TECHNICAL
SPECIFICATION

**ISO/TS
17073**

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Soil quality — Determination of trace elements in aqua regia and nitric acid digests — Graphite furnace atomic absorption spectrometry method (GFAAS)

Qualité du sol — Détermination des éléments en traces solubles dans l'eau régale et l'acide nitrique — Spectrométrie d'absorption atomique avec four graphite

Reference number
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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 (see 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 17073 is based upon CEN/TS 16172 *Sludge, treated biowaste and soil — Determination of elements using graphite furnace atomic absorption spectrometry (GF-AAS)*, 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 Fresh compost
Soil	Agricultural soil

Soil quality — Determination of trace elements in aqua regia and nitric acid digests — Graphite furnace atomic absorption spectrometry method (GFAAS)

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 the determination of trace elements in *aqua regia* or nitric acid digests or other extraction procedures of sludge, treated biowaste and soil, using atomic absorption spectrometry with electrothermal atomization in a graphite furnace. The method is applicable for the determination of the following elements:

Arsenic (As), cadmium (Cd), cobalt (Co), lead (Pb), antimony (Sb), thallium (Tl), vanadium (V).

This method may be applied to other elements. The lower working range is approximately 0,01 mg/kg to 0,001 mg/kg, depending on the element to be determined.

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

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 16965, *Soil quality — Determination of trace elements using inductively coupled plasma mass spectrometry (ICP-MS)*

3 Principle

Graphite furnace atomic absorption spectrometry (GFAAS) (also known as Electrothermal Atomic Absorption Spectrometry (ETAAS)), discrete sample aliquots are dispensed into a graphite tube (of which there are several types), which can be heated to over 2 500 °C very rapidly and in a controlled manner. By increasing the temperature stepwise, the processes of drying, thermal decomposition of the matrix and thermal dissociation into free atoms occurs. Atomic absorption spectrometry is based on the ability of free atoms to absorb light. A light source emits light specific for a certain element (or elements). When the light beam passes through the atom cloud in the heated graphite furnace, the light is selectively absorbed by atoms of the chosen element(s). The decrease in light intensity is measured with a detector at a specific wavelength. The concentration of an element in the sample is determined by comparing the absorbance of the sample with the absorbance of calibration solutions. The signal-peak produced is, under optimum conditions, sharp and symmetrical, and of narrow half-width. The peak area is for most elements proportional to the concentration of the element in solution. The measurements are made at the wavelengths given in Table 2.

Table 2 — Wavelengths of the elements

Element	Wavelength nm
Arsenic	193,7
Cadmium	228,8
Cobalt	240,7
Lead	217,0
Antimony	217,6
Thallium	276,8
Vanadium	318,4

Zeeman background correction and platform use is common practice.

If necessary, interferences may be overcome by adding a matrix modifier to the samples before analysis, or by performing the calibration with standard addition technique.

The results are given as the mass of analyte (micrograms or milligrams) per kilogram of dried sample materials.

4 Interferences and sources of errors

The sample solutions prepared from digestion of samples may contain large amounts of substances that may affect the results. High concentrations of chloride may cause low results, because the volatility of many elements is increased and analyte loss may occur during the pyrolysis step. High chloride concentrations interfere with TI determinations and result in severe losses of the analyte, avoid *aqua regia* digestions and use only nitric acid digestion according to ISO 16729. Matrix effects may be overcome, partially or completely, by optimization of the temperature programme, the use of pyrolytically coated tubes or platforms, the use of chemical modifiers, the standard addition technique and the use of background correction.

5 Reagents

Use only reagents of recognized analytical grade and water grade 1 as specified in ISO 3696.

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.

5.1 **Hydrochloric acid,** HCl, $\rho(\mathrm{HCl}) \sim 1{,}17$ g/ml. $c(\mathrm{HCl}) \sim 12$ mol/l, $w(\mathrm{HCl}) \sim 370$ g/kg.

The same batch of hydrochloric acid shall be used throughout the procedure.

5.2 **Nitric acid,** HNO_3, $\rho(\mathrm{HNO_3}) \sim 1{,}4$ g/ml, $c(\mathrm{HNO_3}) \sim 15$ mol/l, $w(\mathrm{HNO_3}) \sim 650$ g/kg.

The same batch of nitric acid shall be used throughout the procedure.

5.3 **Nitric acid,** diluted 1 + 3 (volume fraction).

Add 250 ml of nitric acid (5.2) to 500 ml of water in a 1 000 ml volumetric flask and fill to the mark with water.

5.4 ***Aqua regia*****,** diluted 1 + 3 (volume fraction).

Dilute 210 ml of hydrochloric acid (5.1) and 70 ml of nitric acid (5.2) with about 500 ml of water in a 1 000 ml volumetric flask, and dilute to the mark.

