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International Co-operative Programme on Assessment and 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 XI

Soil Solution Collection and Analysis

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1. Introduction

In addition to the direct effects of stress factors on the forest canopy, forest condition is also influenced by soil-mediated effects via the tree root system. In this respect, soil solution is the matrix mediating between the solid soil and the roots because all nutrients, as well as toxic compounds, pass into the roots via the soil solution. Thus, soil solution chemistry is a valuable indicator for monitoring the effects of air pollution and other stress factors on forest ecosystems. The chemical composition of the soil solution is governed by a range of biogeochemical processes that comprise the input of atmospheric deposition into the soil, interactions between the soil solid and liquid phases and the soil gas phase, soil biological processes, and chemical equilibrium reactions. Determination of the chemical composition of the soil solution provides real-time, continuous information about nutrient availability and the possible inhibition of nutrient uptake caused by the effects of toxic elements (e.g. Al^{3+}) on plant roots and mycorrhizas. The continuous monitoring of soil solution also provides a direct insight into the relationships between forest condition and environmental stress factors, specifically air pollution (e.g. acidifying deposition) and short-term climatic events, and facilitates the prediction of future trends in soil condition. In addition, determination of the composition of the soil solution, together with the estimation of soil water fluxes, can be used to calculate element fluxes through the soil and the output of compounds from the soil into the groundwater and other ecosystems. Together with the assessment of other element fluxes (e.g. litterfall), it is possible to determine input-output budgets of forest ecosystems in relation to deposition, climate change, as well as of forestry management practices.

2. Scope and application

This part of the Manual aims at providing a consistent methodology for collecting high quality, harmonized and comparable forest soil solution data at selected ICP Forests Level II intensive monitoring plots. Soil solution is assessed at level II and level II core plots, but not at level I. Harmonization of the procedures employed in the collection of soil solution samples and in the chemical analyses is essential to ensure full comparability of the chemical soil solution data. In order to ensure that the national data is acceptable in the international database, as well as for use in evaluations, the National Focal Centers and their scientific partners participating in the ICP Forests programme should follow the methods and procedures outlined in this manual.

3. Objectives

The harmonised collection and analysis of soil solution at the Level II plots across Europe have the following objectives:

1. to determine and monitor long-term trends in soil solution chemistry in response to natural and anthropogenic stress factors (e.g. acidifying deposition, climate change).
2. to determine input-output budgets of elements from forest ecosystems in relation to deposition and forestry management practices.

3. to quantify the temporal and spatial variability of soil solution parameters for the major forest soil types in order to improve the adequacy and precision of soil solution assessment and to understand its dynamics and spatial patterns.

The third objective can be obtained only by using a limited selection of intensive monitoring plots equipped with an adequate number of lysimeters. The overall sampling design (e.g. number of replicate samples and sampling depths) should enable the estimation of plot-based averages of element concentrations, variation and precision level required for the statistical verification of differences between plots and of changes over time.

4. Location of measurements and sampling

4.1 Soil solution sampling techniques

Soil solution can be collected by 1) non-destructive or 2) "semi-destructive" methods. Non-destructive methods involve the installation of a soil solution collector (tension lysimeters) that samples the soil solution at the same point over time. Disturbance to the soil/site associated with the installation of this type of lysimeter is normally relatively minimal and of only short duration. Semi-destructive sampling mainly concerns zero-tension lysimeters, the installation of which can cause major, long-term changes to the soil hydrology and aeration of the sampling point.

The standard method to be used in the ICP Forests soil solution monitoring programme is tension lysimetry. In 2006, 72% of all samplers were tension lysimeters. The sampling techniques differ considerably with respect to the soil solution fraction sampled, the effects of sampling on the site, as well as the extent to which they provide information about temporal and spatial variation in the properties of soil solution (Haines et al., 1982; Hendershot and Courchesne, 1991; Marques et al. 1996). The different soil solution fractions sampled by the four techniques are shown in Annex 1.

4.2 Sampling design at plot scale

4.2.1 Location of the soil solution sampling points

Soil solution sampling with non-destructive and semi-destructive methods (lysimetry) should be carried out on the plots so that soil solution sampling can be integrated with throughfall and litterfall sampling, as well as with soil moisture measurements, i.e. implemented on the same location. If it is not possible to install the lysimeters on the plot they can be placed in the buffer zone surrounding the plot.

4.2.2 Sampling depths

It is mandatory to sample soil solution at fixed depths because the evaluations to be carried out on soil solution and other ecosystem components will primarily be based on fixed depths (e.g. water and element fluxes and budgets). In addition to the fixed depth interval, the genetic horizon(s) in which the lysimeters have been installed, should also be reported. The same horizon designations should be used as in the profile description of the plot (see submanual X).

The reference point for depth determination is the center (mid-point) of the active sampling zone of the soil solution collector, whatever its type. Tension lysimeters should be installed at three depths (Table 1) at least: 1) in the midpoint of the 0-20 cm mineral soil layer (0 cm line = interface

between the organic layer and underlying mineral soil) in order to sample the soil solution passing through the organic layer, 2) within the rooting zone (mid-point of the lysimeter at 20-40 cm in order to be able to monitor the concentrations of nutrients and toxic elements near the fine roots, and 3) below the rooting zone (mid-point of the lysimeter 40- 80 cm layer) in order to be able to estimate the output of elements. Note that the sample obtained from these fixed depths represents soil solution from both above and below the fixed depth; during dry periods the volume of soil sampled will be much greater than that during wet periods, i.e. the actual layer of soil sampled can vary considerably.

Zero-tension lysimeters should be installed immediately below the organic layer at 0 cm depth, at 20-40 cm and at 40-80 cm. The reason why lysimeters should be installed at fixed depths is because these are the depths of the mandatory soil sampling procedure and the soil moisture probes. In order to sample all relevant pedogenetic horizons, soil solution may be sampled optionally below 80 cm in addition to the mandatory depth intervals.

Table 1: Depth agreements of soil solution measurements with other soil assessments

Layer type	Soil		Soil Solution	
	Soil properties	**Moisture probe**	Zero-tension	Tension lysimeter
OFH, Forest floor	OL, OF, OH	> 5 cm thick	-	-
(M05, M51, M01, H01)	0-5/5-10 0-10	0-20 cm	0-5 cm	0-20 cm
(M12, H12)	10-20		-	
(M24, H24)	20-40	20-40 cm	20-40 cm	20-40 cm
(M48, H48)	40-80	40-80 cm	40-80 cm	40-80 cm

4.2.3 Location and number of replicates

4.2.3.1 Number of replicates

The number of samples at the same sampling depth required to obtain a plot mean that is within ± 20% of the population mean, with a confidence level of 95%, is at least 10 for most elements (Grossmann and Kloss, 1994, de Vries and Leeters, 1994, Manderscheid and Matzner, 1995). However, the number of samples required to meet this criterion also varies according to the element/ion in question. The spatial variation of element/ion concentrations in soil solution collected by 20 replicate tension lysimeters and expressed by coefficients of variance as percentages have been reported to range from 12% to 79% (Grossmann and Kloss, 1994) and from 5% to 128% (Manderscheid and Matzner, 1995). Fölster et al. (2003) were able to achieve statistically reliable temporal trends for sulphate and base cations by the use of 3 to 7 replicate lysimeters.

