
Soil quality — Determination of cadmium, chromium, cobalt, copper, lead, manganese, nickel and zinc in aqua regia extracts of soil — Flame and electrothermal atomic absorption spectrometric methods

Qualité du sol — Dosage du cadmium, chrome, cobalt, cuivre, plomb, manganèse, nickel et zinc dans les extraits de sol à l'eau régale — Méthodes par spectrométrie d'absorption atomique avec flamme et atomisation électrothermique



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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.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 11047 was prepared by Technical Committee ISO/TC 190, *Soil quality*, Subcommittee SC 3, *Chemical methods and soil characteristics*.

Annex A of this International Standard is for information only.

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Soil quality — Determination of cadmium, chromium, cobalt, copper, lead, manganese, nickel and zinc in aqua regia extracts of soil — Flame and electrothermal atomic absorption spectrometric methods

WARNING — The procedures in this International Standard should be carried out by competent, trained persons. Some of the techniques and reagents, including the use of equipment, are potentially very dangerous. Users of this International Standard who are not thoroughly familiar with the potential dangers and related safe practices should take professional advice BEFORE commencing any operation.

1 Scope

This International Standard specifies two methods for the determination, by atomic absorption spectrometry, of one or more of cadmium, chromium, cobalt, copper, lead, manganese, nickel and zinc, in aqua regia extracts of soil obtained in accordance with ISO 11466. The choice of method for any element depends on the amount of that element expected to be in a sample, and both methods might be needed to cover all the elements in one sample. The methods are applicable when the extractable element content is above or below the amount given in table 1 (as milligrams per kilogram, dry matter), as appropriate. The two methods are described separately as follows:

Method A – Determination of cadmium, chromium, cobalt, copper, lead, manganese, nickel and zinc by flame atomic absorption spectrometry.

Method B – Determination of cadmium, chromium, cobalt, copper, lead, manganese, nickel and zinc by electrothermal atomic absorption spectrometry.

Many of the procedures and reagents are common to both methods, and to the different elements within each method. Users are advised, however, to read the whole standard carefully before embarking on any of the procedures.

Table 1 — Indicative limits of soil contents (mg/kg dry matter) for elements extractable in aqua regia in accordance with ISO 11446

Element	Method A (flame AAS)	Method B (electrothermal AAS)
Cadmium	> 2	< 2
Chromium	> 12	< 12
Cobalt	> 12	< 12
Copper	> 5	< 5
Lead	> 15	< 15
Manganese	> 2	< 2
Nickel	> 12	< 12
Zinc	> 2	< 2

NOTE 1 Indicative limits given in table 1 are appropriate to the equipment and techniques available at the time of publication of this International Standard. Technical improvements may change this position in the future.

NOTE 2 This International Standard refers specifically to the use of atomic absorption spectrometry. Users of this International Standard 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 International Standard. Results should be established with control charts, for each element, within the laboratory. No result should be accepted which falls outside an agreed limit. Quality control procedures based on a widely accepted statistical technique should be used to establish such limit, to ensure that these are stable and that no long-term drift is occurring. Certified Reference Materials should be used regularly to maintain the integrity of the in-house reference materials and, thereby, the quality control system.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*

ISO 5725-1:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions*

ISO 11465:1993, *Soil quality — Determination of dry matter and water content on a mass basis — Gravimetric method*

ISO 11466: 1994, *Soil quality — Extraction of trace elements soluble in aqua regia*

3 Method A — Determination of cadmium, chromium, cobalt, copper, lead, manganese, nickel and zinc by flame atomic absorption spectrometry

3.1 Principle

The method is based on the atomic absorption spectrometric measurement of the concentration of the element in an aqua regia extract of the sample, prepared in accordance with ISO 11466, using the instrumental conditions given in table 2.

Table 2 — General analytical conditions for flame atomic absorption spectrometry

Element	Wavelength (nm)	Flame type	Lanthanum chloride	Main Interferences	Background correction
Cadmium	228,8	Oxidizing air/ acetylene	No	Fe	Deuterium
Chromium	357,9	Reducing air/ acetylene or acetylene/N ₂ O	Yes No	Fe, Al Ca, Mg	Halogen
Cobalt	240,7	Oxidizing air/ acetylene	No		Deuterium
Copper	324,8	Oxidizing air/ acetylene	No		Deuterium
Lead	217,0	Oxidizing air/ acetylene	No		Deuterium
Manganese	279,5	Oxidizing air/ acetylene or acetylene/N ₂ O	Yes No	Fe, Si	Deuterium
Nickel	232,0	Oxidizing air/ acetylene	No	Fe	Deuterium
Zinc	213,9	Oxidizing air/ acetylene	No		Deuterium

NOTE The wavelengths given are the most sensitive. Interferences are generally lower if the nitrous oxide flame is used for determination of chromium and manganese. Users should be aware that small changes in gas volume ratios can have significant effects on the intensity of the analytical signal and can also change the linearity of the instrument response. Also difference in acid strength, which will vary slightly from digest to digest, can have a measurable effect on some elements with some instruments especially if background correction is not used. Users should, therefore, familiarize themselves with these aspects of their instrument's performance.

