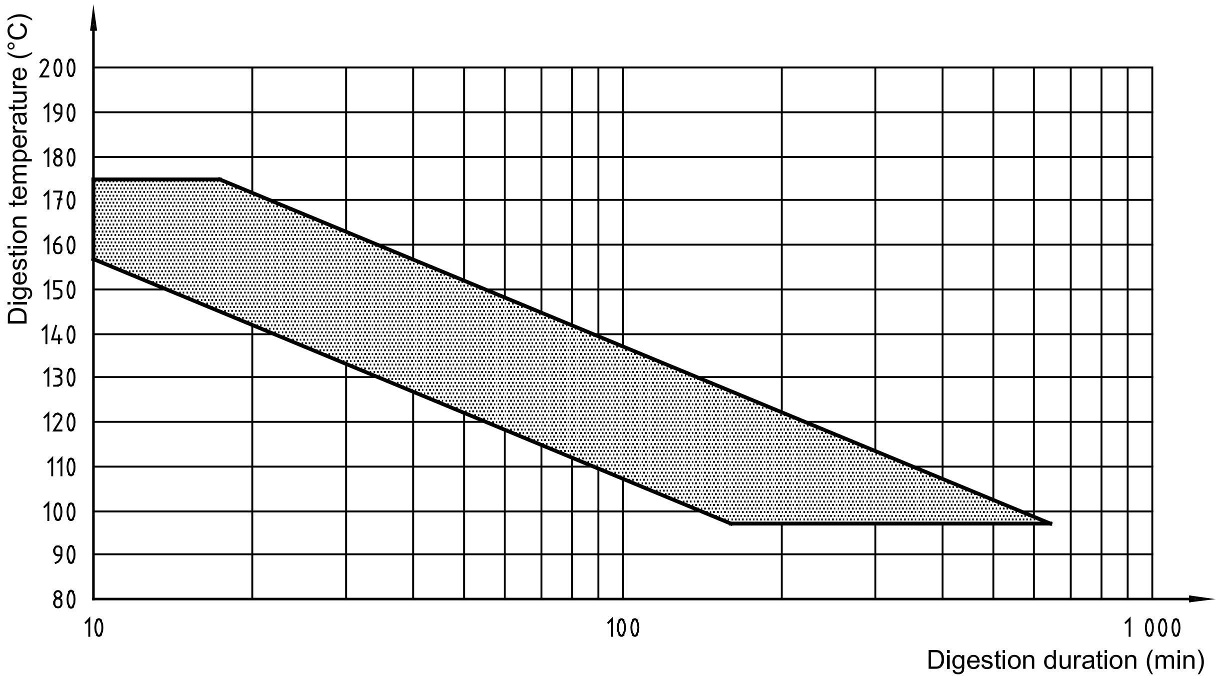

Figure 1 — Domain of permitted digestion temperature and duration

8.4 Sample transfer

Decant the sample into a suitable acid-cleaned volumetric flask (6.7). In order to transfer the analytes quantitatively, wash the digestion vessel (6.1) with water (5.1) and decant the washings. Collect the water in the same volumetric flask.

If the transfer of particles that might interfere with the subsequent analysis cannot be avoided by simple decantation, decant the digest through a filter paper (6.5), collecting the filtrate in a suitable acid-cleaned volumetric flask (6.7). Wash the digestion vessel with water (5.1) and decant the washings through the filter paper (6.5). Collect the filtrate in the same volumetric flask.

Fill the volumetric flask to the mark after addition of reagents required for subsequent sample handling and analysis.

The extract is ready for determination.

Examples of performance checks are given in annex E.

9 Test report

The test report can be prepared separately or in conjunction with the test report of the subsequent analytical method. Either of these shall include the following information:

a) a reference to this part of ISO 15587, i.e. ISO 15587-2;

b) the identity of the water sample;

c) the volume of the test portion and its uncertainty if higher than 0,5 %;

d) the conditions of digestion;

e) any deviation from this method.