Three replicates per depth are mandatory. It is also strongly advised that two extra lysimeters are installed at each depth in order to ensure that at least 3 samples are obtained at each sampling. It should be noted that 3 replicate samples provide information on the trends in soil solution chemistry at specific points of the plot, rather than a fully representative estimate of the site. If soil solution monitoring is being used in input-output budget studies, then it is strongly advised to install at least 10 replicates (see also Bille-Hansen, 2002).

It is strongly recommended to analyze at least three samples separately from each sampling depth on each sampling occasion. The soil solution samples have to be stored in a

refrigerator/cold room (+5°C). Pooling of soil solution samples from one depth should be avoided because otherwise no information is obtained about the spatial variation (variance) of the results for the depth in question. This information is essential when investigating time trends at the national or European level. The volume of the soil solution sample should always be recorded.

If pooling has to be carried out in order to obtain sufficient volume for the chemical analyses, then this should be done by combining the whole samples or by volume weighting in the laboratory. Pooling to only one sample precludes the estimation of spatial variation and missing values can result in biased means if the spatial variation between the individual lysimeters is high. This problem can be avoided to some extent if the spatial variation between the lysimeters has been quantified in a pilot study or for single sampling periods during the soil solution monitoring. The values of missing samples can then be estimated using regression equations. In that case these 'estimated' values should be flagged as such in the database.

4.2.3.2 Selection of sites for replicates

The lysimeters should be randomly or systematically located on the plot or buffer zone in order to obtain a representative sample, although this may be limited by the presence of stones or tree stems. It is advisable to keep a minimum distance of 1 m from the tree base. Lysimeters should be installed in a way to prevent interference with replicate lysimeters, or lysimeters installed in other soil depths, or other assessments. Lysimeters that have already been installed can be maintained, but new lysimeters should be installed in accordance with the above.

4.2.3.3 Numbering of samplers

On each plot, each lysimeter must be given an identification number (ID), i.e. all lysimeters at one plot must be numbered uniquely and permanently. Only such a numbering of samplers guarantees consistency of plot information and data. That means that all samplers at one plot should be first given an (running) ID and then be described by assigning sampler type, sampled horizon and sampled depth (midpoint of lysimeter). For each sampler these attributes must remain the same for all monitoring years. If soil solution from samplers with the same attributes (sampled layer, sampled depth and sampler type) is pooled before analysis the numbering of these bulked samples must also remain the same over the years. Table 2 gives an example of correct sampler numbering

Table 2: An example of sampler numbering .

Country	Plot	Sampler_No (Sampler_ID)	Sampler Type	Layer	Sampling depth (m)	Year	Analysis / Reporting
X	X	1	1	M	0.20	2003	Single
X	X	2	1	M	0.20	2003	Single
X	X	3	2	O	0.05	2003	Bulked
X	X	4	1	M	0.80	2003	Bulked
X	X	1	1	M	0.20	2004	Single
X	X	2	1	M	0.20	2004	Single
X	X	3	2	O	0.05	2004	Bulked
X	X	4	1	M	0.80	2004	Bulked

If a lysimeter needs replacement there are two options. If the sampler is replaced at the same spot, sampling depth, horizon and if the lysimeter is of the same type as before, the sampler ID should be kept to allow for time trend analysis.

If the sampler is removed and another sampler is placed at another spot within the same plot, soil depth, horizon (for example in the case of big disturbances) or if the sampler even is of another type, it must be given a new number (ID) that has not yet been used at this plot.

Replacement of samplers can be reported using the field "Other Observations" in the reduced plot file (PSS). Further information on data reporting is given in subchapter 6.1.

4.3 Sampling equipment and installation

4.3.1 Tension lysimetry

Tension lysimeter systems usually consist of a porous body, i.e. a suction cup or suction plate, which is connected via tubing to a collection vessel and a vacuum system (Fig. 1). Suction cups may be mounted to a shaft of the same diameter, which reaches to the soil surface or into a pit used for the installation of the lysimeters. Tension lysimeters can be installed at depths up to ca. 3 m. However, their use in the organic layer is restricted because it is usually difficult to maintain capillary contact with the humus material during dry periods. Plate lysimeters can usually only be installed close to the soil surface because insertion at greater depths results in considerable disturbance to the soil profile.

Tension lysimetry utilizes vacuum to draw soil solution, via capillary connections, into the lysimeter. The vacuum is also used to lift the soil solution samples up into collection vessels located at or close to the ground surface. Vacuum may be generated by means of a hanging water column or a vacuum pump. The vacuum can be applied to the lysimeter with constant, decreasing or variable tension. A continuous vacuum system with a constant tension is the recommended method. Normally 30 - 60 kPa vacuum are used for soil solution sampling (Beier et al. 1989). A decreasing tension is applied, when the collection vessel is evacuated using a pump. Soil solution is extracted from the soil until the tension rises above the soil water tension. In a variable tension lysimeter system, the tension is continuously regulated to a level that is slightly lower than soil water tension (approximately 5 to 20 kPa). In each case the height difference between porous body and collection vessel has to be considered when the necessary vacuum is calculated (0.1 kPa per cm height difference).

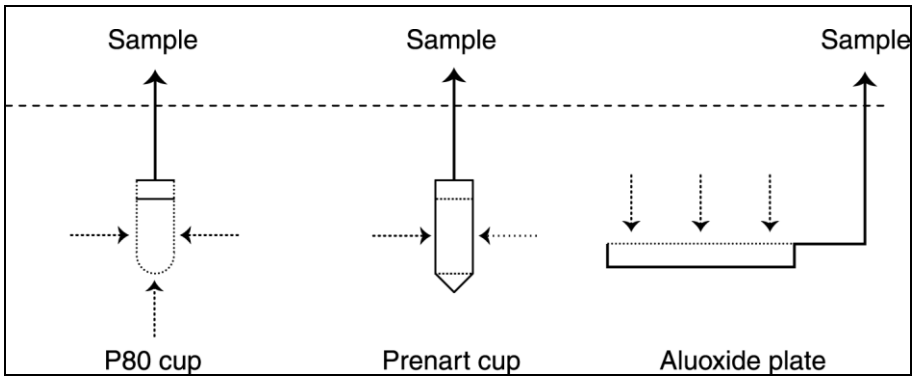

Figure 1: Examples of different types of tension lysimeters.

The suction cups and plates are mainly based on three types of material: ceramic (e.g. P80 and Aluoxide), plastic and sintered glass (Fig. 1). Most plastic materials are hydrophobic, which would make it difficult to obtain soil solution after dry periods. However, the hydrophobic property of plastic can be overcome if mixing the plastic material with silica flour or stainless steel powder.

4.3.2 Zero-tension lysimetry

There are two types of zero-tension lysimeter currently in use in the ICP Forests:

- plate lysimeters
- funnel lysimeters.

