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Monitoring of Air Pollution Effects on Forests (ICP Forests)

MANUAL

on

methods and criteria for harmonized sampling, assessment,
monitoring and analysis of the effects of air pollution on forests

Part X

Sampling and Analysis of Soil

(Annex I - Methods for Soil Analysis)

Version 2025-1

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Annex I – Methods for Soil Analysis

Soil Analysis Method 1 (SA01) Pre-treatment of Samples

Pre-treatment of Samples	
Method sheet	SA01
Reference methods	ISO 11464
Method suitable for	Organic Layer; Mineral Layer

I Relevance in ICP Forests

All samples (organic and mineral) have to be prepared according to the standard methodology in order to maintain comparability among participating countries.

Priority	Level I	Level II
Organic Layer		
<i>OL</i>	<i>Optional</i>	<i>Optional</i>
<i>OF+OH, H-layers</i>	<i>Mandatory</i>	<i>Mandatory</i>
Mineral layer		
<i>0- 10 cm ¹</i>	<i>Mandatory</i>	<i>Mandatory</i>
<i>10 – 20 cm</i>	<i>Mandatory</i>	<i>Mandatory</i>
<i>20 – 40 cm</i>	<i>Mandatory</i>	<i>Mandatory</i>
<i>40 – 80 cm</i>	<i>Optional</i>	<i>Mandatory</i>

¹ Optionally this layer may be split in two layers: 0 – 5 cm AND 5 – 10 cm

II Principle

a. *Organic layer*

After removal of living material (such as mosses, roots, etc.) and objects > 2 cm, collected samples (preferably not less than 500 g fresh material) should be transported to the laboratory as soon as possible and should be air dried or dried at a temperature of 40 °C. They can then be stored until analysis. The sample is subsequently crushed or milled to size < 2 mm.

When the samples are bulked in the field and only a subsample is taken to the laboratory, the fresh mass (kg/m²) of each organic sublayer should be measured in the field. Further it is strongly recommended to measure the thickness of each organic sublayer in each subsample in the field. Firstly, because the horizon thickness (in cm in terms of the upper and lower limit) is mandatory to report in the profile description file (PFH form). Secondly, the thickness of the individual forest floor layers proves to be very useful as a cross check during data analysis.

b. *Mineral layer*

After removal of living material (such as mosses, roots, etc.) and objects > 2 cm, collected samples (preferably not less than 500 g fresh soil) should be transported to the laboratory as soon as possible and should be air dried or dried at a temperature of 40 °C. They can then be stored until analysis.

Living macroscopic roots and all material, mineral and organic, with a diameter larger than 2 mm, should be removed from the samples by dry or wet sieving. The particles not passing the 2-mm sieve (after crushing), may be weighed separately for the determination of the coarse fragments content (SA05). The fraction smaller than 2 mm is used for the soil analysis. The mineral soil samples are crushed and sieved above a 2 mm sieve. Further grinding is allowed in accordance with ISO 11464 for the analysis of Carbonate content (SA07), Total Organic Carbon (SA08), total Nitrogen (SA09), Total Elements (SA12) and Aqua Regia Extractant Determinations (SA11).

Important Note: further grinding will change the test sample properties (e.g. specific surface area, sample homogeneity) compared to 2mm-sieved samples and will generally lead to higher reported concentrations of some aqua regia extractable elements depending on soil texture class and mineralogy. This may have implications for data analysis of time series.

In order to preserve methodological consistency of long-time data series, it is therefore required to conduct a comparative study when changing the extraction method (reflux vs. microwave) or milling procedure to determine the affected elements and magnitude of the effect on local soil samples. This study needs to be reported to the Expert Panel on Soil and Soil Solution.

The sample material for storage should be kept without preservative under normal room conditions with minimal temperature and humidity fluctuations, shielded from incident light.

III Apparatus

Drying oven.

Crusher, mill, mortar and pestle.

Plate sieve, mesh sieve

IV Reagents

No reagents.

V Procedure

Drying

Spread the material in a layer not thicker than 5 cm. If necessary, the sample is crushed while still damp and friable and again after drying. Dry the complete sample in a drying oven at a temperature of 40 °C, until the loss in mass of the sample is not greater than 5 % (m/m) per 24 h. Break down the size of larger clods (greater than 15 mm) to accelerate the drying process.

Removal of fraction < 2 mm

Remove stones and large objects by hand picking and sieving (< 2 mm). Minimise the amount of fine material adhered. Weigh separately the fraction not passing the 2 mm sieve for determination of coarse fragment content. Crush (not ground) the clods greater than 2 mm taking care that crushing of original particles is minimised. Homogenise the < 2 mm fraction.

Sieving and Milling

The organic sample is crushed or milled to size < 2 mm.

The mineral soil samples are crushed and sieved above a 2 mm sieve. Further grinding is allowed for the analysis of Carbonate content (SA07), Total Organic Carbon (SA08), Total Nitrogen (SA09), Total Elements (SA12) and aqua regia extractable elements (SA11).

Subsampling

For the preparation of an analysis subsample, split up (by hand, using a sample divider or by mechanical subsampling) the sample into representative portions until the required sample number and sample size is obtained.

VI Calculation

No calculations.

VII Report

The mineral fractions (> 2 mm) obtained after sieving with a 2 mm sieve may be used for determination of coarse fragments (SA05).

VIII Reference

ISO 11464. 2006. Soil Quality – Pretreatment of samples for physico-chemical analysis. International Organization for Standardization. Geneva, Switzerland. 9 p. [available at www.iso.org].

Soil Analysis Method 2 (SA02): Determination of Soil Moisture Content

Soil Moisture Content	
Method sheet	SA02
Reference method	ISO 11465
Method suitable for	Organic Layer; Mineral Layer

I Relevance in ICP Forests

Recalculation of results obtained by lab analysis to “oven-dry mass”.

Priority	Level I	Level II
Organic Layer		
<i>OL</i>	<i>Optional</i>	<i>Optional</i>
<i>OF+OH, H-layers</i>	<i>Mandatory</i>	<i>Mandatory</i>
Mineral layer		
<i>0- 10 cm</i> ¹	<i>Mandatory</i>	<i>Mandatory</i>
<i>10 – 20 cm</i>	<i>Mandatory</i>	<i>Mandatory</i>
<i>20 – 40 cm</i>	<i>Mandatory</i>	<i>Mandatory</i>
<i>40 – 80 cm</i>	<i>Optional</i>	<i>Mandatory</i>

¹ Optionally this layer may be split in two layers: 0 – 5 cm AND 5 – 10 cm

II Principle

Calculation and reporting of the results of soil analysis is done on basis of "oven-dry" soil. The moisture content of air-dry soil is determined prior to soil analysis. To recalculate the analysis results on dry mass basis, the moisture content of the sample has to be determined by oven-drying a sample to constant mass. The difference in mass is used to calculate water content on a mass basis.

III Apparatus

Moisture tins or flasks (25 – 100 ml) with closely fitting lid

Drying oven

Analytical balance (accuracy 0.001 g)

Note: The use of an automated apparatus for measuring soil moisture content is allowed as long as it is based on the same principle.

IV Reagents

No reagents.

V Procedure

Mineral Layer: Transfer 5-15 g air-dried fine earth (fraction < 2 mm) to a dried, tared moisture tin and weigh. Dry at 105±5 °C (lid removed) until constant mass is reached.

Organic Layer : Transfer 5 – 10 g air dried organic layer material to a dried, tared moisture tin and weigh. Dry at 105 °C (lid removed) for 24 hours.

Remove tin from oven, close with lid, cool in desiccator and weigh.

VI Calculation

The moisture content in mass percentage is obtained by :

$$\text{Moist\%} = \frac{A - B}{B - \text{tare tin}} * 100$$

Where:

A : Mass of tared moisture tin and air-dried soil sample

B : Mass of tared moisture tin and oven-dried soil sample

The corresponding moisture correction factor for analytical results or for amount of sample to be weighed in for analysis is:

$$\text{moisture correction factor(MCF)} = \frac{100 + \text{moist\%}}{100}$$

Note: when reporting the results of Carbonate Content (SA07), Total Organic Carbon (SA08), Total Nitrogen (SA09), Exchangeable acidity, Free H⁺, Exchangeable elements (SA10), Aqua Regia Extractable elements (SA11), Total elements (SA12), Acid Oxalate Extractable Fe, Al and P (SA13), the results on air-dry basis should be multiplied by the moisture correction factor (MCF) to obtain the result on oven-dry basis.

VII Report

Report moisture content (in %) with 1 decimal place.

VIII Reference

ISO 11465. 1993: Soil Quality – Determination of dry matter and water content on a mass basis – Gravimetric method. International Organization for Standardization. Geneva, Switzerland. 3 p. [available at www.iso.org].

Soil Analysis Method 3 (SA03): Determination of Particle Size Distribution

Particle Size Distribution	
Method sheet	SA03
Reference methods	ISO 11277
Method suitable for	Mineral Layer
Method code	Sample preparation: MA02 Determination: DG02, DG03, DG04

I Relevance in ICP Forests

Particle Size Distribution : USDA-FAO texture Classification and Clay Percentage

Priority	Level I	Level II
Organic Layer	-	-
Mineral layer		
0 – 10 cm	<i>Mandatory</i> ^{1, 2}	<i>Mandatory</i> ¹
10 – 20 cm	<i>Mandatory</i> ^{1, 2}	<i>Mandatory</i> ¹
20 – 40 cm	<i>Optional</i>	<i>Mandatory</i> ¹
40 – 80 cm	<i>Optional</i>	<i>Mandatory</i> ¹

¹ if not determined in the first soil survey

² an estimation of clay content based on finger test is allowed

This laboratory method can also be used to determine the soil texture of the pedological horizons, reported in the PFH form.

Particle Size Distribution : Silt and Sand Percentage

Priority	Level I	Level II
Organic Layer	-	-
Mineral layer		
0 – 10 cm	<i>Optional</i>	<i>Mandatory</i> ¹
10 – 20 cm	<i>Optional</i>	<i>Mandatory</i> ¹
20 – 40 cm	<i>Optional</i>	<i>Mandatory</i> ¹
40 – 80 cm	<i>Optional</i>	<i>Mandatory</i> ¹

¹ if not determined in the first soil survey

II Principle

Separation of the mineral part of the soil into various size fractions and determination of the proportion of these fractions. The analysis includes all soil material, i.e. including gravel and coarser material, but the procedure below is applied to the fine earth fraction (< 2 mm) only. Of paramount importance in this analysis is the pretreatment of the sample aimed at complete dispersion of the primary particles. Therefore, generally, cementing materials (usually of secondary origin) such as organic matter, salts, iron oxides and carbonates such as calcium carbonate are removed. After shaking with a dispersing agent, sand (63 µm-2 mm) is separated from clay and silt with a 63 µm sieve (wet sieving). The clay (< 2 µm) and silt (2-63 µm) fractions are determined by the pipette method (sedimentation).

III Apparatus

Sampling pipette (10 to 50 ml) with safety bulb and water reservoir, held in frame

Constant temperature room or thermoregulated bath ($20 - 30\text{ °C} \pm 0.5\text{ °C}$)

Glass sedimentation cylinders (approx. diam. 50 mm, approx. length 350 mm) graduated 500 ml volume with rubber bungs or stirrer

Stirrer and rod

Glass weighing vessels (with masses known to 0.0001 g)

Mechanical shaker (30 – 60 revolutions/min)

Sieves (2 mm – 63 μm)

Balance (accuracy 0.0001 g)

Drying oven

Stopwatch (accuracy 1 s)

Glass filter funnel capable of holding the 63 μm sieve

Wash bottle

Desiccator

650 ml glass beaker with cover glass, 100 ml measuring cylinder, 25 ml pipette

Hot plate or bunsen burner

Electrical conductivity meter (accuracy 0.1 dS/m)

Optional: Centrifuge and 300 ml centrifuge bottle

IV Reagents

Hydrogen peroxide (H_2O_2), 30% volume fraction.

Dispersing agent: 3.3 % sodium hexametaphosphate and 0.7 % soda solution:

Dissolve 33 g sodium hexametaphosphate (NaPO_3)₆ and 7 g soda (Na_2CO_3) in water in a 1 l volumetric flask and make to volume. Both chemicals should be dried overnight at 105 °C prior to use. This solution is unstable and shall be replaced after one month.

Antifoaming agent (preferably octan-2-ol, alternatives are ethanol or methanol)

Calcium chloride solution (CaCl_2), conc. 1 mol/l

Hydrochloric acid (HCl), conc. 1 mol/l

V Procedure

Test sample

Depending on the soil type, weigh 10 (clay) to 30 g (sand) air-dried soil (fraction < 2 mm). Place the sample in the 650 ml glass beaker or 300 ml centrifuge bottle.

Destruction of organic matter

Add 30 ml water to the test sample (add if necessary a few drops of octan-2-ol to allow thoroughly wetting). Add 30 ml of the 30 % hydrogen peroxide solution and mix using the glass or plastic rod (add if necessary a few drops of octan-2-ol to control foaming). Cover and leave overnight. The next day, place the vessel on a hot plate or bunsen burner and warm. Control foaming with octan-2-ol and stir frequently. To avoid drying out, add water if necessary. Bring the suspension to a gentle boil until all signs of bubbling due to the decomposition of hydrogen peroxide have ceased. If undecomposed organic material is still present, cool the beaker and repeat the treatment with hydrogen peroxide.

If using a centrifuge bring the volume to 150 – 200 ml by addition of water. Centrifuge the bottle until obtaining a clear supernatant (recommended 15 min at a minimum relative centrifugal force (RCF) of 400 g) and remove this supernatant by decanting or by using a suction device.

If a centrifuge is not available the mineral residues may be flocculated by adding 25 ml of 1 mol/l calcium chloride solution, stirring and bringing to about 250 ml with water. Let stand until the supernatant is clear, then siphon or decant this from the residue. Add another 250 ml of water and repeat the washing procedure until the dark residues of the decomposed organic matter have gone (if using this method, take care to check the electrical conductivity (next step) before adding the salt).

Removal of soluble salts and gypsum

After destruction of organic matter add water until obtaining a soil:water ratio of 1:4 – 1:6 (v:v). Shake for 1 h using a shaking machine. Centrifuge to obtain a clear supernatant and measure electrical conductivity (E_c) on this supernatant. If $E_c > 0.4$ dS/m soluble salts and gypsum is present in considerable amounts and have to be removed. Remove the supernatant, add 250 ml water and shake for 1 h. Centrifuge and measure electrical conductivity again. Repeat this washing procedure until $E_c < 0.4$ dS/m.

Removal of carbonates

A distinction is made on basis of the presence or absence of calcium carbonate:

- (1) Calcareous soils: $\text{pH}(\text{H}_2\text{O}) > 6.8$
- (2) Non-calcareous soils: $\text{pH}(\text{H}_2\text{O}) < 6.8$

Where the carbonate content is greater than about 2 % mass fraction, add to the washed, centrifuged soil (above) 4 ml of 1 mol/l hydrochloric acid for each percent of carbonate, plus an excess of 25 ml of acid. Make up to about 250 ml with water, and place the suspension on the water bath at about 80 °C for 15 min, stirring the suspension from time to time. Leave the suspension to stand overnight. If the soil flocculates sufficiently to leave a perfectly clear supernatant, then this can be siphoned off or decanted, otherwise centrifugation and decantation will be necessary. Repeat the washing and decantation with water until the E_c of the supernatant is less than 0,4 dS/m.

If the carbonate content is less than about 2 % mass fraction, then only an initial 25 ml of 1 mol/l hydrochloric acid solution is required. It is recommended, therefore, that 20 ml of 1 mol/l calcium chloride solution is added at the same time as the acid. The rest of the procedure is identical as for a higher carbonate content.

Note: if the carbonate content is that high that the results of the particle size distribution become unreliable, this should be mentioned in the Data Accompanying Report.

Dispersion

Add sufficient water to the vessel so that the total volume is between 150 ml and 200 ml, shake the contents until all the soil is in suspension, and add 25 ml of dispersing agent from a pipette. Shake the bottle for 18 h on the end-over-end shaker.

Wet sieving at 63 μm

Place a 63 μm aperture sieve in the large glass funnel, and place the funnel in the stand so that the neck of the funnel is inside one of the 500 ml sedimentation tubes. Transfer the dispersed suspension from the centrifuge bottle quantitatively onto the sieve, and wash the soil using a jet of water from the wash-bottle until the water runs clear. The total volume of the washings should not exceed 500 ml.

Remove the sieve from the funnel and wash the residue on the sieve into an evaporating dish by means of a gentle spray from the wash-bottle. To alleviate sieve blockage, use the glass or plastic rod and rubber sleeve. Place this dish in an oven between 105 °C and 110 °C until the residue is dry. Record the mass to 0.0001 g (m_{fs}).

Wash any particles adhering to the inside of the funnel into the sedimentation tube. Make up the suspension in the sedimentation tube to 500 ml with water.

