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# Soil quality — Determination of trace elements using inductively coupled plasma mass spectrometry (ICP-MS)

## National foreword

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# Soil quality — Determination of trace elements using inductively coupled plasma mass spectrometry (ICP-MS)

*Qualité du sol — Détermination des éléments en traces par spectrométrie de masse avec plasma induit par haute fréquence (ICP-MS)*

Reference number
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# Contents

# Foreword

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

# Introduction

ISO/TS 16965 is based upon CEN/TS 16171, *Sludge, treated biowaste and soil — Determination of elements using inductively coupled plasma mass spectrometry (ICP-MS)*, which was developed by CEN/TC 400, *Project Committee — Horizontal standards in the fields of sludge, biowaste and soil*.

This Technical Specification is applicable and validated for several types of matrices as indicated in Table 1.

**Table 1 — Matrices for which this Technical Specification is applicable and validated**

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

# Soil quality — Determination of trace elements using inductively coupled plasma mass spectrometry (ICP-MS)

**WARNING — Persons using this Technical Specification should be familiar with usual laboratory practice. This Technical Specification 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 Technical Specification be carried out by suitably trained staff.**

## 1 Scope

This Technical Specification specifies a method for the determination of the following elements in *aqua regia* or nitric acid digests or other extraction solutions of sludge, treated biowaste and soil:

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

The working range depends on the matrix and the interferences encountered.

The limit of detection is between 0,1 mg/kg dry matter and 2,0 mg/kg dry matter for most elements.

The limit of detection will be higher in cases where the determination is likely to have interferences (see Clause 4) or in the case of memory effects (see e.g. 8.2 of ISO 17294-1:2004).

## 2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 11466, *Soil quality — Extraction of trace elements soluble in aqua regia*

ISO 16729, *Soil quality — Digestion of nitric acid soluble fractions of elements*

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

ISO 17294-1:2004, *Water quality — Application of inductively coupled plasma mass spectrometry (ICP-MS) — Part 1: General guidelines*

## 3 Principle

Digests with nitric acid or *aqua regia* of samples of sludge, treated biowaste or soil (see ISO 11466 and ISO 16729) are analysed by ICP-MS to get a multi-elemental determination of analytes.

The method measures ions produced by a radio-frequency inductively coupled plasma. Analyte species originating in the digest solution are nebulised and the resulting aerosol is transported by argon gas into the plasma. The ions produced by the high temperatures of the plasma are entrained in the plasma gas and introduced, by means of an interface, into a mass spectrometer, sorted according to their mass-to-charge ratios and quantified with a detector (e.g. channel electron multiplier).

# 4 Interferences

## 4.1 General

Interferences shall be assessed and valid corrections applied. Interference correction shall include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix.

Detailed information on spectral and non-spectral interferences is given in Clause 6 of ISO 17294-1:2004.

## 4.2 Spectral interferences

### 4.2.1 Isobaric elemental interferences

Isobaric elemental interferences are caused by isotopes of different elements of closely matched nominal mass-to-charge ratio and which cannot be separated due to an insufficient resolution of the mass spectrometer in use (e.g. $^{114}$Cd and $^{114}$Sn).

Element interferences from isobars may be corrected by taking into account the influence from the interfering element (see ISO 17294-1:2004). The isotopes used for correction shall be free of interference if possible. Correction options are often included in the software supplied with the instrument. Common isobaric interferences are given in Table A.1.

### 4.2.2 Isobaric molecular and doubly-charged ion interferences

Isobaric molecular and doubly-charged ion interferences in ICP-MS are caused by ions consisting of more than one atom or charge, respectively. Examples include $^{40}$Ar$^{35}$Cl$^+$ and $^{40}$Ca$^{35}$Cl$^+$ ion on the $^{75}$As signal or $^{98}$Mo$^{16}$O$^+$ ions on the $^{114}$Cd$^+$ signal. Natural isotope abundances are available from the literature.

The accuracy of correction equations is based upon the constancy of the observed isotopic ratios for the interfering species. Corrections that presume a constant fraction of a molecular ion relative to the "parent" ion have not been found to be reliable, e.g. oxide levels can vary with operating conditions. If a correction for an oxide ion is based upon the ratio of parent-to-oxide ion intensities, this shall be determined by measuring the interference solution just before the sequence is started. The validity of the correction coefficient should be checked at regular intervals within a sequence.