Zero-tension lysimeter systems consist of a plate or funnel, which is connected to a collection vessel (Fig. 2). A plate lysimeter usually has three vertical walls and an outlet port, which is placed at the roof of a tunnel, which is dug into the wall of a pit or trench. The installation of zero-tension lysimeters in stony soils can be difficult. Plate lysimeters can be easily installed under the organic layer on any type of soil, but successful installation in e.g. till soils can be problematic and cause considerable changes in the overlying soil (e.g. aeration and hydrological changes caused by trench excavation).

One type of funnel lysimeter consists of a 20-cm-diameter plastic funnel containing acid-washed, fine quartz fitted to the top of a plastic collector bottle. For funnel lysimeters, a soil core is taken and placed onto a funnel. Funnel lysimeters have been successfully installed using special large-diameter soil augers on relatively stony soils down to depths of 40 cm. One problem with funnel lysimeters is that the roots leading into the overlying soil profile are always cut during installation. This means that soil solution chemistry will be altered until the roots have grown back into the soil core. For instance, there is frequently a flush of DOC and macronutrients in the soil solution following installation owing to the cessation of nutrient uptake by the roots and an increase in mineralization of organic material.

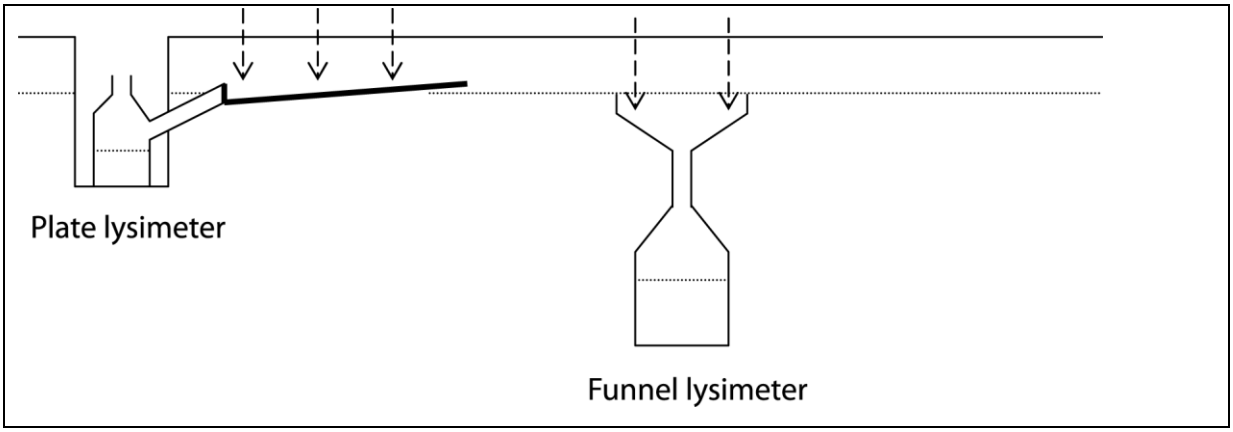

Figure 2: Examples of different types of zero-tension lysimeters.

4.3.3 Materials suitable for use in lysimeter systems

All materials used in lysimeter systems (e.g. suction cups, tubing, collection vessels) should not interfere (contamination or adsorption) with the solutes of interest. If the properties of materials used are unknown, they should be tested for possible interference before use. A summary of the materials used in lysimeter systems is given in Annex 2. The materials considered to be sufficiently free of contaminants are as follows: ceramic material, aluminium oxide, glass sinter, silica flour, stainless steel powder, polyamide (PA), polyethylene (PE), polytetrafluoroethylene (PTFE; e.g. Teflon), polyvinylidene fluoride (PVDF) and polypropylene (PP).

As the properties of the materials listed differ from each other, their suitability in relation to prevailing climatic and edaphic conditions should be taken into account. Due to its hydrophobic nature, teflon has proven to be unsuitable for soils susceptible to long drought periods interrupted by stormy events. These repeated drying and wetting processes of soil are typical in

Mediterranean climate zone. When sampling for heavy metals, plastic materials are more appropriate than ceramic or aluminium oxide. Ceramic and aluminium oxide lysimeters have been reported to adsorb significant amounts of heavy metals (except Pb) from soil solutions with a pH > 4.0 (Grossmann et al. 1990). The cation exchange capacity of these materials also affects the soil solution sample. However, suction cups made from plastics may also absorb heavy metals at low concentrations (Andersen et al. 2002).

A number of plastic materials are available for the tubing used in lysimeter systems (e.g. PE, PVC). However, PA tubing should be avoided because the softener (benzene sulphonamide) added to certain grades of PA tubing is water soluble and will result in elevated DOC, total N and total S concentrations in the soil solution samples.

The collection vessels used in collecting water samples from tension lysimeters are invariably made of glass owing to the relatively high vacuum applied. Glass bottles should have a plastic coating as an implosion protection. Glass bottles should be made of clear borosilicate glass, and preferably of laboratory grade. The volume of the sampling vessel has to be adjusted to the amount of soil solution expected. An overflow protector prevents the sample to flow into the vacuum system or to contaminate other samples.

Transport of the samples to the laboratory should be carried out preferably with laboratory bottles made of polyethylene (PE).

All parts of the lysimeter system that will be in contact with the soil solution sample should be acid washed (1 N HCl), followed by rinsing 5 times with deionized water (see Beier et al. 1989), prior to installation in the field.

4.3.4 Installation

All circumstances, which may have an influence on soil solution composition have to be recorded during the installation process and documented in the sampling layout and equipment section of the Data Accompanying Report Form (DAR). These include (if applicable):

- Materials of the equipment used (porous bodies, tubing, collection vessels, connectors, glue etc.)
- Dimensions of the equipment used (length, diameter of tubing, inner volume of porous body, volume of collection vessels etc.)
- Drilling angle
- Backfilling of augered holes

4.3.4.1 Tension lysimeters

Care should be taken during installation of the lysimeters in order to minimize disturbance to the soil profile. For the installation of a suction cup a hole is drilled with an auger having a diameter slightly larger than that of the cup. The hole can be made vertically or at an angle (e.g. 45°) to the ground surface, or horizontally from the wall of a soil pit. Installing the lysimeter at an angle from vertical has the advantage that the soil layer above the lysimeter is not disturbed. To avoid contamination, it is necessary to prevent material from the overlying horizons to fall into the hole, especially if the soil is very loose. Horizontal installation from a pit will minimize this problem.

Plate lysimeters can be best installed from the wall of a pit or trench by digging a horizontal tunnel and pressing the plate to the roof of the tunnel. The tunnel will then be backfilled. For installation at the interface humus layer/mineral soil the humus layer should be lifted up and material from the mineral soil corresponding to the height of the lysimeter plate must be removed. The lysimeter plate can then be inserted into the cavity.