3.2 Reagents

All reagents shall be of recognized analytical grade. Use deionized water or water distilled from an all-glass apparatus, conforming to grade 2 of ISO 3696.

The water used for blank determinations and for preparing reagents and standard solutions shall have a concentration of the element to be determined that is negligible compared with the lowest concentration of that element in the sample solutions.

3.2.1 Hydrochloric acid, 37 %; $\rho \sim 1,18$ g/ml

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

3.2.2 Nitric acid, 65 %; $\rho \sim 1,42$ g/ml

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

3.2.3 Nitric acid, diluted 1 + 3 (V/V)

Add 250 ml of nitric acid (3.2.2) to 500 ml of water in a 1000 ml volumetric flask and fill to the mark with water.

3.2.4 Sulfuric acid, 98 %; $\rho \sim 1,84$ g/ml.

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

3.2.5 Sulfuric acid, diluted 1 + 9 (V/V).

Add slowly with swirling or stirring (magnetic stirrer bar) 100 ml of sulfuric acid (3.2.4) to 700 ml of water in a 1000 ml volumetric flask, mix, cool and fill to the mark with water.

3.2.6 Lanthanum chloride solution, 37 g/l lanthanum.

Dissolve 100 g of lanthanum(III) chloride, $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$, in 700 ml water. Then quantitatively transfer it to a 1000 ml volumetric flask and fill to the mark with water.

3.2.7 Blank solution without lanthanum – for calibration

Dilute 210 ml of hydrochloric acid (3.2.1) and 70 ml of nitric acid (3.2.2) with 500 ml water in a 1000 ml volumetric flask and fill to the mark with water.

3.2.8 Blank solution with lanthanum – for calibration

Dilute 210 ml of hydrochloric acid (3.2.1) and 70 ml of nitric acid (3.2.2) with 500 ml water in a 1000 ml volumetric flask. Add 100 ml lanthanum chloride solution (3.2.6) and fill to the mark with water.

3.2.9 Acetone**3.3 Preparation of stock and standard solutions of individual elements**

The stock solutions of all the elements shall be replaced after a maximum of one year, but the standard solutions shall be renewed monthly as a minimum. If stock solutions are prepared directly from metals, care needs to be taken to ensure that the metal used is free of surface oxide layers. Stock solutions of metals are available commercially, and may be used, but their use should be controlled by appropriate laboratory procedures which meet accepted good laboratory practice. Records shall be kept of such control data.

3.3.1 Cadmium solutions

WARNING — Cadmium is highly toxic. Safety measures shall be taken to avoid ingestion.

3.3.1.1 Cadmium, stock solution corresponding to 1000 mg/l of cadmium.

Weigh, to the nearest $\pm 0,0002$ g, approximately 1,0000 g of cadmium metal (minimum purity 99,5 %) and dilute it in a covered 250 ml glass beaker with 40 ml of nitric acid (3.2.3). Then add 100 ml of water. Boil to expel nitrous fumes, cool, transfer to a 1000 ml volumetric flask and fill to the mark with water.

3.3.1.2 Cadmium, standard solution corresponding to 20 mg/l of cadmium.

Pipette 20,00 ml of the stock cadmium solution (3.3.1.1) into a 1000 ml volumetric flask. Add 20 ml of nitric acid (3.2.3) and fill to the mark with water.

3.3.2 Chromium solutions**3.3.2.1 Chromium, stock solution corresponding to 1000 mg/l of chromium.**

Dissolve $2,8290 \text{ g} \pm 0,0002 \text{ g}$ of potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, dried at 130°C for 24 h, in a covered 400 ml glass beaker with 40 ml of water. Add 5 ml of sulfuric acid (3.2.4), cool, transfer to a 1000 ml volumetric flask and fill to the mark with water.

3.3.2.2 Chromium, standard solution corresponding to 20 mg/l of chromium.

Pipette 20,00 ml of the stock chromium solution (3.3.2.1) into a 1000 ml volumetric flask. Add 20 ml of nitric acid (3.2.3) and fill to the mark with water.

3.3.3 Cobalt solutions

3.3.3.1 Cobalt, stock solution corresponding to 1000 mg/l of cobalt.

Weigh, to the nearest $\pm 0,0002$ g, approximately 1,0000 g of cobalt metal (minimum purity 99,5 %) and dissolve it in a covered 250 ml glass beaker with 10 ml of nitric acid (3.2.3) and 10 ml of hydrochloric acid (3.2.1). Then add 100 ml of water, boil to expel nitrous fumes, cool, transfer to a 1000 ml volumetric flask and fill to the mark with water.

3.3.3.2 Cobalt, standard solution corresponding to 20 mg/l of cobalt.

Pipette 20,00 ml of the stock cobalt solution (3.3.3.1) into a 1000 ml volumetric flask, add 20 ml of nitric acid (3.2.3) and fill to the mark with water.

3.3.4 Copper solutions

3.3.4.1 Copper, stock solution corresponding to 1000 mg/l of copper.

Weigh, to the nearest $\pm 0,0002$ g, approximately 1,0000 g of copper metal (minimum purity 99,5 %) and dissolve it in a covered 250 ml glass beaker with 40 ml of nitric acid (3.2.3). Then add 100 ml of water, boil to expel nitrous fumes, cool, transfer to a 1000 ml volumetric flask and fill to the mark with water.