Another possibility to remove isobaric molecular interferences is the use of an instrument with collision/reaction cell technology. The use of high resolution ICP-MS avoids these interferences and additionally double-charged ion interferences.

The response of the analyte of interest shall be corrected for the contribution of isobaric molecular and doubly-charged interferences if their impact can be higher than three times the detection limit or higher than half the lowest concentration to be reported.

More information about the use of correction factors is given in ISO 17294-1.

### 4.2.3 Non-spectral interferences

Physical interferences are associated with sample nebulisation and transport processes as well as with ion-transmission efficiencies. Nebulisation and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement. Solids can be deposited on the nebuliser tip of a pneumatic nebuliser and on the cones.

It is recommended to keep the level of total dissolved solids below 0,2 % (2 000 mg/l) to minimize deposition of solids in the sample introduction system of the plasma torch. An internal standard can be used to correct for physical interferences if it is carefully matched to the analyte, so that the two elements are similarly affected by matrix changes. Other possibilities to minimize non-spectral interferences are matrix matching, particularly matching of the acid concentration, and standard addition.

When intolerable physical interferences are present in a sample, a significant suppression of the internal standard signals (to less than 30 % of the signals in the calibration solution) will be observed. Dilution of the sample (e.g. fivefold) usually eliminates the problem.

## 5 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.

Preferably, nitric acid preservation should be applied in order to minimize interferences by chloropolyatom molecules. Bi, Hg, Hf, Mo, Sn, Sb, Te, W and Zr may need hydrochloric acid for preservation.

**5.1 Water,** grade 1 as specified in ISO 3696 for all sample preparations and dilutions.

**5.2 Nitric acid,** $c(\mathrm{HNO_3}) = 15$ mol/l.

NOTE Nitric acid is available both as $c(\mathrm{HNO_3}) \approx 1{,}4$ g/ml [$w(\mathrm{HNO_3}) = 650$ g/kg] and $c(\mathrm{HNO_3}) = 1{,}42$ g/ml [$w(\mathrm{HNO_3}) \approx 720$ g/kg]. Both are suitable for use in this method, provided the content of the analytes of interest is minimal.

**5.3 Hydrochloric acid,** $c(\mathrm{HCl}) = 12$ mol/l, $\rho \approx 1{,}18$ g/ml.

### 5.4 Single-element standard stock solutions

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

These solutions are considered to be stable for more than one year, but in reference to guaranteed stability, the recommendations of the manufacturer should be considered.

### 5.5 Anion standard stock solutions

$\mathrm{Cl^-}$, $\mathrm{PO_4^{3-}}$, $\mathrm{SO_4^{2-}}$, $\rho = 1\,000$ mg/l each.

Prepare these solutions from the respective acids. The solutions are commercially available.

These solutions are considered to be stable for more than one year, but in reference to guaranteed stability, the recommendations of the manufacturer should be considered.

### 5.6 Multi-element standard stock solutions

Depending on the scope, different multi-element standard stock solutions may be necessary. In general, when combining multi-element standard stock 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, Hf and Zr.

Mercury standard stock solutions can be stabilized by adding 1 mg/l Au in nitric acid (5.2) or by adding hydrochloric acid (5.3) up to 0,6 %.

NOTE When Au is to be used as modifier, the instrument is not suitable for accurate Au determination.

Multi-element standard stock solutions with more elements are allowed provided that these solutions are stable.

**5.6.1 Multi-element standard stock solution A** at the mg/l level may contain the following elements:

Ag, Al, As, B, Ba, Be, Bi, Cd, Ce, Co, Cr, Cu, Fe, Hg, Li, Mn, Nd, Ni, Pb, Pr, Sc, Se, Si, Sm, Sr, Te, Th, Ti, Tl, U, V, Zn.

Use nitric acid (5.2) for stabilization of multi-element standard stock solution A.

Other elements of interest may be added to the standard stock solution, provided that these solutions are stable.

