



**International
Standard**

ISO 22036

**Environmental solid matrices —
Determination of elements using
inductively coupled plasma optical
emission spectrometry (ICP-OES)**

Matrices solides environnementales — Dosage d'éléments par spectroscopie d'émission optique avec plasma induit par haute fréquence (ICP-OES)

**Second edition
2024-01**

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Foreword

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

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO document should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

ISO draws attention to the possibility that the implementation of this document may involve the use of (a) patent(s). ISO takes no position concerning the evidence, validity or applicability of any claimed patent rights in respect thereof. As of the date of publication of this document, ISO had not received notice of (a) patent(s) which may be required to implement this document. However, implementers are cautioned that this may not represent the latest information, which may be obtained from the patent database available at www.iso.org/patents. ISO shall not be held responsible for identifying any or all such patent rights.

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 190, *Soil quality*, Subcommittee SC 3, *Chemical and physical characterization*, in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 444, *Environmental characterization of solid matrices*, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This second edition cancels and replaces the first edition (ISO 22036:2008), which has been technically revised.

The main changes are as follows:

- the content of ISO 22036:2008 and EN 16170:2017 has been merged;
- the Scope has been widened to include treated biowaste, waste, sludge and sediment;
- the document has been developed parallel with CEN according to the Vienna Agreement;
- applicable digestion and extraction methods have been updated;
- the text has been editorially revised.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

This document is applicable and validated for several types of matrices as indicated in [Table 1](#) (see [Annex A](#) for the results of validation).

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

Matrix	Materials used for validation
Sludge	Municipal sludge Industrial sludge Sludge from electronic industry Ink waste sludge Sewage sludge
Biowaste	Compost Composted sludge
Soil	Agricultural soil Sludge amended soils
Waste	City waste incineration fly ash ("oxidised" matrix) City waste incineration bottom ash ("silicate" matrix) Ink waste sludge (organic matrix) Electronic industry sludge ("metallic" matrix) BCR 146R (sewage sludge) BCR 176 (city waste incineration ash)
Sediments	ISE 859 (Sediment from de Bilt / Netherlands)

The choice of calibration method depends on the extractant and can be adapted to the extractant concentration.

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Environmental solid matrices — Determination of elements using inductively coupled plasma optical emission spectrometry (ICP-OES)

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

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

1 Scope

This document specifies a method for the determination of the following elements in aqua regia, nitric acid or mixture of hydrochloric (HCl), nitric (HNO₃) and tetrafluoroboric (HBF₄)/hydrofluoric (HF) acid digests of soil, treated biowaste, waste, sludge and sediment:

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

The method is also applicable to other extracts or digests originating from, for example, DTPA extraction, fusion methods or total digestion methods, provided the user has verified the applicability.

The method has been validated for the elements given in [Table A.1](#) (sludge), [Table A.2](#) (compost) and [Table A.3](#) (soil). The method is applicable for other solid matrices and other elements as listed above, provided the user has verified the applicability.

This method is also applicable for the determination of major, minor and trace elements in aqua regia and nitric acid digests and in eluates of construction products (EN 17200^[22]).

NOTE Construction products include e.g. mineral-based products; bituminous products; metals; wood-based products; plastics and rubbers; sealants and adhesives; paints and coatings.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

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

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at <https://www.iso.org/obp>

— IEC Electropedia: available at <https://www.electropedia.org/>

- 3.1
blank calibration solution**
solution prepared in the same way as the *calibration solution* (3.3) but leaving out the analytes
- 3.2
blank test solution**
solution prepared in the same way as the *test sample solution* (3.10) but omitting the test portion
- 3.3
calibration solution**
solution used to calibrate the instrument, prepared from *stock solutions* (3.8) by adding acids, buffer, reference element and salts as needed
- 3.4
instrumental detection limit**
lowest concentration that can be detected with a defined statistical probability using a clean instrument and a clean solution
- 3.5
laboratory sample**
sample intended for laboratory inspection or testing
[SOURCE: ISO 11074:2015, 4.3.7, modified — Notes to entry have been removed.]
- 3.6
linearity**
straight-line relationship between the mean result of measurement and the quantity (concentration) of the analyte
- 3.7
method detection limit
MDL**
lowest concentration that can be detected using a specific analytical method with a defined statistical probability for defined maximum matrix element concentrations
- 3.8
stock solution**
solution with accurately known analyte concentration(s), prepared from pure chemicals
- 3.9
test sample**
portion of material, resulting from the *laboratory sample* (3.5) by means of an appropriate method of sample pretreatment, and having the size (volume/mass) necessary for the desired testing or analysis
[SOURCE: ISO 11074:2015, 4.3.16]
- 3.10
test sample solution**
solution prepared after extraction or digestion of the *test sample* (3.9) according to appropriate specifications

4 Principle

Inductively coupled plasma optical emission spectrometry (ICP-OES) can be used to determine elements in solution. The solution is dispersed by a suitable nebulizer; and the resulting aerosol is transported into the plasma. In a radio-frequency inductively coupled plasma, the solvent is evaporated; the dried salts are then vaporized, dissociated, atomized and ionized. The atoms or ions are excited thermally; and the number of photons emitted during transition to a lower energy level are measured with optical emission spectrometry. The spectra are dispersed by a grating spectrometer; and the intensities of the emission lines are monitored by photosensitive devices. The identification of the element takes place by means of the wavelength of the

radiation (energy of photons), while the concentration of the element is proportional to the intensity of the radiation (number of photons). The ICP-OES method can be used to perform multi-element determinations using an optical system.

[Annex B](#) shows examples of recommended wavelengths and detection limits for one particular instrument. Data given are valid for a synthetic soil matrix (500 mg/l Al, Ca, Fe in 30 ml aqua regia filled up to 100 ml with deionized water) with an optimized instrument. Using other instruments can lead to different detection limits. Adoption of other wavelengths is possible.

This document refers specifically to the use of ICP-OES. Users of this document are advised to operate their laboratories to accepted quality control procedures. Certified reference materials (CRM) should be used to establish the amounts of the relevant elements in in-house reference materials. The latter can be used for routine quality control of the procedures given in this document.

Results shall be established with control charts, for each element, within the laboratory. No result shall be accepted which falls outside an agreed limit. Quality control procedures based on widely accepted statistical techniques shall be used to establish such limits, that these are stable and that no long-term drift is occurring. CRM should be used regularly to maintain the integrity of the in-house reference materials and, thereby, the quality control system.

5 Interferences

5.1 General

The accurate and precise determination of trace element concentrations requires the correction of signal contributions not caused by the analyte of interest ('interferences'). Such interferences can result in both lower and higher results and thus shall be accounted for during analytical method development. [5.2](#) and [5.3](#) characterize possible interferences in ICP-OES and discuss procedures to detect and remedy their influence on the analytical result. Interferences are classified either as spectral or non-spectral.