5.5 Standard stock solutions

Both single-element standard stock solutions and multi-element standard stock solutions with concentration of 1 000 mg/l, 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.

Alternatively, the standard stock solutions may be prepared as indicated in Table A.1.

5.6 Standard solutions

Use the same acid as the digested samples when preparing the standard and the calibration solutions.

5.6.1 Standard solution corresponding to 10 mg/l of element

Pipette 10 ml of the actual standard stock solution (5.5) into a 1 000 ml volumetric flask. Add 20 ml of nitric acid (5.3) or 20 ml of *aqua regia* (5.4), fill to the mark with water and mix well.

5.6.2 Standard solution corresponding to 0,1 mg/l of element

Pipette 5 ml of the standard solution (5.6.1) into a 500 ml volumetric flask. Add 10 ml of nitric acid (5.3) or 10 ml of *aqua regia* (5.4), fill to the mark with water and mix well. Prepare this solution on the day of use.

5.7 Calibration solutions

Before each batch of determinations, prepare, from the standard solutions of each element (5.6.1 or 5.6.2), at least four calibration solutions covering the linear range of the calibration curve for the element to be determined. Use nitric acid (5.3) or *aqua regia* (5.4) to adapt the acid concentration in calibration solutions to digest sample solution used. Calibration solutions shall be prepared on the day of use. Use the set of standard solutions containing the same acid as the digested samples.

5.8 Calibration blank solutions

Prepare a calibration blank solution in the same way as the calibration solutions, but add no standard solution. Use a 100 ml volumetric flask. Use nitric acid (5.3) or *aqua regia* (5.4) to adapt the acid concentration to that in calibration solutions (5.7). Cool if necessary and dilute to volume with water.

5.9 Palladium nitrate/magnesium nitrate modifier

Dissolve 0,259 g of $Mg(NO_3)_2 \cdot 6H_2O$ in 100 ml of water. Mix the palladium nitrate solution [10 g/l $Pd(NO_3)_2$] with twice the volume of magnesium nitrate solution. Observe the manufacturer's recommendations. 10 µl of the mixed solution is equal to 15 µg of Pd and 10 µg of $Mg(NO_3)_2$. $Pd(NO_3)_2$ solution is commercially available (10 g/l). Prepare the solution freshly every month. The palladium solution is stable for more than one month.

5.10 Magnesium nitrate modifier

Dissolve 0,865 g of $Mg(NO_3)_2 \cdot 6H_2O$ in 100 ml of water. 10 µl of this solution is equal to 50 µg of $Mg(NO_3)_2$. Observe the manufacturer's recommendations.

5.11 Ammonium dihydrogen phosphate modifier

Dissolve 2,0 g of $NH_4H_2PO_4$ in 100 ml of water. 10 µl of this solution is equal to 200 µg of $NH_4H_2PO_4$. Observe the manufacturer's recommendations.

5.12 Ammonium dihydrogen phosphate / magnesium nitrate modifier

Dissolve 2,0 g of $NH_4H_2PO_4$ and 0,173 g of $Mg(NO_3)_2 \cdot 6H_2O$ in 100 ml of water. 10 µl of this solution is equal to 200 µg of $NH_4H_2PO_4$ and 10 µg of $Mg(NO_3)_2$. Observe the manufacturer's recommendations.

5.13 Purge gas, argon, Ar (> 99,99 %).

6 Apparatus

6.1 Usual laboratory apparatus

All glass or plastic ware shall be cleaned carefully before trace element determinations, e.g. by immersion in 5 % (volume fraction) aqueous nitric acid solution for overnight, followed by rinsing with water before use. The nitric acid shall be replaced each week.

NOTE It has been found convenient to keep separate sets of glass or plastics ware for the determinations given in this Technical Specification, in order to reduce the possibility of within-laboratory contamination. Similarly, it can be convenient to carry out the acid cleaning step overnight. Certain kinds of plastic are affected by nitric acid, so care should be taken in the choice of plastic. Because of the high sensitivity of electro-thermal atomic absorption spectrometry, stringent precautions should be taken to clean all glass or plastic ware and avoid contamination of sample, standard and calibration solutions from foreign material and dust from the laboratory atmosphere.

6.2 Atomic absorption spectrometer

The atomic absorption spectrometer shall be equipped with an electro-thermal atomizer, the necessary hollow cathode lamps or electrodeless dischard lamps appropriate to the element of interest and operated at a current recommended for the lamp by the instrument manufacturer, an automatic background correction device, and a computerized read-out or a high speed chart recorder. Background correction shall be used with electrothermal atomic absorption spectrometry, the minimum acceptable technical specification (below 350 nm wavelength) of which is that based on deuterium.