Calibration

Calibration sampling pipette

Clean and dry the pipette thoroughly and immerse the tip in water. Draw water into the pipette into the safety bulb. Drain off the water in the safety bulb through the outlet tube. Drain the pipette into a weighing bottle of known mass, and determine the internal volume of the pipette. Repeat this exercise three times and take the average of the three volumes as the internal volume of the pipette to the nearest 0.05 ml (V_c ml).

Calibration dispersing agent

Pipette 25 ml of dispersing agent solution into one of the glass sedimentation tubes, and fill the tube to the 500 ml mark with water. Mix the contents of the tube thoroughly. Place the tube in the constant temperature environment, and leave the tube for at least 1 h. Between any of the times at which samples may be taken from the sampling tube (Table SA03-1), take a sample (V_c ml) of the dispersing agent solution from the sedimentation tube using the sampling pipette. Drain the pipette into a weighing vessel of known mass, and dry the contents of the vessel between 105 °C and 110 °C. Allow the vessel to cool in the desiccator and determine the mass of the residue in the vessel to 0.0001 g (m_r).

Follow this procedure each time a new batch of dispersing agent is prepared.

Sedimentation

Place the sedimentation tube in the constant temperature environment. Agitate (at least 30 times/min for a minimum of 2 min) the contents of the sedimentation tube vigorously, either by means of the stirrer, or by inserting a bung in the tube, followed by end-over-end shaking. Replace the tube upright in the constant-temperature environment and start the timer.

About 15 s before a sample is to be taken (Table SA03-1), lower the pipette, with the tap of the safety bulb closed, vertically into the soil suspension, and centrally in the sedimentation tube, until the tip is the appropriate depth (± 1 mm) below the suspension surface (Table SA03-1). Take care to disturb the suspension as little as possible, and complete the operation within

about 10 s. Open the tap of the safety bulb and withdraw a sample of the suspension such that the pipette and a part of the safety bulb are full. This sampling operation shall take about 10 s. Withdraw the pipette from the suspension so that the tip of the pipette is clear of the top of the sedimentation tube. Run the surplus present in the safety bulb into a small beaker by the outlet tube. Wash with water from the water reservoir until no suspension remains in this part of the system.

Place a weighing vessel of known mass (to 0.0001 g) under the tip of the pipette and open the tap so that the contents of the pipette are delivered to the vessel. Wash any suspension left on the inner walls of the pipette into the vessel by allowing water from the water reservoir to run through the system. Place the weighing vessel and contents in the oven between 105 °C and 110 °C, and evaporate to dryness. Cool the vessel in the desiccator, weigh the vessel and its contents to the nearest 0.0001 g, and determine the mass of the residue the nearest 0.0001 g (ms_1). Clean the outside of the pipette of any adhering sediment, and take the other sample (fraction < 2 µm), in accordance with the times given in Table SA03-1, using the same pipetting procedure given above. Call the additional sample masse ms_2 .

Table SA03-1: Pipette sampling times and fraction at different temperatures

Temperature (°C)	Time (after mixing) of starting sampling operation	
	Fraction: < 63 µm	Fraction: < 2 µm
	Sampling depth 200 mm ± 1 mm	Sampling depth 100 mm ± 1 mm
20	56 s	7 h 44 min 16 s
21	54 s	7 h 34 min 04 s
22	53 s	7 h 23 min 53 s
23	52 s	7 h 13 min 13 s
24	51 s	7 h 03 min 02 s
25	49 s	6 h 52 min 50 s
26	48 s	6 h 44 min 02 s
27	47 s	6 h 35 min 42 s
28	46 s	6 h 26 min 53 s
29	45 s	6 h 18 min 33 s
30	44 s	6 h 09 min 45 s

VI Calculation

Fractions < 63 µm

Calculate the mass of solids in suspension in 500 ml (mf_1 , mf_2) in grams, for each pipette sampling time from the equation:

$$\text{Mass < 63 } \mu\text{m in 500 ml : } mf_1 = ms_1 (500/V_c)$$

$$\text{Mass < 2 } \mu\text{m in 500 ml : } mf_2 = ms_2 (500/V_c)$$

where:

mf_x is the mass (g) of solid in suspension in 500 ml;

ms_x is the mass (g) of material from the xth pipette sampling;

V_c is the calibrated volume of the pipette.

Each fraction however, still contains a part of dispersing agent, which has to be corrected. The mass of solid material in 500 ml of dispersant solution, m_d , in grams, is given by:

$$\text{Mass dispersing agent in 500 ml: } m_d = m_r (500/V_c)$$

where:

m_r is the mass of residue, in grams;

V_c is the calibrated volume of the pipette, in millilitres.

This gives the final fraction masses:

$$\begin{array}{llll} \text{Clay} & \text{Mass fraction} < 2 \mu\text{m} & = & m_{f_2} - m_d \\ \text{Silt} & \text{Mass fraction } 2 - 63 \mu\text{m} & = & m_{f_1} - m_{f_2} \end{array}$$

Fraction 63 μm - 2 mm

Mass of the fraction 63 μm - 2 mm = m_{f_s}

Proportion of fraction

The method of calculation assumes that the sample mass is the sum of the constituent fractions, and not the mass of the test sample. The mass of sample < 2 mm is thus the sum of the masses of the fractions obtained by wet sieving at 63 μm and the masses of the fractions obtained by calculation. Denote this total sample mass as m_t in grams.

Calculate the proportion in each fraction <2 mm as follows:

Proportions = mass of fraction/ m_t

VII Report

It is an agreed convention that the percentage of each particle size grade is reported on the basis of oven-dry soil free of organic matter (1 decimal place).

Note: With this calculation, the clay, silt and sand fractions are obtained in percentage of the sum of the constituent fractions (after removal of carbonates and organic matter).

USDA-FAO texture classification is based on the USDA-FAO textural triangle (FAO, 1990) as shown in Figure 1.

VIII References

ISO 11277. 2020: Soil Quality – Determination of particle size distribution in mineral soil material – Method by sieving and sedimentation. International Organization for Standardization. Geneva, Switzerland. 38 p. [available at www.iso.org].

FAO. 1990: Guidelines for soil description, 3rd (revised) edition.

Soil Analysis Method 4 (SA04): Determination of Bulk Density

Bulk Density	
Method sheet	SA04
Reference methods	ISO 11272
Method suitable for	Mineral Layer

I Relevance in ICP Forests

Priority	Level I	Level II
Organic Layer	-	-
Mineral layer		
<i>0 – 10 cm</i>	<i>Mandatory^{1,2,3}</i>	<i>Mandatory^{2,3}</i>
<i>10 – 20 cm</i>	<i>Mandatory^{1,2,3}</i>	<i>Mandatory^{2,3}</i>
<i>20 – 40 cm</i>	<i>Mandatory^{1,2,3}</i>	<i>Mandatory^{2,3}</i>
<i>40 – 80 cm</i>	<i>Optional</i>	<i>Optional</i>

¹ may also be obtained by using pedo-transfer functions

² only mandatory in non-stony soils

³ in case of re-assessment (if the parameter was already measured according to the reference method in a previous survey, the measurement is optional)

II Principle

The dry bulk density (BD) is the ratio between the mass of oven dry soil material and the volume of the undisturbed fresh sample. ISO11272 defines dry bulk density as the ratio of the oven-dry mass of the solids to the volume (the bulk volume includes the volume of the solids and of the pore space) of the soil.

Non-gravelly soils (when coarse fragments content < 5%)

Several methods can be applied for the determination of bulk density, going from simple methods such as digging out holes of known volume to sophisticated gamma radiometry methods. The recommended method (core method) uses steel cylinders of known volume (100 cm³, 400 cm³) that are driven in the soil vertically by percussion. Sampling large volumes results in smaller relative errors but requires heavy equipment. The method cannot be used if stones or large roots are present or when the soil is too dry or too hard.

Soils with high stone or root content or when the soil is too dry or too hard

In these conditions it is advised to use measuring methods based on the following principle (excavation method): a hole on a horizontal surface is dug and then filled with a material with a known density (e.g. sand which packs to a calibrated volume or water separated from the soil material by an elastic membrane). The obtained soil from the hole, is dried to remove the water and the dry mass is weighed. Methods measuring the volume of clods or aggregates should be avoided because they tend to underestimate macroporosity.

The volumetric percentage of the coarse fragments needs to be determined in order to calculate the bulk density of the fine earth.

Stony soils

Soils with a high content of gravel (0.2 – 6 cm) and/or the presence of stones (6 – 20 cm) and boulders (> 20 cm), have a low volume of fine earth. Core samplers normally used in forest monitoring are not able to representatively collect stones or large portions of coarse fragments in the field. In these cases, the above recommended excavation method will produce good

results but may be considered very expensive, time-consuming and destructive. So, alternatively, a combined approach is described where the quantity of bulk density of both fine earth and coarse fragments (SA05) has to be estimated / sampled in the field.

Methods are according to the prevailing conditions (i.e. coarse fragment content and size) at each individual sampling site:

- In case of coarse fragment content of more than 5 %, the fine earth fraction must be sieved and weighed. Its volume must then be determined either directly or indirectly by establishing the coarse fragment volume. Furthermore, the density of the coarse fragments (specific weight) must be known or established.
- In case of content of coarse fragments > 20 mm, representative sampling is no longer possible with a core sampler. Then the coarse fragment content must be determined by additional sampling using a shovel or spade and/or estimations in the soil profile.
- In case of coarse fragments content of > 60 mm, representative volume sampling is not possible and sampling with mini-core samplers is combined with an estimation in the profile pit.

In the analysis each method or each combined method leads to the determination of (partially) different parameters which means that different calculation formulas are needed.

Note: The determination of the bulk density of the fine earth is incorrect when the sample contains significant portions of roots in addition to the coarse fragment portions. In these cases, this must be corrected.

III Apparatus

Core sample holders, thin-walled metal cylinders with a volume of 100 cm³ to 400 cm³, a steel cap for driving into the soil, and a driver (or root auger, hollow stem auger, AMS core sampler with liner or alike)

Oven (heated and ventilated, temperature 105 ± 2 °C)

Desiccator

Balance (accuracy 1/1000 of measured value).

Spade, shovel

Metal sieves (2 mm, 20 mm, 60 mm)

IV Reagents

No reagents.

V Procedure

Case 1: *Non-gravelly soils (when coarse fragments content < 5%)*

Press or drive a core sample holder of known volume without deflection and compaction into either a vertical or horizontal soil surface far enough to fill the sampler. Carefully remove the sample holder and its contents to preserve the natural structure, and trim the soil extending

beyond each end of the sample holder with a straight-edged knife or sharp spatula. The soil sample volume is thus equal to the volume of the sample holder. Take at least five core samples from each soil layer. Place the holders containing the samples in an oven at 105 °C until constant mass is reached (minimum 48 h). Remove the samples from the oven and allow them to cool in the desiccator. Weigh the samples on the balance immediately after removal from the desiccator (m_i). Control mass is reached when the differences in successive weighings of the cooled sample, at intervals of 4 h, do not exceed 0,01% of the original mass of the sample.

Case 2: *Mineral soil with a coarse fragment content of more than 5% that can be sampled with a core sampler or any other representative sampler (coarse fragments < 20 mm)*

The mineral soil sample is collected in the field with core samplers from the undisturbed soil. In the laboratory the sample is then dried at a temperature of 105 °C for at least 48 hours to constant mass and weighed.

The sample is then passed through a 2 mm metal sieve and the sieve residue washed in order to break down clumpy fine earth material and to rinse off earth adhering to the stones. The washed sieve residue (= coarse fragment portion) is shaken into a beaker, dried at a temperature of 105°C in a drying oven and then weighed.

Case 3: *Mineral soil, which cannot be sampled with a core sampler or any other representative sampler (coarse fragments > 20 mm)*

Case 3.1.: *Combination of representative volume sampling with a core sampler and estimation of coarse fragments > 20 mm*

The mineral soil sample is collected in the field with core samplers from the undisturbed soil. In the laboratory the sample is dried at a temperature of 105 °C for at least 48 hours to constant mass and weighed.

The sample is passed through a 2 mm metal sieve and the sieve residue washed in order to break down clumpy fine earth material and to rinse off earth adhering to the stones. The washed sieve residue (= coarse fragment portion) is shaken into a beaker, dried at a temperature of 105 °C in a drying oven and then weighed. After that, the sieve residue is passed through a 20 mm sieve and the 2 – 20 mm sieve fraction (fine and medium gravel) weighed.

For the coarse fragment portion > 20 mm an estimation from the profile description must be available.

Case 3.2.: *Combination of representative volume sampling with a core sampler, disturbed sample and estimation of coarse fragments more than 60 mm at the profile*

The mineral soil sample is collected in the field with a core sampler from the undisturbed soil. In addition, a larger sample volume, which must be representative for the coarse fragment fraction 2 – 60 mm (gravel), is collected with a shovel or a spade. In the laboratory the two samples are then dried at a temperature of 105 °C for at least 48 hours to constant mass and weighed.

The core sample is then passed through a 2 mm metal sieve and the sieve residue is washed in order to break down clumpy fine earth material and wash off earth adhering to the stones. The washed sieve residue (= coarse fragment portion) is shaken into a beaker, dried in a drying oven at a temperature of 105 °C and then weighed.

The spade sample is also dried at a temperature of 105 °C to constant mass and then weighed. The spade sample is then passed through a 2 mm sieve and the sieve residue through a 60

mm sieve. The coarse fragment fraction 2 – 60 mm obtained in this way is weighed. For the coarse fragment content > 60 mm an estimation from the profile description must be available.

Case 4: *Representative volume sampling with a corer sampler is not possible, Sampling with mini-core samplers and estimation of coarse fragments more than 2 mm from a large volume sample*

With core sampler caps or mini-core samplers ($n \geq 5$) several samples are taken from the undisturbed soil. In addition, a larger sample volume, which must be representative for the coarse fragment fraction 2 – 60 mm, is collected with a shovel or a spade.

In the laboratory the core sampler caps together with their contents are dried at a temperature of 105 °C for at least 48 hours to constant mass and then weighed together. The empty mass of the core sampler caps is then deducted from the total mass.

The spade sample is dried at a temperature of 105 °C for at least 48 hours to constant mass and then weighed. The sample is then passed through a 2 mm sieve and the sieve residue through a 6 mm sieve. The sieve residue is then passed through a 60 mm sieve as well. The fractions obtained < 2 mm (fine earth), 2 – 6 mm (fine gravel) and 6 – 60 mm (medium and coarse gravel) are weighed.

Alternative to the combined approach of case 2 till case 4 in soils with high stone or root content or if the soil is too dry or too hard:

In case of gravely or stony soils an alternative excavation method consist of excavating a quantity of soil, drying and weighing it, and determining the volume of the excavation by filling it with sand (cf. ISO 11272 – **excavation method**). Note that the excavation method measures the total dry bulk density.

VI Calculation

Case 1: *Non-gravely soils (when coarse fragments content < 5%)*

In case of measurements, the bulk density of the fine earth (BD_{fe}) is approximately equal to the bulk density of total soil. The bulk density (BD_s) the for *non-gravely soils* is calculated as follows:

$$BD_s = BD_{fe} = \frac{M_s}{V_s} \quad (\text{equation SA04.01})$$

where:

BD_s	=	Bulk Density of the sample (kg/m^3)
BD_{fe}	=	Bulk Density of the fine earth (kg/m^3)
M_s	=	Dry Mass of the sample (kg)
V_s	=	Volume of the sample (m^3)

Case 2: *Mineral soil with a coarse fragment content of more than 5% that can be sampled with a core sampler or any other representative sampler (coarse fragments < 20 mm)*

In case of measurement with a core sampler, the bulk density of the fine earth of gravely soils (BD_{fe}) is calculated as follows:

$$BD_{fe} = \frac{M_{fe}}{V_{fe}} = \frac{M_s - M_{cf}}{V_s - V_{cf}} = \frac{M_s - M_{cf}}{V_s - \frac{M_{cf}}{\rho_{cf}}} \quad (\text{equation SA04.02})$$

where:

BD_{fe}	=	Bulk density of the fine earth (kg/m^3)
M_{fe}	=	Dry Mass of the fine earth taken with core sampler (kg)
V_{fe}	=	Volume of the undisturbed fine earth (m^3)
M_s	=	Dry Mass of the soil sample with gravel taken with core sampler (kg)
M_{cf}	=	Dry Mass of the coarse fragments taken with the core sampler (kg)
V_s	=	Volume of core sampler (m^3)
V_{cf}	=	Volume of the coarse fragments taken with the core sampler (kg)
ρ_{cf}	=	Density of the coarse fragments (approximated by $2650 \text{ kg}/\text{m}^3$)

The fine earth stock (FES) is the amount (kg) of fine earth in the soil layer under consideration expressed per ha. In stony soils, a correction for the volume of coarse fragments is required. It is calculated as follows:

$$FES = BD_{fe} \times d \times 10 \times \left(1 - \frac{V_{cf}}{V_s}\right) = BD_{fe} \times d \times 10 \times \left(1 - \frac{M_{cf}}{\rho_{cf} \times V_s}\right) \quad (\text{equation SA04.03})$$

where:

FES	=	Fine earth stock (t/ha)
BD_{fe}	=	Bulk density of fine earth (kg/m^3)
d	=	Thickness of the sampled layer (m)
V_{scf}	=	Volume of coarse fragment taken with core sampler (respectively core of root auger) (m^3)
M_{cf}	=	Dry Mass of coarse fragment taken with core sampler (respectively core of root auger) (kg)
ρ_{cf}	=	Density of the coarse fragments (approximated by $2650 \text{ kg}/\text{m}^3$)
V_s	=	Volume of core sampler (m^3)

Notes:

- If the core sampler sample cakes strongly as a consequence of drying, it might make sense to pulverise the sample with a crusher prior to sieving. The big stones should be removed beforehand. .
- In the case of non-cohesive soil (sand), there is no need to wash or dry the stones.

