

Determination of elements in aqua regia and nitric acid digests by flame atomic absorption spectrometry

1 Scope

This Horizontal Standard includes principles and procedures for the determination of metals in aqua regia and nitric acid digests of sludge, soil and treated biowaste and neighbouring samples, using flame atomic absorption.

The method detection limit for each element depends on the sample matrix as well as of the instrument. For water samples with a simple matrix (i.e. low concentration of dissolved solids and particles), the method detection limits will be close to instrument detection limits. In digests containing higher concentrations of dissolved solids, interference effects may lead to an increase in the method detection limit.

NOTE This Horizontal Standard refers specifically to the use of atomic absorption spectrometry. Users of this Horizontal 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 Horizontal Standard. Results should be established with control charts, for each element, within the laboratory. No results 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. CRM's should be used regularly to maintain the integrity of the in-house reference materials and, thereby, the quality control system.

42 Normative references

This Horizontal Standard incorporates by dated or undated references, provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendment to or revisions of these publications apply to this Horizontal Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies.

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.
ISO 15587-2: 2002	Water quality – Digestion for the determination of selected elements in water- Part 2: Nitric acid digestion.
ISO 11047:1998	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.
Draft Horizontal	Digestion of soil, sludge, and biowaste and wast for the extraction of aqua regia soluble elements.

3 Principle

The method is based on the atomic absorption spectrometric measurement of the concentration of the element in an aqua regia or nitric acid extract of the sample, prepared in accordance with ISO 11466 or ISO 15587-2, using the instrumental conditions given in table 1.

Table 1. General conditions for flame atomic absorption spectrometry

Element	Wavelength nm	Flame type	Lanthanum chloride	Main interferences	Background correction
Aluminium	309,3	Reducing acetylene/ N ₂ O	Yes	Fe	Deuterium
Antimony	217,6	Oxidizing air/acetylene	No		Deuterium
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
Iron	248,3	Oxidizing air/acetylene	No	Co, Ni, Si	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
Molybdenum	313,3	Reducing acetylene/ N ₂ O	No	Ca, Sr, Fe	Deuterium
Nickel	232,0	Oxidizing air/acetylene	No	Fe	Deuterium
Silver	328,1	Oxidizing air/acetylene	No	Al, halides	Deuterium
Thallium	276,8	Oxidizing air/acetylene	No		Deuterium
Vanadium	318,4	Reducing acetylene/ N ₂ O	No	Fe, Al	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 the 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 especially if background correction is not used. Users should, therefore, familiarize themselves with these aspects of their instrument's performance.

4 Reagents

All reagents shall be of recognized analytical grade. Use deionized water or water distilled from all-glass apparatus, conforming to grade 1 of ISO 3696 ($\leq 0,01$ mS/m, or better).

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.

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

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

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

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

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

Add 250 ml of nitric acid (4.3) to 500 ml of water in a 1000 ml volumetric flask and fill to the mark with water.

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

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

4.5 Sulfuric acid, diluted 1 + 9 (V/V)

Add slowly with swirling or stirring (magnetic stirrer bar) 100 ml of sulfuric acid (4.4) to 700 ml water in a 1000 ml volumetric flask, mix, cool and fill to the mark with water.

4.6 Lanthanum chloride solution, 37 g/l lanthanum

Dissolve 100 g 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.

4.7.1 Blank solution without lanthanum, aqua regia

Dilute 210 ml of hydrochloric acid (4.1) and 70 ml of nitric acid (4.2) with 500 ml water in a 1000 ml volumetric flask and fill to the mark with water.

4.7.2 Blank solution without lanthanum, nitric acid

Dilute 210 ml of hydrochloric acid (4.1) and 70 ml of nitric acid (4.2) with 500 ml water in a 1000 ml volumetric flask and fill to the mark with water.

4.8.1 Blank solution with lanthanum, aqua regia

Dilute 210 ml of hydrochloric acid (4.1) and 70 ml of nitric acid (4.2) with 500 ml water in a 1000 ml volumetric flask. Add 100 ml lanthanum chloride solution (4.6) and fill to the mark with water.

4.8.2 Blank solution with lanthanum, nitric acid

Dilute 210 ml of hydrochloric acid (4.1) and 70 ml of nitric acid (4.2) with 500 ml water in a 1000 ml volumetric flask. Add 100 ml lanthanum chloride solution (4.6) and fill to the mark with water.

4.9 Acetone

4.10 Stock and standard solutions

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.

4.10.1 Aluminium solutions

4.10.1.1 Aluminium, stock solution corresponding to 1000 mg/l of aluminium

Weigh, to the nearest $\pm 0,0002$ g, approximately 1,0000 g aluminium metal and dissolve it with a minimum amount of hydrochloric acid (1+1). Transfer to a 1000 ml volumetric flask and fill to the mark with water.

4.10.1.2 Aluminium, standard solution corresponding to 20 mg/l of aluminium

Pipette 20,00 ml of the aluminium stock solution (4.10.1.1) into a 1000 ml volumetric flask. Add 20 ml of nitric acid (4.3), fill to the mark with water and mix well.

4.10.1.3 Aluminium calibration solutions, aqua regia

Pipette 5,00 ml, 10,00 ml, 20,00 ml, 30,00 ml and 40,00 ml of aluminium standard solution (4.10.1.2) into a series of 100 ml volumetric flasks. Add 21 ml of hydrochloric acid solution (4.1) and 7 ml of nitric acid (4.2). Dilute to the mark with water and mix well.

