TECHNICAL SPECIFICATION

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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)

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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 documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2. www.iso.org/directives

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

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, $c(HNO_3) = 15$ mol/l.

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

5.3 Hydrochloric acid, $c(HCl) = 12$ 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

Cl^-, PO_4^{3-}, 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:

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

and for digests also

$\rho(C)$ = 1 000 mg/l; $\rho(Fe)$ = 500 mg/l; $\rho(Na)$ = 500 mg/l and $\rho(Al)$ = 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