Case 3: Mineral soil, which cannot be sampled with a core sampler or any other representative sampler (coarse fragments > 20 mm)

Case 3.1. Combination of representative volume sampling with a core sampler and estimation of coarse fragments > 20 mm

The bulk density of the fine earth (BD_{fe}) is calculated using equation SA04.02.

The FES is calculated as follows:

$$FES = BD_{fe} \times d \times 10 \times \left(1 - \frac{V_{cf>20}}{100} - \frac{M_{cf(2-20)}}{\rho_{cf} \times V_s}\right) \quad (\text{equation SA04.04})$$

where:

FES	=	Fine earth stock (t/ha)
BD_{fe}	=	Bulk density of fine earth (kg/m^3)
d	=	Thickness of the sampled layer (m)
$M_{cf(2-20)}$	=	Dry Mass of coarse fragment between 2 and 20 mm taken with core sampler (respectively core of root auger) (kg)
$V_{cf>20}$	=	Percentage volume of coarse fragment of the fraction > 20 mm estimated at the profile (%)
ρ_{cf}	=	Density of the coarse fragments (approximated by $2650 \text{ kg}/\text{m}^3$)

V_s = Volume of core sampler (m^3)

Notes: see Case 2

Case 3.2. Combination of representative volume sampling with a core sampler, disturbed sample and estimation of coarse fragments more than 60 mm at the profile

The bulk density of the fine earth (BD_{fe}) is calculated using equation SA04.02.

The fine earth stock (FES) is calculated as follows:

$$FES = BD_{fe} \times d \times 10 \times \left(1 - \frac{V_{cf>60}}{100} - \frac{M_{ds(2-60)}}{BD_{cf}} \times \frac{BD_{fe}}{M_{ds} - M_{ds(2-60)} + BD_{fe} \times \frac{M_{ds(2-60)}}{\rho_{cf}}} \right)$$

(equation SA04.05)

where:

FES = Fine earth stock (t/ha)

BD_{fe} = Bulk density of fine earth (kg/m^3)

d = Thickness of the sampled layer (m)

$M_{ds(2-60)}$ = Dry Mass of coarse fragment between 2 and 60 mm of the disturbed sample (kg)

$V_{cf>60}$ = Percentage volume of coarse fragment > 60 mm estimated at the profile (%)

ρ_{cf} = Bulk density of the coarse fragments (approximated by $2650 kg/m^3$)

M_{ds} = Total dry mass of the disturbed sample (kg)

Notes: see Case 2

Case 4: Representative volume sampling not possible, Sampling with mini-core samplers

From the mass of the sample < 6 mm and the mass of the coarse fragment fraction 2 mm – 6 mm, factor f, which is approximately the coarse fragment portion in the core sampler cap, is calculated as follows:

$$f = \frac{M_{ds(2-6)}}{M_{ds(<6)}} \quad (\text{equation SA04.06})$$

where:

$M_{ds(2-6)}$ = Mass of coarse fragment of the fraction 2 - 6 mm of the disturbed sample (kg)

$M_{ds(<6)}$ = Mass of the sample < 6 mm in the aliquot of the disturbed sample (kg)

For the coarse fragment content > 60 mm an estimation from the profile must be available.

The bulk density of the fine earth (BD_{fe}) is calculated using the following formula:

$$BD_{fe} = \frac{M_{TOT} MINI \times (1 - f)}{V_{TOT} MINI - \frac{M_{TOT} MINI \times f}{\rho_{cf}}} \quad (\text{equation SA04.07})$$

where:

$M_{TOT} MINI$ = Mass of mini-core sampler (kg)

$V_{TOT} MINI$ = Volume of mini-core sampler (m^3)

ρ_{cf} = Density of the coarse fragments (kg/m^3) (approximated by $2650 kg/m^3$)

The fine earth stock (FES) is calculated using equation SA04.05.

VII Report

The dry bulk density of the fine earth (BD_{fe}) is reported in kg/m³ with no decimal places.

In the case of stony or gravelly soils the bulk density of the fine earth fraction (BD_{fe}) (< 2 mm) should be reported together with the coarse fragment content (vol %) (See also SA05).

Furthermore, the bulk density of the coarse fragments should be known, but this may be approximated as 2650 kg.m⁻³. In the case that pedotransfer functions are used (Level I), the calculation procedure should be reported as well.

Note that the “excavation method” described in ISO11272, asks for the total dry bulk density of the soil (BDs), while in this programme the bulk density of the fine earth (BD_{fe}) should be reported.

VIII Reference

ISO 11272. 2017. Soil Quality – Determination of dry bulk density. 2nd edition. International Organization for Standardization. Geneva, Switzerland. 14 p. (available at www.iso.org)

DIN ISO 11272, Normenausschuß Wasserwesen (NAW) in the Dt. Inst. für Normung e.V. [Eds.] (2001): Bodenbeschaffenheit - Bestimmung der Trockenrohddichte (Soil composition, Determination of bulk density)

Riek, W., Wolff, B., 2006: Evaluierung von Verfahren zur Erfassung des Grobbodenanteils von Waldböden – Erarbeitung von Empfehlungen für die Anwendung dieser Verfahren im Rahmen der Bodenzustandserhebung im Wald (BZE II)“. Eberswalde (Evaluation of methods to determine the coarse fragment portion of forest soils – Drawing up recommendations for the use of these methods in forest soil surveys)

Soil Analysis Method 5 (SA05): Determination of Coarse Fragments

Coarse Fragments	
Method sheet	SA05
Reference methods	ISO 11464, ISO 11277
Method suitable for	Mineral horizons

I Relevance in ICP Forests

Priority	Level I	Level II
Organic Layer	-	-
Mineral layer		
0 – 10 cm	<i>Mandatory</i> ^{1,2}	<i>Mandatory</i>
10 – 20 cm	<i>Mandatory</i> ^{1,2}	<i>Mandatory</i> ^{1,2}
20 – 40 cm	<i>Mandatory</i> ^{1,2}	<i>Mandatory</i> ^{1,2}
40 – 80 cm	<i>Optional</i> ¹	<i>Optional</i> ¹

¹ may be obtained by estimation

² in case of re-assessment (if the parameter was already measured according to the reference method in a previous survey), the measurement is optional

II Principle

The abundance of coarse fragments can be measured in the laboratory, but is usually estimated during routine soil profile description (see Annex II). When the estimation is based on such a visual observation, one should take into account the volume of the macropores (packing pores between the stones) which is often underestimated.

The most straightforward way to determine the volumes in the field of stones and boulders is by digging pits. This method, however, encounters practical problems such as hard manual work and destructive sampling. The 'Finnish method' or 'rod penetration method' is described here as an example of a non-destructive method. This method estimates the proportion (*volume %*) of coarse gravel (2 – 6 cm), stones (6 – 20 cm) and boulders (> 20 cm) in the 0 – 30 cm mineral layer by pushing a graduated metal rod down through the organic layer and as far as possible into the mineral soil.

Coarse fragments are separated from the fine earth fraction during the preparation of soil samples (SA01). The content of coarse fragments, *cf. (mass %)*, is determined by weighing the residue left on a 2 mm sieve after washing and drying in the laboratory.

III Apparatus

Field estimation: *The 'Finnish method' or 'rod penetration method'*

graduated metal rod (diameter 10 mm, length 80 – 100 cm)

Laboratory measurement

No apparatus, using data obtained in preparation of soil sample (SA01).

IV Reagents

Field estimation: *The 'Finnish method' or 'rod penetration method'*

No reagents.

Laboratory measurement

No reagents, using data obtained in preparation of soil sample (SA01).

V Procedure

Field estimation: *The 'Finnish method' or 'rod penetration method'*

The volume of stones is estimated in the 0-30 cm mineral soil layer. A steel rod (d = 10 mm, length = 80...100 cm, with a tip of hard metal, gradation lines at 10 cm intervals, see Figure 1) is pushed down (through the organic layer) into the mineral soil with sufficient force that the rod will stop if it comes into contact with a stone of 2 cm or larger (moderate push). The measuring rod is pushed down into the mineral soil at e.g. 20 or 30 systematically located (using a tape measure or even paces) points. The depth of penetration is measured with respect to the surface of the ground. If there is an organic layer present, then its thickness has to be measured using the rod or by taking a sample of the organic layer and measuring its thickness, and then subtracted from the penetration depth. In Finland, penetration is measured and organic layer samples are taken at the same time. The average penetration value and stoniness of the 0-30 cm mineral soil layer is calculated as follows (only 5 points in this example):

Penetration depth (cm)	Organic layer thickness (cm)	Penetration depth – organic layer thickness (cm)	Penetration in the ≤30 layer (cm)
12	2	10	10
40	4	36	30
4	4	0	0
35	3	32	30
22	5	17	17
			Average = 17.4

The great advantage of the rod method is that a large number of measurements can be made easily and quickly over the whole plot. The inaccuracy and other drawbacks of the method outweigh the lack of representability involved in measuring (estimating) stoniness in a very restricted number of soil pits.



Figure 2: Penetration rod



Figure 3: Tip of the penetration rod

Laboratory measurement

No procedure, using data obtained in preparation of soil sample (SA01).

VI Calculation

Field estimation

0 – 30 cm layer

$$\text{Volume of stones (\%)} = 83 - 2.75 * \text{average penetration (cm)} \quad [\text{Equation SA05.01}]$$

The volume of stones in the example = $83 - 2.75 * 17.4 = 35\%$ in the 0-30 cm layer. According to equation SA05.01, the volume of stones is 0.5 % when the average penetration into the mineral soil is 30 cm, and volume of stones is 83 % when the average penetration is 0 cm.

It is possible to estimate the stoniness of thinner layers if the empirical relationship between penetration depth and volumetric stone percentage remains the same. The relevant equations are as follows:

0-10 cm layer

$$\text{Volume of stones (\%)} = 83 - 8.25 * \text{average penetration (cm) for the layer}$$

0-20 cm layer

$$\text{Volume of stones (\%)} = 83 - 4.125 * \text{average penetration (cm) for the layer.}$$

The constant maximum depth of each penetration should be set so that it reaches the target mineral soil depth, e.g., 30, 20 or 10 cm, through the thickest possible organic layer. On upland

soils an extra 10 cm is commonly added to the target depth, e.g., there is a target depth of 40 cm if the studied layer is 0-30 cm, or to 30 cm if the layer is 0-20 cm.

Note: Equation SA05.01 is based on a very specific material [Finnish till (morainic) soils] but has not been tested on other soils, and in some respects it is somewhat illogical (see Eriksson and Holmgren, 1996). It is therefore of utmost importance that the equation is calibrated locally before it can be applied on other soil types.

Laboratory measurement

The content of coarse fragments, *cf* (mass%), is determined by weighing the residue left on a 2 mm sieve after washing and drying according to:

$$cf(\text{mass}\%) = \frac{\text{mass_of_soil_fraction} > 2\text{mm}}{\text{mass_of_the_total_oven_dry_soil}} \times 100$$

In order to convert the content by mass to an expression by volume, the bulk density of both the coarse fragments and the fine earth should be determined.

$$cf(\text{vol}\%) = \frac{BD_s}{BD_{cf}} * cf(\text{mass}\%)$$

where:

BD_s	=	Bulk density of the total soil (kg/m ³)
BD_{cf}	=	Bulk density of the coarse fragments (approximated by 2650 kg/m ³)
$cf(\text{vol}\%)$	=	Volumetric percentage of coarse fragments in the soil (%)
$cf(\text{mass}\%)$	=	Mass percentage of coarse fragments in the soil (%)

VII Report

The amount of coarse fragments (stones and gravel with a diameter > 2 mm) has to be reported for the individual mineral layers in volume % without decimals.

Note: The Rod penetration method only allows reporting for the 0 – 10 cm, 0 – 20 cm or 0- 30 cm layer and for the coarse fragments > 2 cm

VIII References

- Eriksson, C.P., Holmgren, P. 1996. Estimating stone and boulder content in forest soils – evaluating the potential of surface penetration methods. *Catena* 28: 121 – 134.
- ISO 11464. 2006. Soil Quality – Pretreatment of samples for physico-chemical analysis. International Organization for Standardization. Geneva, Switzerland. 9 p. [available at www.iso.org].
- ISO 11277. 1998. Soil Quality – Determination of particle size distribution in mineral soil material – Method by sieving and sedimentation. International Organization for Standardization. Geneva, Switzerland. 30 p. [available at www.iso.org].
- Mikkelsen, J. Cools, N., Langohr, R. 2006 Guidelines for Forest Soil Profile Description, adapted for optimal field observations within the framework of the EU Forest Focus Demonstration Project. BIOSOIL. Partly based on the 4th edition of the Guidelines for Soil Profile Description and Classification (FAO, 2006).
- Tamminen, P. 1991. Kangasmaan ravinnutunnusten ilmaiseminen ja viljavuuden alueellinen vaihtelu Etelä-Suomessa. Summary: Expression of soil nutrient status and regional variation in soil fertility of forested sites in Southern Finland. *Folia Forestalia* 777: 1-40.

- Viro, P., 1947. Metsämaan raekoostumus ja viljavuus varsinkin maan kivisyyttä silmällä pitäen. Summary: The mechanical composition and fertility of forest soil taking into consideration especially the stoniness of the soil. Communicationes Instituti Forestalis Fenniae 35, 115.
- 1952. Kivisyyden määrittämisestä. Summary: On the determination of stoniness. Communicationes Instituti Forestalis Fenniae 40, 23.
 - 1958. Suomen metsämaiden kivisyydestä. Summary: Stoniness of forest soil in Finland. Communicationes Instituti Forestalis Fenniae 49, 45

Soil Analysis Method 6 (SA06): Determination of Soil pH

pH	
Method sheet	SA06
Reference methods	ISO 10390
Method suitable for	Organic Layer; Mineral Layer
Method code	Sample preparation: MA02 Pretreatment: PA01 and PA02 Determination: DF01

I Relevance in ICP Forests

$pH(\text{CaCl}_2)$

Priority	Level I	Level II
Organic Layer		
<i>OL</i>	-	-
<i>OF+OH, H-layers</i>	<i>Mandatory</i>	<i>Mandatory</i>
Mineral layer		
<i>0 – 10 cm</i>	<i>Mandatory</i>	<i>Mandatory</i>
<i>10 – 20 cm</i>	<i>Mandatory</i>	<i>Mandatory</i>
<i>20 – 40 cm</i>	<i>Optional</i>	<i>Mandatory</i> ²
<i>40 – 80 cm</i>	<i>Optional</i>	<i>Mandatory</i> ²

² in case of re-assessment (if the parameter was already measured according to the reference method in a previous survey), the measurement is optional

$pH(\text{H}_2\text{O})$

Priority	Level I	Level II
Organic Layer	Optional	Optional
<i>OL</i>	-	-
<i>OF+OH, H-layers</i>	<i>Optional</i>	<i>Optional</i>
Mineral layer		
<i>0 – 10 cm</i>	<i>Optional</i>	<i>Optional</i>
<i>10 – 20 cm</i>	<i>Optional</i>	<i>Optional</i>
<i>20 – 40 cm</i>	<i>Optional</i>	<i>Optional</i>
<i>40 – 80 cm</i>	<i>Optional</i>	<i>Optional</i>

II Principle

The pH of the soil is potentiometrically measured in the supernatant suspension of 1:5 (volume fraction). This liquid is made up of a 0.01 mol/l solution of calcium chloride in water for $pH(\text{CaCl}_2)$ or deionised water for $pH(\text{H}_2\text{O})$.