5.2 Spectral interferences

Spectral interferences result in a change of the analyte instrumental signal, from a (partial) overlap of the analyte emission by emission lines or spectra of other sample constituents (direct spectral interference, inter-element or molecular (band) interference), by broad-band, continuous spectra, for example, from recombination of sample constituents, or by spectrally overlapping signals resulting from stray light or spectrally non-resolved molecular emissions.

Spectral interferences result in increased background signals that can obscure a weak analyte emission line completely. Accordingly, using spectrally interfered analyte emission lines can reduce the analytical capabilities and ultimately produce wrong results. Selecting a non-interfering analyte emission line, if available, can normally reduce or avoid deleterious spectral interference effects.

Broad-band spectral background emissions and stray light can normally be accounted for by subtraction of the background signal measured in immediate vicinity to the analyte emission line and extrapolated to the analyte wavelength position ('off-peak' background correction).

Spectral scans of samples compared with single element solutions in the analyte regions may indicate when alternate wavelengths are desirable because of severe spectral interference.

Such measurements also show if the background signal is best determined based on the interpolation of a measurement on one side or on both sides of the analytical emission line or peak. The position selected for the background-intensity measurement, on one or both sides of the analytical line, is determined by the complexity of the spectrum adjacent to the analyte line. The position used should be as free as possible from spectral interference, and should reflect the same change in background intensity as occurs at the analyte wavelength measured.

For routine measurements, background measurement positions with no spectral off-peak interferences (as e.g. inter-element or molecular band interferences) shall be chosen, ensuring that the background

signal measured off-peak is not interfered and allows an accurate background signal determination from its extrapolation to the analytical line wavelength position. If no interference-free off-peak background measurement position can be found, a suitable correction shall be applied to allow background signal determination from extrapolation of an off-peak background signal measurement.

Another possibility to avoid spectral interferences is the use of alternative emission wavelengths for the analyte of interest, if available. Finally, a correction of spectral interferences can also be performed by (typically multi-dimensional) mathematical spectral modelling approaches or (often iterative) correction formulae accounting for inter-element effects. To achieve accurate results with systems employing inter-element correction formulae, analyte and interfering elements shall be measured simultaneously. Spectral interferences that remain undetected and uncorrected lead to wrong positive results for the interfered analyte(s) in the sample under investigation. [Table B.1](#) lists recommended and alternative wavelengths of elements.

Modern ICP-OES systems are often equipped with multi-dimensional mathematical spectral modelling algorithms pre-set by the manufacturer for interference correction. Such approaches typically do not require the selection of dedicated wavelength positions for background signal measurements during method development, but instead utilize complete wavelength regions around the analyte emission line for modelling and correction. As with all interference correction techniques, the use of multi-dimensional spectral modelling algorithms requires a careful verification of their effectiveness and of the resulting accuracy, in the sample matrix of interest, to avoid wrong analytical results. This can, for example, be done by analysing matrix-matched samples of known analyte concentration(s), advisably in the range expected for the real samples or required from the analytical task at hand, e.g. the control of limiting values.

5.3 Non-spectral interferences

Apart from the spectral interferences described in [5.2](#), non-spectral interferences can also occur, reducing the analytical accuracy and precision if undetected and uncorrected for. Non-spectral interferences can be subdivided into physical, chemical and memory interferences.

Physical interferences are effects that occur in conjunction with sample transport and nebulization. Differences in sample viscosity or surface tension can result in significant interference effects, especially for samples with high concentrations of acids or dissolved solids. Physical interferences can be reduced by sample dilution, by adjustment of acid concentrations among the samples, by matrix matching or using suitable sample introduction equipment, e.g. 'slurry nebulizers' for samples with high TDS (total dissolved solids). Physical interferences can be corrected for by the application of suitable reference element within the analytical methodology.

The formation of molecular compounds, together with sample evaporation and ionization effects are all examples of chemical interferences. Excluding the easily ionizable elements effect (EIEE) relevant under axial plasma observation, chemical interferences typically do not occur significantly in ICP-OES techniques. However, should chemical interferences still arise, they can normally be minimized by a careful choice of the plasma parameters (e.g. RF power, observation height, nebulizer gas flow rate, 'robust plasma'), by suitably buffering the samples, by matrix-matching or by employing the method of standard additions. In general, chemical interferences are highly dependent on the type of sample matrix and the analyte element(s) of interest.

If large amounts of easily ionizable elements, for example, alkaline or earth-alkaline elements (I. and II. Group of the periodic table), reach the ICP, the plasma ionization equilibrium, i.e. the ratio of neutral atom to ion and electron number densities, can shift, resulting in a changed emission line excitation probability for neutral or ionized analyte atoms. Ultimately, this results in different analyte signals for the same amount of analyte in samples containing different amounts of easily ionizable elements. Especially for the easily ionizable elements themselves, the EIEE leads to substantial calibration function non-linearities that can result in significant analytical errors.

Since the EIEE is a plasma effect, its occurrence is independent from the plasma-viewing orientation (radially or axially) employed. However, its effect on the analytical result is dependent on the plasma-viewing orientation. For an axially viewed plasma, all processes along the analytical channel viewed contribute to the analytical signal; accordingly, the EIEE influence on the measurement results is relevant and shall be accounted and/or corrected for in any case. Possibilities to do so include the use of an ionization buffer

(e.g. CsCl) added to all samples, or to employ radial plasma view for the elements affected. For radial view, where only a small plasma region contributes to the measurement signal, the influence of the EIEE on the analytical results can usually be ignored. However, radially viewing the plasma often also results in lower measurement sensitivities. Accordingly, such trade-offs in figures of merit shall be accounted for during any analytical method development.

Memory-Interferences (“memory effects”) occur when the analyte signals of the current sample are influenced (usually resulting in positive deviations from the correct value) by the sample(s) measured before. Memory effects can result from sample deposits or accumulation in pump tubing, nebulizer, spray chamber or plasma torch. Occurrence of memory effects is element-specific and often can be reduced by rinsing the complete system thoroughly with a suitable clean rinse solution before the introduction of a new sample. Possible memory effects during analytical measurements shall be assessed and reduced, e.g. by an inter-sample rinse with a clean rinse solution for an appropriate time. The required rinse time is element-specific and shall be determined during method development, usually by defining a maximum tolerable background signal resulting from samples measured before, for each analyte affected by memory interferences.

6 Reagents

For the determination of elements at trace and ultra-trace level, the reagents shall be of adequate purity. The concentration of the analyte or interfering substances in the reagents and the water should be negligible compared to the lowest concentration to be determined.