3.3.4.2 Copper, standard solution corresponding to 20 mg/l of copper.

Pipette 20,00 ml of the stock copper solution (3.3.4.1) into a 1000 ml volumetric flask. Add 20 ml of nitric acid (3.2.3) and fill to the mark with water.

3.3.5 Lead solutions

3.3.5.1 Lead, stock solution corresponding to 1000 mg/l of lead.

Weigh, to the nearest $\pm 0,0002$ g, approximately 1,0000 g of lead metal (minimum purity 99,5 %) and dissolve it in a covered 250 ml glass beaker with 40 ml of nitric acid (3.2.3). Then add 100 ml of water, boil to expel nitrous fumes, cool, transfer to a 1000 ml volumetric flask and fill to the mark with water.

3.3.5.2 Lead, standard solution corresponding to 20 mg/l of lead.

Pipette 20,00 ml of the stock lead solution (3.3.5.1) into a 1000 ml volumetric flask. Add 20 ml of nitric acid (3.2.3) and fill to the mark with water.

3.3.6 Manganese solutions

3.3.6.1 Manganese, stock solution corresponding to 1000 mg/l of manganese.

Clean manganese metal by transferring several grams of electrolytic manganese (minimum purity 99,5 %) to a 250 ml glass beaker containing about 150 ml of dilute sulfuric acid (3.2.5). Stir and allow the manganese to settle for several minutes. Decant, wash several times with water and finally with acetone (3.2.9). Decant the surplus acetone, dry the metal for 2 min at 105 °C and cool in a desiccator.

Weigh, to the nearest $\pm 0,0002$ g, approximately 1,0000 g of such cleaned manganese metal and dissolve it in a covered 250 ml glass beaker with 20 ml of hydrochloric acid (3.2.1) and 20 ml of nitric acid (3.2.3). Then add 100 ml of water, boil to expel nitrous fumes, cool, transfer to a 1000 ml volumetric flask and fill to the mark with water.

3.3.6.2 Manganese, standard solution corresponding to 20 mg/l of manganese.

Pipette 20,00 ml of the stock manganese solution (3.3.6.1) into a 1000 ml volumetric flask. Add 20 ml of nitric acid (3.2.3) and fill to the mark with water.

3.3.7 Nickel solutions

3.3.7.1 Nickel, stock solution corresponding to 1000 mg/l of nickel.

Weigh, to the nearest $\pm 0,0002$ g, approximately 1,0000 g of nickel metal (minimum purity 99,5 %) and dissolve it in a covered 250 ml glass beaker with 10 ml of hydrochloric acid (3.2.1) and 10 ml of nitric acid (3.2.3). Then add 100 ml of water, boil to expel nitrous fumes, cool, transfer to a 1000 ml volumetric flask and fill to the mark with water.

3.3.7.2 Nickel, standard solution corresponding to 20 mg/l of nickel.

Pipette 20,00 ml of the stock nickel solution (3.3.7.1) into a 1000 ml volumetric flask. Add 20 ml of nitric acid (3.2.3) and fill to the mark with water.

3.3.8 Zinc solutions

3.3.8.1 Zinc, stock solution corresponding to 1000 mg/l of zinc.

Weigh, to the nearest $\pm 0,0002$ g, approximately 1,0000 g of zinc metal (minimum purity 99,5 %) and dissolve it in a covered 250 ml glass beaker with 40 ml of nitric acid (3.2.3). Then add 100 ml of water, boil to expel nitrous fumes, cool, transfer to a 1000 ml volumetric flask and fill to the mark with water.

3.3.8.2 Zinc, standard solution corresponding to 20 mg/l of zinc.

Pipette 20,00 ml of the stock zinc solution (3.3.8.1) into a 1000 ml volumetric flask. Add 20 ml of nitric acid (3.2.3) and fill to the mark with water.

3.4 Apparatus

3.4.1 Ordinary laboratory apparatus

All glassware shall be cleaned carefully before trace element determinations, e.g. by immersion in warm 5 % (V/V) aqueous nitric acid solution for a minimum of 6 h, followed by rinsing with water before use. The nitric acid shall be replaced each week.

NOTE It is convenient to keep separate sets of glassware for the determinations given in this International Standard, in order to reduce the possibility of within-laboratory contamination. Similarly, it may be convenient to carry out the acid cleaning step overnight.

3.4.2 Atomic absorption spectrometer

This shall be equipped with: a hollow cathode lamp or an electrode-less discharge lamp appropriate to the element of interest (operated at the current recommended for the lamp by the instrument manufacturer), a background correction system, a burner suitable for an air/acetylene or nitrous oxide/acetylene flame (operated according the manufacturer's instructions). Deuterium background correction is the minimum technical specification acceptable for background correction for measurement wavelengths below 350 nm and a halogen lamp for measurement wavelengths above 350 nm. Other systems (e.g. Zeeman polarization, Smith-Hieftje) are equally acceptable and, in certain circumstances, can be superior.

WARNING — It is essential that the manufacturer's safety recommendations are strictly observed when using these flames.

3.5 Procedure

3.5.1 Test portion

Use aqua regia extracts of soil in accordance with ISO 11466.