**5.6.2 Multi-element standard stock solution B** at the mg/l level may contain the following elements:

Mo, Sb, Si, Sn, W, Zr.

Use hydrochloric acid (5.3) for stabilization of multi-element standard stock solution B.

Other elements of interest may be added to the standard stock solution, provided that these solutions are stable.

**5.6.3 Multi-element standard stock solution C** at the mg/l level may contain the following elements:

Ca, Mg, Na, K, P, S.

Use nitric acid (5.2) for stabilization of multi-element standard stock solution C.

### 5.7 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.

Add acids (5.2 and 5.3) 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.

Check the stability of the diluted calibration solutions.

### 5.8 Internal standard solution

Internal standards can either be added to every flask or added online. It is essential that the same concentration of internal standard is added to all standards. The elements In, Lu, Re, Ge and Rh have been found suitable for this purpose.

The choice of elements for the internal standard solution depends on the analytical problem. The solution of this/these internal standard(s) should cover the mass range of interest. The concentrations of the selected elements (used as internal standard) should be negligibly low in the digests of samples.

Generally, a suitable final concentration of the internal standard in samples and calibration solutions is 1 µg/l to 50 µg/l (for a high and stable count rate). The use of a collision/reaction cell may require higher concentrations.

### 5.9 Calibration blank solution

Prepare the calibration blank solution by diluting acids (5.2, 5.3) with water (5.1) to the same concentrations as used in the calibration solutions and samples.

### 5.10 Test blank solution

The test blank solution shall contain all of the reagents in the same volumes and handled in the same way throughout the procedure as the samples. The test blank solution contains the same acid concentration in the final solution as the test solution after the digestion method is applied.

### 5.11 Optimization solution

The optimization solution serves for mass calibration and for optimization of the instrumental settings, e.g. adjustment of maximal sensitivity with respect to minimal oxide formation rate and minimal formation of doubly charged ions. It should contain elements covering the total mass range, as well as elements prone to a high oxide formation rate or to the formation of doubly charged ions. The composition of the optimization depends on the elements of interest, instrument and manufacturer's instructions. An optimization solution containing e.g. Mg, Cu, Rh, In, Ba, La, Ce, U and Pb is suitable. Li, Be and Bi are less suitable because they tend to cause memory effects at higher concentrations.

The mass concentrations of the elements used for optimization should allow count rates of more than $10^4$ counts per second.

### 5.12 Interference check solution

The interference check solutions serve to determine the correction factors for the corresponding equations. High demands are made concerning the purity of the basic reagents due to the high mass concentrations.

Interference check solutions shall contain all the interferences of practical relevance given in ISO 17294-1, at a concentration level at the same range as expected in the samples (see also 10.5).

Leaving out an interfering element according to ISO 17294-1 is permitted if it can be demonstrated that its impact is negligible and lasting.

In extraordinary situations the other interfering elements according to ISO 17294-1 shall also be investigated for relevance.

EXAMPLE An example of the composition of an interference check solution is:

$\rho(\mathrm{Ca})$ = 2 500 mg/l; $\rho(\mathrm{Cl^-})$ = 2 000 mg/l; $\rho(\mathrm{PO_4^{3-}})$ = 500 mg/l and $\rho(\mathrm{SO_4^{2-}})$ = 500 mg/l

and for digests also

$\rho(\mathrm{C})$ = 1 000 mg/l; $\rho(\mathrm{Fe})$ = 500 mg/l; $\rho(\mathrm{Na})$ = 500 mg/l and $\rho(\mathrm{Al})$ = 500 mg/l (see[1]).

## 6 Apparatus

### 6.1 General requirements

The stability of samples, measuring, and calibration solutions depends to a high degree on the container material. The material shall be checked according to the specific purpose. For the determination of elements in a very low concentration range (<1 µg/kg), glass or polyvinyl chloride (PVC) should not be used. Instead, it is recommended to use perfluoroalkoxy (PFA), hexafluoroethene propene (FEP) or quartz containers, cleaned with diluted, high quality nitric acid or hot, concentrated nitric acid in a closed system. For the determination of elements in a higher concentration range, containers made from high density polyethylene (HDPE) or polytetrafluoroethene (PTFE) are also suited for the collection of samples. Immediately before use, all containers should be washed thoroughly with diluted nitric acid (e.g. $w(HNO_3) = 10$ %), and then rinsed several times with water (5.1).