6.1 Water, with an electrical conductivity less than $0,1 \text{ mS m}^{-1}$ (equivalent to resistivity greater than $0,01 \text{ M}\Omega \text{ m}$ at $25 \text{ }^\circ\text{C}$). The water used should be obtained from a purification system that delivers ultrapure water having a resistivity greater than $0,18 \text{ M}\Omega \text{ m}$ (usually expressed by manufacturers of water purification systems as $18 \text{ M}\Omega \text{ cm}$). For all sample preparations and dilutions.

6.2 Nitric acid, HNO_3 , e.g. $\rho(\text{HNO}_3) = 1,4 \text{ g/ml}$, $c(\text{HNO}_3) \approx 15 \text{ mol/l}$, $w(\text{HNO}_3) \approx 65 \text{ } \%$ (m/m) to $70 \text{ } \%$ (m/m).

6.3 Hydrochloric acid, HCl , e.g. $\rho(\text{HCl}) = 1,18 \text{ g/ml}$, $c(\text{HCl}) \approx 12 \text{ mol/l}$, $w(\text{HCl}) \approx 32 \text{ } \%$ (m/m) to $37 \text{ } \%$ (m/m).

6.4 Tetrafluoroboric acid (HBF_4), $c(\text{HBF}_4) \approx 6 \text{ mol/l}$, $w(\text{HBF}_4) \approx 38 \text{ } \%$ (m/m) to $48 \text{ } \%$ (m/m).

6.5 Hydrofluoric acid (HF), $c(\text{HF}) \approx 23 \text{ mol/l}$, $w(\text{HF}) \approx 40 \text{ } \%$ (m/m) to $45 \text{ } \%$ (m/m).

6.6 Boric acid ($\text{B}(\text{OH})_3$), solid.

NOTE Boric acid can be used to mask the fluoride ions. However, there is a risk of incorrect analysis results due to contaminated boric acid.

6.7 Boric acid ($\text{B}(\text{OH})_3$) solution, e.g. $4 \text{ } \%$ (m/m) solution

Dissolve 40 g of boric acid (6.6) in 1 l of water (6.1).

6.8 Single element standard stock solutions

For example, Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Ho, Hg, In, Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nd, Ni, P, Pb, Pd, Pr, Pt, Rh, Ru, S, Sb, Sc, Se, Si, Sm, Sn, Sr, Ta, Tb, Te, Th, Tm, Ti, Tl, V, W, Y, Yb, Zn, Zr, $\rho(\text{element}) = 1 \text{ 000 mg/l}$ each.

Both single element standard stock solutions and multi element standard stock solutions with adequate specification stating the acid used and the preparation technique are commercially available. Single-element standard stock solutions can be made from high purity metals.

For stability of the solutions, refer to the manufacturer guarantee statement.

6.9 Multi-element standard stock solutions

6.9.1 General

Depending on the scope, different multi-element standard stock solutions may be necessary. In general, when combining multi-element standard solutions, their chemical compatibility and the possible hydrolysis of the components shall be regarded. Care shall be taken to prevent chemical reactions (e.g. precipitation).

The multi-element standard stock solutions are considered to be stable for several months if stored in the dark. This does not apply to multi-element standard stock solutions that are prone to hydrolysis, in particular solutions of Bi, Mo, Sn, Sb, Te, W, and Zr.

6.9.2 Multi-element standard stock solution A

This solution at the mg/l level can contain the following elements:

Al, As, B, Ba, Be, Bi, Cd, Co, Cr, Cu, Fe, Ga, In, Li, Mn, Ni, Pb, Se, Sr, Te, Tl, U, V, Zn.

Use nitric acid (6.2) for stabilisation of multi-element standard stock solution A.

6.9.3 Multi-element standard stock solution B

This solution at the mg/l level can contain the following elements:

Ge, Mo, Sb, Si, Sn, Ti, W, Zr, P, S.

Use hydrochloric acid (6.3) for stabilisation of multi-element standard stock solution B.

Other elements of interest can be added to the standard stock solution, provided that the resulting multi-element solution is stable.

6.9.4 Multi-element standard stock solution C

This solution at the mg/l level can contain the following elements:

Ca, Mg, Na, K

Use nitric acid (6.2) for stabilisation of multi-element standard stock solution C.

6.9.5 Multi-element standard stock solution D

This solution at the mg/l level can contain the following elements:

Ce, Dy, Er, Eu, Gd, Ho, La, Nd, Pr, Sc, Sm, Tb, Tm, Th, Yb.

Use nitric acid (6.2) for stabilisation of multi-element standard stock solution D.

6.9.6 Multi-element standard stock solution E

This solution at the mg/l level can contain the following elements:

Au, Ir, Pd, Pt, Rh, Ru.

Use hydrochloric acid (6.3) for stabilisation of multi-element standard stock solution E.

6.10 Multi-element calibration solutions

Prepare in one or more steps calibration solutions at the highest concentration of interest. If more concentration levels are needed, prepare those similarly in an equidistant concentration range.

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Add acids (6.2 or 6.3 or a mixture of 6.2, 6.3, 6.4, 6.5 and 6.7) to match the acid concentration of samples closely.

If traceability of the values is not established, check the validity by comparison with a (traceable) independent standard.

The stability of calibration solution can be checked by comparison with freshly prepared solutions on a regular basis.

Care should be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. Other elements combinations are also possible and depend on the analytical task. To avoid cross-contamination, only pure chemicals should be used. The diluted solutions should be stored in clean PFA-, FEP-fluorocarbon, HDPE or PP bottles.

Applying digestion with aqua regia or nitric acid to sludge, treated biowaste or soil, ubiquitous elements like Al, Na, K, Ca, Mg, Ti and Fe can be co-extracted resulting in concentrations of several hundreds of mg/l. The efficiency of the method selected to compensate spectral interferences, background subtraction, transport interference shall be checked by analysis of control samples and interference control samples. Otherwise, the sample matrix elements shall be adapted in calibration solutions for each batch of sample types.

Alternatively, the standard addition method shall be used.

6.11 Reference element solution

The choice of elements for the reference element (synonymously called internal standard) solution depends on the analytical problem. The reference elements shall not be analytes; and the concentrations of the selected elements should be negligibly low in the digests of samples. The elements Y, Rh and Lu have been found suitable for this purpose.

Generally, a suitable concentration of the reference element in samples and calibration solutions is 1 mg/l to 10 mg/l.

6.12 Calibration check solution

Prepare the calibration check solution using an independent multi-element standard stock solution, adapted to the same acid concentrations at an upper concentration level.

6.13 Interference check solution

If interferences cannot be excluded, prepare an interference check solution to detect the interference, with known concentrations of interfering elements. The choice of the concentration and interfering element are matrix dependent.

Avoid two or more interferences for an analyte in the same interference check solution. Spike the sample with the analytes of interest, particularly those with known interferences at 0,5 mg/l to 1 mg/l. In the absence of measurable analyte, overcorrection can go undetected because a negative value can be reported as zero. If the particular instrument displays overcorrection as a negative number, this spiking procedure is not necessary.