3.5.2 Blank test

Carry out a blank test at the same time as the extraction with aqua regia using cleaned quartz sand instead of the soil sample and follow the same procedure, using the same quantities of all the reagents for the determination.

3.5.3 Preparation of the calibration solutions

Before each batch of determinations, prepare from the 20 mg/l element standard solution (see 3.3) at least five calibration solutions covering the range of concentrations to be determined, as below. Fresh calibration solutions for all these elements shall be prepared at least monthly.

3.5.3.1 Cadmium calibration solutions

Pipette 1,00 ml, 2,00 ml, 4,00 ml, 6,00 ml, 8,00 ml, 10,00 ml of cadmium standard solution (3.3.1.2) into a series of 100 ml volumetric flasks. Add to each flask 21 ml of hydrochloric acid (3.2.1) and 7 ml of nitric acid (3.2.2). Dilute to the mark with water and mix well.

These solutions correspond to cadmium concentrations of 0,2 mg/l, 0,4 mg/l, 0,8 mg/l, 1,2 mg/l, 1,6 mg/l and 2,0 mg/l, respectively.

3.5.3.2 Chromium calibration solutions

Pipette 5,00 ml, 10,00 ml, 20,00 ml, 30,00 ml and 40,00 ml portions of chromium standard solution (3.3.2.2) into a series of 100 ml volumetric flasks. Add to each flask 21 ml of hydrochloric acid (3.2.1) and 7 ml of nitric acid (3.2.2). Dilute to the mark with water and mix well.

For measurement with an air/acetylene flame, add 10 ml of lanthanum chloride solution (3.2.6) before diluting to the mark.

These solutions correspond to chromium concentrations of 1,0 mg/l, 2,0 mg/l, 4,0 mg/l, 6,0 mg/l and 8,0 mg/l, respectively.

3.5.3.3 Cobalt calibration solution

Pipette 5,00 ml, 10,00 ml, 20,00 ml, 30,00 ml and 40,00 ml portions of cobalt standard solution (3.3.3.2) into a series of 100 ml volumetric flasks. Add to each flask 21 ml of hydrochloric acid (3.2.1) and 7 ml of nitric acid (3.2.2). Dilute to the mark with water and mix well.

These solutions correspond to cobalt concentrations of 1,0 mg/l, 2,0 mg/l, 4,0 mg/l, 6,0 mg/l and 8,0 mg/l, respectively.

3.5.3.4 Copper calibration solutions

Pipette 5,00 ml, 10,00 ml, 20,00 ml, 30,00 ml and 40,00 ml portions of copper standard solution (3.3.4.2) into a series of 100 ml volumetric flasks. Add to each flask 21 ml of hydrochloric acid (3.2.1) and 7 ml of nitric acid (3.2.2). Dilute to the mark with water and mix well.

These solutions correspond to copper concentrations of 1,0 mg/l, 2,0 mg/l, 4,0 mg/l, 6,0 mg/l and 8,0 mg/l, respectively.

3.5.3.5 Lead calibration solutions

Pipette 5,00 ml, 10,00 ml, 20,00 ml, 30,00 ml and 40,00 ml portions of lead standard solution (3.3.5.2) into a series of 100 ml volumetric flasks. Add to each flask 21 ml of hydrochloric acid (3.2.1) and 7 ml of nitric acid (3.2.2). Dilute to the mark with water and mix well.

These solutions correspond to lead concentrations of 1,0 mg/l, 2,0 mg/l, 4,0 mg/l, 6,0 mg/l and 8,0 mg/l, respectively.

3.5.3.6 Manganese calibration solutions

Pipette 2,00 ml, 5,00 ml, 10,00 ml, 20,00 ml, 30,00 ml and 40,00 ml portions of manganese standard solution (3.3.6.2) into a series of 100 ml volumetric flasks. Add to each flask 21 ml of hydrochloric acid (3.2.1) and 7 ml of nitric acid (3.2.2). Dilute to the mark with water and mix well.

For measurement with an air/acetylene flame, add 10 ml of lanthanum chloride solution (3.2.6) before diluting to the mark.

These solutions correspond to manganese concentrations of 0,4 mg/l, 1,0 mg/l, 2,0 mg/l, 4,0 mg/l, 6,0 mg/l and 8,0 mg/l, respectively.

3.5.3.7 Nickel calibration solutions

Pipette 5,00 ml, 10,00 ml, 20,00 ml, 30,00 ml and 40,00 ml portions of nickel standard solution (3.3.7.2) into a series of 100 ml volumetric flasks. Add to each flask 21 ml of hydrochloric acid (3.2.1) and 7 ml of nitric acid (3.2.2). Dilute to the mark with water and mix well.

These solutions correspond to nickel concentrations of 1,0 mg/l, 2,0 mg/l, 4,0 mg/l, 6,0 mg/l and 8,0 mg/l, respectively.

3.5.3.8 Zinc calibration solutions

Pipette 1,00 ml, 2,00 ml, 4,00 ml, 6,00 ml, 8,00 ml, 10,00 ml portions of zinc standard solution (3.3.8.2) into a series of 100 ml volumetric flasks. Add to each flask 21 ml of hydrochloric acid (3.2.1) and 7 ml of nitric acid (3.2.2). Dilute to the mark with water and mix well.