The limit of detection of most elements is affected by contamination of solutions and this depends predominantly on the cleanliness of laboratory air.

The use of piston pipettes is permitted and also enables the preparation of smaller volumes of calibration solutions. The application of dilutors is also allowed. Every charge of pipette tips and single-use plastics vessels shall be tested for impurities.

Dispensing of a volume of less than 50 µl by means of a pipette should be avoided.

For more detailed information on the instrumentation see Clause 5 of ISO 17294-1:2004.

## 6.2 Mass spectrometer

A mass spectrometer with inductively coupled plasma (ICP) suitable for multi-element and isotope analysis is required. The spectrometer should be capable of scanning a mass range from 5 $m/z$ (amu) to 240 $m/z$ (amu) with a resolution of at least 1 $m_r/z$ peak width at 5 % of peak height ($m_r$ = relative mass of an atom species; $z$ = charge number). The instrument may be fitted with a conventional or extended dynamic range detection system.

Quadrupole ICP-MS, high-resolution ICP-MS, time-of-flight ICP-MS and collision/reaction cell ICP-MS instrumentation are suitable for measurement.

## 6.3 Mass-flow controller

A mass-flow controller on the nebuliser gas supply is strongly recommended. Mass-flow controllers for the plasma gas and the auxiliary gas are preferred. A cooled spray chamber (cold water or Peltier element) may be beneficial in reducing some types of interferences (e.g. from polyatomic oxide species).

## 6.4 Nebuliser with variable speed peristaltic pump

The speed of the pump shall not be too low and the number of rolls as high as possible to provide a stable signal.

## 6.5 Gas supply

**6.5.1 Argon,** Ar, with high purity grade, i.e. > 99,99 %.

**6.5.2 Reaction gas**, e.g. helium (He), hydrogen ($H_2$), oxygen ($O_2$), ammonia gas ($NH_3$), or methane ($CH_4$) with high purity grade, i.e. > 99,99 %.

## 6.6 Storage bottles, for the stock, standard, calibration and sample solutions

Preferably made from perfluoroalkoxy (PFA) or hexafluoroethene propene (FEP). For the determination of elements in a higher concentration range (>1 µg/kg), high density polyethylene (HDPE) or polytetrafluoroethene (PTFE) bottles may be suitable.

# 7 Procedure

## 7.1 Test sample solution

The test sample solution is a particle-free digest or extraction solution prepared according to ISO 11466 or ISO 16729 or other extraction procedures.

## 7.2 Test portion solution

The test portion solution may be directly obtained from the test sample solution or may be diluted to accommodate the measurement range or to dilute the matrix.

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

Ensure that all elements are present in a non-volatile form. Volatile species shall be converted to non-volatile ones, e.g. sulfide oxidation by hydrogen peroxide.

## 7.3 Instrument set up

Adjust the instrumental parameters of the ICP-MS system in accordance with the manufacturer's instructions. A guideline for method and instrument set up is given in ISO 17294-1:2004.

Define the isotopes and the need for corresponding corrections. See 6.3.2 of ISO 17294-1:2004 for a method to determine these factors. Alternatively, apply multivariate calibration procedures.

Define the rinsing times depending on the length of the flow path; in the case of wide working range of analyte mass concentrations in the measuring solutions, allow longer rinsing periods.

The use of an internal standard is mandatory. Add the internal standard stock solution (5.8) to the interference check solution (5.12), to all multi-element calibration solutions (5.7), to the blank calibration solutions (5.9), and to all measuring solutions.

NOTE 1 Online dilution and mixing of the sample flow with internal standard solution by means of the peristaltic pump of the nebuliser is commonly used. In such case the calibration solutions are diluted the same way as the sample solutions.

The mass concentration of the internal standard elements shall be the same in all solutions. Generally a suitable concentration of the internal standard element in sample and calibration solutions is 1 µg/l to 50 µg/l (for a high and stable count rate).

Adjust the instrument to working condition. This takes usually 30 min.