This interference check should be made once at installation of a new instrument.

7 Apparatus

7.1 Inductively coupled argon plasma emission spectrometer

The ICP atomic emission spectrometer consists of a sample introduction system, the plasma (as an excitation source), an optical system, a detector and a computer. The sample introduction system usually consists of a rotation tube pump for sample transport to the nebulizer, the nebulizer and a spray chamber. The most

common nebulizers are the concentric nebulizer, the cross-flow nebulizer and the V-groove nebulizer. They are made from glass, quartz, polytetrafluoroethylene (PTFE) or plastics.

Also many types of spray chambers are applied in commercial systems. The most common, beside the cyclonic type with a baffle is the Scott type where double concentric tubes separate larger droplets from the fine aerosol which is introduced into the plasma torch.

The torch consists of three concentric tubes (Fassel type). Quartz is the most commonly used material. The injector tube can be made of HF-acid resistant material, e.g. aluminium oxide, sapphire or platinum. The plasma gas flow and the auxiliary gas flow rates depend on the type of construction and are around 10 l/min to 20 l/min and 0 l/min to 3 l/min, respectively. All gas flows shall be controlled by a flow controller.

At the end of the torch a coil with up to five windings is placed, through which a high alternating current flows to excite the plasma. The frequency used is 27 MHz or 40 MHz with a power of 600 W to 2 000 W.

The emission from the plasma can be observed either from the side (radial view) or both sides (dual radial view) or from the torch central symmetrical axis (axial view).

NOTE 1 The computerized registration of light intensities by several element lines is converted into concentrations using appropriate software packages from the instrument manufacturers.

NOTE 2 The instruments for ICP-OES come in different varieties, i.e. axial or radial viewing or a combination of both.

NOTE 3 To run the ICP with a large number of samples an autosampler can be used.

7.2 Argon gas supply of high purity, e.g. $\geq 99,95\%$.

7.3 Volumetric flasks

7.4 Volumetric pipettes

8 Procedure

8.1 Cleaning of glassware

All glassware used in the determination of trace element concentrations shall be cleaned carefully before use, for examples, by immersion in 5 % (v/v) aqueous nitric acid solution for a minimum of 6 h, followed by rinsing with water (6.1) before use. The nitric acid shall be replaced each week.

8.2 Instrument performance parameters

Due to differences between various models of instruments, no detailed instructions can be given to operate the specific instrument. The instruction provided by the manufacturer for waiting time, for instrument stability, gas flow rates, plasma conditions, nebulizer conditions, sample uptake rates, etc., should be followed.

The following performance parameters should be assessed with typical matrix concentrations:

- selection of appropriate analyte wavelength;
- working range and linearity;
- long- and short-term stabilities, coefficient of variation [relative standard deviation (RSD)] of measurements;
- limit of detection of the method for each analyte and of each type of sample [method detection limit (MDL)];
- verification of inter-element corrections;

- verification of routines for correcting spectral interferences;
- rinsing time between samples and standards;

The performance of the measuring equipment shall be checked with appropriate quality control solutions before measuring test samples (tuning).

8.3 Instrument optimization

The manufacturer's instructions for operating conditions shall be followed to assess maximum signal-to-background ratio of the least sensitive elements, such as As, Se, Pb and Tl.

8.4 Instrument set-up

8.4.1 General requirements

Set up the instrument according to the manufacturer's instructions and ignite the plasma. Verify that the instrument configuration and performance criteria satisfy the safety and analytical requirements (e.g. laboratory environment conditions, power, exhaustion requirements). The plasma shall be allowed to become thermally stable before starting the measurement (usually at least 15 min stabilization time prior to calibration).

8.4.2 Software method development, wavelength selection

Develop a method (set of instrument parameters) depending on the type of samples and matrices to be measured.

Define the wavelengths of the analytes of interest and the need for corresponding corrections according to [Annex C](#). Define the rinsing times to blank level depending on the length of the flow path. The time for rinsing the sample introduction system between the subsequent samples shall be long enough to rinse all the analytes of interest from the system.

NOTE 1 The information given is intended as guidance for indicating potential interferences. Other instruments with other spectral resolution can exhibit different interferences.

NOTE 2 ICP-OES has excellent multi-element capability. Nevertheless, it does not mean that all elements can be analysed during one measurement run. The sensitivity of determination depends on numerous parameters (nebuliser flow, radio-frequency power, viewing height etc.). The optimal instrument settings cannot be reached for all elements at once.

8.4.3 Inter-element correction

Investigate whether the interfering elements in [Table C.1](#) result in measured values higher than three times the instrumental limit of detection or 0,5 times the lowest concentration to be reported. If this is the case, correct for interference. See [Annex C](#) for determining the inter-element correction factors (IEC factors).

8.4.4 Reference element

If the type of samples to be measured strongly varies, matrix matching may not be possible. The reference element correction method can be applied independently from the calibration procedure.

If the reference element procedure insufficiently reduces matrix effects, apply standard addition calibration (see [8.5.2](#)).

The use of a reference element is recommended. Add the reference element solution ([6.11](#)) to all solutions to be measured. One possibility is the on-line dilution and mixing the sample flow with a flow of reference element solution by the peristaltic pump of the nebuliser.

The mass concentration of the reference element shall be the same in all solutions. Divide the response of the analyte by the response of the reference element in all solution(s) and use this ratio in the calibration function.

8.4.5 Long-term stability

Long-term stability (one day, several hours) assessment is a measurement of the instrument drift. A common procedure is to compensate the drift by the reference element technique (using a reference element). A possible drift can also be detected by analysing a calibration standard or the quality control sample at regular intervals between samples. With these measured values, an apparent instrument drift can be compensated by a mathematical procedure. The individual behaviour of each instrument shall be checked.

8.4.6 Preliminary instrument check

The repeatability and sensitivity of the system shall be checked on a daily basis.

NOTE This can be done by measuring a 1 mg/l solution of As, Al, Ca, Mn, Pb with a minimum of five replicates, with the selected integration time.

Nebulizer condition, steady even flow rate of the peristaltic pump, gas flow rate, torch conditions, etc., shall be controlled before measurement of samples.

Check the wavelength calibration as often as required by the manufacturer.

8.5 Calibration

8.5.1 Linear calibration function

The standard calibration method, which is used to measure the light emission intensities of analyte lines in the calibration and test sample solutions, is crucial. With the assistance of a linear calibration curve, the concentrations are calculated in the unknown sample solutions. The linearity over a broad concentration range shall be checked for setting the calibration range. Only Alkaline element lines in particular suffer from non-linear calibration curves, due to ionization and self-absorption effects, and can be calculated by second-order curve fit with appropriate regression lines.