Annex A
(informative)

Digestion in an open system using electrical heating

A.1 Principle

A test portion of a water sample, which may contain up to 20 g/l suspended solids and up to 5 g/l organic carbon, is digested by boiling the test portion under reflux with nitric acid during a period between 120 min and 480 min.

A.2 Reagents

Use the reagents as specified in clause 5.

A.3 Apparatus

Usually, borosilicate glass is suitable for parts in contact with the digestion solution. If low concentrations of leachable elements are to be analysed, other construction materials may be used, for instance quartz (high temperatures) and polyethene or polypropene (low temperatures). Examples of leachable elements are B, Na, K and Al.

A.3.1 **Digestion vessel**, made of borosilicate glass, and having a nominal volume of 100 ml.

A.3.2 **Reflux condenser**, a straight-through type, with conical ground-glass joints and made of borosilicate glass.

Water-cooled condensers with a minimum effective length of at least 200 mm have been found suitable.

A.3.3 **Roughened glass beads**, having a diameter of 2 mm to 3 mm and acid-washed [for instance with warm nitric acid (5.2) diluted to 10 % by volume with grade 1 water (5.1)].

A.3.4 **Temperature-controlled heating apparatus**, capable of heating the contents of the digestion vessel to reflux temperature.

A.3.5 **Volumetric flask**, made of borosilicate glass, and having a nominal volume of 100 ml.

A.3.6 **Graduated pipettes** or **dispensers**.

A.4 Sampling

Preserve and handle water samples in accordance with ISO 5667-3.

Take a test portion of 40 ml ± 0,2 ml from a well-shaken homogeneous water sample.

If suspended solids make it impossible to deliver a representative test portion of a known volume, the test portion may be delivered otherwise, for instance by weighing. Calculate the volume from the determination of its mass, possibly corrected for the mass and density of solids. Report the uncertainty of the volume if it is higher than 0,2 ml.

A.5 Procedure

Carefully acid-wash the digestion equipment in contact with the digestion solution and volumetric ware [for instance with warm nitric acid (5.2) diluted to 10 % by volume with grade 1 water (5.1)].

Take a test portion of 40 ml ± 0,2 ml and transfer it to the digestion vessel (A.3.1).

Add the roughened glass beads (A.3.3).

Add 10,0 ml ± 0,2 ml of nitric acid (5.2). If excessive foaming occurs, add one or more drops of antifoaming agent (5.3).

Swirl and allow the mixture to stand until any visible reaction has stopped.

Connect the digestion vessel to the reflux condenser (A.3.2).

Place the digestion vessel in the temperature-controlled heating apparatus (A.3.4).

Increase the temperature slowly until reflux conditions are reached, ensuring that the condensation zone is lower than one third of the height of the condenser.

Maintain the boiling temperature for a period between 120 min and 480 min. As the boiling point (103 °C at 101,3 kPa) decreases with altitude, add 20 min to the minimum of 120 min for every 1 000 m above sea level.

Once the digestion period is completed, allow the digestion vessel to cool.

Rinse the reflux condenser with grade 1 water (5.1) and decant the washings. Collect the water in the digestion vessel.

Dismount the digestion vessel from the digestion system.

Decant the sample into the acid-cleaned volumetric flask (A.3.5).

In order to transfer the analytes quantitatively, wash the digestion vessel with grade 1 water (5.1) and decant. Collect the water in the same volumetric flask.

Fill the volumetric flask to the mark after addition of reagents, which are required for subsequent sample handling and analysis.

The extract is ready for determination.

A.6 Test report

The test report can be prepared separately or in conjunction with the test report of the subsequent analytical method. Either of these shall include the following information:

f) a reference to this part of ISO 15587, i.e. ISO 15587-2;

g) the identity of the water sample;

h) the volume of the test portion and its uncertainty if higher than 0,5 %;

i) the conditions of digestion;

j) any deviation from this method.