It is recommended to install the lysimeters without slurrying. Only if a good hydraulic contact between the suction cup and the soil cannot be achieved (e.g. in stony or sandy soils), a slurry of the material taken by the auger from the bottom of the hole can be used. If this material is not very fine-textured, hydraulic contact can be improved by sieving soil taken at a corresponding depth in a pit dug outside the subplot/plot. The fine material passing through the sieve is used to prepare the slurry. If acid-washed, quartz powder has to be used, then great care should be taken to ensure that all traces of elements (especially Ca) have been removed by prolonged washing. Bentonite may not be used as this can release ions that affect the soil solution chemistry.

If the cup does not have a shaft, the hole should be backfilled with material from the corresponding horizons. Soil from the auger is an obvious source of backfill material, but additional material is usually required from a nearby source.

If lysimeters are installed vertically or near-vertically, water should be prevented from seeping down the tube running from the ground surface down to the lysimeter. This can be avoided by completely burying the lysimeter tube in the soil, or by attaching a collar of a flexible inert material around the top of the tube. If the lysimeters are connected with thin tubing, this problem can be avoided by running the tubing horizontally through the humus layer towards the collection vessel. Replacement of the part of the tubing that runs above ground can be facilitated by inserting a connector at the point where the tubing passes down into the ground. This also reduces the likelihood of losing a lysimeter because, if the above-ground tubing is pulled up (or gnawed by animals), the part of the tubing leading down to the lysimeter remains intact.

The collection vessels used in tension lysimetry should be located close to the ground surface in dark and dry containers. The containers have to be isolated to prevent the samples from freezing and warming up.

4.3.4.2 Zero-tension lysimeters

To install zero-tension plate lysimeters, a pit has to be dug and the lysimeter installed into the wall. This should be done immediately next to the selected location of the lysimeter so that it can be installed with as little disturbance to the overlying soil as possible. Plate lysimeters can also be installed immediately below the humus layer by cutting at one or two sides of a square of humus larger than the plate, and then carefully lifting the intact humus “mat”. Part of the underlying mineral soil is then removed so that the lysimeter plate slopes towards the collector tube on the side of the plate. The humus mat is then carefully replaced. It is important to cut as few as possible roots of the trees and ground vegetation in order to reduce the disturbance of the humus layer to a minimum.

The funnel lysimeters are installed by first removing an intact soil core (larger than the diameter of the funnel) down to the required depth using a special auger, and the lysimeters are then placed in a shaft sunk below the removed soil core. The soil core is then carefully replaced. Soil solution is removed from the lysimeters by means of a plastic tube leading down into the collection bottle (for details of the construction, see Derome et al. (1991).

In the case of zero-tension lysimeters the collection vessels are usually located in a pit below the depth of the lysimeter to allow the soil solution to flow freely into the vessels. The collection vessels should be stored in isolated containers to prevent the samples from freezing and warming up.

4.4 Sample collection

It is recommended that wooden walkways be used to access the sampling points in order to minimise soil compaction and damage to the surrounding ground vegetation.

4.4.1 Determination of the soil solution volume

It is recommended to determine the volume of each soil solution sample in the field using graded collection vessels, graded cylinders or a portable balance (weight). If soil solution samples are to be pooled in the field, then the samples from the same sampling depth should be mixed in a suitable plastic container. Before reuse, clean the container to avoid cross-contamination.

4.4.2 Sampling frequency

Ideally, the sampling period should be no longer than two weeks, in order to minimise artefacts due to microbial activity in the collection vessels. The risk of data loss due to contamination should also be considered. It is worse to lose one of relatively few long-term samples than to lose one of many short-term samples. It is recommended to use fortnightly or even weekly sampling. If it is not possible to analyze samples so frequently, for example for financial reasons, pooling of samples to collective samples representing periods of up to one month is allowed. However, one month or four weeks is the maximum period over which samples can be pooled, even in case of insufficient volume of the sample. Pooling should be done by combining the whole samples or by volume weighting in the laboratory. If frequent sampling is not practical, sampling may be carried out monthly or a time interval of every two or three weeks, depending mainly on climate, access to the plot and method used. On plots with other intensive monitoring activities, e.g. deposition, litterfall and soil moisture measurements, soil solution sampling periods should be synchronized as far as possible with these measurements.

Sampling frequency, pooling method and sample volumes should be recorded and submitted.

4.4.3 Protection from spoilage

Protecting the samples in the field from spoilage caused by microbial activity is one of the most important aspects of soil solution sampling. The location of the samples (i.e. belowground with zero-tension lysimeters or aboveground with tension lysimeters) and the length of time that the samples remain in the collection vessel varies depending on the type of lysimeter used and on the length of the sampling period (i.e. continuous or discontinuous sampling). There are a number of ways of ensuring that the samples remain pristine.

Keeping the soil solution in a cool (< +4°C), dark location within the lysimeter system is the recommended means of minimising biological activity. The use of organic or inorganic preservatives is permitted, but should be avoided as far as possible because it may interfere with the chemical analyses. If preservatives or other additives are applied, they should be recorded.

4.4.4 Replacement of collecting vessels

It is preferable not to replace the collecting vessel after each sampling period since it is soil solution from the same lysimeter that is collected each time. This will help to minimise the risk of contamination through human error. However, if there are signs of algal and fungal growth in the vessel, then it should be immediately replaced with a clean, acid-washed vessel. All vessels should be removed and acid-washed in the laboratory at suitable intervals.

Any lysimeter tubing that is lying on the ground surface should be protected against sunlight. It is recommended that this tubing would be replaced each year.

4.4.5 Transport

Transportation to the laboratory should be carried out as quickly as possible using closed boxes containing cold packs. If the transportation distance is long, it is recommended to use express post or a courier service that can guarantee delivery within 24 hours (preferably to arrive at the

laboratory the following morning). Thermal insulated transport boxes should be used for this purpose.

5. Measurements

5.1 Measurements and reporting units

5.1.1 Selected variables

The parameters to be determined on the samples are listed in Table 3 according to whether their determination is mandatory or optional. Although the list includes both mandatory and optional parameters, in practice all the cations and anions that are present in significant amounts in the samples are required for calculating ion balances (see Part XVI: Quality Assurance and Control in Laboratories). The concentrations of Zn and Cu are also important for nutrient cycling studies because they are important micronutrients. It is also strongly recommended to measure additionally Al_{labile} , at least during one monitoring year, to get an idea of the distribution between labile and non-labile aluminium in soil solution.