Before each series of measurements check the sensitivity and the stability of the system and minimize interferences, e.g. by using the optimization solution (5.12).

Check the resolution and the mass calibration as often as required by the manufacturer.

NOTE 2 ICP-MS 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, lens voltage, lens voltage mode, etc.). The optimal instrument settings cannot be reached for all elements at once.

## 7.4 Calibration

### 7.4.1 Linear calibration function

If more than two concentration levels, including zero, are used, apply weighted linear regression to obtain the linear calibration function.

NOTE 1 ICP-MS provides a large measurement range. The dispersion of blank measurements is usually much smaller than the dispersion at full scale. Ordinary linear regression assumes that the dispersion is constant over the entire range. As a consequence a much higher percentage of the calculated intercepts is out of the range expected from the spread of blanks: a non-zero blank value is calculated that is actually not there. Weighted linear regression forces the line through points of low dispersion, resulting in the expected intercept dispersion.

NOTE 2 An alternative, but less efficient, approach is ordinary linear regression where the line is forced through the blank value or through zero.

If weighted linear regression is not possible, apply linear regression forced through the blank value or through zero. In the latter case check regularly by running a blank whether the assumption on the absence of a blank value is justified.

NOTE 3 Weighted linear regression is not suitable for lower element concentrations.

A two point calibration is allowed if the calibration function is linear, which usually is the case. Check regularly for linearity with a calibration solution of known dilution.

Instead of one measurement per level more measurements can be performed to reduce the uncertainty of the calibration line.

### 7.4.2 Standard addition calibration

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). Minimize 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.

### 7.4.3 Determination of correction factors

The need for the use of correction factors is determined during method development. In order to evaluate and to update the correction factors, measure the interference check solutions (5.12) at regular intervals within a sequence.

NOTE For example, the interference correction factor for $^{40}Ar^{35}Cl^+$ on $^{75}As$ is determined by recording the signal at mass 75 and 35 of a $Cl^-$ solution; the ratio of the net signal at mass 75 and net signal at mass 35 is the correction factor. For the isobaric molecular interference of $^{98}Mo^{16}O^+$ the correction factor is determined by the recording of the signal at mass 114 and 98 of a Mo solution.

### 7.4.4 Variable isotope ratio

Take into account the possible discrepancies in the isotope composition between the calibration solutions and the measuring solutions (e.g. relevant for Li, Pb, U).

## 7.5 Sample measurement

Run at least one measurement using multi-element calibration solutions (5.7) and a calibration blank solution (5.9).

Run the interference check solution(s) (5.12) to establish interference correction or to check presence of interference.

Every 25 samples or less and at the beginning and end, run a calibration blank solution (5.9) and a multi-element calibration solution (5.7) of an independent source.

Every (e.g.) 50 samples and at the end of a run, analyse an interference check solution (5.12).

Run all samples including one or more test blank solution (5.10).

Run at least one post digestion spiked sample from the series to check recovery. If standard addition calibration is applied to all samples, leave out recovery check.

Some elements (e.g. Ag, B, Be, Hg, Li, Th) are rinsed very slowly from the sample inlet system. Check whether a high sample count rate has an effect on the next measurement result.

Whenever an unknown sample matrix is encountered, check:

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

## 8 Calculation

Calculate the element concentration in the digested solid sample using Equation (1):

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

where

$w_i$ is the mass fraction of the element in the solid sample *i*, expressed in micrograms per gram (µg/g) or milligrams per kilogram (mg/kg) corrected to dry matter at 105 °C;

$\rho_1$ is the concentration of the element in the test portion solution (7.2), expressed in micrograms per litre (µg/l);

$\rho_0$ is the concentration of the element in the test blank solution (5.10), expressed in micrograms per litre (µg/l);

$f$ is the dilution factor of the test portion solution (7.2);

$V$ is the volume of the test solution (digest solution), expressed in litres (l);

$m$ is the mass of the digested test portion, expressed in grams (g);

$w_{\mathrm{dm}}$ is the dry matter fraction of the sample, in percent (%);

$C$ is the correction factor for dry mass $C = 100/w_{\mathrm{dm}}$.

## 9 Expression of results

State as many significant figures as are acceptable according to the precision of the measuring values, but not more than three significant figures.