6.3 Automated sample introduction system

Depending on the concentration levels to be determined, new autosampler cups may be cleaned with distilled water. The autosampler system shall be capable of delivering fixed volumes up to 70 µl.

6.4 Graphite tubes

Pyrolytically coated graphite tubes with platforms, or other corresponding tubes, are preferably used for high and medium volatile elements, while elements of low volatility should be atomized from the wall. Provided satisfactory results are achieved, the manufacturer's recommendations regarding the use of graphite tubes and platforms should be followed.

6.5 Chemical modification

Chemical modifiers are used to overcome spectral and/or non-spectral interferences in a sample (matrix effects). By measuring a sample with and without addition of an analyte, and comparison of the recovery of the analyte with a calibration standard, the existence of a non-spectral interference is often recognized. In order to ascertain that the modification works, the same procedure is repeated with the addition of a chosen chemical modifier.

In general, the aim of chemical modification is to allow a pyrolysis temperature that is high enough to remove the bulk of concomitants before the atomization step. The combination of Pd and $Mg(NO_3)_2$ is regarded as a "universal" modifier that is used for a lot of elements. The combination of Pd and a reducing agent, like ascorbic acid, is sometimes used instead of Pd/$Mg(NO_3)_2$. The background absorption tends to be high with $Mg(NO_3)_2$. Other modifiers are also used. In Table 3 some examples of chemical modifiers are given for the elements in this standard. Other chemical modifiers may be used, but potential memory effects shall be observed.

Table 3 — Examples of chemical modifiers

Element	Chemical modifiers	Amounts[a] µg
As	$Pd(NO_3)_2 + Mg(NO_3)_2$	15 + 10
Cd	$Pd + Mg(NO_3)_2$ or $NH_4H_2PO_4 + Mg(NO_3)_2$	15 + 10 or 200 + 10
Co	$Mg(NO_3)_2$	50
Pb	$Pd + Mg(NO_3)_2$ or $NH_4H_2PO_4 + Mg(NO_3)_2$	15 + 10 or 200 + 10
Sb	$Pd + Mg(NO_3)_2$ or Ni (as nitrate)	15 + 10 or 20
Tl	$Pd + Mg(NO_3)_2$	15 + 10
V	No modifier required	

[a] These amounts are only recommendations. Significantly lower amounts may be required in some atomizers. See also recommendations from instrument manufacturers.

If chemical modifiers are used, add them both to calibration blank solutions (5.8), calibration solutions (5.7), test blank solutions (7.3), test sample solutions (7.2) and quality control solutions. To achieve the recommended amounts in Table 3, 10 µl of modifier solution shall be added. Preferably inject the modifier solution with the autosampler directly into the atomizer after the sample solution is delivered.

7 Procedure

7.1 Graphite furnace programme

A temperature programme for the graphite furnace usually includes four steps:

- drying;
- pyrolysis;
- atomization;
- cleaning.

Preferably, as a start, use the temperatures and times recommended by the manufacturer. Interrupt the argon flow during the atomization step. Always use background correction.

NOTE Alternative wavelengths (with different sensitivities) may be used. For example, for lead, the wavelength 217,0 nm may be used, where the sensitivity is about twice of that at 283,3 nm. However, the noise is higher and the risk for interferences is greater. In the case of high concentrations, a wavelength with lower sensitivity may be used. For evaluation the integrated absorbance (peak area) is recommended.

7.2 Test sample solution

The test sample solution is an aliquot of the particle free digest solution prepared according to ISO 11466 or ISO 16965 or other extraction procedures.

To be within the calibration range of the very sensitive electrothermal absorption method and to protect the graphite tubes from high acid concentrations, it is recommended to dilute the sample solutions 1 + 3 with water.

7.3 Test blank solution

Prepare the test blank solution at the same time as the extraction with *aqua regia* or nitric acid or other extraction procedure is performed. Follow the same procedure, using the same quantities of all reagents for the determination, but omit the test sample. The dilution of the test blank solution shall be kept in the same manner as the test sample solutions.

7.4 Determination

Set up the instrument parameters and align the electrothermal atomizer according to the manufacturer's instructions to take full advantage of the background correction system. Set up the autosampler similarly. Use the temperature programme recommended by the instrument manufacturer for the element and select a sample volume to be within working range. Set the instrument baseline to zero. Check the zero stability within the atomization system by running the pre-set heating programme for blank firing of the graphite atomizer. Check the lack of spectral interferences by running real sample solutions with standard additions. Repeat the blank firing to ensure baseline stability.

Using the autosampler, inject into the atomiser the predetermined volume (up to 70 µl) of each of the diluted test solutions. Add a fixed volume of modifier solution, atomize and note the instrument response. If information on the concentrations to expect is roughly known, sort the test sample solutions into groups of three or four with similar concentrations of the analyte, starting with the lowest. Be careful to note any memory effects caused by particular samples, especially at high analyte levels.