Table 3: Parameters to be determined on soil solution samples (Mandatory/Optional refers to Level II core plots)

Variable	Reporting Unit	Mandatory/Optional
Sample volume per lysimeter	ml	Mandatory
pH	pH unit	Mandatory
Conductivity	µS/cm	Mandatory
Ca	mg/L	Mandatory
Mg	mg/L	Mandatory
Na	mg/L	Mandatory
K	mg/L	Mandatory
NH4-N	mg N/L	Mandatory
SO4-S	mg S/L	Mandatory
NO3-N	mg N/L	Mandatory
Cl	mg/L	Mandatory
Alkalinity	µmolc/L	Mandatory if pH >5
Total N	mg/L	Mandatory
DOC	mg/L	Mandatory
Altotal	mg/L	Mandatory (if pH <5)
Allabile	mg/L	Optional
Fe	mg/L	Mandatory (if pH <5)
Mn	mg/L	Mandatory (if pH <5)
Ptotal	mg/L	Optional
Zn	µg/L	Optional
Cu	µg/L	Optional
Cr	µg/L	Optional
Ni	µg/L	Optional
Pb	µg/L	Optional
Cd	µg/L	Optional
Si	mg/L	Optional

In case the sample volume obtained is inadequate for determination of all mandatory parameters priority ranking of analysis/parameters is needed. Therefore, each participating country should elaborate a national priority list of determinations. As the required amount of soil solution for a spesific parameter is dependent on the equipment and methods used in each laboratory, it is not possible to produce a general priority list valid for all participating laboratories.

Participating countries and laboratories are free in their selection of analytical methods as long as the analytical work is performed in accordance with the guidelines. Standardised analytical methods and procedure should be used, preferably ISO or EN/CEN methods. Methods suitable for the analysis of soil solution and soil extracts are given in Table 4. Detailed descriptions are given in Annex 4 of Part XIV (Sampling and Analysis of Deposition). Methods that are **not** recommended, since they tend to give poor results in laboratory inter-comparisons, are given at the end of Annex 4 of Part XIV. A list of ISO and EN/CEN methods is given in Annex 5 of Part XIV. The lists of possible methods are not complete, and only include the most frequently used methods. The tables also give some information about any additional pre-treatment necessary for specific analytical methods. More details can be found in the ISO and EN/CEN standards.

Table 4: Recommended soil solution analysis methods

Parameter	Method/Instrument	Additional pre-treatment required	Comments
pH	• Potentiometry		Determined in the laboratory. Two-point calibration must be used.
Conductivity	• Conductimetry at 25°C		Conductivity measurements made in the field can help to give a rough estimate of the quality of the sample and to reject contaminated samples.
Total alkalinity	• Titrimetric determination (Gran, two end-point, titration to pH 4.5 with correction for extra acid)		Mandatory for all samples with pH > 5. One end-point titration without correction should **not** be used
Sulphate	• Ion chromatography (IC) • Spectrophotometry, e. g. the Thorin method or Methyl-thymol-blue method (CFA) • Potentiometric determination • ICP/OES (S_{total})		IC is the recommended method. The use of ICP for soil solution samples requires correction for organic S at high DOC concentrations. Spectrophotometric methods should not be used for coloured samples without correction.
Nitrate	• Ion chromatography (IC) • Spectrophotometry, e.g. azo dye after reduction to nitrite (CFA)		IC is the recommended method. Spectrophotometric methods should not be used for coloured samples without correction or dialysis.

Chloride	• Ion chromatography (IC) • Potentiometric detection (CFA, FIA) • Spectrophotometry, e.g. Hg-thiocyanate method (CFA)		IC is the recommended method.
Total phosphorus (P_{total})	• Spectrophotometry, molybdenum blue method • ICP/OES		Ion chromatography is not recommended due to the high limit of quantification. Spectrophotometry: P_{total} is determined as PO_4 after digestion with strong oxidising agents.
Ammonium	• Spectrophotometry e. g. indophenol method (CFA) or ammonia diffusion cell method (FIA) • Ion chromatography (IC)		IC : high Na concentrations may interfere with the analysis; the limit of quantification is also often too high FIA : filtration and dialysis of the samples is necessary: however, automated FIA systems include this.
Na, K, Mg, Ca	• AAS Flame • AES Flame (only for Na and K) • ICP/OES • Ion chromatography (IC)		Note: differing results are possible depending on the methods used: IC determines ions, AAS and ICP total elements
Al, Mn and heavy metals (e.g. Cu, Cd, Pb, Zn)	• AAS Graphite furnace • ICP/MS • ICP/OES • ICP/OES with ultrasonic nebulizer	The samples are preserved with nitric acid. Pre-concentration of samples may be necessary	Instruments with low quantification limits are necessary due to the low concentrations, Control of blanks and avoidance of contamination is important.

Al labile	• AAS Graphite furnace • ICP/MS • ICP/OES • ICP/OES with ultrasonic nebulizer	Labile Al can be determined by a number of different techniques (Wickstrøm et al. 2000). The simplest technique is to remove this fraction by passing the sample through a cation exchange column. The difference between the Al concentration before and after passage through the column is equal to the labile Al concentration.	The work load on the laboratory can be considerable if labile Al has to be determined on a large number of samples as soon as possible after they arrive at the laboratory. This problem can be reduced by carrying out the determination in two stages: 1) immediate fractionation of Al_{total} using a cation exchange column, and 2) preservation of the two solutions to be analysed for Al with suprapure 65% HNO3, and subsequent determination up to 2-3 weeks after fractionation (Derome et al. 1998).
Total nitrogen (N_{total})	• Elementary analysis • Spectrophotometry after oxidation to nitrate using persulphate in borate buffer solution or UV-digestion • total N analyser with chemiluminescence detection		
Organic nitrogen	• N_{total} analysis, and nitrate and ammonium analysis		Organic N = N_{total} – (NO_3-N + NH_4-N + NO_2-N (if present))
Dissolved org. carbon (DOC)	• Infrared spectroscopy after oxidation to CO_2 • Flame ionisation after reduction to CH_4 • UV absorbance (254 nm)	Use glass fibre membrane filters (not cellulose acetate/nitrate)	UV absorbance is not the optimal method and should only be used by laboratories without TOC analyser

5.1.2 Analysis

The volume of work necessary in order to reach an acceptable level of analytical quality according to ISO and EN norms is quite important, especially during the first 1-3 years of monitoring activity. The volume of work depends especially on the current quality level of each laboratory. The chapters below try to guide as well as possible the ICP Forests laboratories in their work in concentrating on the most essential information taken from a variety of ISO and EN/CEN guidelines.

5.1.3 Reception at the laboratory, initial checks and temporary storage

Upon reception of the samples at the laboratory, the delivery should be checked immediately, and discrepancies noted, for the following:

- the accompanying forms are included in the delivery

- the number of sample bottles corresponds to that stated on the accompanying forms
- the bottles are properly closed and no leakage has occurred
- damage to the box or bottles
- presence of visible contamination
- initial pH and conductivity check for indications of contamination
- registration in the laboratory sample book

The samples (wet-only and bulk deposition, throughfall or stemflow) should be stored (protected from light at max. +4ºC) in such a manner that there will be minimal changes in the chemical parameters to be determined before the samples are analysed (any changes in concentration should be smaller than the precision of the analyses). If sub-samples are taken for pH and conductivity measurements prior to pre-treatment, then these sub-samples should be stored in the same way.

The samples should be pre-treated and analysed as soon as possible. Excessively long storage times (e.g. > 5 days) should be avoided in order to prevent chemical changes caused by microbial activity in the samples.