## 10 Performance characteristics

### 10.1 General

The performance of this analytical method has been validated in connection with EN 16173 and EN 16174. Validation data will be included after verification.

### 10.2 Blank

The result of the calibration blank check shall be less than 3 times the instrumental limit of detection or 0,5 times the lowest concentration to be reported.

### 10.3 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.

### 10.4 Internal standard response

The relative response of the internal standard in a spiked sample shall be between 70 % and 130 % of the response of the internal standard blank or calibration check solution. If not, clean the cones and recalibrate.

### 10.5 Interference

In high matrix measurements the limit of detection of the analytes of interest should be determined in interference check solution containing relevant interferences.

EXAMPLE 1 Assume that the concentration for calcium in an interference check solution based upon a relevant matrix is 200 mg/l. As long as the contribution of interference of Ca on the interfered isotope (Ni60) is lower than three times the instrumental detection limit or lower than 0,5 times the lowest concentration to be reported (and if the concentration of the interferent (Ca) in the test sample is lower than 200 mg/l) the concentration of the interfered isotope (Ni60) can be reported.

EXAMPLE 2 Assume that the contribution of interference by the same 200 mg/l calcium solution is e.g. 0,5 µg/l and the maximum allowed contribution is 1 µg/l (either 3 times $L_{\mathrm{DI}}$ or 0,5 times the lowest concentration to be reported) then the maximum concentration of the interfering element (Ca) in the test sample on the interfered isotope (Ni60) is 400 mg/l ( = 1/0,5 · 200 mg/l assuming a linear relation). Otherwise Ni60 cannot be reported prior to further investigation of the interference.

NOTE These examples refer to the following assumptions: the contribution of corrected and uncorrected isobaric molecular and doubly-charged ions should neither be higher than 3 times the instrumental detection limit in trace analysis nor be higher than half the lowest concentration to be reported.

### 10.6 Recovery

Spike recovery shall be between 75 % and 125 % or difference between results for the original sample and the fivefold-diluted sample shall be less than 20 % when the concentration in fivefold-diluted sample is higher than three times the instrumental detection limit or twice the lowest concentration to be reported. Spike concentration should be within 0,4 times and 2,5 times the analyte concentration.

### 10.7 Precision

The performance characteristics of the method data have been evaluated based on the repeatability results and the performance data of digests (see ISO 11466 and ISO 16729).

## 11 Test report

The test report shall contain at least the following information:

a) a reference to this Technical Specification (ISO/TS 16965);

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 Technical Specification or which are optional, as well as any factor which may have affected the results.

# Annex A
(informative)

## Selected isotopes and spectral interferences for quadrupole ICP-MS instruments

For selected isotopes and spectral interferences for quadrupole ICP-MS instruments see ISO 17294-1.

**Table A.1 — Examples of equations for isobaric overlay**

| **Element** | **Recommended isotope and inter-element correction** |
|---|---|
| As | $^{75}As - 3{,}127(^{77}Se - 0{,}815\ ^{82}Se)$ or<br>$^{75}As - 3{,}127(^{77}Se - 0{,}3220\ ^{78}Se)$ |
| Ba | $^{138}Ba - 0{,}0009008\ ^{139}La - 0{,}002825\ ^{140}Ce$ |
| Cd | $^{114}Cd - 0{,}02684\ ^{118}Sn$ |
| Ge | $^{74}Ge - 0{,}1385\ ^{82}Se$ |
| In | $^{115}In - 0{,}01486\ ^{118}Sn$ |
| Mo | $^{98}Mo - 0{,}1106\ ^{101}Ru$ |
| Ni | $^{58}Ni - 0{,}04825\ ^{54}Fe$ |
| Pb | $^{208}Pb + ^{207}Pb + ^{206}Pb$ |
| Se | $^{82}Se - 1{,}009\ ^{83}Kr$ |
| Sn | $^{120}Sn - 0{,}01344\ ^{125}Te$ |
| V | $^{51}V - 3{,}127(^{53}Cr - 0{,}1134\ ^{52}Cr)$ |
| W | $^{184}W - 0{,}001242\ ^{189}Os$ |

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