All acids, salts, buffers, detergents and releasers which are present in the test sample solution shall also be present in the calibration solutions in the same concentration. The use of a reference element is highly recommended and should be added to the calibration solutions. The reference element shall not be present in the sample. Therefore, only negligible or very low concentrations should originally be present in extract or digestion solutions.

A minimum of four calibration standards plus a blank calibration standard shall cover the calibration range.

The calibration function is only valid under specific operational conditions and should be re-established if these conditions are changed. The calibration function does not need to be renewed for every batch of samples. For routine analysis, it is sufficient to check the calibration function by a two-point calibration, if the deviation is not more than 5 %.

The accuracy of the concentration of this calibration solution shall be assured. Apply linear regression to obtain the calibration function. For analysing traces apply linear regression forced through the blank value. Check regularly by running a blank sample whether the assumption on the absence of a blank value is justified. After the failure of a control sample it is sufficient to recalibrate with 2 points. The blank value should be less than 50 % of the minimum concentration of interest.

In soil extracts, especially in aqua regia extracts of soil, ubiquitous elements such as Al, Na, K, Ca, Mg, Ti and Fe can be co-extracted, resulting in element concentrations of several hundreds of mg/l. The efficiency of the method selected to compensate spectral interferences, background subtraction, transport interference shall be checked by analysis of control samples and interference control samples. Otherwise the sample matrix elements shall be adapted in calibration solutions for each batch of sample types. If this is not practicable, the standard addition method shall be used.

8.5.2 Standard addition calibration

In case the sample matrix deviates too much from the matrix of the calibration samples (Al, Ca, Fe 500 mg/l) alternatively the standard addition calibration can be used. Since the matrix is perfectly adjusted here, the highest possible accuracy is obtained.

Add a known amount of standard solution of the analyte and an equal amount of blank solution to two separate but equal portions of the sample solution (or its dilution). Minimise dilution or correct for spike dilution. The added amount of standard solution should be between 0,4 times and 2 times the expected sample mass concentration. Measure both solutions as a sample solution. Determine the 'measured spike concentration' as the difference in mass concentration between the two spiked sample portions. Use the ratio 'true spike concentration' versus 'measured spike concentration' as a correction factor for the initially measured concentration of the sample portion.

8.6 Solutions to be prepared

8.6.1 General

Two types of blank solution are required for the analysis: the blank calibration solution (8.6.2) and the blank test solution (8.6.3) prepared during test sample processing.

8.6.2 Blank calibration solution

This solution is prepared by adding the same amount of acids, buffer concentration or salt concentration as in the calibration and test sample solutions. A sufficient quantity should be prepared to flush the system between standards and samples, and to be used as a quality control sample. If a reference element is applied, add the same concentration as used in standards and samples.

8.6.3 Blank test solution

This solution is prepared during the extraction or dissolution process of the sample. Carry out a blank test at the same time as the extraction or dissolution of soil samples; and follow the sample procedure, using the same quantities of all the reagents for the determination, but omitting the test portion. If a reference element is used, add the same concentration as in standards and samples.

Carry out a blank test at the same time as the extraction or digestion of the soil sample, following the same procedure.

8.6.4 Calibration solutions

Prepare mixed calibration solutions covering the range of concentrations to be measured by combining appropriate volumes of the stock solutions in volumetric flasks. Care should be taken when preparing the mixed calibration solutions to ensure that the elements are compatible and stable together. Add appropriate volumes of acids and/or the solutions used for the soil extraction so that the matrix of the calibration solutions corresponds with the matrix of the sample solutions. Fill up the volumetric flasks to the mark with water or acid to adjust the same acidity as in the sample solutions.

Matrix matching of the blank calibration solution and the calibration solutions concerning the main components such as Al, Ca, Fe, K, Mg and Na is recommended, if high concentrations of these elements are present in the sample solution.

Y or Lu is commonly used as a reference element. If the reference element technique is to be used, the reference element shall be added to all calibration solutions, the quality control solution and the sample solutions, so that all solutions contain the reference element in the same concentration.

8.6.5 Test sample solutions

The test sample solution is a particle-free digest or extraction solution prepared according to e.g. ISO 54321^[3], EN 16173^[20], EN 13656^[17], ISO 16729^[12], ISO 17586^[13], ISO 14870^[11], ISO 19730^[14], ISO 14869-1^[8], ISO 14869-2^[9] or ISO 14869-3^[10] or other standards, as appropriate.

8.6.6 Test solutions

The test solution is an aliquot of the test sample solution. It can be directly obtained from the test sample solution or can be diluted to be within the measurement range or to dilute the matrix.

The acidity of calibration solutions shall match the acid concentration in test solutions.

8.7 Measurement procedure

After stabilization of the instrument and verification of stable conditions (8.4.6), carry out measurements on blank calibration and calibration solutions, calibration verification solution, blank test and test sample solutions and quality control solutions. The rinse time between solutions shall be long enough not to contaminate the next solution.

The temperature of all calibration, quality control and test solutions should be within 2 °C of each other at the time of ICP-OES measurement.

After a sufficient delay (depending on sample flow rate stability), read and record the emission intensity of the solution at least three times and average the values, if they fall within an acceptable range.

NOTE The definition of an acceptable range is outside the scope of this document. Refer to [Clause 4](#) concerning quality control procedures.

Whatever the basis for the latter in the laboratory, it should conform to well-established practices, such as those based on CRM, in-house reference materials, verification of calibration accuracy, recovery rate of spiked samples, linearity check, control charts and other measures.

If an unknown type of matrix is to be handled, determine in addition the element concentration by the standard addition method. If the analytical results according to the standard addition method and the standard calibration method are equal, the calibration curve method can be applied. Run the interference check solution(s) (6.13) to establish interference correction or to check for presence of interference.

Run all test solutions including one or more blank test solutions (8.6.3).

Run after calibration and at the end of the sequence a blank calibration solution (8.6.2) and a calibration check solution (6.12). Depending on the stability of the spectrometer and the sample matrix, a calibration check solution should also be analysed at regular intervals in between.

If during analysis of a sample matrix problems are encountered, for example, when the results of the internal standard do not meet the requirements, post digestion spiking of the sample can be performed. Whenever an unknown matrix is encountered, check:

- matrix effects by running the spike sample;
- matrix effects by running a fivefold diluted sample;
- inter-element interference analysing at a different wavelength.

9 Calculation

By reference to the calibration graph obtained, the software calculates the concentration of each element corresponding to the intensities of the test sample solution (see 8.6.5) and of the blank test solution (8.6.3).