Annex B
(informative)

Digestion in an open system using microwave-assisted heating

B.1 Principle

A test portion of a water sample, which may contain up to 20 g/l suspended solids and up to 5 g/l organic carbon, is digested by boiling the test portion under reflux in a flask heated by microwave unit with nitric acid during a period between 120 min and 480 min.

B.2 Reagents

Use the reagents specified in clause 5. Verify their purity by performing a blank test.

B.3 Apparatus

Usually, borosilicate glass is suitable for parts in contact with the digestion solution. If low concentrations of leachable elements are to be analysed, other construction materials may be used, for instance quartz (high temperatures) and polyethene or polypropene (low temperatures). Examples of leachable elements are B, Na, K and Al.

B.3.1 **Digestion vessel**, made of borosilicate glass, and having a nominal volume of 50 ml.

B.3.2 **Reflux condenser**, made of borosilicate glass.

B.3.3 **Roughened glass beads**, having a diameter of 2 mm to 3 mm (or **anti-bumping granules**), acid-washed [for instance with warm nitric acid (5.2) diluted to 10 % by volume with grade 1 water (5.1)].

B.3.4 **Microwave unit**, consisting of a programmer and microwave module capable of heating the digestion vessel to the boiling point.

B.3.5 **Volumetric flask**, made of borosilicate glass, and having a nominal capacity of 50 ml.

B.3.6 **Graduated pipettes** or **dispensers**.

B.4 Sampling

Water sample preserved and handled in accordance with ISO 5667-3.

Take a test portion of 20,0 ml ± 0,1 ml from a well-shaken homogeneous water sample.

If suspended solids make it impossible to deliver a representative test portion of a known volume, the test portion may be delivered otherwise, for instance by weighing. Calculate the volume from the determination of its mass, possibly corrected for the mass and density of solids. Report the uncertainty of the volume if it is higher than 0,1 ml.

B.5 Procedure

Carefully acid-wash the digestion equipment in contact with the digestion solution and volumetric ware [for instance with warm nitric acid (5.2) diluted to 10 % by volume with grade 1 water (5.1)].

Take a test portion of 20,0 ml ± 0,1 ml and transfer it to the digestion vessel (B.3.1).

Add the roughened glass beads (B.3.3).

Add 5,0 ml ± 0,1 ml of nitric acid (5.2). If excessive foaming occurs, add one or more drops of antifoaming agent (5.3).

Swirl and allow the mixture to stand until any visible reaction has stopped.

Connect the digestion vessel to the reflux condenser (B.3.2).

Place the digestion vessel in the microwave unit (B.3.4).

Program the microwave unit to heat to reflux conditions (103 °C).

Maintain the boiling temperature for a period between 120 min and 480 min. As the boiling point (103 °C at 101,3 kPa) decreases with altitude, add 20 min to the minimum of 120 min for every 1 000 m above sea level.

Once the digestion period is completed, allow the digestion vessel to cool.

Rinse the reflux condenser with grade 1 water (5.1) and decant the washings. Collect the water in the digestion vessel.

Dismount the digestion vessel from the digestion system.

Decant the sample into the acid-cleaned volumetric flask (B.3.5).

In order to transfer the analytes quantitatively, wash the digestion vessel with grade 1 water (5.1) and decant the washings. Collect the water in the same volumetric flask.

Fill the volumetric flask to the mark after addition of reagents, which are required for subsequent sample handling and analysis.

The extract is ready for determination.

B.6 Test report

The test report can be prepared separately or in conjunction with the test report of the subsequent analytical method. Either of these shall include the following information:

a) a reference to this part of ISO 15587, i.e. ISO 15587-2;

b) the identity of the water sample;

c) the volume of the test portion and its uncertainty if higher than 0,5 %;

d) the conditions of digestion;

e) any deviation from this method.