These solutions correspond to zinc concentrations of 0,2 mg/l, 0,4 mg/l, 0,8 mg/l, 1,2 mg/l, 1,6 mg/l and 2,0 mg/l, respectively.

3.5.4 Calibration

Set up the atomic absorption spectrometer according to the manufacturer's instructions at the appropriate wavelength using appropriate conditions (see table 2), and with the suitable background correction system in operation. Aspirate a calibration solution (3.5.3) and optimize the aspiration conditions, burner height and flame conditions. Adjust the response of the instrument to zero absorbance whilst aspirating water.

Aspirate the set of calibration solutions in ascending order and, as a zero member, the blank calibration solution (3.2.7 or 3.2.8). After a delay of more than 10 s, read the absorbance of each solution at least twice and, if the values fall within an accepted range, average the values. Care should be taken to ensure that, when using the more concentrated standards, the absorbance is < 1 , and preferably not more than 0,7.

NOTE 1 Nickel shows severe curvature above about 0,5 absorbance units even with a spectral bandwidth of 0,2 nm.

NOTE 2 The definition of an accepted range is outside the scope of this International Standard. However, users are reminded of NOTE 2 in clause 1, 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 control charts, confidence limits, and the statistics of normal and non-normal distributions.

3.5.5 Plotting calibration graphs

Plot a graph for each element with the concentrations of the calibration solutions [from which has been subtracted the blank calibration reading for the solution (3.2.7 or 3.2.8)], in milligrams per litre, as abscissa, and the corresponding absorbance values as ordinate.

3.6 Determination of test portion

3.6.1 General

Aspirate the blank test solution (3.5.2) and the test portion (3.5.1) separately into the flame, and measure the absorbance for that element. Read the solutions at least twice and, if the values fall within an accepted range, average the values (see NOTE 2 in 3.5.4). After each measurement, aspirate water and re-adjust the zero if necessary. If the concentration of the element in the test portion exceeds the calibration range, dilute the test solution with the blank solution (3.2.7 or 3.2.8) accordingly. Particular elements might need special precautions (3.6.2).

If an unknown type of sample is to be handled, determine the concentration of each element by the standard addition method. If the analytical results according to the standard addition method and the calibration curve are equal, the calibration curve method can be applied.

NOTE The temperatures of all calibration and test solutions should be within 1 °C of each other at the time of atomic absorption measurement.

3.6.2 Special factors

3.6.2.1 Chromium

For measurement with an air/acetylene flame, add 10 ml of lanthanum chloride solution (3.2.6) to the blank, each standard and sample flask.

NOTE The efficiency of the extraction of chromium from soils by aqua regia depends strongly on the nature of chromium compounds present, and the analytical signal is strongly affected by matrix elements (see table 2) in the extract.

3.6.2.2 Manganese

For measurement with an air/acetylene flame, add 10 ml of lanthanum chloride solution (3.2.6) to the blank, each standard and sample flask.

3.6.2.3 Nickel

For wavelength $\lambda = 232,0$ nm, select a spectral bandwidth of 0,2 nm to separate the analytical line from adjacent non-absorbing lines.

3.7 Calculation

By reference to the calibration graph obtained, determine the concentration of the element corresponding to the absorbances of the test portion (3.5.1) and of the blank test solution (3.5.2). Calculate the content (w) of the element M in the sample using the following equation:

$$w_{(M)} = \frac{(\rho_1 - \rho_0)}{w} \cdot f \cdot V$$

where

$w_{(M)}$ is the mass fraction of the element M in the sample, in milligrams per kilogram;

ρ_1 is the concentration of the element, in milligrams per litre, corresponding to the absorbance of the test portion (3.5.1);

ρ_0 is the concentration of the element, in milligrams per litre, corresponding to the absorbance of the blank test solution (3.5.2);

f is the dilution factor of the diluted test portion (3.5.1), if applicable;

V is the volume, in litres, of the test portion taken for the analysis; 0,1 litres in accordance with ISO 11466;

m is the mass of the sample, in kilograms, corrected for water content in accordance with ISO 11465, and treated in accordance with ISO 11466.

3.8 Precision

An interlaboratory test yielded the data given in annex A, table A.1. Repeatability and reproducibility were calculated according to ISO 5725-1.

3.9 Expression of results

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

EXAMPLE: $w(\text{Cd}) = 8,5 \text{ mg/kg}$

$w(\text{Cd}) = 12 \text{ mg/kg}$

3.10 Test report

The test report shall contain the following information:

- a reference to this International Standard;
- a reference to the method used;
- complete identification of the sample;
- the results of the determination;
- any details not specified in this International Standard, or which are optional, as well as any factor which may have affected the results.

4 Method B — Determination of cadmium, chromium, cobalt, copper, lead, manganese, nickel and zinc by electrothermal atomic absorption spectrometry

4.1 Principle

In electrothermal atomization atomic absorption spectrometry, discrete sample aliquots are dispensed into a graphite tube (of which there are several types), which can be heated to over 2 800 °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 occur. The signal-peak produced is, under optimum conditions, sharp and symmetrical, and of narrow half-width. The height of the peak is, for most elements, proportional to the concentration of the element in solution, although for certain elements it is preferable to work from peak area. The measurements are made at the wavelengths given in table 3.