Calculate the mass fraction (w) of the element (E) of the sample for each element using [Formula \(1\)](#):

$$w_i = \frac{(\rho_1 - \rho_0) \cdot f \cdot V \cdot C}{m} \quad (1)$$

with

$$C = 100 / w_{\text{dm}} \quad (2)$$

where

- w_i is the mass fraction of the element in the solid sample i , expressed in milligrams per kilogram (mg/kg) corrected to dry matter;
- ρ_1 is the concentration of the element in the test solution ([8.6.6](#)), expressed in milligrams per litre (mg/l);
- ρ_0 is the concentration of the element in the blank test solution ([8.6.3](#)), expressed in milligrams per litre (mg/l);
- f is the dilution factor of the test solution ([8.6.6](#)), if applicable;
- V is the volume of the test portion taken for analysis, e.g. 100 ml for aqua regia extraction in accordance with EN 16173 or EN 16174, expressed in millilitres (ml);
- m is the mass of the digested test portion, expressed in grams (g);
- C is the correction factor for dry mass;
- w_{dm} is the dry matter fraction of the sample, determined according to ISO 11465 or EN 15934, in percent (%).

10 Expression of results

The measurement uncertainty reported for the results should reflect the results from quality control measurements and incorporate the deviation between the individual readings for the sample in question. In general, values shall not be expressed to a degree of accuracy greater than three significant figures. The rounding of values depends on the statistics of the quality control procedures mentioned earlier and the requirements of the analysis.

EXAMPLE $w_{\text{Cd}} = 8,54 \text{ mg/kg}$

$w_{\text{Cd}} = 12,6 \text{ mg/kg}$

11 Performance characteristics

11.1 Calibration check

For demonstration of calibration traceability, a calibration verification solution with certified concentration and known measurement uncertainty shall be used. Additionally, this solution or a calibration solution may be used for drift control during the measurement cycle. The accepted deviation shall be in the limit of the laboratory quality control policy.

11.2 Interference

The magnitude of uncorrected background and spectral interference shall not be higher than three times the instrumental detection limit or 0,5 times the lowest concentration to be reported.

Successive values of a correction factor shall not differ by more than 20 %.

11.3 Recovery

The post digestion spike recovery shall be between 75 % and 125 %; or the difference between results for the original sample and the fivefold-diluted sample shall be less than 10 % when the concentration after dilution is higher than ten times the instrumental detection limit or higher than twice the lowest concentration to be reported. Spike concentration should be within 0,4 times and 2 times the analyte concentration. If the recovery is not within these limits, a matrix effect should be suspected.

11.4 Performance data

The performance characteristics have been determined in an international validation study. The results of this study are given in [Annex A](#).

12 Test report

The test report shall contain at least the following information:

- a) a reference to this document; i.e. ISO 22036:2023
- b) all information necessary for identification of the sample;
- c) information about the pretreatment and method of digestion of the sample;
- d) results of the determination as indicated in [Clause 9](#);
- e) any details not specified in this document or which are optional, as well as any factor which may have affected the results;
- f) any deviation from the procedure;
- g) any unusual features observed;
- h) a date of the test.

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Annex A (informative)

Repeatability and reproducibility data

Repeatability and reproducibility data have been added from a European interlaboratory comparison organized by the German Federal Institute for Materials Research and Testing BAM in 2013 (EN 16171:2016). The results of this study are summarised in [Tables A.1](#) to [A.3](#) for respectively digestion of nitric acid soluble fractions of elements (EN 16173), digestion of aqua regia soluble fractions of elements using thermal heating under reflux conditions (EN 16174 method A) and digestion of aqua regia soluble fractions of elements using microwave heating with temperature control (EN 16174 method B).

Repeatability and reproducibility data have been reported as a result of the European interlaboratory comparison organized by VITO NV in Mol (Belgium) and Synlab Analytics & Services B.V. in Rotterdam (The Netherlands) for the validation of EN 13656. The validation was performed on the following types of matrices: city waste incineration ash (BCR176/BCR176R), ink waste sludge (organic matrix), electronic industry sludge ("metallic" matrix), sediment, coal fly ash, steel slag, copper slag, city waste incineration fly ash ("oxidised" matrix), city waste incineration bottom ash ("silicate" matrix), sewage sludge (BCR 146R).

Repeatability and reproducibility data have been reported as a result of the European interlaboratory comparison organized by VITO NV in Mol (Belgium) and Synlab Analytics & Services B.V. in Rotterdam (The Netherlands) for the validation of ISO 54321. The validation was performed on the following types of matrices: municipal sludge, industrial sludge, sludge from electronic industry, ink waste sludge, sewage sludge, biowaste, compost, composted sludge, agricultural soil, sludge amended soil, city waste incineration fly ash ("oxidised" matrix), city waste incineration bottom ash ("silicate" matrix), ink waste sludge (organic matrix), electronic industry sludge ("metallic" matrix), BCR 146R (sewage sludge), BCR 176 (city waste incineration ash).

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Table A.1 — Repeatability and reproducibility data for sludge

Element	Extraction method	l	n	n_0	n_{ev}	$\bar{\bar{x}}$	s_r	$C_{V,r}$	s_R	$C_{V,R}$
Ag	EN 16173	22	66	0	22	5,439	0,313	5,8	0,959	17,6
	EN 16174, Method A	23	66	1	22	6,070	0,126	2,1	0,650	10,7
	EN 16174, Method B	24	69	1	23	6,146	0,241	3,9	0,926	15,1
As	EN 16173	20	57	1	19	4,381	0,511	11,7	0,872	19,9
	EN 16174, Method A	20	54	2	18	4,373	0,337	7,7	1,386	31,7
	EN 16174, Method B	21	60	1	20	4,213	0,592	14,0	1,005	23,8
Cd	EN 16173	20	60	0	20	1,007	0,058	5,7	0,181	18,0
	EN 16174, Method A	19	54	1	18	1,002	0,041	4,1	0,141	14,0
	EN 16174, Method B	22	63	1	21	0,976	0,042	4,3	0,192	19,7
Co	EN 16173	24	69	1	23	2,555	0,120	4,6	0,58	22,5
	EN 16174, Method A	22	63	1	21	2,329	0,110	4,9	0,35	15,0
	EN 16174, Method B	25	75	0	25	2,838	0,280	9,9	0,7	24,8
Cr	EN 16173	25	69	2	23	18,60	0,64	3,5	2,63	14,2
	EN 16174, Method A	23	66	1	22	18,99	0,64	3,4	1,95	10,3
	EN 16174, Method B	26	75	1	25	19,86	0,74	3,7	2,7	13,6
Cu	EN 16173	25	75	0	25	967,4	24,7	2,6	99,7	10,3
	EN 16174, Method A	23	66	1	22	959,7	13,3	1,4	79,7	8,3
	EN 16174, Method B	26	75	1	25	978,3	19,0	1,9	104,1	10,6
Ni	EN 16173	25	72	1	24	18,23	0,67	3,7	2,35	12,9
	EN 16174, Method A	23	66	1	22	18,30	0,48	2,6	2,07	11,3
	EN 16174, Method B	26	75	1	25	18,97	0,73	3,9	2,55	13,4
Key										
L number of participating laboratories										
n number of analytical results after outlier rejection										
n_{ev} number of evaluated datasets										
n_0 number of outlier laboratories										
$\bar{\bar{x}}$ total mean of results (without outliers) in milligram per kilogram (mg/kg)										
s_R reproducibility standard deviation in milligram per kilogram (mg/kg)										
$C_{V,R}$ coefficient of variation of reproducibility in per cent (%)										
s_r repeatability standard deviation in milligram per kilogram (mg/kg)										
$C_{V,r}$ coefficient of variation of repeatability in per cent (%)										