Annex C
(informative)

Digestion in a closed system using microwave assisted heating

C.1 Principle

A test portion of a water sample, which may contain up to 20 g/l suspended solids and up to 5 g/l total organic carbon, is mixed with nitric acid and heated in a microwave oven at a temperature beyond the boiling point and maximally to 175 °C. At the boiling point (103 °C at 101,3 kPa), the minimum duration to release the digestible fraction is 120 min. The maximum duration is set at four times the minimum duration at that temperature. By convention, both the required minimum and maximum duration are assumed to halve with every 15 °C increase in temperature above the boiling point.

After digestion the digest is clarified, if necessary.

C.2 Reagents

Use the reagents as specified in clause 5. Verify their purity by performing a blank test.

C.3 Apparatus

C.3.1 Digestion vessel, made of inert material (e.g. fluorocarbon body and cap), suited for safe application in the temperature range, and having a nominal volume of 100 ml.

C.3.2 Microwave oven, either temperature control or power control in combination with pressure measurement.

The accuracy of the temperature and pressure measurement or control shall guarantee working inside the shaded area of Figure 1. This includes traceability to national or international temperature and pressure standards.

The microwave unit shall ensure equal distribution of energy over the samples.

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

C.3.3 Volumetric flask, made of borosilicate glass, nominal capacity 50 ml.

C.3.4 Thermometer, calibrated against a national or International Standard. The calibrated range shall cover at least 10 °C to 50 °C, capable of measuring the temperature to the nearest 0,1 °C.

C.3.5 Graduated pipettes or **dispensers**.

C.4 Sampling

Preserve and handle water samples in accordance with ISO 5667-3.

Take a test portion of 20,0 ml ± 0,1 ml from a well-shaken homogeneous water sample.

If suspended solids make it impossible to deliver a representative test portion of a known volume, the test portion may be delivered otherwise, for instance by weighing. Calculate the volume from the determination of its mass, possibly corrected for the mass and density of solids. Report the uncertainty of the volume if it is higher than 0,1 ml.

C.5 Procedure

Carefully acid-wash the digestion equipment in contact with the digestion solution and volumetric ware [for instance with warm nitric acid (5.2) diluted to 10 % by volume with grade 1 water (5.1)].

Take a test portion of 20,0 ml ± 0,1 ml and transfer it to the digestion vessel (C.3.1).

Add 5,0 ml ± 0,1 ml of nitric acid (5.2). If excessive foaming occurs, add one or more drops of antifoaming agent (5.3).

Swirl and allow the mixture to stand until any visible reaction has stopped.

Cap the digestion vessel and weigh it.

Position the digestion vessel in the microwave oven (C.3.2).

Always fill all positions of power-controlled microwave equipment.

Increase the temperature of the digestion mixture slowly to temperature T_d.

Maintain digestion for a period Δt.

Choose the values of T_d and Δt so as to remain within the set of values shown by the shaded area in Figure 1.

Once the digestion period is completed, allow the digestion vessel to cool down to room temperature.

Weigh the digestion vessel and accept the digest if the mass loss is consistent with the mass loss of a well documented reference material known to lead to acceptable results.

Uncap and vent the digestion vessel in a fume hood.

Decant the sample into the acid-cleaned volumetric flask (C.3.3).

In order to transfer the analytes quantitatively, wash the digestion vessel with grade 1 water (5.1) and decant the washings. Collect the water in the same volumetric flask.

Fill the volumetric flask to the mark after addition of reagents, which are required for subsequent sample handling and analysis.

The extract is ready for determination.

C.6 Procedure to establish the relationship between microwave power and temperature for power-controlled systems with pressure measurement

C.6.1 General

Several closed microwave-assisted digestion systems control power rather than temperature. These instruments have facilities to measure the pressure of the vessel. The procedure to establish the relationship between digestion temperature and power setting is given in clause C.6.2 and C.6.3.

C.6.2 Power calibration

Perform power calibration periodically. Changes of more than 10 W in the upper power range require recalibration. Usually, two calibrations per year are sufficient.