NOTE Although a technique is given for the determination of manganese and zinc, users of this International Standard are advised that the flame method is usually more than adequate for these elements, as manganese and zinc are ubiquitous in the environment, often in relatively large amounts.

Table 3 — General conditions for electrothermal atomic absorption spectrometry

Element	Wavelength nm	Atomization conditions	Recommended background correction techniques
Cadmium	228,8	Platform recommended	Zeeman, Deuterium
Chromium	357,9	No platform	Zeeman or Smith-Hieftje
Cobalt	240,7	No platform	Zeeman, Deuterium
Copper	324,8	Platform recommended	Zeeman or Smith-Hieftje is better
Lead	217,0	Platform recommended	Zeeman, Deuterium
Manganese	279,5	Platform recommended	Zeeman or Smith-Hieftje is better
Nickel	232,0	No platform	Zeeman, Deuterium
Zinc	213,9	Platform recommended	Zeeman, Deuterium

4.2 Reagents

Refer to 3.2.

4.3 Stock and standard solutions

Stock solutions of 1000 mg/l for all elements are prepared as in 3.3. These are used to prepare the standard solutions given below. Stock solutions shall be replaced after one year as a maximum, and standard solutions with concentrations of 10 mg/l (first dilution step) shall be renewed monthly as a minimum.

4.3.1 Cadmium, standard solution corresponding to 10 mg/l of cadmium.

Pipette 10,00 ml of the cadmium stock solution (3.3.1.1) into a 1000 ml volumetric flask. Add 20 ml of nitric acid (3.2.3), fill to the mark with water and mix well.

4.3.1.1 Cadmium, standard solution corresponding to 0,4 mg/l of cadmium.

Pipette 20,00 ml of the cadmium standard solution (4.3.1) into a 500 ml volumetric flask. Add 10 ml of nitric acid (3.2.3), fill to the mark with water and mix well. Prepare this solution on the day of use.

4.3.1.2 Cadmium, standard solution corresponding to 0,02 mg/l of cadmium.

Pipette 5,00 ml of the cadmium standard solution (4.3.1.1) into a 100 ml volumetric flask. Add 2 ml of nitric acid (3.2.3), fill to the mark with water and mix well. Prepare this solution on the day of use.

4.3.2 Chromium, standard solution corresponding to 10 mg/l of chromium.

Pipette 10,00 ml of the chromium stock solution (3.3.2.1) into a 1000 ml volumetric flask. Add 20 ml of nitric acid (3.2.3), fill to the mark with water and mix well.

4.3.2.1 Chromium, standard solution corresponding to 0,4 mg/l of chromium.

Pipette 20,00 ml of the chromium standard solution (4.3.2) into a 500 ml volumetric flask. Add 10 ml of nitric acid (3.2.3), fill to the mark with water and mix well. Prepare this solution on the day of use.

4.3.3 Cobalt, standard solution corresponding to 10 mg/l of cobalt.

Pipette 10,00 ml of the cobalt stock solution (3.3.3.1) into a 1000 ml volumetric flask. Add 20 ml of nitric acid (3.2.3), fill to the mark with water and mix well.

4.3.3.1 Cobalt, standard solution corresponding to 0,4 mg/l of cobalt.

Pipette 20,00 ml of the cobalt standard solution (4.3.3) into a 500 ml volumetric flask. Add 10 ml of nitric acid (3.2.3), fill to the mark with water and mix well. Prepare this solution on the day of use.

4.3.4 Copper, standard solution corresponding to 10 mg/l of copper.

Pipette 10,00 ml of the copper stock solution (3.3.4.1) into a 1000 ml volumetric flask. Add 20 ml of nitric acid (3.2.3), fill to the mark with water and mix well.

4.3.4.1 Copper, standard solution corresponding to 0,4 mg/l of copper.

Pipette 20,00 ml of the copper standard solution (4.3.4) into a 500 ml volumetric flask. Add 10 ml of nitric acid (3.2.3), fill to the mark with water and mix well. Prepare this solution on the day of use.

4.3.5 Lead solutions, standard solution corresponding to 10 mg/l of lead.

Pipette 10,00 ml of the lead stock solution (3.3.5.1) into a 1000 ml volumetric flask. Add 20 ml of nitric acid (3.2.3), fill to the mark with water and mix well.

4.3.5.1 Lead, standard solution corresponding to 0,4 mg/l of lead.

Pipette 20,00 ml of the lead standard solution (4.3.5) into a 500 ml volumetric flask. Add 10 ml of nitric acid (3.2.3), fill to the mark with water and mix well. Prepare this solution on the day of use.

4.3.6 Manganese, standard solution corresponding to 10 mg/l of manganese.

Pipette 10,00 ml of the manganese stock solution (3.3.6.1) into a 1000 ml volumetric flask. Add 20 ml of nitric acid (3.2.3), fill to the mark with water and mix well.