5.1.4 Pre-treatment of the samples

A separate sub-sample should be taken, prior to filtration, for the determination of pH and conductivity (as stated in ISO 10523 and ISO 7888). However, this is done only if the volume of the sample is sufficient for the other chemical analyses. This sub-sample should not be used for any of the other analyses. Many types of pH electrode release K^+ into the sample and therefore a separate aliquot of the sample should be used to avoid contamination. Similarly, if electrical conductivity is measured on the same aliquot of sample, then this should be done before pH measurement.

The sample should be filtered through a 0.45 µm membrane filter in order to remove any solid material and to stabilise the sample for the subsequent analyses. Filtration considerably decreases the possibility of microbially-induced changes (e.g. nitrogen transformations) in the samples as it removes all micro-organisms (except viruses). Thus, the stability and lifetime of the samples are increased. The make/type of membrane filter used should be tested beforehand in order to ensure that there is no release of soluble or particulate, carbon-containing material/compounds from the membrane. Filter paper should not be used owing to possible contamination by NH_4 and carbon. Many types of membrane release small amounts of particulate material (containing carbon) when first used, and this will affect the DOC determination. However, this problem can be avoided by "rinsing" the membrane in the membrane holder with a known volume of pure water or (preferably) sample prior to filtration of the sample proper. Each laboratory should determine the minimum amount of rinsing water required. Tests on a number of membrane types have shown that ca. 50 ml is sufficient.

After filtration, sub-samples should be taken to be used for the determination of metals by e.g. AAS or ICP techniques. These sub-samples should be acidified, e.g. with suprapure 65% HNO_3 to pH < 2 in order to avoid the absorption of metal cations on the inside surface of plastic bottles (if used), as well as possible changes caused by microbial activity. The preserved samples can be stored for several weeks prior to analysis by AAS, ICP etc.

Another subsample should be stored at +4°C and analysed as soon as possible for all other parameters. The maximum storage times for sub-samples for the individual analyses should be determined by the individual laboratories. The sub-samples should not be frozen, as there is evidence in the literature to show that this has an effect on the samples and analysis results. pH

measurement should also be repeated at this stage if it is required for determining the ion balance of the sample.

The use of preservatives in the laboratory (chloroform, formaldehyde, mercury compounds, iodine etc.) is not recommended owing to occupational health hazards, the danger of damaging laboratory equipment (e.g. ion chromatograph columns), and possible interference in certain analyses.

5.2 Quality Assurance and Quality Control

In a period in which the general demand for higher quality assurance is growing, it is of high importance that within the expert panel soil and soil solution the participating organizations maintain a definable and acceptable level, in both field sampling and laboratory analysis. This level should allow the production of data on a European level with known analytical errors and ranges, as this will also be the case for field methods. Thus the data can be transmitted to any user with error ranges allowing a more optimal use for all types of calculations on the European level.

5.2.1 Quality Assurance in the field

In order to obtain representative samples, the location of the lysimeters has to be carried out and documented carefully taking into account other measuring activities implemented in the same plot. Distance to nearest throughfall and litterfall collector, soil moisture probes, as well as to the nearest tree base, has to be reported in the Data Accompanying Report Form (DAR).

5.2.2 Quality Assurance in the laboratory

see Part XVI: Quality Assurance for Laboratories

5.2.2.1 Plausibility limits and numerical precision

Each country should develop its own plausible ranges by determining the 2.5 - 97.5 percentile range for each parameter under study. In order to get feasible values for data validation and laboratory quality checking the ranges have to be calculated on the basis of the country-specific data.

Table 5: As an example of plausible ranges (based on 2.5 - 97.5 percentile range) values calculated from the whole European soil solution data set.

Parameter	Unit	Plausible range	
		Lower limit	Upper limit
Electrical conductivity	µS/cm 25°C	10	500
pH	-	3.5	8.5
Alkalinity	$\mu mol_c/l$	< LOQ (0)	7000
DOC	mg/l	< LOQ (1)	85
Na	mg/l	< LOQ (0.2)	22
K	mg/l	< LOQ (0.05)	8.5
Ca	mg/l	< LOQ (0.12)	75
Mg	mg/l	< LOQ (0.05)	15
Al_{total}	mg/l	< LOQ (0.02)	15
Al_{labile}	mg/l	< LOQ (0)	9
Fe	mg/l	< LOQ (0)	1.2
Mn	mg/l	< LOQ (0)	1.9
P_{total}	mg/l	< LOQ (0)	0.6

NO_3-N	mg/l	< LOQ (0)	15
NH_4-N	mg/l	< LOQ (0)	3.0
SO_4-S	mg/l	< LOQ (0.2)	25
Cl	mg/l	< LOQ (0.16)	40
Zn	µg/l	< LOQ (0.03)	680
Cu	µg/l	< LOQ (0)	130
Cr	µg/l	< LOQ (0)	10
Ni	µg/l	< LOQ (0.26)	45
Pb	µg/l	< LOQ (0)	100
Cd	µg/l	< LOQ (0)	8.5
Si	mg/l	< LOQ (0.2)	10

5.2.2.2 Data completeness

Table 3 outlines for all the physical and chemical soil solution parameters whether and under which conditions they are mandatory or optional to report. When a country/federal state decides to report optional parameters, they should also fulfil the data quality requirements.

5.2.2.3 Data quality objectives or tolerable limits

see Part XVI: Quality Assurance for Laboratories, Chapter 3.4.1.2.1

All reported values should have been measured according to the methods described in Annex 3.

5.2.2.4 Data quality limits

The laboratory results are considered of sufficient quality when the laboratory received a qualification for the concerning parameter(s) after participation in the Interlaboratory Comparisons (see Part XVI: Quality Assurance for Laboratories, Chapter 3.4.1.2.1).

In the validation procedure of the soil solution data attention should be given to a number of factors that influence the results directly or indirectly. For example the sample volume is an important factor, because an inverse relationship exists between ion concentrations and sample volumes. Therefore it is also interesting to look at the relationship between the amount of precipitation and ion concentrations. Long dry periods may stimulate the decomposition of organic matter, which may lead to elevated concentrations of certain ions, in particular in the B-horizon. Precipitation volume and sample volume should be included as covariables when statistical analyses are performed.

Another point of attention is the sample composition in the case that soil solution samples are pooled before analysis (which will probably be done by several countries, because analysing individual samples is too expensive). A pooled sample should be composed of sufficient subsamples of the same depth because the missing of samples from lysimeters located on places with a different soil composition could clearly influence mean ion concentrations. Therefore it is recommended to include the number of lysimeters and the number of locations in the plot that are represented in the sample as covariables in statistical analyses.

6. Data handling

6.1 Data submission procedures and forms

Forms for data submission and explanatory items are found on the ICP Forests web page, at http://www.icp-forests.org/Manual.htm. Forms to be used are PSS (reduced plotfile), SSM (mandatory soil solution parameters), SSO (optional soil solution parameters) and DAR (data accompanying report).

6.2 Data validation

Data checks should be done as soon as results from the laboratory analyses are available. Data validation and quality assurance should be applied in accordance with the guidelines for QA/QC procedures in the laboratory that are given in the Part XVI of the Manual: Quality Assurance for Laboratories.