The calibration method required for laboratory microwave units depends on the type of electronic system used by the manufacturer to provide partial microwave power. Few units have an accurate and precise linear relationship between percent power settings and absorbed power. Where linear circuits have been utilized, the calibration curve can be determined by a two-point calibration method. Otherwise, use the multiple-point calibration method.

The multiple-point calibration involves the measurement of absorbed power over a large range of power settings. Calibration shall cluster about the customary working power range. Nonlinearity has been commonly encountered at the upper end of the calibration.

Measure the power at 100 % and 50 % using the procedure below and calculate the power setting corresponding to the required microwave power from the (two-point) line. Measure the absorbed power at that partial power setting. If the measured absorbed power does not correspond to the specified power to within 10 W, use the multiple-point calibration.

Equilibrate a large amount of water, for instance 1 000 g, to room temperature in a beaker that does not significantly absorb microwave energy (polyethene, polypropene; glass is not recommended).

Measure the temperature to within ± 0,1 °C.

Position the covered beaker in the microwave oven in the normal sample path.

Run the microwave at a specific power setting for a specific period of time, for instance 2 min.

Remove the beaker.

Stir the water vigorously.

Measure the temperature to within ± 0,1 °C.

Determine the microwave power P, expressed in watts, using equation (C.1).

$$P = \frac{\Delta T \times m \times c_p}{t} \qquad \text{(C.1)}$$

where

ΔT is the difference in temperature, expressed in degrees Celsius, between the final temperature and the initial temperature;

m is the mass, expressed in gram, of water;

c_p is the specific heat capacity at constant pressure for water [= 4,18 J/(g×°C)];

t is the time, expressed in seconds.

C.6.3 Temperature calibration

At constant room temperature T_a, measure the digestion pressure p, expressed in kilopascals, at different power settings using 20,0 ml ± 0,1 ml of (blank) water (5.1) mixed with 5,0 ml ± 0,2 ml nitric acid (5.2).

Use all digestion positions of the microwave oven and use an identical test portion for every position.

Calculate the digestion temperature T_d, expressed in degrees Celsius, corresponding to the pressure p, expressed in kilopascals, of diluted nitric acid from the approximation:

$$T_d = 38,9 + 3,00 \times (\ln p)^2 \tag{C.2}$$

Obtain for every power setting the corresponding microwave power from the relationship established in C.6.2.

Establish the relationship between the digestion temperature and the microwave power in the calibration graph.

Re-evaluate the temperature calibration graph each time changes are made in the microwave system, for instance for the type of digestion vessel (geometry, material), composition of digested sample or digestion volume.

Use the relationship for sample analysis in the following way:

- Choose the temperature T_d for sample digestion.
- Obtain the required microwave power using the temperature calibration graph determined above.
- Obtain the power setting using the power calibration graph of C.6.2.

NOTE 1 The applicability of the procedure is limited for temperatures less than 120 °C because of the influence of air expansion inside the vessel.

NOTE 2 Power-controlled microwave energy raises the digest temperature above room temperature. Therefore, the temperature calibration graph is valid for the room temperature during the calibration. If room temperature during digestion of samples differs, the actual temperature will be ($T_{a,sample} - T_{a,cal}$) higher than calculated. Check whether digestion conditions are still inside the domain of Figure 1.

C.7 Test report

The test report can be prepared separately or in conjunction with the test report of the subsequent analytical method. Either of these shall include the following information:

a) a reference to this part of ISO 15587, i.e. ISO 15587-2;

b) the identity of the water sample;

c) the volume of the test portion and its uncertainty if higher than 0,5 %;

d) the conditions of digestion;

e) any deviation from this method.

Annex D
(informative)

Digestion in a closed system using an autoclave

D.1 Principle

A test portion of a water sample, which may contain up to 20 g/l suspended solids and up to 5 g/l total organic carbon, is mixed with nitric acid and heated in an autoclave to a temperature beyond the boiling point and maximally to 175 °C. At the boiling point (103 °C at 101,3 kPa), the minimum duration to release the digestible fraction is 120 min. The maximum duration is set at four times the minimum duration at that temperature. By convention, both the required minimum and maximum duration are assumed to halve with every 15 °C increase in temperature above the boiling point.