4.3.6.1 Manganese, standard solution corresponding to 0,4 mg/l of manganese.

Pipette 20,00 ml of the manganese standard solution (4.3.6) into a 500 ml volumetric flask. Add 10 ml of nitric acid (3.2.3), fill to the mark with water and mix well. Prepare this solution on the day of use.

4.3.7 Nickel, standard solution corresponding to 10 mg/l of nickel.

Pipette 10,00 ml of the nickel stock solution (3.3.7.1) into a 1000 ml volumetric flask. Add 20 ml of nitric acid (3.2.3), fill to the mark with water and mix well.

4.3.7.1 Nickel, standard solution corresponding to 0,4 mg/l of nickel.

Pipette 20,00 ml of the nickel standard solution (4.3.7) into a 500 ml volumetric flask. Add 10 ml of nitric acid (3.2.3), fill to the mark with water and mix well. Prepare this solution on the day of use.

4.3.8 Zinc, standard solution corresponding to 10 mg/l of zinc.

Pipette 10,00 ml of the zinc stock solution (3.3.8.1) into a 1000 ml volumetric flask. Add 20 ml of nitric acid (3.2.3), fill to the mark with water and mix well.

4.3.8.1 Zinc, standard solution corresponding to 0,4 mg/l of zinc.

Pipette 20,00 ml of the zinc standard solution (4.3.8) into a 500 ml volumetric flask. Add 10 ml of nitric acid (3.2.3), fill to the mark with water and mix well. Prepare this solution on the day of use.

4.3.8.2 Zinc, standard solution corresponding to 0,02 mg/l of zinc.

Pipette 5,00 ml of the zinc standard solution (4.3.8.1) into a 100 ml volumetric flask. Add 2 ml nitric acid (3.2.3), fill to the mark with water and mix well. Prepare this solution on the day of use.

4.4 Apparatus

4.4.1 Usual laboratory apparatus

All glass or plastic ware shall be cleaned carefully before trace element determinations, e.g. by immersion in warm 5 % (V/V) aqueous nitric acid solution for a minimum of 6 h, 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 plastic ware for the determinations given in this International Standard, 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 electrothermal 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.

4.4.2 Atomic absorption spectrometer

This shall be equipped with an electrothermal atomizer, a hollow cathode lamp or electrodeless discharge lamp 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.

NOTE Deuterium background correction is appropriate for cadmium, zinc and lead, if the limited application of deuterium background correction for some instruments to about 0,6 to 0,8 absorbance is not exceeded. Smith-Hieftje or Zeeman background correction is required for all elements if the background signal is high. To increase the analyte-to-background-signal ratio, application of a graphite tube with a pyrolytic platform together with matrix modifiers such as diammonium hydrogen phosphate $(\text{NH}_4)_2\text{HPO}_4$, reduced palladium or other, plus peak integration read out, are recommended for samples with high acid and matrix load. Pyrolytic graphite has the additional advantage that carry-over from sample to sample is likely to be greatly reduced for most elements, in comparison with non-pyrolytic graphite. Users of this International Standard should not assume that the routine instrumental settings recommended by manufacturers will necessarily give the best results with complex matrices such as those dealt with in this International Standard. Careful development of temperature programmes is essential.

4.4.3 Automated sample introduction system, capable of delivering fixed volumes up to 70 μl .

4.5 Procedure

4.5.1 Test portion

The soil samples shall be extracted with aqua regia in accordance with ISO 11466. To cover the calibration range of the very sensitive electrothermal atomic absorption method and to protect the graphite tubes from high acid concentrations, it is recommended to dilute the sample solutions 1 + 4 with water, as follows. Pipette 20,00 ml of each sample solution into a 100 ml volumetric flask and fill to the mark with water.

4.5.2 Blank test

Carry out a blank test at the same time as the extraction with aqua regia using cleaned quartz sand instead of the soil sample and following the same procedure, using the same quantities of all the reagents for the determination.

To prepare the blank test solutions diluted 1 + 4, pipette 20,00 ml of the above solution into a 100 ml volumetric flask and fill to the mark with water.

4.5.3 Preparation of calibration solutions

Before each batch of determinations, prepare, from the standard solutions of each element (4.3), at least four calibration solutions covering the range of concentrations to be determined, as below. Calibration solutions shall be prepared on the day of use.

4.5.3.1 Blank solution for calibration

Dilute 210 ml of hydrochloric acid (3.2.1) and 70 ml of nitric acid (3.2.2) with 500 ml of water in a 1000 ml volumetric flask and fill to the mark with water.

4.5.3.2 Blank solution for calibration, diluted 1 + 4

Dilute 20,00 ml of blank solution (4.5.3.1) with water in a 100 ml volumetric flask and fill to the mark with water.

4.5.3.3 Cadmium calibration solutions

Pipette 2,00 ml, 5,00 ml, 10,00 ml, 20,00 ml and 30,00 ml of cadmium standard solution (4.3.1.2) into a series of 100 ml volumetric flasks. Add 20 ml of the blank solution (4.5.3.1) and fill to the mark with water and mix well.

These solutions correspond to cadmium concentrations of 0,0004 mg/l, 0,001 mg/l, 0,002 mg/l, 0,004 mg/l and 0,006 mg/l, respectively.