6.3 Transmission to co-ordinating centres

All validated data should be sent yearly to each national focal centre and to the European central data storage facility at the ICP Forests Programme Coordinating Centre. Detailed time scheduled is provided by the relevant bodies.

6.4 Data processing guidelines

Caution should be taken when interpreting soil solution data from recently installed lysimeters as chemical reactions with the porous cup or disturbance of the soil due to installation may affect the results. The samples from the first 2 or 3 sampling events after installation should therefore be discarded. In the case of funnel lysimeters, a period of one year for the roots to grow back is required. In long-term monitoring, however, this is not a problem.

Because soil solution may be influenced by a lot of parameters (deposition, meteorology, soil context, tree species and age, forest health, harvesting…) data series should be interpreted plot by plot.

6.4.1 Calculation of leaching fluxes

Soil water fluxes are required for determining input-output budgets of ions in the monitoring plots. Since soil water fluxes usually cannot be measured directly, they have to be estimated indirectly using models (Kutílek & Nielsen 1994), see also Part IX of the Manual: Meteorological Measurements.

For any substance, leaching flux is calculated by multiplying its concentration in soil solution with soil water flux estimated at the same depth and time interval.

Estimated water fluxes can also be used as weights in calculation of annual means from periodic soil solution concentrations, in the same way as for annual deposition.

6.5 Data reporting

Data should be accompanied by a "Data accompanying report" Form (DAR) including all information requested by the European central data storage facility. The DAR should include all details on sampling and analytical procedures in a standardised way. In addition, irregularities in sampling and analytical procedure, estimated values and encountered errors in the validation, should be documented. Missing values and values below the quantification limit (not the detection limit) should be clearly coded. Definitions of the quantification and detection limits can be found in Section 3.2.3 of the submanual on Quality Assurance and Quality Control in Laboratories. General remarks for data reporting are also given in the Forms and Explanatory Items of the respective monitoring year.

7. References

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8. Annexes

Annex 1. The soil water fractions sampled by zero-tension lysimetry, tension lysimetry and centrifuge drainage.

Annex 2. Materials used for the construction of tension soil water samplers.

Annex 3. Overview of analytical EN/ISO methods for different parameters in water, soil or plant samples and extracts and digestion solutions.

Annex 1

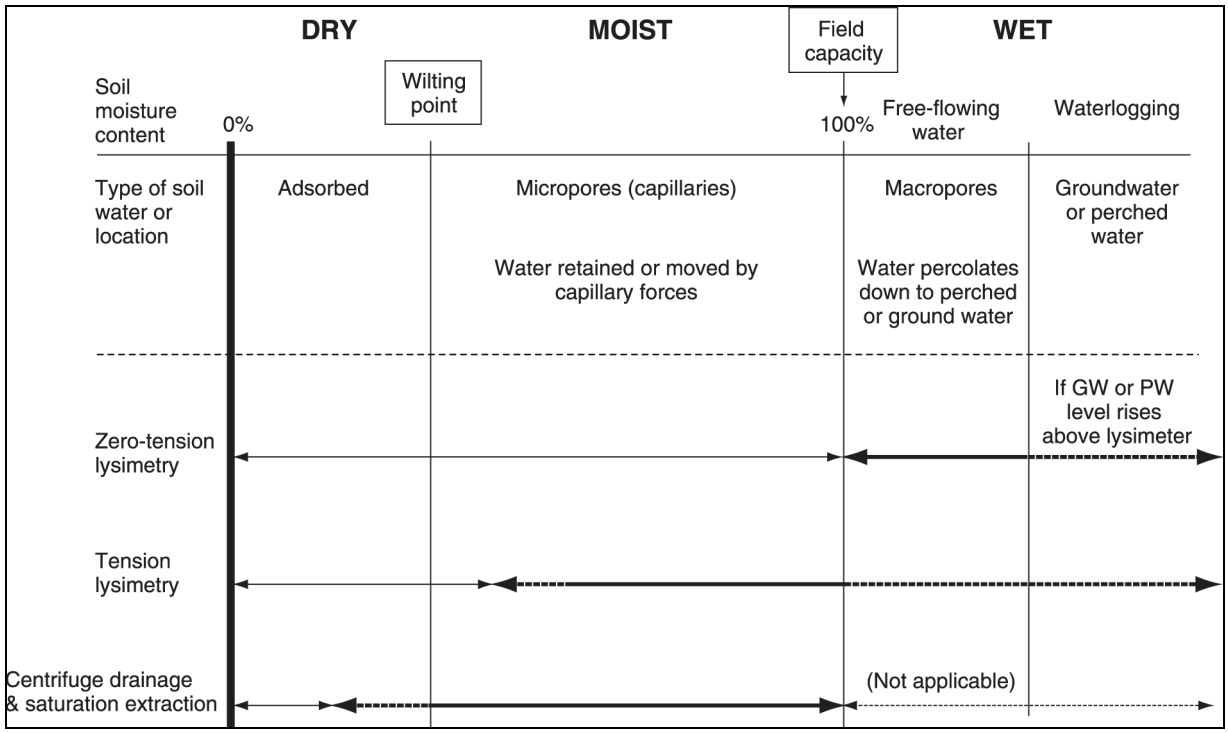

Figure A1-1: The soil water fractions sampled by zero-tension lysimetry, tension lysimetry and centrifuge drainage (thick lines). The thin lines indicate the fractions that cannot be sampled. The actual fractions sampled by tension lysimetry can vary depending on the size of the vacuum applied and the moisture content of the soil during sampling (dotted lines).

Annex 2

Table A2-1: Materials used for the construction of tension soil water samplers.

Material	Type	Special properties	Disadvantages
Ceramic	P 80 Czeratzki Alundum Soilmoisture	cheap, widely used, well known	retains P, may weather/ release ions (e.g. Al, Si), relatively fragile, high exchange capacity
Teflon	Morrison Prenart	chemically inert, easy to install, robust, adjustable to pore size according to soil type	expensive, may release low Ca, may absorb heavy metals
Glass	Fritted Sintered	cheap	fragile, adsorption/ desorption may release Na, Si
Nylon	Filter	low ion exchange capacity	relatively fragile, may release N, C and S compounds, expensive
Polyvinylidene fluoride	Filter	low ion exchange capacity	relatively fragile, expensive, some material eaten by animals
Plastic	Filter Porous Supralene	no adsorption/desorption	some retain Al

Annex 3

Table A3-1: Overview of analytical EN/ISO methods for different parameters in water, soil or plant samples and extracts and digestion solutions.