III Apparatus

End-over-end shaking machine

pH meter with appropriate electrode

Thermometer (accuracy 1 °C)

Sample bottle (capacity at least 50 ml) with cap

Accurate measuring spoon

IV Reagents

Water (grade 2)

Calcium chloride (CaCl₂), conc. 0.01 mol/l

make a solution of 1.47 g CaCl₂·2H₂O/liter water

pH buffer solutions

V Procedure

Preparation of the suspension

Take a representative sample (at least a volume of 5 ml) of the air-dried soil (fraction < 2 mm) using the accurate measuring spoon. Place the test sample in the sample bottle and add five times its volume of calcium chloride solution (pH-CaCl₂) or deionised water (pH-H₂O). Shake or mix the suspension for 60 min +/- 10 min, using the mechanical shaker or mixer, and wait for at least for 1 hour before measuring but not longer than 3 hours. Ingress of air during standing after shaking should be avoided.

Calibration of pH meter

Calibrate the pH-meter as prescribed in the manufacturer's manual, using the buffer solutions.

pH measurement

Measure the pH in the suspension at 20°C ± 2°C immediately after or whilst being stirred. The stirring should be at such a rate to achieve a reasonable homogeneous suspension of the soil particles, but entrainment of air should be avoided. Read the pH after stabilisation of the value is reached.

VI Calculations

No calculations.

VII Report

Note the recorded values to two decimal places.

VIII Reference

ISO 10390. 2021. Soil, treated biowaste and sludge – Determination of pH. International Organization for Standardization. 3rd edition. Geneva, Switzerland. 8 p. [available at www.iso.org].

Soil Analysis Method 7 (SA07): Determination of Carbonate Content

Carbonates	
Method sheet	SA07
Reference methods	ISO 10693, EN 15936
Method suitable for	Organic Layer, Mineral Layer
Method code	Sample preparation: MA02, MA03, MA04, MA05 Determination: DA04, DA07, DA08

I Relevance in ICP Forests

Priority	Level I	Level II
Organic Layer		
<i>OL</i>	-	-
<i>OF+OH, H-layers</i>	<i>Mandatory</i> ¹	<i>Mandatory</i> ¹
Mineral layer		
<i>0 – 10 cm</i>	<i>Mandatory</i> ¹	<i>Mandatory</i> ¹
<i>10 – 20 cm</i>	<i>Mandatory</i> ¹	<i>Mandatory</i> ¹
<i>20 – 40 cm</i>	<i>Optional</i>	<i>Optional</i>
<i>40 – 80 cm</i>	<i>Optional</i>	<i>Optional</i>

¹ Only mandatory if pH(CaCl₂) > 5.5 or in calcareous soils

II Principle

The soil sample is treated with a strong acid. The volume of the carbon dioxide produced is measured by using a calcimeter (Scheibler unit), and is compared with the volume of carbon dioxide produced by pure calcium carbonate.

Alternatively, when the laboratory is determining the total organic carbon by dry combustion, using the **indirect method** (see SA08 where TOC = TC - TIC), the measurement of the total inorganic carbon (TIC) according to EN 15936 (2012) can be used to report the carbonate content.

In case the **direct method** (see SA08) for TOC is used, the TIC content can be derived by analysing the sample twice. Once with acid treatment and once without acid treatment. The TIC content is derived indirectly by TIC = TC – TOC.

III Apparatus

Calcimeter (Scheibler unit)

Analytical balance (accuracy 0.0001 g)

Reaction vessels (capacity 150 ml)

Plastic cups (which can pass through the neck of the reaction vessel)

Tong

Watch glass

IV Reagents

Distilled water

Hydrochloric acid (HCl), conc. 4 mol/l

Dilute 340 ml of concentrated hydrochloric acid ($\rho = 1.19$ g/ml) to 1000 ml with water.

Calcium carbonate (CaCO_3), pure.

V Procedure

Preparation

The mass of the test portion is determined based on the carbonate content. For a preliminary test on carbonate content, add some hydrochloric acid to a portion of the soil on a watch glass. The carbonate content of the sample can be estimated on the basis of the intensity and duration of effervescence (Table SA07-1). Determine from Table SA07-1 the mass of test portion (air-dried soil fraction < 2 mm).

Table SA07-1: Mass of test portion for determination of carbonate content based on intensity of effervescence

Intensity of effervescence	Carbonate content (g/kg)	Mass of test sample (g)
None or only limited	< 20	10
Clear, but for a short time	20 – 80	5
Strong, for a long time	80 – 160	2.5
Very strong, for a long time	> 160	$\leq 1^1$

¹ use sample that is crushed to a particle size of less than 250 μm

Measurement

Transfer the sample into the reaction vessels and add 20 ml of water. Fill the plastic cup with 7 ml of hydrochloric acid and place this, using tongs in the reaction vessel containing the test portion. Take care that there is no contact between the hydrochloric acid and the soil before the reaction vessel is connected to the calcimeter (Scheibler unit). Warm the reaction vessel by hand.

Connect the reaction vessel to the calcimeter. Carefully add the hydrochloric acid from the cup to the soil by tilting the reaction vessel at an angle. The gas produced will lower the water level in the tube on the right and at the same time will raise the water level in the tube on the left. Shake for 5 min and note the volume when it no longer varies. If it still varies, continue shaking until the volume is stable, but not longer than 1 h. At the end of the shaking period, bring the water level in both tubes to the same height and measure the volume of gas in the calibrated tube with an accuracy of 0.1 ml.

Calibration

Determinations of samples, blanks and the calcium carbonate used as standard material, shall be performed simultaneously in a room where temperature and pressure do not vary too much during the measurement.

Weigh the standards of 0.200 g and 0.400 g of calcium carbonate, transfer these amounts into the reaction vessels and add 20 ml of water. For the blank determinations, use reaction vessels containing 20 ml of water.

VI Calculations

$$w(\text{CaCO}_3) = 1000 \times \frac{m_2 (V_1 - V_3)}{m_1 (V_2 - V_3)}$$

$w(\text{CaCO}_3)$ = carbonate content of sample (g/kg) on basis of air dried soil

m_1 = mass (g) of test sample

m_2 = mean mass (g) of standards

V_1 = volume (ml) of CO_2 produced by test sample

V_2 = mean volume (ml) of CO_2 produced by standards

V_3 = volume change (ml) in blank determinations (can be negative)

In case the total inorganic carbon content was determined by dry combustion, following formula needs to be used to convert between TIC and CaCO_3 , all expressed in g/kg:

$$\begin{aligned} \text{TIC} &= \text{CaCO}_3 \times 0.12 \\ \text{and CaCO}_3 &= \text{TIC}/0.12 = \text{TIC} \times 8.33 \end{aligned}$$

VII Report

The results of the carbonate (g/kg) must be reported without decimals on the basis of oven-dried soil.

VIII Reference

ISO 10693. 1995. Reviewed and confirmed in 2021. Soil Quality – Determination of carbonate content - Volumetric method. International Organization for Standardization. Geneva, Switzerland. 7 p. [available at www.iso.org].

ISO 10694. 1995. Reviewed and confirmed in 2021. Soil Quality – Determination of organic and total carbon after dry combustion (elementary analysis). International Organization for Standardization. Geneva, Switzerland. 7 p. [available at www.iso.org]

NBN EN 15936. 2012. Sludge, treated biowaste, soil and waste - Determination of total organic carbon (TOC) by dry combustion.

Soil Analysis Method 8 (SA08): Determination of Organic Carbon Content

Organic Carbon	
Method sheet	SA08
Reference methods	ISO 10694
Method suitable for	Organic Layer, Mineral Layer
Method code	Sample preparation: MA02, MA03, MA04, MA05 Determination: DA01, DA02

I Relevance in ICP Forests

Priority	Level I	Level II
Organic Layer		
<i>OL</i>	-	-
<i>OF+OH, H-layers</i>	<i>Mandatory</i>	<i>Mandatory</i>
Mineral layer		
<i>0 – 10 cm</i>	<i>Mandatory</i>	<i>Mandatory</i>
<i>10 – 20 cm</i>	<i>Mandatory</i>	<i>Mandatory</i>
<i>20 – 40 cm</i>	<i>Mandatory</i>	<i>Mandatory</i>
<i>40 – 80 cm</i>	<i>Optional</i>	<i>Optional</i>

II Principle

The carbon present in the soil is oxidised to carbon dioxide (CO₂) by heating the soil to at least 900 °C in a flow of oxygen-containing gas that is free from carbon dioxide. The amount of carbon dioxide released is then measured by titrimetry, gravimetry, conductometry, gas chromatography or using an infrared detection method, depending on the apparatus used.

When the soil is heated to a temperature of at least 900 °C, any carbonates present are completely decomposed.

Total organic carbon can be determined directly or indirectly. Direct determination consists of previous removal of any carbonates present by treating the soil with hydrochloric acid. Indirect determination consists of a correction of the total carbon content for the carbonates present.

III Apparatus

Glassware

Analytical balance (accuracy 0.0001 or 0.00001 g)

Apparatus for determination of total carbon content (temperature at least 900 °C)

Crucibles proper for the apparatus

IV Reagents

Combustion gas - chemicals and catalysts proper to the apparatus

Calibration substances

Hydrochloric acid (HCl), conc. 4 mol/l

V Procedure

Laboratory sample

Use sample of air-dried soil (fraction < 2 mm) of known moisture and carbonate content.

Calibration of the apparatus

Calibrate the apparatus as described in the relevant manual using the calibration substances.

Direct determination of organic carbon content

Add an excess of hydrochloric acid (4 mol/l) to the crucible containing a weighed quantity of air-dried soil and mix. Wait 4 h and dry the crucible for 16 h at a temperature of 60 °C to 70 °C. The amount of test portion taken for analysis depends on the expected carbon content and on the apparatus used. Weigh out m_1 g of the air-dried sample in a crucible. Carry out the analyses in accordance with the manufacturer's manual for the apparatus.

Indirect determination of organic carbon content

The procedure is identical to the direct determination of organic carbon content, without adding hydrochloric acid. The measured total carbon content is calculated according to the amount of test portion taken for analysis which depends on the expected total carbon content and on the apparatus used. Weigh out m_1 g of the air-dried sample in a crucible. Carry out the analyses in accordance with the manufacturer's manual for the apparatus.

VI Calculation

Direct determination of organic carbon content

The organic carbon content (on basis of air-dried soil) is obtained by:

$$w_{C,o} = 1000 \times \frac{m_2}{m_1} \times 0.2727$$

where

$w_{C,o}$	=	Organic carbon content (g/kg) on basis of air-dried soil
m_1	=	Mass (g) of test portion
m_2	=	Mass (g) of released CO ₂
0.2727	=	Conversion factor for CO ₂ to C

Indirect determination of organic carbon content

The total carbon content (on basis of air-dried soil) is obtained by :

$$w_{C,t} = 1000 \times \frac{m_2}{m_1} \times 0.2727$$

where

$w_{C,t}$	=	Total carbon content (g/kg) on basis of air-dried soil
m_1	=	Mass (g) of test portion

$$\begin{aligned} m_2 &= \text{Mass (g) of released CO}_2 \\ 0.2727 &= \text{Conversion factor for CO}_2 \text{ to C} \end{aligned}$$

Calculate the organic carbon content of the sample using a correction for carbonates. The organic carbon content (on basis of air dried soil) is calculated by:

$$w_{C,o} = w_{C,t} - (0.12 \times w_{CaCO_3})$$

where

$$\begin{aligned} w_{C,o} &= \text{Organic carbon content (g/kg) on basis of air-dried soil} \\ w_{C,t} &= \text{Total carbon content (g/kg) on basis of air-dried soil} \\ 0.12 &= \text{Conversion factor} \\ w_{CaCO_3} &= \text{Carbonate content (g/kg) on basis of air-dried soil} \end{aligned}$$

VII Report

Report organic carbon content (in g/kg) with 1 decimal place on the basis of oven-dried soil.

VIII Reference

ISO 10694. 1995. Reviewed and confirmed in 2021. Soil Quality – Determination of organic and total carbon after dry combustion (elementary analysis). International Organization for Standardization. Geneva, Switzerland. 7 p. [available at www.iso.org].

Soil Analysis Method 9 (SA09): Determination of Total Nitrogen Content

Total Nitrogen	
Method sheet	SA09A
Reference methods	ISO 13878
Method suitable for	Organic Layer, Mineral Layer
Method code	Sieving/milling: MA02, MA03, MA04, MA05 Determination: DA01, DA02

I Relevance in ICP Forests

Priority	Level I	Level II
Organic Layer		
<i>OL</i>	-	-
<i>OF+OH, H-layers</i>	<i>Mandatory</i>	<i>Mandatory</i>
Mineral layer		
<i>0 – 10 cm</i>	<i>Mandatory</i>	<i>Mandatory</i>
<i>10 – 20 cm</i>	<i>Mandatory</i>	<i>Mandatory</i>
<i>20 – 40 cm</i>	<i>Optional</i>	<i>Optional</i>
<i>40 – 80 cm</i>	<i>Optional</i>	<i>Optional</i>

II Principle

The nitrogen content of a soil is determined by heating to a temperature of at least 900 °C in the presence of oxygen gas. Mineral and organic nitrogen compounds are oxidised and/or volatilised. The combustion products are oxides of nitrogen (NO_x) and molecular nitrogen (N₂). After transforming all nitrogen forms into N₂, the content of total nitrogen is measured using thermal conductivity.

III Apparatus

Laboratory glassware

Analytical balance (accuracy 0.0001 or 0.00001 mg)

Apparatus for determination of total nitrogen content (temperature at least 900 °C)

Crucibles proper for the apparatus

IV Reagents

Combustion gas - chemicals and catalysts proper to the apparatus

Calibration substances

V Procedure

Laboratory sample

Use fraction of air-dried soil (fraction < 2 mm) of known moisture content. If a soil mass of less than 2 g is required for nitrogen analysis, mill a representative subsample further, to pass a sieve of an aperture specified in the manufacturer's manual to ensure sufficient test reproducibility.

Calibration of the apparatus

Calibrate the apparatus as described in the relevant manual using the calibration substances.

Determination of total nitrogen content

The amount of test sample for analysis depends on the expected total nitrogen content and on the apparatus used. Weigh out m_1 g of the air-dried sample or subsample into a crucible. Carry out the analyses in accordance with the manufacturer's manual for the apparatus.

Normally the primary results are given as milligrams nitrogen (X_1) or a mass fraction of nitrogen (X_2), expressed as a percentage, referred to the mass of air-dry soil used (m_1).

VI Calculation

Calculate the total content of nitrogen (w_N), in milligrams per gram, on the basis of the air-dried soil according to the following equations:

- For primary results given in milligrams of nitrogen:

$$w_N = \frac{X_1}{m_1}$$

- For primary results, given as percent mass fraction of nitrogen:

$$w_N = 10 \cdot X_2$$

where

w_N : total nitrogen content (g/kg) on basis of air-dried soil

m_1 : mass (g) of test portion

X_1 : primary result as milligrams N

X_2 : primary result as percentage N

VII Report

Report total nitrogen (in g/kg) with 2 decimals on the basis of oven-dried soil.

VIII Reference

ISO 13878. 1998. Reviewed and confirmed in 2020. Soil Quality – Determination of total nitrogen content by dry combustion ("elemental analysis"). International Organization for Standardization. Geneva, Switzerland. 5 p. [available at www.iso.org].

Total Nitrogen Modified Kjeldahl method	
Method sheet	SA09B
Reference methods	ISO 11261
Method suitable for	Organic Layer, Mineral Layer
Method code	Sieving/milling: MA02, MA03, MA04, MA05 Pretreatment: PB08 Determination: DF08

I Relevance in ICP Forests

Priority	Level I	Level II
Organic Layer		
<i>OL</i>	-	-
<i>OF+OH, H-layers</i>	<i>Mandatory</i>	<i>Mandatory</i>
Mineral layer		
<i>0 – 10 cm</i>	<i>Mandatory</i>	<i>Mandatory</i>
<i>10 – 20 cm</i>	<i>Mandatory</i>	<i>Mandatory</i>
<i>20 – 40 cm</i>	<i>Optional</i>	<i>Optional</i>
<i>40 – 80 cm</i>	<i>Optional</i>	<i>Optional</i>

II Principle

The modified Kjeldahl method determines the total nitrogen content (including ammonium-N, nitrate-N, nitrite-N and organic N) of a soil. The method is based on a Kjeldahl digestion, but instead of selenium (Kjeldahl method) titanium dioxide is used as the catalyst.