4.5.3.4 Chromium calibration solutions

Pipette 5,00 ml, 10,00 ml, 15,00 ml and 20,00 ml of chromium standard solution (4.3.2.1) into a series of 100 ml volumetric flasks. Add 20 ml of the blank solution (4.5.3.1) and fill to the mark with water and mix well.

These solutions correspond to chromium concentrations of 0,02 mg/l, 0,04 mg/l, 0,06 mg/l and 0,08 mg/l, respectively.

4.5.3.5 Cobalt calibration solutions

Pipette 5,00 ml, 10,00 ml, 20,00 ml and 30,00 ml of cobalt standard solution (4.3.3.1) into a series of 100 ml volumetric flasks. Add 20 ml of the blank solution (4.5.3.1) and fill to the mark with water and mix well.

These solutions correspond to cobalt concentrations of 0,02 mg/l, 0,04 mg/l, 0,08 mg/l and 0,12 mg/l, respectively.

4.5.3.6 Copper calibration solutions

Pipette 5,00 ml, 10,00 ml, 15,00 ml and 20,00 ml of copper standard solution (4.3.4.1) into a series of 100 ml volumetric flasks. Add 20 ml of the blank solution (4.5.3.1) and fill to the mark with water and mix well.

These solutions correspond to copper concentrations of 0,02 mg/l, 0,04 mg/l, 0,06 mg/l and 0,08 mg/l, respectively.

4.5.3.7 Lead calibration solutions

Pipette 5,00 ml, 10,00 ml, 15,00 ml and 20,00 ml of lead standard solution (4.3.5.1) into a series of 100 ml volumetric flasks. Add 20 ml of the blank solution (4.5.3.1) and fill to the mark with water and mix well.

These solutions correspond to lead concentrations of 0,02 mg/l, 0,04 mg/l, 0,06 mg/l and 0,08 mg/l, respectively.

4.5.3.8 Manganese calibration solutions

Pipette 1,00 ml, 2,00 ml, 5,00 ml and 7,50 ml of manganese standard solution (4.3.6.1) into a series of 100 ml volumetric flasks. Add 20 ml of the blank solution (4.5.3.1) and fill to the mark with water and mix well.

These solutions correspond to manganese concentrations of 0,004 mg/l, 0,008 mg/l, 0,02 mg/l and 0,03 mg/l, respectively.

4.5.3.9 Nickel calibration solutions

Pipette 5,00 ml, 10,00 ml, 15,00 ml and 20,00 ml of nickel standard solution (4.3.7.1) into a series of 100 ml volumetric flasks. Add 20 ml of the blank solution (4.5.3.1) and fill to the mark with water and mix well.

These solutions correspond to nickel concentrations of 0,02 mg/l, 0,04 mg/l, 0,06 mg/l and 0,08 mg/l, respectively.

4.5.3.10 Zinc calibration solutions

Pipette 5,00 ml, 10,00 ml, 20,00 ml and 30,00 ml of zinc standard solution (4.3.8.2) into a series of 100 ml volumetric flasks. Add 20 ml of the blank solution (4.5.3.1) and fill to the mark with water and mix well.

These solutions correspond to zinc concentrations of 0,001 mg/l, 0,002 mg/l, 0,004 mg/l and 0,006 mg/l, respectively.

4.6 Calibration and determination

4.6.1 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. Determine the optimum electrothermal atomizer parameters for the particular type of atomizer and sample volume (up to 70 µl) as recommended by the instrument manufacturer to cover the optimal 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.

4.6.2 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 possible, sort the test 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.

4.6.3 Using an autosampler, inject a fixed volume of solution. Add a fixed volume of modifier solution and atomize the diluted blank calibration solution (4.5.3.2), the calibration solutions (4.5.3), the diluted blank test solution (4.5.2) and the diluted test solutions (4.5.1) in order of increasing instrument response. If the peak height (or peak area) of the test portion 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 reproducibility is acceptable according to the quality control system in use in the laboratory (see NOTE 2 in 3.5.4), average the readings. Check the instrument again for absence of memory effects, especially at high analyte levels, by running the blank firing programme after high readings. Reset the baseline to zero if necessary.

If an unknown type of sample is to be handled, each element concentration shall be determined by means of the standard addition method. If the analytical results according to the standard addition method and calibration curve method are equal, the calibration curve method can be applied.

NOTE The reproducibility of the instrument readings expressed as an absolute difference, coefficient of variation, or a standard deviation, will vary depending on the concentration of the element in the extracts.

4.7 Plotting the graph

Plot a graph having the element concentration of the calibration solutions (from which has been subtracted the blank calibration reading), in milligrams per litre, as abscissa, and the corresponding values of the peak height (or area) as ordinate.

4.8 Calculation

By reference to the calibration graph obtained, determine the concentration of the element corresponding to the absorbance of the test portion (4.5.1) and of the diluted blank test solution (4.5.2). Calculate the content (w) of the element in the sample using the following equation:

$$w_{(M)} = \frac{(\rho_1 - \rho_0)}{w} \cdot f \cdot V$$

where

$w_{(M)}$ is the mass fraction of the element M in the sample, in milligrams per kilogram;

ρ_1 is the concentration of the element, in milligrams per litre, corresponding to the absorbance of the diluted test portion (4.5.1);