Element, ion	Matrix: W=water S =soil P=plant E=salt extract DS=digestion solution	Method	Norm/Standard
Alkalinity		Titrimetric determination	ISO 9963-1
			ISO 9963-2
Al	S	XRF	EN 15309
	W, E, DS	AAS-Flame	EN ISO 12020
	W, E, DS	ICP-OES	EN ISO 11885
	W, E, DS	ICP-MS	EN ISO 17294-2
As	S	XRF	EN 15309
	W, E, DS	ICP-OES	EN ISO 11885
	W, E, DS	ICP-MS	EN ISO 17294-2
	W, E, DS	AAS-hydride technique	EN ISO 11969
	W, E, DS	AAS- graphit furnace	EN ISO 15586
Ba	S	XRF	EN 15309
	W, E, DS	ICP-OES	EN ISO 11885
	W, E, DS	ICP-MS	EN ISO 17294-2
B	W, E, DS	ICP-MS	EN ISO 17294-2
	W, E, DS	ICP-OES	EN ISO 11885
Cd	S	XRF	EN 15309
	W, E, DS	AAS- graphit furnace	EN ISO 5961
	W, E, DS	AAS- graphit furnace	EN ISO 15586
	W, E, DS	ICP-OES	EN ISO 11885
	W, E, DS	ICP-MS	EN ISO 17294-2
Ca	S	XRF	EN 15309
	W, E, DS	AAS-Flame	EN ISO 7980
	W, E, DS	ICP-OES	EN ISO 11885
	W, E, DS	ICP-MS	EN ISO 17294-2
Cl_{tot}	S	XRF	EN 15309
Cl-Cl^-	W	IC	EN ISO 10304-1, 2 u.-4
	W	Cont flow photometry, potentiometry	EN ISO 15682
Cr	S	XRF	EN 15309
	W, E, DS	AAS- graphit furnace	EN 1233
	W, E, DS	AAS- graphit furnace	EN ISO 15586
	W, E, DS	ICP-OES	EN ISO 11885
	W, E, DS	ICP-MS	EN ISO 17294-2
	W, E, DS	AAS-Flame	DIN ISO 11047
Co	S	XRF	EN 15309
	W, E, DS	AAS- graphit furnace	EN ISO 15586
	W, E, DS	ICP-OES	EN ISO 11885
	W, E, DS	ICP-MS	EN ISO 17294-2

	W, E, DS	AAS-Flame	DIN ISO 11047
Fe	S	XRF	EN 15309
	W, E, DS	ICP-OES	EN ISO 11885
K	S	XRF	EN 15309
	W, E, DS	AAS-Flame	ISO 9964-2
	W, E, DS	AES-Flame	ISO 9964-3
	W, E, DS	ICP-OES	EN ISO 11885
	W	IC	EN ISO 14911
	W, E, DS	ICP-MS	EN ISO 17294-2
C_{tot}	S, P	elemental analysis	ISO 10694
	W, E	elemental analysis	EN 1484
	W, E	elemental analysis	ISO 8245
$C\text{-}C_{org}$	S, P	elemental analysis	ISO 10694
C-DOC	W, E	elemental analysis	EN 1484
	W, E	elemental analysis	ISO 8245
$C\text{-}CO_3$	S, P	elemental analysis	ISO 10694
	S, P	volumetric analysis	ISO 10693
	W, E	elemental analysis	EN 1484
	W, E	elemental analysis	ISO 8245
Cu	S	XRF	EN 15309
	W, E, DS	AAS- graphit furnace	EN ISO 15586
	W, E, DS	ICP-OES	EN ISO 11885
	W, E, DS	ICP-MS	EN ISO 17294-2
	W, E, DS	AAS-Flame	DIN ISO 11047
Mg	S	XRF	EN 15309
	W, E, DS	AAS-Flame	EN ISO 7980
	W, E, DS	ICP-OES	EN ISO 11885
	W, E, DS	ICP-MS	EN ISO 17294-2
Mn	S	XRF	EN 15309
	W, E, DS	ICP-OES	EN ISO 11885
	W, E, DS	ICP-MS	EN ISO 17294-2
	W, E, DS	AAS-Flame	DIN ISO 11047
Mo	S	XRF	EN 15309
	W, E, DS	ICP-OES	EN ISO 11885
	W, E, DS	ICP-MS	EN ISO 17294-2
	W, E, DS	AAS- graphit furnace	EN ISO 15586
Na	S	XRF	EN 15309
	W, E, DS	AAS-Flame	ISO 9964-1 + 3
	W, E, DS	ICP-OES	EN ISO 11885
	W, E, DS	ICP-MS	EN ISO 17294-2
	W	IC	EN ISO 14911
Ni	S	XRF	EN 15309
	W, E, DS	AAS- graphit furnace	EN ISO 15586
	W, E, DS	ICP-OES	EN ISO 11885
	W, E, DS	ICP-MS	EN ISO 17294-2
	W, E, DS	AAS-Flame	DIN ISO 11047
P_{tot}	S	XRF	EN 15309
	W, E, DS	ICP-OES	EN ISO 11885
	W, E	photometry	EN ISO 15681-1 u. 2
	W, E	cont. flow photometry	EN ISO 6878
	W, E, DS	ICP-MS	EN ISO 17294-2
$P\text{-}PO_4$	W	IC	EN ISO 10304-1 u. 2

	W, E	photometry	EN ISO 15681-1 u. 2
	W, E	cont. flow photometry	EN ISO 6878
Pb	S	XRF	EN 15309
	W, E, DS	AAS- graphit furnace	EN ISO 15586
	W, E, DS	ICP-OES	EN ISO 11885
	W, E, DS	ICP-MS	EN ISO 17294-2
	DS	AAS-flame + graphit furnace	ISO 11047
Hg	W, DS	AAS-hydride technique	EN 1483
	W, DS	AAS-hydride technique	ISO 16772
	W, E, DS	atomic fluorescence spectrometry	EN 13506
	W	atomic fluorescence spectrometry	EN ISO 17852
S_{tot}	S	XRF	EN 15309
	W, E, DS	ICP-OES	EN ISO 11885
	S, P	elemental analysis	ISO 15178
S-SO_4	W	IC	DIN EN ISO 10304-1 + 2
	W	ICP-OES	EN ISO 11885 (only with correction of S org.)
Si_{tot}	S	XRF	EN 15309
	W, E, DS	ICP-OES	EN ISO 11885
Si-SiO_4	W	photometry	EN ISO 16264
N_{tot}	P, S	elemental analysis	ISO 13878
	W, E, DS	chemiluminescence	EN 12260
	W, E, DS	photometry	ISO 14255
	W, E, DS	photometry	ISO 11905-1
	W, E, DS	chemiluminescence	ISO 11905-2
N-NH_4	W	IC	EN ISO 1491
	W	photometry	EN ISO 11732
	W	photometry	ISO 7150-1 + 2
N-NO_3	W	IC	EN ISO 10304-1 + 2
	W	photometry	EN ISO 13395
	W, E	photometry	ISO 14255
Zn	S	XRF	EN 15309
	W, E, DS	ICP-OES	EN ISO 11885
	W, E, DS	ICP-MS	EN ISO 17294-2
	W, E, DS	AAS- graphit furnace	ISO 11047
pH	W, E	potentiometry	ISO 10523
	W, E	potentiometry	ISO 10390
Cond.	W	conductivity	EN 27888
	W	conductivity	ISO 11265