III Apparatus

Digestion flasks or tubes (50 ml)

Digestion stand

Distillation apparatus

Burette (intervals of 0.01ml or smaller)

IV Reagents

- Salicylic acid / Sulfuric acid: Dissolve 25g of salicylic acid in 1 litre of concentrated sulfuric acid ($\rho = 1.84 \text{ g/cm}^3$)
- Potassium sulfate catalyst mixture: Grind and thoroughly mix the following substances;
 - 200 g of potassium sulfate
 - 6 g of copper (II) sulfate pentahydrate
 - 6 g of titanium dioxide with the crystal structure of anatase

- Sodium thiosulfate pentahydrate: Crush the crystals of Sodium thiosulfate pentahydrate until they form a powder that passes through a sieve with an aperture of 0.25mm
- Sodium hydroxide: $c(\text{NaOH}) = 10 \text{ mol/l}$
- Boric acid solution: $\rho(\text{H}_3\text{BO}_3) = 20 \text{ g/l}$
- Mixed indicator: Dissolve 0.1 g of bromocresol green and 0.02 g of methyl red in 100 ml of ethanol
- Sulfuric acid: $c(\text{H}^+) = 0.01 \text{ mol/l}$

V Procedure

Place a test portion from 0.2g (expected N-content 0.5%) to 1g (expected N-content of 0.1%) of the air-dried soil sample in the digestion flask.

Add 4 ml of salicylic/sulfuric acid and swirl the flask until the acid is thoroughly mixed with the soil. Let the mixture stand for at least several hours (or overnight).

Add 0.5 g of sodium thiosulfate through a dry funnel with a long stem that reaches down into the bulb of the digestion flask. Heat the mixture cautiously on the digestion stand until frothing has ceased.

Cool the flask and add 1.1g of the catalyst mixture, heat until the digestion mixture becomes clear.

Boil the mixture gently for up to 5 h. (in most cases a boiling period of 2h. is sufficient) so that the sulfuric acid condenses about 1/3 of the way up to the neck of the flask. Make sure that the temperature of the solution does not exceed 400°C.

Allow the flask to cool down after the digestion and add about 20ml of water slowly while shaking. Then swirl the flask to bring any insoluble material into suspension and transfer then the contents to the distillation apparatus. Rinse three times with water to complete the transfer.

Add 5 ml of boric acid to a 100 ml conical flask. Place the flask under the condenser of the distillation apparatus, make sure that the end of the condenser dips into the solution.

Add 20 ml of sodium hydroxide to the funnel of the apparatus and run the alkali slowly into the distillation chamber.

Distil about 40 ml of the condensate and rinse the end of the condenser.

Add a few drops of indicator to the distillate and titrate with sulfuric acid to a violet endpoint or use a potentiometric titration with endpoint $\text{pH}=5$.

Notes:

Carry out a blank test in which the same procedure is performed without soil.

A potentiometric titration is also possible (endpoint of titration should be $\text{pH} = 5$).

If steam distillation is used, a distillation rate up to about 25ml/min is applicable. Stop the distillation when about 100ml of distillate have been collected.

VI Calculation

The total nitrogen content is calculated by use of the following formula:

$$w_N = \frac{(V_1 - V_0) \times c(H^+) \times M_N}{m} \times \frac{100 + w_{H_2O}}{100}$$

Where

W_N	=	The total nitrogen content (mg/g = g/kg)
V_1	=	Volume of the sulfuric acid used in the titration of the sample (ml)
V_0	=	Volume of the sulfuric acid used in the titration of the blank sample (ml)
$c(H^+)$	=	Concentration of H+ in the sulfuric acid (moles/litre)
M_N	=	The molar mass of nitrogen (= 14 g/mol)
m	=	Mass of the air-dried soil sample (g)
w_{H_2O}	=	Water content of the soil sample, based on oven-dried soil (% by mass)

VII Report

Report total nitrogen in g/kg with 2 decimals on the basis of oven-dried oil.

VIII Reference

ISO 11261. 1995. Reviewed and confirmed in 2021. Soil Quality – Determination of total nitrogen – Modified Kjeldahl method. International Organization for Standardization. Geneva, Switzerland. 4 p. [available at www.iso.org].

Soil Analysis Method 10 (SA10): Determination of Exchangeable Cations (Al, Ca, Fe, K, Mg, Mn, Na), Free H⁺ and Exchangeable Acidity

Exchangeable acidity and exchangeable cations	
Method sheet	SA10
Reference Methods	ISO 11260 & ISO 14254
Method suitable for	Organic Layer, Mineral Layer
Method code	Sample preparation: MA02 Pretreatment: PA03 Determination: DB**

I Relevance in ICP Forests

Basic exchangeable cations (Ca, Mg, K, Na)

Priority	Level I	Level II
Organic Layer		
OL	-	-
OF+OH, H-layers	Mandatory ¹	Mandatory ¹
Mineral layer		
0 - 10 cm	Mandatory	Mandatory
10 – 20 cm	Mandatory	Mandatory
20 – 40 cm	Optional	Mandatory ²
40 – 80 cm	Optional	Mandatory ²

¹ in calcareous soil (CaCO₃ > 20 g kg⁻¹), this parameter is optional

² in case of re-assessment (if the parameter was already measured according to the reference method in a previous survey), the measurement is optional

Acid exchangeable cations (Al, Fe, Mn), free H⁺ acidity and Exchangeable acidity

Priority	Level I	Level II
Organic Layer		
OL	-	-
OF+OH, H-layers	Mandatory ¹	Mandatory ¹
Mineral layer		
0 - 10 cm	Mandatory ¹	Mandatory ¹
10 – 20 cm	Mandatory ¹	Mandatory ¹
20 – 40 cm	Optional	Mandatory ^{1,2}
40 – 60 cm	Optional	Mandatory ^{1,2}

¹ in calcareous soils (CaCO₃ > 20 g kg⁻¹), this parameter is optional

² in case of re-assessment (if the parameter was already measured according to the reference method in a previous survey), the measurement is optional

II Principle

The soil is first saturated with respect to barium by treating the soil one single time with a 0,1 mol/l barium chloride solution.

Concentrations of the exchangeable basic cations sodium, potassium, calcium and magnesium and the exchangeable acid cations iron, manganese, aluminium are determined in the 0.1 mol/l barium chloride extract of the soil using spectrometry.

To determine exchangeable acidity, the 0.1 mol/l extract is titrated with a 0.05 mol/l NaOH solution up to pH = 7.8. Determination of the free H⁺ acidity is realised using a method in which

sodium fluoride is added to the soil extract before the titration (Aluminium ions are complexed and only the free H⁺ acidity is detected during the titration process).

Note: *the reference method deviates from ISO 11260 & ISO 14254 in the sense that one single barium chloride extraction must be used instead of three extractions*

Alternatively the free H⁺ acidity can be determined by the “German calculation method” based on the pH of the barium chloride solution before and after extraction (König *et al.* 2005). The exchangeable acidity is subsequently calculated based on the sum of the acid cations and the free H⁺.

III Apparatus

Centrifuge + centrifuge tubes

Mechanical shaker

Laboratory glassware

Magnetic stirrer

Funnel (diam. approx. 110 mm)

Filter paper (diam. 150 mm)

PE-bottles

pH-meter

Burette

Atomic Absorption Spectrometer (AAS) / Flame Emission Spectrometer (FES) / Inductively Coupled Plasma Spectrometer (ICP)

IV Reagents

Barium chloride (BaCl₂) solution, conc. 0.1 mol/l

Sodium hydroxide (NaOH) solution, conc. 0.05 mol/l

Sodium fluoride (NaF) solution, conc. 1 mol/l

pH buffer solutions

Calibration substances

V Procedure

Laboratory sample

Use 2.5 g air-dried soil (particle size < 2 mm) of known moisture content.

Leaching procedure

Place the laboratory sample in a 50 ml centrifuge tube. Add 30 ml barium chloride solution and shake for 2 hours. Centrifuge at 3000 g for 10 min. Transfer the supernatant liquid through a filter into a PE-bottle. Retain the extract for analysis (Volume V).

If the filtered extract solution is not enough for the measurement of all cations and pH the extract solution can be diluted (for example 1:5) with barium chloride solution. This has to be considered when calculating the concentrations in the extract. Alternatively it is allowed to use higher volumes of barium chloride solution, but the ratio soil to solution must always be the same (e.g. 5.0 g soil and 60 ml barium chloride solution)!

Note: According to ISO 11260 & ISO 14254 three BaCl₂ extractions should be done and each time shaken for 1 hour in contrast to this analytical method (SA10).

Determination of exchangeable cations (Ca, Mg, K, Na, Al, Fe, Mn)

Measure the exchangeable cations in the extract using one of the spectrometric determination methods.

Determination of free H⁺

Pipette 25 ml of the extract (Volume V_s). Add 1.25 ml of the sodium fluoride (1 mol/l) solution. Titrate with the sodium hydroxide (0.05 mol/l) solution to a pH value of 7.8. Titrate a blank in the same way.

Note: If 25 ml is not sufficient for the titration, new BaCl₂ extract, in accordance to ISO 11260, should be obtained and used.

Determination of exchangeable acidity

Pipette 25 ml of the extract into a container of sufficient capacity to also receive the electrodes of the pH-meter. Insert the electrodes and titrate with the sodium hydroxide (0.05 mol/l) solution until a pH value of 7.8 is reached and remains stable for 30 s. Repeat the procedure for a blank 0.1 mol/l BaCl₂ solution extract.

Note: If 25 ml is not sufficient for the titration, new BaCl₂ extract, in accordance to ISO 11260, should be obtained and used.

VI Calculation*Determination of exchangeable cations (Ca, Mg, K, Na, Al, Fe, Mn)*

Calculation according to apparatus taking into account following equivalent mass in g/mol:

Na ⁺	= 22,99 = 8,99	Ca ²⁺	= 20,04	Fe ³⁺	= 18,62	Al ³⁺	
K ⁺	= 39,10 = 1,01	Mg ²⁺	= 12,16	Mn ²⁺	= 27,47	H ⁺	

Calculation of the ion equivalents per g soil:

$$IE = \frac{c * V}{m * EQ * 10}$$

where

IE ion equivalent in cmol/kg

- c element concentration in the extract in mg/l
 V volume of the added BaCl₂-solution in ml (30 ml)
 m mass of the soil sample in g (2,5 g)
 EQ equivalent mass of the element in g/mol

Determination of exchangeable acidity

The total exchangeable acidity on basis of air-dried soil is given by:

$$E_A = \frac{(V_a - V_B) \cdot C_{NaOH} \cdot 100 \cdot V}{V_s \cdot m}$$

where

- E_A total exchangeable acidity (cmol/kg) of the soil on basis of air-dried soil
 V_A volume NaOH (ml) used for the test sample
 V_B volume NaOH (ml) used for the blank
 C_{NaOH} concentration of NaOH (mol/l)
 V_S volume (ml) pipetted for analysis
 m mass (g) of the laboratory sample
 V final volume (ml) of the extract

Determination of free H⁺

For free H⁺ acidity use the same equation as for exchangeable acidity but use the volumes V_a and V_b for the volume NaOH used in the titration for free acidity.

Alternative method for the determination of free H⁺ ("German" calculation method)

Calculation of the Proton equivalent per gram soil:

$$H^+ (\text{cmol} / \text{kg}) = 10^{-1} * \frac{(10^{-pH_p} - 10^{-pH_0}) * V * 1000}{m * 0,88} - \frac{c(Al) * V}{m * M(Al) * \left(1 + \frac{10^{-pH_p}}{10^{-5,85}}\right)}$$

Or

$$H^+ (\text{cmol} / \text{kg}) = 10^{-1} * \frac{(10^{-pH_p} - 10^{-pH_0}) * V * 1000}{m * 0,88} - \frac{c(Al) * V}{m * M(Al) * F}$$

Where

F = the Ulrich/Prenzel factor. Values of the F factor for different pH values can be read from Table SA10-1.

- H⁺ = Free H⁺ in cmol/kg
 10⁻¹ = Conversion factor between units (μmol/g to cmol/kg)
 pH_P = pH-value of the BaCl₂ extract after the leaching procedure
 pH₀ = pH-value of the pure BaCl₂-extract
 V = Final Volume of the extract in ml (30 ml)
 m = Mass of the laboratory sample in g (2.5 g)
 c(Al) = Concentration of the Aluminium in the BaCl₂ extract in mg/l
 M(Al) = Molar mass of Aluminium in g/mol (26,98 g/mol)
 F = Ulrich/Prenzel factor (cf. Table SA10-1)

Note: As alternative method, the exchangeable acidity can be calculated as the sum of the exchangeable acid cations (Al, Fe, Mn, free H⁺).

Table SA10-1: The Ulrich/Prenzel factor (F) for a range of pH_p values (König and Fortmann, 1996)

pH	F	pH	F	pH	F	pH	F	pH	F	pH	F
		4.6	18.8	4.1	57.2	3.6	179	3.1	563	2.6	1774
		4.59	19.2	4.09	58.5	3.59	183	3.09	576	2.59	1816
		4.58	19.6	4.08	59.9	3.58	187	3.08	590	2.58	1858
		4.57	20.1	4.07	61.3	3.57	192	3.07	604	2.57	1900
		4.56	20.5	4.06	62.7	3.56	196	3.06	618	2.56	1943
		4.55	21	4.05	64.1	3.55	201	3.05	632	2.55	1993
		4.54	21.4	4.04	65.6	3.54	205	3.04	647	2.54	2035
		4.53	21.9	4.03	67.1	3.53	210	3.03	662	2.53	2084
		4.52	22.4	4.02	68.6	3.52	215	3.02	677	2.52	2134
		4.51	22.9	4.01	70.2	3.51	220	3.01	693	2.51	2183
		4.50	23.4	4	71.8	3.5	225	3	709	2.5	2233
		4.49	23.9	3.99	73.5	3.49	230	2.99	721	2.49	2289
		4.48	24.4	3.98	75.1	3.48	235	2.98	743	2.48	2341
		4.47	25	3.97	76.9	3.47	241	2.97	757	2.47	2401
		4.46	25.5	3.96	78.6	3.46	246	2.96	778	2.46	2451
		4.45	26.1	3.95	80.4	3.45	252	2.95	792	2.45	2511
		4.44	26.7	3.94	82.3	3.44	258	2.94	813	2.44	2571
		4.43	27.3	3.93	84.2	3.43	264	2.93	827	2.43	2631
		4.42	27.9	3.92	86.2	3.42	270	2.92	848	2.42	2691
		4.41	28.5	3.91	88.1	3.41	276	2.91	870	2.41	2751
		4.4	29.2	3.9	90.1	3.4	283	2.9	891	2.4	2821
		4.39	29.8	3.89	92.2	3.39	289	2.89	912	2.39	2881
		4.38	30.5	3.88	94.3	3.38	296	2.88	933	2.38	2961
		4.37	31.2	3.87	96.5	3.37	303	2.87	954	2.37	3021
		4.36	31.9	3.86	98.7	3.36	310	2.86	976	2.36	3091
		4.35	32.6	3.85	101	3.35	317	2.85	997	2.35	3161
		4.34	33.4	3.84	103	3.34	325	2.84	1024	2.34	3241
		4.33	34.1	3.83	106	3.33	332	2.83	1046	2.33	3311
		4.32	34.9	3.82	108	3.32	340	2.82	1067	2.32	3391
		4.31	35.7	3.81	111	3.31	348	2.81	1095	2.31	3471
		4.3	36.5	3.8	113	3.3	356	2.8	1117	2.30	3551
4.8	12.2	4.29	37.3	3.79	116	3.29	364	2.79	1145	2.29	3631
4.79		4.28	38.2	3.78	118	3.28	373	2.78	1173	2.28	3721
4.78		4.27	39	3.77	121	3.27	381	2.77	1202	2.27	3801
4.77	13	4.26	39.9	3.76	124	3.26	390	2.76	1230	2.26	3891
4.76	13.3	4.25	40.8	3.75	127	3.25	399	2.75	1258	2.25	3981
4.75	13.6	4.24	41.7	3.74	130	3.24	408	2.74	1286	2.24	4071
4.74	13.9	4.23	42.7	3.73	133	3.23	418	2.73	1315	2.23	4171
4.73	14.2	4.22	43.9	3.72	136	3.22	430	2.72	1350	2.22	4271
4.72	14.5	4.21	44.7	3.71	139	3.21	438	2.71	1378	2.21	4371
4.71	14.8	4.20	45.1	3.70	142	3.20	448	2.70	1413	2.20	4471
4.7	15.1	4.19	46.7	3.69	146	3.19	458	2.69	1442	2.19	4571
4.69	15.5	4.18	47.3	3.68	149	3.18	469	2.68	1477	2.18	4681
4.68	15.8	4.17	48.9	3.67	152	3.17	480	2.67	1512	2.17	4791
4.67	16.1	4.16	50	3.66	156	3.16	491	2.66	1548	2.16	4901
4.66	16.5	4.15	51.1	3.65	159	3.15	502	2.65	1583	2.15	5001
4.65	16.8	4.14	52.3	3.64	163	3.14	514	2.64	1618	2.14	5131
4.64	17.2	4.13	53.5	3.63	167	3.13	526	2.63	1654	2.13	5251
4.63	17.6	4.12	54.7	3.62	170	3.12	538	2.62	1695	2.12	5371
4.62	18	4.11	56	3.61	175	3.11	551	2.61	1731	2.11	5501
4.61	18.4	4.10	57.2	3.60	179	3.10	563	2.60	1774	2.10	5621
pH	F	pH	F	pH	F	pH	F	pH	F	pH	F

VII Report

Report (in $\text{cmol}_{(+)}/\text{kg}$) total exchangeable acidity, the exchangeable cations Al, Ca, K, Mg, Na, and free H^+ with 2 decimals; and Fe and Mn with 3 decimals on the basis of oven-dried soil.