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Table A.1 (continued)

Element	Extraction method	<i>l</i>	<i>n</i>	<i>n</i> ₀	<i>n</i> _{ev}	$\bar{\bar{x}}$	<i>s</i> _r	<i>C</i> _{V,r}	<i>s</i> _R	<i>C</i> _{V,R}
Pb	EN 16173	23	69	0	23	27,98	0,92	3,3	3,68	13,1
	EN 16174, Method A	21	60	1	20	27,30	0,68	2,5	3,30	12,1
	EN 16174, Method B	24	69	1	23	29,20	1,11	3,8	4,42	15,2
Sn	EN 16173	22	63	1	21	11,57	2,21	19,1	8,14	70,3
	EN 16174, Method A	20	54	2	18	33,85	0,76	2,2	7,21	21,3
	EN 16174, Method B	23	69	0	23	35,05	1,30	3,7	3,61	10,3
V	EN 16173	25	72	1	24	5,564	0,223	4,0	0,612	11,0
	EN 16174, Method A	23	66	1	22	5,365	0,102	1,9	0,601	11,2
	EN 16174, Method B	26	75	1	25	5,971	0,251	4,2	0,885	14,8
Zn	EN 16173	25	72	1	24	1 035	25	2,4	125	12,0
	EN 16174, Method A	23	69	0	23	1 017	22	2,2	100	9,8
	EN 16174, Method B	25	0	75	25	1 044	24	2,3	127	12,2

Key

l number of participating laboratories
n number of analytical results after outlier rejection
*n*_{ev} number of evaluated datasets
*n*₀ number of outlier laboratories
 $\bar{\bar{x}}$ total mean of results (without outliers) in milligram per kilogram (mg/kg)
*s*_R reproducibility standard deviation in milligram per kilogram (mg/kg)
*C*_{V,R} coefficient of variation of reproducibility in per cent (%)
*s*_r repeatability standard deviation in milligram per kilogram (mg/kg)
*C*_{V,r} coefficient of variation of repeatability in per cent (%)

Table A.2 — Repeatability and reproducibility data for compost

Element	Extraction method	<i>l</i>	<i>n</i>	<i>n</i> ₀	<i>n</i> _{ev}	$\bar{\bar{x}}$	<i>s</i> _r	<i>C</i> _{V,r}	<i>s</i> _R	<i>C</i> _{V,R}
Ag	EN 16173	10	9	1	27	0,229	0,031	13,7	0,187	81,4
	EN 16174, Method A	11	11	0	33	0,318	0,063	19,8	0,267	83,8
	EN 16174, Method B	10	7	3	21	0,175	0,018	10,5	0,043	24,6
As	EN 16173	20	19	1	57	5,395	0,413	7,7	1,283	23,8
	EN 16174, Method A	20	19	1	57	5,322	0,388	7,3	1,147	21,6
	EN 16174, Method B	21	18	3	54	5,482	0,314	5,7	1,208	22,0

NOTE For an explanation of symbols, see [Table A.1](#).

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Table A.2 (continued)

Element	Extraction method	l	n	n_0	n_{ev}	\bar{x}	s_r	$C_{V,r}$	s_R	$C_{V,R}$
Cd	EN 16173	19	19	0	57	0,550	0,040	7,3	0,132	24,0
	EN 16174, Method A	19	19	0	57	0,554	0,025	4,6	0,127	23,0
	EN 16174, Method B	21	18	3	54	0,504	0,040	8,0	0,137	27,2
Co	EN 16173	25	25	0	75	6,679	0,230	3,4	0,93	13,9
	EN 16174, Method A	22	22	0	66	6,613	0,350	5,3	1,09	16,4
	EN 16174, Method B	26	26	0	78	7,184	0,270	3,8	1,32	18,4
Cr	EN 16173	25	25	0	75	29,33	1,84	6,3	6,96	23,7
	EN 16174, Method A	23	22	1	66	28,60	1,53	5,3	5,17	18,1
	EN 16174, Method B	26	25	1	75	34,13	2,01	5,9	7,82	22,9
Cu	EN 16173	25	25	0	75	45,13	1,18	2,6	4,60	10,2
	EN 16174, Method A	23	22	1	66	45,48	2,77	6,1	4,72	10,4
	EN 16174, Method B	26	25	1	75	45,81	2,06	4,5	6,84	14,9
Ni	EN 16173	25	24	1	72	22,49	0,86	3,8	3,03	13,5
	EN 16174, Method A	23	21	2	63	22,36	0,66	3,0	3,13	14,0
	EN 16174, Method B	26	24	2	72	23,50	0,60	2,5	3,94	16,8
Pb	EN 16173	23	23	0	69	32,04	1,57	4,9	3,80	11,9
	EN 16174, Method A	21	21	0	63	32,18	1,69	5,3	3,70	11,5
	EN 16174, Method B	24	22	2	66	33,18	1,35	4,1	3,28	9,9
Sn	EN 16173	14	13	1	36	1,678	0,150	9,0	1,098	65,5
	EN 16174, Method A	19	15	4	44	2,596	0,216	8,3	0,763	29,4
	EN 16174, Method B	21	21	0	61	2,886	0,736	25,5	1,121	38,9
V	EN 16173	25	24	1	72	24,19	1,59	6,6	6,91	28,6
	EN 16174, Method A	23	21	2	63	24,74	0,81	3,3	4,84	19,6
	EN 16174, Method B	26	26	0	78	29,84	1,66	5,6	8,16	27,3
Zn	EN 16173	25	25	0	75	168,3	4,4	2,6	16,7	9,9
	EN 16174, Method A	23	21	2	63	162,1	4,4	2,7	19,1	11,8
	EN 16174, Method B	25	24	1	72	164,4	4,3	2,6	21,7	13,2

NOTE For an explanation of symbols, see [Table A.1](#).