Using the autosampler, inject a fixed volume of the solution (e.g. 20 µl), add for each solution a fixed volume of modifier solution (e.g. 10 µl) and atomize the solution. Measure in that way the calibration blank solution (5.8), the calibration solutions (5.7), the diluted test blank solution (7.3) and the diluted test sample solutions (7.2) in order of increasing instrument response. If the peak area of a test solution exceeds the value of the highest calibration solution, a smaller volume of the test portion shall be used.

Atomize each solution at least twice and, if the precision is acceptable according to the quality control system in use in the laboratory and average the readings. Check the instrument again for absence of memory effect, especially at high analyte levels, by running the blank firing programme after high readings. Reset the baseline to zero if necessary.

7.5 Calibration

7.5.1 Standard calibration technique

Perform the calibration with a calibration blank solution (5.8) and four equidistant calibration solutions (5.7) for an appropriate concentration range. It should be stressed that the linearity of the calibration curve is often limited.

Correct the absorbance values of the calibration solutions by subtracting the absorbance value of the blank calibration solution. For plotting a calibration curve or for calculation of the calibration function, use the resulting values together with the analyte concentrations of the calibration solutions. Usually, the calculation is done by a computer programme integrated into the AAS system.

7.5.2 Standard addition technique

To compensate the effect of non-spectral interferences, if chemical modification is not used or does not eliminate matrix effects, the standard addition technique may be applied provided the calibration curve is linear in the absorbance range used. The standard addition technique cannot be used to correct for spectral interferences, such as unspecific background absorption, and shall not be used if interferences are changing the signal with a factor of more than three.

Transfer equal volumes of the test sample solution to three vessels (e.g. autosampler cups). Add a small amount of standard solution to two of the vessels, calculated that the resulting concentration in the samples will be respectively about 100 % and 200 % higher than what is expected in the original sample. Add an equal amount of water to the third vessel. Mix the solutions well. Measure the integrated absorbance of each solution, and the plot a diagram where the concentration added is given on the abscissa and the measured absorbance on the ordinate. Determine the analyte concentration in the calibration blank solution (5.8) or test blank solution (7.3) in the same way.

8 Calculation

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

$$w_i = \frac{(\rho_1 - \rho_0) \times f \times V \times 100}{m} \tag{1}$$

where

w_i	is the mass fraction of the element in the solid sample, expressed in milligrams per kilogram (mg/kg) corrected to dry matter at 105 °C;
ρ_1	is the concentration of the element in the test sample solution (7.2), expressed in milligrams per litre (mg/l);
ρ_0	is the concentration of the element in the test blank solution (7.3), expressed in milligrams per litre (mg/l);
f	is the dilution factor of the test sample 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 kilograms (kg);

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 Test report

The test report shall contain at least the following information:

a) a reference to this Technical Specification (ISO/TS 17073);

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)

Examples of instrumental parameter settings

There may be great differences between instruments from different manufacturers, and between old and new models. It is recommended to use the temperatures proposed by the manufacturers as a start. Generally, the settings shown in Table A.1 may be applied.

Table A.1 — Proposed general instrument set-up

Element	**Wave-length** nm	**Slit width** nm	**Pyrolysis temperature** °C		**Atomization temperature** °C	
			Without modifier	**With modifier** [a]	**Without modifier**	**With modifier**[a]
As	193,7	0,7	-	1 300	-	2 300
Cd	228,8	0,7	300	900 / 900	1 250	1 100 / 1 800
Co	240,7	0,2	1 100	1 400	2 200	2 400
Pb	217,0	0,7	600	1 200 / 600	1 500	2 000 / 1 900
Sb	217,6	0,7	900	1 200 / 1 100	1 900	1 900 / 2 400
Tl	276,8	0,7	600	1 000	1 350	1 650
V	318,4	0,7	1 400	-	2 650	-

[a] The alternate temperature values are for the cases where two alternative chemical modifiers are recommended

Bibliography

[1] EN 14346, *Characterization of waste — Calculation of dry matter by determination of dry residue or water content*

[2] EN 16179, *Sludge, treated biowaste and soil — Guidance for sample pretreatment*

[3] ISO 11047, *Soil quality — Determination of cadmium, chromium, cobalt, copper, lead, manganese, nickel and zinc — Flame and electrothermal atomic absorption spectrometric methods*

[4] ISO 11465, *Soil quality — Determination of dry matter and water content on a mass basis — Gravimetric method*

[5] U.S. Environmental Protection Agency, Method 200.9 – *Determination of Trace Elements by Stabilized Temperature Graphite Furnace Atomic Absorption,* Rev. 2.2, 1994

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