VIII References

- ISO 11260. 2018. Reviewed and confirmed in 2024. Soil Quality – Determination of effective cation exchange capacity and base saturation level using barium chloride solution. International Organization for Standardization. Geneva, Switzerland. 12 p. [available at www.iso.org].
- ISO 14254. 2018. Reviewed and confirmed in 2023. Soil Quality – Determination of exchangeable acidity using barium chloride solution as extractant. International Organization for Standardization. Geneva, Switzerland. 6 p. [available at www.iso.org].
- König, N., Fortmann, H. 1996. Probenvorbereitungs-, Untersuchungs- und Element-bestimmungsmethoden des Umweltlabors der Niedersächsischen Forstlichen Versuchsanstalt und des Zentrallabors II des Forschungszentrums Waldökosysteme, Teil 4: Probenvorbereitungs- und Untersuchungsmethoden, Qualitätskontrolle und Datenverarbeitung; Berichte des Forschungszentrums Waldökosyst. B, Bd. 49, Untersuchungsmethode Boden AKEG1.1
- Gutachterausschuss Forstliche Analytik 2005: Handbuch Forstliche Analytik. König, N., Bartens, H. (eds.): Loseblatt-Sammlung der Analysemethoden im Forstbereich, 433 pg. (Method A3.2.1.3)

Soil Analysis Method 11 (SA11): Aqua Regia Extractant Determinations P, Ca, K, Mg, Mn, Cu, Pb, Cd, Zn, Al, Fe, Cr, Ni, S, Hg, Na

Aqua Regia extractant determinations P, Ca, K, Mg, Mn, Cu, Pb, Cd, Zn, Al, Fe, Cr, Ni, S, Hg, Na	
Method sheet	SA11
Reference method	ISO 11466
Method suitable for	Organic Layer, Mineral Layer
Method code	Sample preparation: MA02 Pretreatment: PB01 Determination: DB**

I Relevance in ICP Forests

Aqua Regia extractant determinations (P, Ca, K, Mg, Mn)

Priority	Level I	Level II
Organic Layer		
<i>OL</i>	<i>Optional</i>	<i>Optional</i>
<i>OF+OH, H-layers</i>	<i>Mandatory</i>	<i>Mandatory</i>
Mineral layer		
<i>0 - 10 cm</i>	<i>Optional</i>	<i>Optional</i>
<i>10 – 20 cm</i>	<i>Optional</i>	<i>Optional</i>
<i>20 – 40 cm</i>	<i>Optional</i>	<i>Optional</i>
<i>40 – 80 cm</i>	<i>Optional</i>	<i>Optional</i>

Aqua Regia extractant determinations (Cu, Pb, Cd, Zn)

Priority	Level I	Level II
Organic Layer		
<i>OL</i>	<i>Optional</i>	<i>Optional</i>
<i>OF+OH, H-layers</i>	<i>Mandatory</i>	<i>Mandatory</i>
Mineral layer		
<i>0 - 10 cm</i>	<i>Mandatory</i>	<i>Mandatory</i>
<i>10 – 20 cm</i>	-	-
<i>20 – 40 cm</i>	-	-
<i>40 – 80 cm</i>	-	-

Aqua Regia extractant determinations (Al, Fe, Cr, Ni, S, Hg, Na)

Priority	Level I	Level II
Organic Layer		
<i>OL</i>	<i>Optional</i>	<i>Optional</i>
<i>OF+OH, H-layers</i>	<i>Optional</i>	<i>Optional</i>
Mineral layer		
<i>0 - 10 cm</i>	<i>Optional</i>	<i>Optional</i>
<i>10 – 20 cm</i>	-	-
<i>20 – 40 cm</i>	-	-
<i>40 – 80 cm</i>	-	-

II Principle

According to the reference method (ISO 54321), the dried sample is extracted with a hydrochloric/nitric acid mixture by standing for 16 h at room temperature or after the first strong reactions have ceased (after 2 hours), followed by boiling under **reflux** for 2 h. The extract is then clarified and made up to volume with nitric acid.

Alternatively, the digestion of the sample under pressure in closed vessels (microwave digestion) is allowed (at 175°C +/- 5°C for 10 min +/- 1 min) followed by filtration according to ISO Standard 12914 (2012).

Elements are determined by spectrometry (atomic absorption or ICP/OES or ICP/MS).

III Apparatus

Analytical balance (accuracy 0.001 g)

Reference method (reflux):

Desiccator (2 l)

Reaction vessel (250 ml)

Reflux condenser

Absorption vessel, non return type, containing 15 ml of nitric acid (0.5 mol/l) (only necessary for determination of mercury)

Roughened glass beads or antibumping granules

Temperature-controlled heating apparatus

Funnel (diam. approx. 110 mm)

Volumetric flask (110 ml)

Filter paper (diam. 150 mm, pore size approx. 8 µm)

Microwave digestion (alternative)

Microwave apparatus (laboratory-grade microwave oven with temperature-feedback control mechanisms, temperature accuracy +/- 2.5°C) with rotating turntable (min. speed of 3 min⁻¹)

Microwave extraction vessels with internal volumetric flasks, of capacity 50 ml or 100 ml

Filter papers, cellulose-based, 0.45 µm, hardened and resistant to aqua regia

Atomic Absorption Spectrometer (AAS) / Flame Emission Spectrometer (FES) / Inductively Coupled Plasma Spectrometer (ICP) / Colorimeter

IV Reagents

Water (grade 2)

Hydrochloric acid (HCl) concentration 12 mol/l, $\rho \approx 1.19$ g/ml

Nitric acid (HNO₃) concentration 15.8 mol/l, $\rho \approx 1.42$ g/ml

Nitric acid (HNO₃) concentration 0.5 mol/l

The aqua regia extractant is the mixture of the HCl:HNO₃ in a 3 to 1 ratio.

Anti-foaming agent

V Procedure

Method A by reflux (reference method)

Laboratory sample

Weigh 3.000 g air-dried soil (particle size < 2 mm) of known moisture content in the 250 ml reaction vessel.

Moisten with about 0.5 ml to 1.0 ml of water and add, while mixing, 21 ml of hydrochloric acid followed by 7 ml of nitric acid (15.8 mol/l), drop by drop if necessary, to reduce foaming. Connect the condenser (and the absorption vessel) to the reaction vessel, and allow to stand for 16 h at room temperature to allow for slow oxidation of the organic matter in the soil.

The amount of aqua regia is sufficient only for oxidation of about 0.5 g of organic carbon. If there is more than 0.5 g of organic carbon in the 3 g subsample, proceed as follows. Allow the first reaction with the aqua regia to subside. Then add an extra 1 ml of nitric acid (15.8 mol/l) only to every 0.1 g of organic carbon above 0.5 g. Do not add more than 10 ml of nitric acid at any time, and allow any reaction to subside before proceeding further.

Raise the temperature of the reaction mixture slowly until reflux conditions are reached and maintain for 2 h, ensuring that the condensation zone is lower than 1/3 of the height of the condenser, then allow to cool.

Allow the reaction vessel to stand so that most of any insoluble residue settles out of suspension. (Add the contents of the absorption vessel to the reaction vessel, via the condenser, rinsing both the absorption vessel and condenser with a further 10 ml of nitric acid (0.5 mol/l)). Decant the relatively sediment-free supernatant carefully onto a filter paper, collecting the filtrate in a 100 ml volumetric flask. Allow all the initial filtrate to pass through the filter paper, then wash the insoluble residue onto the filter paper with a minimum of nitric acid (0.5 mol/l). Collect this filtrate with the first. before proceeding further. The extract thus prepared is ready for the determination of trace elements, by an appropriate method.

Method B by microwave digestion

Weigh at least 0.5 g to max. 2.0 g \pm 0.1 g (based on dry mass) of the test sample (particle size < 250 μ m), and transfer to the microwave extraction vessel.

Moisten the test portion with a few drops of water. Add separately 6 ml \pm 0.1 ml of hydrochloric acid and then 2 ml \pm 0.1 ml of nitric acid to the extraction vessel 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.

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 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 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.

Maintain the extraction at 175 °C for 10 min ± 1 min. Then allow the extraction vessel to cool to room temperature following the manufacturer's manual. 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.

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 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 before subsequent measurement. Alternatively, centrifugation at 2000 to 3000 rotations.min⁻¹ for 10 min can be sufficient to clear the supernatant.

Determination of elements (P, Ca, K, Mg, Mn, Cu, Pb, Cd, Zn, Al, Fe, Cr, Ni, S, Na)

Measure the elements cations in the extract using one of the spectrometric determination methods.

Notes:

- 1) *ISO 11047 can be used as a guideline for the determination of Cd, Cr, Cu, Pb, Mn, Ni and Zn.*
- 2) Particular attention needs to be paid to the cleaning of the laboratory equipment. It is recommended to thoroughly clean all laboratory equipment (e.g. vessels) and, as a minimum, leave the equipment standing overnight in 1 % to 5 % nitric acid.

VI Calculation

Determination of elements (P, Ca, K, Mg, Mn, Cu, Pb, Cd, Zn, Al, Fe, Cr, Ni, S, Hg, Na)

Calculation according to apparatus.

VII Report

Report aqua regia extract determinations (mg/kg) with 1 decimals and Cd with 2 decimals on the basis of oven-dried soil.

VIII References

- ISO 11047. 1998. Reviewed and confirmed in 2020. Soil Quality – Determination of cadmium, chromium, cobalt, copper, lead, manganese nickel and zinc. Flame and electrothermal atomic absorption spectrometric methods. International Organization for Standardization. Geneva, Switzerland. 6 p. [available at www.iso.org].
- ISO 54321. 2020. Soil, treated biowaste, sludge and waste — Digestion of aqua regia soluble fractions of elements: replaces standards ISO 11466, 12914 and 16174. 38 p. [available at www.iso.org]

Soil Analysis Method 12 (SA12): Determination of Total Elements Ca, Mg, Na, K, Al, Fe, Mn

Total Elements: Ca, Mg, Na, K, Al, Fe, Mn	
Method 1 : Dissolution with hydrofluoric and perchloric acids	
Method sheet	SA12A
Reference methods	ISO 14869
Method suitable for	Organic Layer, Mineral Layer
Method code	Sample preparation: MA05 Pretreatment: PC03 Determination: DB**

I Relevance in ICP Forests

Priority	Level I	Level II
Organic Layer		
<i>OL</i>	-	-
<i>OF+OH, H-layers</i>	-	-
Mineral layer		
<i>0 – 10 cm</i>	-	<i>Optional</i>
<i>10 – 20 cm</i>	-	<i>Optional</i>
<i>20 – 40 cm</i>	-	<i>Optional</i>
<i>40 – 80 cm</i>	-	<i>Optional</i>

II Principle

This method specifies the complete dissolution, using hydrofluoric and perchloric acids, of the following elements in soils:

Al, Ba, Cd, Ca, Cs, Cr, Co, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V, Zn.

This procedure may be appropriate for the subsequent determination of other elements provided their concentrations are high enough relative to the sensitivity of the measurement methods. The low acid concentration of the final solution allows the use of a large range of analytical devices and the volatilisation of silicon simplifies analytical procedures.

The dried and ground sample is pre-treated to destroy organic matter, and then digested with a mixture of hydrofluoric and perchloric acids. After evaporation to near dryness, the residue is dissolved in dilute hydrochloric or nitric acid. Hydrofluoric acid decomposes silicates by the reaction of F with Si to form volatile SiF₄. As it evaporates last, perchloric acid forms readily-soluble perchlorate salts.

To minimise the danger of acid ejection due to violent oxidation of organic matter by perchloric acid, two alternative procedures have been adopted to destroy organic matter prior to digestion:

- dry ashing at 450 °C;
- pretreatment with nitric acid.

III Apparatus

Mill

Drying oven and desiccator

Analytical balance (accuracy 0.0001 g)

Crucible of fused silica or platinum (10 - 30 ml)

Furnace (temperature 450 °C)

Evaporating dishes made of polytetrafluoroethylene (PTFE)

Hot plate (150 °C)

Fume hood

Volumetric flask of polypropylene (50 ml)

Atomic Absorption Spectrometer (AAS) / Flame Emission Spectrometer (FES) / Inductively Coupled Plasma Spectrometer (ICP)

IV Reagents

Water (grade 2)

Hydrofluoric acid (HF), conc. 27.8 mol/l, $\rho = 1.16$ g/ml

Perchloric acid (HClO₄), conc. 11.6 mol/l, $\rho = 1.67$ g/ml

Hydrochloric acid (HCl), conc. 12.1 mol/l, $\rho = 1.19$ g/ml

Nitric acid (HNO₃), conc. 15.2 mol/l, $\rho = 1.41$ g/ml

V Procedure

Attention!

Always use latex gloves while working with HF and keep the ointment against HF acid bites ready for eventual accidents!

Laboratory sample

Use air-dried soil milled as fine as possible. Weigh precisely 0.250 g of the milled sample.

Destruction organic matter

Dry ashing

Transfer soil sample to a crucible. Place the crucible in the furnace and allow the temperature to reach 450 °C, progressively over 1 h. Maintain this temperature for 3 h. Allow the furnace to cool to room temperature and transfer the ash quantitatively to a PTFE evaporating dish with a minimum amount of water. Using a platinum crucible of about 30 ml avoids ash being transferred to a PTFE dish and allows digestion to be performed in the same container as dry ashing.

Nitric acid pre-treatment

Transfer soil sample to an evaporating dish and add 5 ml of nitric acid. Place the dish on the hot plate at 150 °C and evaporate until approximately 1 ml of nitric acid remains. Note that several successive additions of nitric acid may be necessary until the emission of nitrous

vapours ceases to remove all the organic matter. In such cases, remove the dish from the hot plate and cool to room temperature before adding the next portion of nitric acid. After the last addition of nitric acid, remove the dish from the hot plate and cool to room temperature.

Total digestion

Add 5 ml of hydrofluoric acid and 1.5 ml of perchloric acid to the pretreated test portion in the PTFE dish or the 30 ml platinum crucible. Heat this mixture on the hot plate until the dense fumes of perchloric acid and silicon tetrafluoride cease. Do not allow the mixture to evaporate to complete dryness. Remove the dish from the hot plate, allow to cool, add 1 ml of hydrochloric acid or 1 ml of nitric acid and approximately 5 ml of water to dissolve the residue. Warm the dish briefly on the hot plate to assist dissolution. Transfer this solution quantitatively to the 50 ml volumetric flask, fill to the mark and mix well.

A solid phase remaining in the resultant solution indicates incomplete dissolution. It may be of no importance with respect to the elements of interest, especially when pure silica constitutes the solid phase, but in that case, the procedure shall be completed by one of the following stages.

- The procedure is stopped at this point and failure of total dissolution with a possible effect on the determination of total contents is noted in the test report.
- The procedure is adjusted to improve the dissolution. One or a combination of the three following treatments is carried out.
- The procedure is started again with a new test portion but a further dose of 5 ml of hydrofluoric acid and 1.5 ml of perchloric acid is added after evaporation of the first one to near dryness. The second dose is also evaporated as above and the procedure is carried on as described above.
- The procedure is started again with a new test portion but after the addition of hydrofluoric and perchloric acids the mixture is left overnight at room temperature before being heated as described above.
- The whole procedure is not changed but the mass of the test portion is reduced.

If a solid phase remains in spite of these further treatments, then failure of total dissolution is mentioned in the test report.

Blank test

Use the same procedure, without the sample, to perform at least one blank test within each batch of digestions.

Determination of total elements (Ca, Mg, K, Na, Al, Fe, Mn)

Measure the total elements in the extract using one of the spectrometric determination methods.

VI Calculation

Determination of total elements (Ca, Mg, K, Na, Al, Fe, Mn)

Calculation according to apparatus.

VII Report

Report total elements (mg/kg) with one decimal place on the basis of oven-dried soil.

VIII References

- ISO 14869-1. 2001. Soil Quality – Dissolution for the determination of total element content - Part 1: Dissolution with hydrofluoric and perchloric acids. International Organization for Standardization. Geneva, Switzerland. 5 p. [available at www.iso.org].

Total Elements: Ca, Mg, Na, K, Al, Fe, Mn	
Method 2 : Total element analysis by fusion with lithium metaborate	
Method sheet	SA12B
Reference methods	ISO 14869
Method suitable for	Organic Layer, Mineral Layer
Method code	Sample preparation: MA03 Pretreatment: PB10 Determination: DB**

I Relevance in ICP Forests

Priority	Level I	Level II
Organic Layer		
<i>OL</i>	-	-
<i>OF+OH, H-layers</i>	-	-
Mineral layer		
<i>0 – 10 cm</i>	-	<i>Optional</i>
<i>10 – 20 cm</i>	-	<i>Optional</i>
<i>20 – 40 cm</i>	-	<i>Optional</i>
<i>40 – 80 cm</i>	-	<i>Optional</i>

II Principle

This method specifies the fusion using lithium metaborate.