Table A.3 — Repeatability and reproducibility data for soil

Element	Extraction method	l	n	n_0	n_{ev}	$\bar{\bar{x}}$	s_r	$C_{V,r}$	s_R	$C_{V,R}$
Ag	EN 16173	13	33	2	11	0,635	0,031	4,9	0,161	25,4
	EN 16174, Method A	16	45	1	15	0,629	0,039	6,2	0,188	29,8
	EN 16174, Method B	16	40	2	14	0,824	0,053	6,5	0,428	52,0
As	EN 16173	23	63	2	21	45,13	0,95	2,1	3,16	7,0
	EN 16174, Method A	22	66	0	22	46,93	0,79	1,7	3,99	8,5
	EN 16174, Method B	24	66	2	22	47,90	1,32	2,8	5,01	10,5
Cd	EN 16173	25	75	0	25	13,26	0,45	3,4	1,78	13,4
	EN 16174, Method A	23	69	0	23	12,89	0,29	2,3	1,30	10,1
	EN 16174, Method B	26	72	2	24	13,06	0,53	4,1	1,44	11,0
Co	EN 16173	24	66	2	22	3,790	0,114	3,0	0,368	9,7
	EN 16174, Method A	22	66	0	22	3,989	0,088	2,2	0,427	10,7
	EN 16174, Method B	25	72	1	24	4,195	0,109	2,6	0,642	15,3
Cr	EN 16173	25	69	2	23	21,79	0,71	3,3	1,77	8,1
	EN 16174, Method A	23	63	2	21	21,86	0,39	1,8	1,67	7,6
	EN 16174, Method B	26	72	2	24	22,70	0,62	2,7	2,98	13,1
Cu	EN 16173	25	72	1	24	35,50	1,22	3,4	2,70	7,6
	EN 16174, Method A	23	63	2	21	35,82	0,59	1,7	2,65	7,4
	EN 16174, Method B	26	72	2	24	36,35	1,30	3,6	3,12	8,6
Ni	EN 16173	25	66	3	22	7,013	0,231	3,3	0,891	12,7
	EN 16174, Method A	23	60	3	20	7,050	0,176	2,5	0,874	12,4
	EN 16174, Method B	26	72	2	24	7,423	0,171	2,3	1,128	15,2
Pb	EN 16173	23	65	1	22	74,01	3,43	4,6	6,27	8,5
	EN 16174, Method A	21	63	0	21	74,94	2,41	3,2	7,82	10,4
	EN 16174, Method B	24	69	1	23	77,53	4,52	5,8	11,81	15,2
Sn	EN 16173	19	53	1	18	3,153	0,753	23,9	1,870	59,3
	EN 16174, Method A	20	57	1	19	10,86	0,86	7,9	2,01	18,5
	EN 16174, Method B	23	66	1	22	11,49	1,64	14,2	1,98	17,2

NOTE For an explanation of symbols, see [Table A.1](#).

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Table A.3 (continued)

Element	Extraction method	l	n	n_0	n_{ev}	\bar{x}	s_r	$C_{V,r}$	s_R	$C_{V,R}$
V	EN 16173	25	75	0	25	6,225	0,299	4,8	0,977	15,7
	EN 16174, Method A	23	69	0	23	6,977	0,181	2,6	0,795	11,4
	EN 16174, Method B	26	75	1	25	7,682	0,307	4,0	1,229	16,0
Zn	EN 16173	25	69	2	23	178,6	3,3	1,8	16,8	9,4
	EN 16174, Method A	23	63	2	21	176,8	4,0	2,3	19,5	11,1
	EN 16174, Method B	25	69	2	23	185,5	3,5	1,9	29,3	15,8

NOTE For an explanation of symbols, see [Table A.1](#).

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Annex B (informative)

Wavelengths and estimated instrumental detection limits

The wavelengths given in [Table B.1](#) are often used, but they are given here only as an example. Adoption of other wavelengths is possible.

These 3-sigma detection limits (LOD) are measured by using 40 s integration time with 10 replicates in synthetical matrix blank (500 mg/l Al, Ca, Fe in 30 ml aqua regia filled up to 100 ml with deionized water). Only LOD of Al, Ca and Fe are measured in 30 ml aqua regia filled up to 100 ml with deionized water.

The LOD, as a mass fraction of the soil sample in mg/kg dry matter, is given assuming that a test sample of 3 g is extracted with 30ml of aqua regia and diluted to 100 ml. The LOD shown in [Table B.1](#) are only examples of a given equipment and laboratory conditions. Each laboratory shall select appropriate wavelengths and determine LOD under its specific laboratory conditions. The limit of detection and the linear range vary for each element with the wavelength, spectrometer, operating conditions and matrix load in the sample solution. Therefore, these detection limits should be verified by each laboratory using reference materials and interlaboratory comparisons.

Table B.1 — Wavelengths and estimated instrumental detection limits

Element	Wavelength nm	LOD	
		solution µg/l	Sample mg/kg
Ag	328,068	1,3	0,042
	338,289	2,9	0,096
Al	167,078	0,6	0,019
	176,641	4,4	0,145
	308,215	10,2	0,337
	309,271	9,7	0,321
	394,401	7,4	0,245
	396,152	4,0	0,132
	As	189,042	2,8
193,759		13,4	0,441
197,262		6,4	0,211
Au	174,05	17,5	0,577
	242,795	1,6	0,053
	267,595	2,8	0,091
B	182,641	0,3	0,010
	208,959	1,2	0,039
	249,677	0,9	0,029
	249,773	0,5	0,016
Ba	233,527	0,2	0,007
	455,404	0,1	0,004
Be	234,861	0,012	0,000 4
	313,042	0,004	0,000 1
	313,107	0,006	0,000 2

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Table B.1 (continued)

Element	Wavelength nm	LOD	
		solution µg/l	Sample mg/kg
Bi	190,241	7,1	0,234
	223,061	3,6	0,118
	306,772	29,0	0,956
Ca	183,801	2,4	0,080
	315,887	1,8	0,059
	317,933	1,3	0,043
	370,603	11,5	0,379
Cd	214,438	0,8	0,027
	226,502	0,6	0,021
	228,802	0,3	0,010
Ce	413,765	8,2	0,271
	418,66	7,9	0,262
	448,691	24,5	0,809
Co	228,616	0,5	0,016
	230,786	0,9	0,029
	238,892	2,6	0,086
Cr	206,149	0,5	0,017
	267,716	0,5	0,018
	283,563	5,2	0,171
	284,325	1,4	0,046
Cu	224,7	2,6	0,085
	324,754	1,1	0,036
	327,396	1,8	0,059
Dy	340,78	3,8	0,124
	353,17	1,0	0,032
	394,468	9,8	0,325
Er	337,271	0,8	0,028
	349,91	1,7	0,058
Eu	381,967	0,2	0,008
	420,505	0,7	0,023
Fe	238,204	0,595	0,020
	239,562	0,612	0,020
	259,941	0,625	0,021
	261,187	1,754	0,058
	275,573	1,492	0,049
Ga	294,364	7,7	0,253
	417,206	13,3	0,438
Gd	335,047	2,7	0,089
	342,247	1,6	0,052
Ge	164,919	14,2	0,468
	265,118	2,4	0,078
Hf	232,247	1,8	0,060