After digestion the digest is clarified, if necessary.

D.2 Reagents

Use the reagents as specified in clause 5. Verify their purity by performing a blank test.

D.3 Apparatus

D.3.1 Digestion vessel, made of inert material, suitable for safe application in the temperature range, and having a nominal volume of 100 ml.

D.3.2 Autoclave, pressure adjustable so as to obtain the required temperature between 103 °C and 175 °C.

The accuracy of the temperature measurement and control shall guarantee working inside the domain of Figure 1. This includes traceability to national or international temperature and pressure standards.

D.3.3 Volumetric flask, made of borosilicate glass, having a nominal capacity of 100 ml.

D.3.4 Filter paper, cellulose-based ashless type, with a median pore size of 8 µm or less.

D.3.5 Graduated pipettes or **dispensers**.

D.4 Sampling

Preserve and handle water samples in accordance with ISO 5667-3.

Take a test portion of 40,0 ml ± 0,2 ml from a well-shaken homogeneous water sample.

If suspended solids make it impossible to deliver a representative test portion of a known volume, the test portion may be delivered otherwise, for instance by weighing. Calculate the volume from the determination of its mass, possibly corrected for the mass and density of solids. Report the uncertainty of the volume if it is higher than 0,2 ml.

D.5 Procedure

Carefully acid-wash the digestion equipment in contact with the digestion solution and volumetric ware [for instance with warm nitric acid (5.2) diluted to 10 % by volume with grade 1 water (5.1)].

Take a test portion of 40,0 ml ± 0,2 ml and transfer it to the digestion vessel (D.3.1).

Add 10,0 ml ± 0,2 ml of nitric acid (5.2). If excessive foaming occurs, add one or more drops of antifoaming agent (5.3).

Swirl and allow the mixture to stand until any visible reaction has stopped.

Cap the digestion vessel and weigh it.

Place the vessel in the autoclave (D.3.2).

Adjust the pressure relief to the value equivalent to the vapour pressure of water at the required digestion temperature T_d. Any value of T_d between 103 °C and 175 °C is permitted.

Run the autoclave.

After having reached T_d, maintain digestion for a period Δt.

Choose the values of T_d and Δt so as to remain within the set of values shown by the shaded area in Figure 1.

Switch off the heating and allow the autoclave to cool down.

Weigh the digestion vessel and accept the digest if the mass loss is consistent with the mass loss of a well documented reference material known to lead to acceptable results.

Uncap and vent the digestion vessel in a fume hood.

Decant the digest through the filter paper (D.3.4), collecting the filtrate in the volumetric flask (D.3.3).

Wash the digestion vessel with grade 1 water (5.1) and decant the washings through the filter paper (D.3.4). Collect the filtrate in the same volumetric flask.

Fill the volumetric flask to the mark after addition of reagents, which are required for subsequent sample handling and analysis.

The extract is ready for determination.

D.6 Test report

The test report can be prepared separately or in conjunction with the test report of the subsequent analytical method. Either of these shall include the following information:

a) a reference to this part of ISO 15587, i.e. ISO 15587-2;

b) the identity of the water sample;

c) the volume of the test portion and its uncertainty if higher than 0,5 %;

d) the conditions of digestion;

e) any deviation from this method.

Annex E
(informative)

Performance checks

The performance of the digestion procedure may be checked by:

- running a test portion of a blank sample so as to check on the requirement on purity;
- running a test portion of certified reference material so as to check on recovery, trueness or reproducibility;
- running a test portion of a control sample so as to check on reproducibility;
- running a field sample with and without the addition of a known amount of (undigested) analyte so as to determine recovery for a field matrix or recovery for specific analyte species.

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