III Apparatus

Platinum crucibles

Muffle furnace

Magnetic stirring devices

Analytical balance (accuracy 0.0001 g)

Filter paper prewashed (with a 10% HNO₃ or HCl solution)

IV Reagents

Lithium metaborate (LiBO₂) on powder

Nitric acid (HNO₃), 4 %

V Procedure

Laboratory sample

Use air-dried soil (milled < 0.4 mm). Weigh 0.4 g of the milled sample.

Destruction organic matter

The sample is put to each platinum crucible and pre-ignited at 850°C for 30 min as to avoid damaging the platinum crucible when it would be mixed with lithium metaborate. The reason for this is that the soil organic matter can cause reduction of the platinum during the fusion.

Fusion

After the crucibles are cooled (usually it takes one night) the pre-ignited soil is mixed thoroughly (by means of a pipette tip) with 2 g of lithium metaborate powder in a platinum crucible and fused for 15 min at 950°C in a preheated muffle furnace. The crucible and flux that is formed are allowed to cool for one night. The reason for this is that if we try to remove them from the furnace immediately after heating by means of something metallic, there will be a reaction between the platinum and the metal.

The crucibles are immersed in a 100 ml beaker and covered with 70-80 ml of 4% nitric acid. A magnetic stirring bar is then placed inside the crucible and stirring can begin immediately. The flux is dissolved in 3 to 4 hr (occasionally it might take a little more) and the solution is made up to 100 ml, filtered through a prewashed (with a 10% HNO₃ or HCl solution) paper filter of 0.45 mm and stored for analysis.

Blank test

Use the same procedure, without the sample, to perform at least one blank test within each batch of digestions.

Determination of total elements (Ca, Mg, K, Na, Al, Fe, Mn)

Measure the total elements in the extract using one of the spectrometric determination methods.

VI Calculation

Determination of total elements (Ca, Mg, K, Na, Al, Fe, Mn)

Calculation according to apparatus.

VII Report

Report total elements (mg/kg) with one decimal place on the basis of oven-dried soil.

VIII References

- Michopoulos, P. 1995. Studies on manganese cycling in forest soils. PhD Thesis. University of Aberdeen.
- Potts, P.J. 1987. A handbook of silicate rock analysis. Blackie, New York.

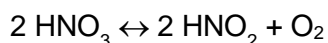
Total Elements: Ca, Mg, Na, K, Al, Fe, Mn Method 3 : Total digestion with HNO₃ and HF	
Method sheet	SA12C
Reference methods	
Method suitable for	Organic Layer, Mineral Layer
Method code	Sample preparation: MA05 Pretreatment: PC03, PD05 Determination: DB**

I Relevance in ICP Forests

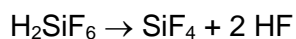
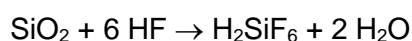
Priority	Level I	Level II
Organic Layer		
OL	-	-
OF+OH, H-layers	-	-
Mineral layer		
0 – 10 cm	-	Optional
10 – 20 cm	-	Optional
20 – 40 cm	-	Optional
40 – 80 cm	-	Optional

II Principle

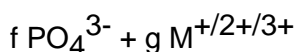
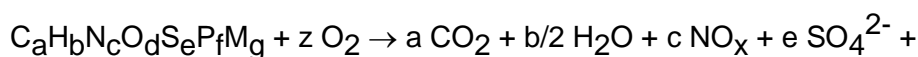
Nitric acid/hydrofluoric acid digestion is a dissolution in which the oxidising effect of nitric acid and the silica-dissolving property of hydrofluoric acid are combined. On the one hand, nitrate (with N^V) is converted to nitrous gases (NO_x, with N^{II-IV}) and the released oxygen causes the oxidation of the substances that are to be digested:



On the other hand, the hydrofluoric acid converts all silicates to fluorosilicic acid, which on fuming disintegrates into volatile silicon tetrafluoride and hydrofluoric acid and thus removes the silicates from the system:



Organic substances are dissolved completely in this digestion:



Mineral substances in the humus are also dissolved completely, with the exception of few special minerals (e.g. certain zircon compounds, topaz).

Digestion is carried out in a pressure vessel with teflon beakers, so that it is possible to carry out the digestion with highly volatile nitric acid and hydrofluoric acid at temperatures ranging from 170° to 190°C.

Disturbances

As the oxidising effect of the HF/HNO₃ mixture is not as strong as that of pure nitric acid, soil samples with high humus content may require pre-digestion with pure nitric acid in order to obtain complete digestion of the organic matter.

Under certain conditions some compounds are not completely digested, such as when they are chemically unstable or when the samples are insufficiently finely ground. In some cases, precipitation of phases of low solubility may occur during digestion. The following elements or precipitations can, for example, be subject to incomplete digestion: oxides of Al and Ti; fluorides of Al, Ca; sulphates of Ba, Pb and Sr.

The risk of contamination is high. Contamination can be effectively contained by rinsing the instruments used with diluted nitric acid.

Pressure vessels to be used are beakers of Teflon or related materials specially developed for this job. This minimizes the danger of memory effects.

III Apparatus and Instruments

- Digestion apparatus with Teflon pressure vessels
- Hot plate with temperature control; alternatively: drying cabinet with temperature control
- Balance (weighing precision +/- 0.1 mg)
- Volumetric flask 50 ml made of Duran-glas or PFA
- PFA bottles 50 ml
- Ceramic spatula
- Pipettes
- Dispenser

IV Reagents

Water, H₂O demin.

Nitric acid (HNO₃), 65% p.a. plus

Hydrofluoric acid (HF), 40% p.a.

Solutions

Rinsing acid 5% p.a. plus: 80 ml concentrated HNO₃ p.a. are measured in a graduation cylinder and topped up in a 1 l beaker with H₂O demin. and then transferred to a 2 l PE bottle with dispenser attachment.

Sample preparation

The samples have to be dried at 40 °C and milled as fine as possible.

V Procedure

Safety measures:

- 1 The work has to be carried out in a suitable fume cupboard!*
- 2 The specific safety measures for the handling of hydrofluoric acid must be observed!*

(a) Digestion

(1) Pre-digestion

(necessary only in the case of topsoil samples with high humus content or for a repeated digestion when a black precipitation is evident after total digestion).

200 mg sample material is weighed to a precision of 0.1 mg with a micro balance and filled into each Teflon beaker. Beneath the fume hood 4 ml conc. HNO_3 is added to the samples with a pipette, taking care that the liquid slowly flows down the beakers' inside wall. Rotate each Teflon beaker carefully by hand to allow the entire sample to be moistened by the acid. Cover beakers with a lid and allow to stand for one hour at room temperature until samples begin to react with the acid. Subsequently the numbered Teflon beakers are placed in the digestion block which is then screwed tight. After this the digestion block is placed into the drying oven or onto the hot-plate and heated slowly (within one hour) to 175°C . This temperature is to be maintained for at least 6 hours and the samples thus digested (possibly overnight).

On the morrow the digestion blocks are allowed to cool down before they are opened. Hold the crucible lids at a slight inclination when opening, while tapping the crucible lightly with the edge of the lid, so that any acid condensation adhering to the inside of the lid may drip back into the crucible. Crucible lids are rinsed with H_2O demin. and put aside for total digestion. Cover with a sheet of tissue to protect them from dust.

The teflon crucibles with the digestion solution are then placed into a fume cupboard and fumed at a maximum temperature of 120°C until nearly dry.

Remarks:

- 1 Use the spatula to place the sample material as deep down into the teflon beaker as possible in order to avoid electrostatic adherence of sample material to the beaker sides.
- 2 Because of the nitrous gases that are released, the hot-plate or drying-oven used for digestion should be placed beneath a fume hood.
- 3 In order to avoid or minimize contamination during fuming, the use of closed fume cupboards is strongly recommended (see Appendix 1).

(2) Total digestion

In case no pre-digestion was necessary, about 200 mg of sample material is weighed into each Teflon beaker with a micro balance. Otherwise total digestion is carried out with the nearly dry samples in the Teflon beakers. Underneath the hood, 4 ml conc. HNO_3 and 2 ml HF are added to humus samples and 2 ml conc. HNO_3 and 2 ml HF to soil samples using a pipette, taking care that the liquid slowly flows down the beakers' inside wall. Rotate each Teflon beaker carefully by hand so that the entire sample is moistened by the acid. Cover beakers with a lid and allow to stand for one hour at room temperature until samples start to react with the acid. If pre-digestion has been carried out, this step can be skipped. Subsequently the numbered Teflon beakers are placed in the digestion block which is then screwed tight. The digestion

block is placed into the drying-oven or onto the hot-plate and heated slowly (within one hour) to 175°C. This temperature is to be maintained for at least 6 hours and the samples thus digested (possibly overnight).

On the morrow the digestion blocks are allowed to cool down before they are opened. Hold the crucible lids at a slight inclination when opening while tapping the crucible lightly with the edge of the lid, so that any acid condensation adhering to the inside of the lid may drip back into the crucible. Crucible lids are rinsed with H₂O demin. and put aside for total digestion. Cover with a sheet of tissue to protect them from dust.

The Teflon crucibles with the digestion solution are then placed into a fume cupboard and fumed at a maximum temperature of 120° C until nearly dry.

Remarks:

1 Always wear latex gloves when handling HF and avail yourself of a specific cream against HF-cauterisation in case of an accident.

2 Use the spatula to place the sample material as deep down into the beaker as possible in order to avoid electrostatic adherence of sample material to the teflon beaker sides.

3 Because of the nitrous gases that are released, the hot-plate or drying-oven used for digestion should be placed beneath a fume hood.

4 In order to avoid or minimize contamination during fuming, the use of closed fume cupboards is strongly recommended.

(3) Ending digestion procedure

The residue left in the Teflon beaker after fuming is combined with 2 ml conc. HNO₃, then add 15 ml H₂O demin. reinst. with a dispenser.

Cover the beakers with lids and place the closed beakers in the digestion block which is then screwed tight. Place the digestion block into the drying-oven or onto the hot-plate and heat to 150° C. This temperature is held for at least one hour until the residue has dissolved.

The digestion block is then opened. The crucibles should now contain clear solutions. (If this is not the case, the digestion and pre-digestion must be repeated.)

In order to remove the digestion solution one beaker at a time is taken from the block and its lid carefully removed. Hold the crucible lids at a slight inclination when opening while tapping the crucible lightly with the edge of the lid, so that any acid condensation adhering to the inside of the lid may drip back into the crucible.

Subsequently the solution is poured directly into a 50 ml graduated flask. Rinse the beaker 3 x with 10 ml demin. each time from the dispenser and then add the rinsing solution to the contents of the graduated flask. The flask is then topped up with H₂O demin., closed and shaken. The digestion solution is finally poured into a 50 ml. PFA-bottle.

Remarks:

1 In case the residue has not completely dissolved, the concluding digestion procedure may be repeated after adding a small quantity of HCl.

2 The cleaning of used vessels and filters:

- Teflon beakers:

After each digestion as well as at the conclusion of the series, these are to be filled to the brim with 5% rinsing acid and closed with their lid. Any discolouration of the inner walls of the Teflon

crucibles should be carefully wiped off with a sheet of tissue paper and H₂O demin. Leave to stand for one hour, then empty the beakers, rinse thoroughly with H₂O demin. and put to dry in a drying-cupboard. Cover with a piece of paper and do not allow the temperature to exceed 60°C.

- *Graduated flasks:*

Fill 50 ml graduated flask right to the top with rinsing acid and close with a bung. Just before re-using the flask, rinse thoroughly with H₂O demin.

- *PFA bottles:*

Pour 25 ml of rinsing acid into the 50 ml bottles, shake for one hour on the shaking machine, then rinse thoroughly with H₂O demin. Subsequently they are dried in the drying cupboard at 50° C, covered with a sheet of paper.

- *Remaining instruments:*

The pipettes used for the conc. HNO₃ and HF must be rinsed thoroughly with H₂O demin. at the end of each day in order to avoid corrosion. Pipette tips may be used for one series only.

(b) Element determination in the digestion solution

All elements can be measured in the digestion solution with ICP (main elements) or ICP with ultrasonic nebulizer or AAS with graphite furnace (heavy metals)

Remarks:

Take care that only matrix adapted acid solutions are used when preparing the standards and intermediate rinsing fluids with the ICP, AAS and with automatic dispensers.

VI Comparability with other methods

(a) Total digestion with HNO₃/HF using a microwave oven (method A3.3.2, Handbuch Forstliche Analytik): the results are fundamentally comparable.

(b) Total digestion with HClO₄/HNO₃/HF using a microwave oven (method A3.3.5, Handbuch Forstliche Analytik): the results are fundamentally comparable; however, the German advisory committee of silvicultural analysis has experienced deficiencies in the evaluation of chromium in HClO₄/HNO₃/HF digestion, especially where humus samples are concerned.

VIII References

DIN Deutsches Institut f. Normung (publisher) (2000): Handbuch der Bodenuntersuchungen, Beuth Verlag, Berlin and Wiley-VCH Verlag, Weinheim, method 11.9a

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Heinrichs, H., Herrmann A.G. 1990. Praktikum der analytischen Geochemie; Springer-Verlag, Berlin, 669 p.

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Picotrace-User Manual

Sulcek, Z., Povondra, P., 1989. Methods of decomposition in inorganic analysis, CRC Press, Boca Raton.

ISO 14869-1:2001 Soil quality -- Dissolution for the determination of total element content -- Part 1: Dissolution with hydrofluoric and perchloric acids

Soil Analysis Method 13 (SA13). Determination of Acid Oxalate Extractable Al, Fe and P

Acid Oxalate Extractable Fe and Al	
Method sheet	SA13
Reference methods	ISRIC, 2002
Method suitable for	Organic Layer, Mineral Layer
Method code	Sample preparation: MA02 Pretreatment: PA05 Determination: DB***

I Relevance in ICP Forests

Priority	Level I	Level II
Organic Layer		
OL	-	-
OF+OH, H-layers	Optional	Optional
Mineral layer		
0 – 10 cm	Optional	Mandatory (Optional for P)
10 – 20 cm	Optional	Mandatory (Optional for P)
20 – 40 cm	Optional	Mandatory ¹ (Optional for P)
40 – 80 cm	Optional	Mandatory ¹ (Optional for P)

¹ In case of re-assessment (if the parameter was already measured according to the reference method in a previous survey), the measurement is optional

II Principle

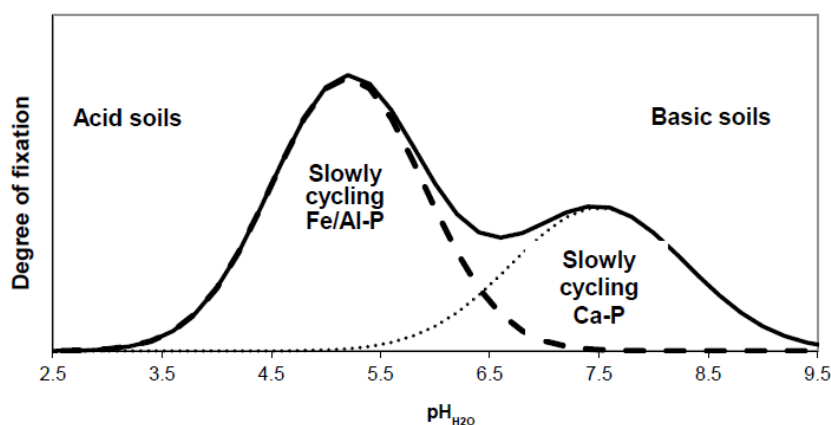


Figure 4: Degree of fixation of phosphorus in soil in relation to the soil acidity pH(H₂O) (Stevenson and Cole 1999)

In the above figure Stevenson and Cole (1999) show that in acid soils with low soil pH, P is strongly absorbed to Fe and Al, while in soils with high pH value, P is absorbed to Ca. The maximum bioavailability of P lies around a pH of 6.

The principle of this analysis is to dissolve the “reactive” or “short range order” (\approx “amorphous”) Al and Fe and a (variable) amount of organically complexed Fe and Al and the P in acid soils by shaking with a complexing acid ammonium oxalate solution. Subsequently the Al, Fe and P is determined in the extract by AAS or ICP-AES. The ammonium oxalate buffer extraction is

sensitive to light, especially UV light. The exclusion of light during the extraction reduces the dissolution effect of crystalline oxides.

Superfloc is added as a flocculent to the solution to remove the fine, suspended, solid particles, often made up of iron minerals (ferrihydrite). While conducting this analysis for classification purposes, no Superfloc should be added.

III Apparatus

Reciprocating shaking machine

Centrifuge

Atomic absorption spectrophotometer (with nitrous oxide/acetylene flame) or Inductive Coupled Plasma Atomic Emission Spectrophotometer (ICP-AES)

Polythene shaking bottles, wide mouth, 100 and/or 250 ml

IV Reagents

In this procedure *distilled* water is used since deionised water may contain Si.

Acid ammonium oxalate solution, 0.2 M in oxalate, pH 3:

- Dissolve 81 g $(\text{COONH}_4)_2 \cdot \text{H}_2\text{O}$ and 54 g $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ in 4.5 l water and make to 5 l. Prepare 1 l of two separate 0.2 M solutions of NH_4 -oxalate (28 g/l) and oxalic acid (25 g/l) and add some of either solution to the mixture until the pH is 3.

Potassium suppressant solution, 10,000 mg/l K:

- Dissolve 19 g KCl in 800 ml water and make up to 1 l.

"Superfloc" solution, 0.2%:

- Dissolve 0.1 g superfloc flocculent in 50 ml water. Stir overnight in the dark. (Note: store in the dark. This solution can be kept for about a week).
- Superfloc is a flocculent used in waste water treatment. E.g. Cyanamid Superfloc N-100 and Floberger Kemflock FA 20H

Diluent solution (5x):

- Make 2.38 g KCl and 25 ml conc. HCl to 1 l with water.

Diluent solution (20x):

- Make 2.01 g KCl, 158 ml acid ammonium oxalate solution and 21 ml conc. HCl to 1l with water.

Standard solutions Fe and Al, 250 mg/l:

- Dilute standard analytical concentrate ampoules (1g/l) according to instruction to make 1000 mg/l solutions. Dilute each to 250 mg/l by pipetting 50 ml into a 200 ml volumetric flask and making up to volume with water.

Mixed standard series of Fe and Al:

- 1 To each of five 250 ml volumetric flasks add 50 ml of the acid oxalate reagent, 25 ml of the KCl suppressant solution and 5 ml conc. HCl (or 10 ml 6 M HCl)

- 2 Of each 250 mg/l standard solution pipette 0-5-10-25-50 ml into the 250 ml volumetric flask (same volumes into same flasks respectively) and make to volume with water. The standard series are then: Fe, Al, 0-5-10-25-50 mg/l.

V Procedure

- 1 Weigh 1 g of fine earth (accuracy 0.01 g) into a 100 ml shaking bottle. Include two blanks and a control sample.
- 2 Add 50.0 ml oxalate reagent and close the bottle. (Note: for soils with relatively high contents of oxalate-extractable material (Al, Fe >2%) use 100.0 ml oxalate reagent and a 250 ml shaking bottle).
- 3 Shake for four hours **in the dark**.
- 4 Transfer about 35 ml to a 50 ml centrifuge tube
- 5 Add 3-4 drops of superfloc solution and swirl well (preferably on a Vortex mixer) and centrifuge.
- 6 Prepare 5x and 20x dilutions:

5x dilution

Pipette 1 ml of the clear supernatant and 4 ml of the diluent solution (5x) into a test tube and homogenise.

20x dilution

Pipette 1 ml of the clear supernatant solution and 19 ml (by varispencer or burette) of the diluent solution (20x) into a wide test tube and homogenise
- 7 Measure Fe by AAS at 248.3 nm using an air/acetylene flame and measure Al by AAS at 309.3 nm using a nitrous oxide/acetylene flame or measure by ICP-AES. Refer to the manufacturer's manual for operation.

Note: In case of over ranged (diluted) extracts, dilute these once more 1+1 with the zero standard solution. Therefore, of the latter an extra 250 or 500 ml should be prepared. Change the calculation accordingly.

VI Calculation

Calculate the oxalate extractable Fe, P and Al, on the basis of the air-dried soil according to the following equation:

$$Fe, Al, P (mg / kg) = \frac{(a - b) \times df}{s} \times mlox. \times 1000$$

where

- a = mg/l Fe, Al, P in diluted sample extract
- b = mg/l Fe, Al, P in diluted blank
- df = dilution factor
- ml ox. = ml of oxalate reagent used (50 or 100)
- s = air dry sample weight in milligram
- 1000 = conversion factor to mg/kg basis

VII Report

Report oxalate extractable Fe, Al and P (mg/kg) with one decimal place on the basis of oven-dried soil.

VIII Reference

ISRIC, FAO. 2002. Procedures for soil analysis. Sixth ed. ISRIC Technical Paper 9. L.P. Van Reeuwijk (ed). Wageningen, The Netherlands.

USDA National Resources Conservation Service, 2004. Survey Laboratory Methods Manual. Soil Investigations report N°.42, Version 4.0, 312-317.

Stevenson, F.J. and Cole, M.A. 1999. Cycles of Soil (Carbon, Nitrogen Phosphorus Sulfur, Micronutrients). John Wiley and Sons Publishers, Hoboken, 427 p.

Soil Analysis Method 14 (SA14): Determination of the Soil Water Retention Characteristic

Soil water retention characteristic (pF analysis) (SWRC)	
Method sheet	SA14
Reference method	ISO 11274
Method suitable for	Mineral and organic soil horizons, undisturbed samples

I Relevance in ICP Forests

Priority	Level I and Level II	Level II core
Organic layer		
<i>OL</i>	-	-
<i>OF-OH, H - layers</i>	<i>Optional</i>	<i>Mandatory if > 5 cm</i>
Mineral layer		
<i>0 – 20 cm</i>	<i>Optional</i>	<i>Mandatory</i>
<i>20 – 40 cm</i>	<i>Optional</i>	<i>Mandatory</i>
<i>40 – 80 cm</i>	<i>Optional</i>	<i>Mandatory</i>
<i>> 80 cm</i>	<i>Optional</i>	<i>Optional</i>
<i>Extra (specific) layer</i>	<i>Optional</i>	<i>Optional</i>

The volumetric water content at matric heads 0, -1, -5, -33 and -1500 kPa plus the dry soil bulk density are mandatory to determine on Level II core plots. Extra observations of the SWRC at pressures -10, -100 and -250 kPa are optional but they greatly improve fitting the soil water retention characteristic (SWRC).

Some matric heads immediately provide information on SWRC parameters: at 0 kPa the maximum water holding capacity (WHC) of the saturated soil sample is determined; depending on definitions and soil texture field capacity (FC) may be inferred from -10 till -100 kPa; permanent wilting point (PWP) is attained at a matric pressure of -1500 kPa and dry bulk density (BD) (lowest pressure at about 10^{-6} kPa) derived in the oven at 105°C.

II Principle

This method sheet describes the determination of the soil water retention in the laboratory, extending from saturated soil (no pressure or suction; 0 kPa) to oven-dry soil (about -10^6 kPa) based on measurements of the drying or desorption curve. All methods described by ISO 11274 are allowed, except method B, using a porous plate and burette apparatus for matric pressures from 0 to -20 kPa.

In order to determine the SWRC, the volumetric water content (θ in volume fraction, $\text{m}^3 \text{m}^{-3}$) is determined at predefined matric potentials (ψ , in kPa).

The volumetric soil water content at matric pressure 0 kPa is approximated by the total porosity of the soil.

The ISO 11274:1998 allows 4 methods to determine matric pressures within specific ranges:

- method using sand, kaolin or ceramic suction tables for determination of matric pressures from 0 kPa to - 50 kPa;
- method using a porous plate and burette apparatus for determination of matric pressures from 0 kPa to - 20 kPa; (single sample)

- method using a pressurized gas and a pressure plate extractor for determination of matric pressures from - 5 kPa to - 1500 kPa;
- method using a pressurized gas and pressure membrane cells for determination of matric pressures from - 33 kPa to - 1500 kPa.

Since method B allows only processing a single sample at the time, use of this method is not recommended. Laboratories are free to apply methods A, C and D according to the ISO 11274 standard. Guidelines for choosing the most appropriate method for specific soil types are given in ISO 11274, chapter 3.

Before applying methods A, C or D, general recommendations for sample preparation are:

- For measurements at pressures from 0 to -50 kPa, use a nylon mesh to retain the soil sample in the sleeve and secure it with an elastic band or tape;
- Ensure maximum contact between the soil core, mesh and the porous contact medium of the suction tables, plates or membranes; remove any small projecting stones if necessary;
- Avoid smearing the surface of (clayey) soils, especially when water saturated;
- Inspect the sample for bioturbation (worms, isopods) or germination of seeds during analysis; the use of a biocide is discouraged;
- Report the temperature at which the water-retention measurements are made;
- Ideally, measurements use field-moist samples [i.e. do not dry the undisturbed samples first (hysteresis effect)]. Prior to analysis, samples are saturated with water.
- Respect wetting times before starting measurements to obtain a saturated sample. General guidelines for wetting times according to ISO 11274 are:
 - sand 1 to 5 days
 - loam 5 to 10 days
 - clay 5 to 14 days or longer
 - peat 5 to 20 days.

Table SA14-1: Overview of matric heads to assess for the determination of the SWRC.

Matric potential ψ			Recommended instrument / Method	Estimator	M/O
cm H ₂ O	pF	kPa			
1	0.0	0	Pycnometer	$\approx \theta_{\text{sat}} = \text{WHC} = \text{Total porosity}$	M
10	1.0	-1	Sand suction table (method A)		M
51	1.7	-5			M
102	2.0	-10		FC sand	O
337	2.5	-33	Kaolin suction table (method A)	FC siltloam	M
1022	3.0	-100	Pressure plate extractor (method C) or Pressure membrane cells (method D)	FC clay	O
2555	3.4	-250			O
15330	4.2	-1500		PWP	M
10 ⁷	7.0	-10 ⁶	Oven	Dry BD	M

Where:

- 1) the pF is the logarithm of the absolute value of the matric potential expressed by the graduation of the water column (cm).
- 2) 1 kPa = 10.22 cm H₂O or 1 cm H₂O column = 0.097885 kPa
- 3) 100 kPa = 1 bar

III Apparatus

Method A: *Determination of the soil water characteristic using sand, kaolin and ceramic suction tables*

- Suction table (watertight, rigid container with outlet in base and close fitting cover)
- Drainage system for suction table, enabling to maintain suction at specific matric pressures
- Sand, silt or kaolin packing material, appropriate for use in suction tables (homogenous, sieved, graded and washed, free of organic material or salts). Material should achieve the required air entry values (see ISO 11274 for details)
- Drying oven capable of maintaining temperature of 105 ± 2 °C
- Balance (accuracy 0.1% of measured value)

Method C: *Determination of soil water characteristic by pressure plate extractor*

- Pressure plate extractor with porous ceramic plate
- Sample retaining rings/soil cores with discs and/or lids
- Air compressor (1700-2000 kPa), nitrogen cylinder or other pressurized gas)
- Pressure regulator and test gauge
- Drying oven capable of maintaining temperature of 105 ± 2 °C
- Balance (accuracy 0.1% of measured value)

Follow the manufacturer's instruction to assemble and operate the apparatus.

Method D: *Determination of soil water characteristic using pressure membrane cells*

- Pressure cells with porous baseplates
- Cellulose acetate membrane
- Pressure regulator
- Air compressor (1700-2000 kPa, nitrogen cylinder or other pressurized gas)
- Drying oven capable of maintaining temperature of 105 ± 2 °C
- Balance (accuracy 0.1% of measured value)

Follow the manufacturer's instruction to assemble and operate the apparatus.

IV Procedure

Method A: *Determination of the soil water characteristic using sand, kaolin and ceramic suction tables*

- Weigh the cores and then place them on a suction table at the desired matric pressure with table cover closed. The reference 0 cm height for setting the suction level is the middle of the core;

- Leave the cores for 7 days (minimum equilibration time). Equilibrium is reached if daily change in mass of the core is less than 0,02 %;
- If equilibrium is reached, weigh the cores, if not, replace cores firmly onto the suction table and wait until equilibrium is reached.

Method C: *Determination of soil water characteristic by pressure plate extractor*

- Take small subsamples from the undisturbed sample: soil cores of approximately 5 cm diameter and between 5 mm and 10 mm in height; smaller samples for lower pressures are used in order to avoid long equilibration times;
- It is acceptable to use disturbed samples at pressures lower than - 100 kPa, providing that the disturbance consists only in breaking off small pieces of soil and not in compressing or remoulding the soil.
- Use at least three replicate samples of each sample and place them on a presaturated plate;
- Wet the samples by immersing the plate and the samples until a thin film of water can be seen on the surface of the samples;
- Create a saturated atmosphere in the extractor;
- Apply the desired gas pressure and keep to a constant level, check for leaks;
- Record on a daily basis the evacuated water from the samples, when no change are observed (volume in a burette remains static) the samples have come to an equilibrium;
- At equilibrium status, soil samples are weighed, oven-dried and reweighed to determine the water content at the predetermined pressures

Method D: *Determination of soil water characteristic using pressure membrane cells*

- Soil subsamples are placed on a porous cellulose acetate membrane
- Equilibrium status is attained when water outflow from the pressure cell ceases and soil water content is determined by weighing, oven-drying and reweighing the sample.
- Gas pressure methods are only suited to determine matric pressures below - 33 kPa

V Calculation

V.1 Volumetric water content

ISO 11274 describes two procedures:

- Procedure for soils containing less than 20 % coarse material (diameter greater than 2 mm)
- Procedure for stony soils; conversion of results to a fine earth basis

1 For soils with less than 20% coarse material:

Calculate the water content mass ratio at matric pressure ψ_i using the formula:

$$WC_{\psi_i} = (M_{\psi_i} - M_{dry}) / M_{dry}$$

where

WC_{ψ_i} is the water content mass ratio at a matric pressure ψ_i , in grams;

M_{ψ_i} is the mass of the soil sample at matric pressure ψ_i , in grams;

M_{dry} is the mass of the oven-dried soil sample, in grams.

Calculate the volumetric water content at matric pressure ψ_i using the formula:

$$\theta_{\psi_i} = [(M_{\psi_i} - M_{dry}) / (V \times \rho_w)] \times 10^{-3}$$

alternatively

$$\theta_{\psi_i} = WC_{\psi_i} \times (\rho_b / \rho_w)$$

where

θ_{ψ_i} is the water content volume fraction at matric pressure ψ_i , expressed in $m^3 m^{-3}$ (volume of water per volume of soil);

M_{ψ_i} is the mass of the soil sample at matric pressure ψ_i , in grams;

M_{dry} is the mass of oven dried soil sample, in grams;

V is the volume of the soil sample in m^3

ρ_w is the density of water, in $kg m^{-3}$

ρ_b is the bulk density of oven dried soil at 105°C, in $kg m^{-3}$.

2 For soils with more than 20% coarse material, data needs conversion to a fine earth basis as follows:

The volumetric water content of the fine earth (θ_f) equals:

$$\theta_f = \theta_t / (1 - \theta_s)$$

where:

θ_f water content of the fine earth, expressed as a volume fraction ($m^3 m^{-3}$);

θ_s volume of non-porous stones, expressed as a fraction of total core volume ($m^3 m^{-3}$);

θ_t is the water content of the total earth, expressed as a fraction of total core volume ($m^3 m^{-3}$);

For porous stones, a different correction should be applied as described in ISO 11274.

If volumetric water content is reported on fine earth basis, this should be clearly reported along with the volume of non-porous stones in the sample.

V.2 Calculation of the total porosity

A value for porosity can be calculated from the bulk density ρ_{bulk} and particle density $\rho_{particle}$:

$$\phi = 1 - \frac{\rho_{bulk}}{\rho_{particle}}$$

Often the particle density or true density of soil is approximated by 2650 $kg.m^{-3}$ (mineral density of quartz). But the direct measurement of the particle density is strongly recommended to be done by the means of a pycnometer.

V.3 Determination of dry bulk density

Determination of dry bulk density is done according to method SA04. The dry bulk density (BD) is recorded in $kg m^{-3}$ with no decimal places.

In the case of stony or gravely soils the bulk density of the fine earth fraction (< 2 mm) should be reported. Furthermore, the bulk density of the coarse fragments should be known, but this may be approximated as 2650 kg.m⁻³.

VI Report

Report for each undisturbed soil sample, the raw volumetric soil water content

($\theta = \text{VWC in m}^3 \text{ m}^{-3}$) with four decimal places using the xx20xx.SWA data form. Report the dry bulk density (BD) in kg m⁻³ without decimal places using the xx20xx.SWC file.

Together with the laboratory results, following field data should be reported: plot ID, sampling data, pit ID, code depth layer, horizon number, sample ring depth (upper and lower side of the ring) in cm below the top of the mineral soil.

VII References

ISO 11274, 1998. Soil Quality – Determination of the water-retention characteristic – Laboratory methods. International Organization for Standardization. Geneva, Switzerland. 20 p. [available at www.iso.org].