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

4.10.1.4 Aluminium calibration solution, nitric acid

Pipette 5,00 ml, 10,00 ml, 20,00 ml, 30,00 ml and 40,00 ml of aluminium standard solution (4.10.1.2) into a series of 100 ml volumetric flasks. Add 7 ml of nitric acid (4.2) and fill to the mark with water and mix well.

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

4.10.2 Antimony solutions

4.10.2.1 Antimony, stock solution corresponding to 1000 mg/l of antimony

Dissolve 2,743 potassium antimonyl tartrate hemihydrate, $K(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O$, in deionized water and dilute to 1000 ml with deionized water in a volumetric flask.

4.10.2.2 Antimony, standard solution corresponding to 20 mg/l of antimony

Pipette 20,00 ml of the antimony stock solution (4.10.1.1) into a 1000 ml volumetric flask. Add 20 ml of nitric acid (4.3), fill to the mark with water and mix well.

4.10.2.3 Antimony calibration solutions, aqua regia

Pipette 5,00 ml, 10,00 ml, 20,00 ml, 30,00 ml and 40,00 ml of antimony standard solution (4.10.1.2) into a series of 100 ml volumetric flasks. Add 21 ml of hydrochloric acid solution (4.1) and 7 ml of nitric acid (4.2). Dilute to the mark with water and mix well.

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

4.10.2.4 Antimony calibration solution, nitric acid

Pipette 5,00 ml, 10,00 ml, 20,00 ml, 30,00 ml and 40,00 ml of antimony standard solution (4.10.1.2) into a series of 100 ml volumetric flasks. Add 7 ml of nitric acid (4.2) and fill to the mark with water and mix well.

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

4.10.3 Cadmium solutions

Warning - Cadmium is highly toxic. Safety measures shall be taken to avoid ingestion.

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

Weigh, to the nearest $\pm 0,0002$ g, approximately 1,0000 g cadmium metal (minimum purity 99,5 %) and dilute it in a covered 250 ml glass beaker with 40 ml nitric acid (4.3). 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.

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

Pipette 20,00 ml of the cadmium stock solution (4.10.3.1) into a 1000 ml volumetric flask. Add 20 ml of nitric acid (4.3), fill to the mark with water and mix well.

4.10.3.3 Cadmium calibration solutions, aqua regia

Pipette 1,00 ml, 2,00 ml, 4,00 ml, 6,00 ml, 8,00 ml and 10,0 ml of cadmium standard solution (4.10.3.2) into a series of 100 ml volumetric flasks. Add 21 ml of hydrochloric acid solution (4.1) and 7 ml of nitric acid (4.2). 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.

4.10.3.4 Cadmium calibration solution, nitric acid

Pipette 1,00 ml, 2,00 ml, 4,00 ml, 6,00 ml, 8,00 ml and 10,0 ml of cadmium standard solution (4.10.3.2) into a series of 100 ml volumetric flasks. Add 7 ml of nitric acid (4.2) and fill 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.

4.10.4 Chromium solutions

4.10.4.1 Chromium, stock solution corresponding to 1000 mg/l of chromium

Dissolve 2,8290 g \pm 0,0002 g potassium dichromate, $K_2Cr_2O_7$, dried at 130 °C for 24 hours, in a covered 400 ml glass beaker with 40 ml of water. Add 5 ml of sulfuric acid (4.4), cool, transfer to a 1000 ml volumetric flask and fill to the mark with water.

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

Pipette 20,00 ml of the chromium stock solution (4.10.4.1) into a 1000 ml volumetric flask. Add 20 ml of nitric acid (4.3), fill to the mark with water and mix well.

4.10.4.3 Chromium calibration solutions, aqua regia

Pipette 5,00 ml, 10,00 ml, 20,00 ml, 30,00 ml and 40,00 ml of chromium standard solution (4.10.4.2) into a series of 100 ml volumetric flasks. Add 21 ml of hydrochloric acid solution (4.1) and 7 ml of nitric acid (4.2). Dilute to the mark with water and mix well.

For measurement with an air acetylene flame, add 10 ml of lanthanum chloride solution (4.6) 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.

4.10.4.4 Chromium calibration solutions, nitric acid

Pipette 5,00 ml, 10,00 ml, 20,00 ml, 30,00 ml and 40,00 ml of chromium standard solution (4.10.4.2) into a series of 100 ml volumetric flasks. Add 7 ml of nitric acid (4.2). Dilute to the mark with water and mix well.

For measurement with an air acetylene flame, add 10 ml of lanthanum chloride solution (4.6) 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.

4.10.5 Cobalt solutions

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

Weigh, to the nearest $\pm 0,0002$ g, approximately 1,0000 g cobalt metal (minimum purity 99,5 %) and dilute it in a covered 250 ml glass beaker with 10 ml nitric acid (4.3) and 10 ml hydrochloric acid (4.1). 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.

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

Pipette 20,00 ml of the cobalt stock solution (4.10.5.1) into a 1000 ml volumetric flask. Add 20 ml of nitric acid (4.3), fill to the mark with water and mix well.

4.10.5.3 Cobalt calibration solutions, aqua regia

Pipette 5,00 ml, 10,00 ml, 20,00 ml, 30,00 ml and 40,00 ml of cobalt standard solution (4.10.5.2) into a series of 100 ml volumetric flasks. Add 21 ml of hydrochloric acid solution (4.1) and 7 ml of nitric acid (4.2). 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.

4.10.5.4 Cobalt calibration solutions, nitric acid

Pipette 5,00 ml, 10,00 ml, 20,00 ml, 30,00 ml and 40,00 ml of cobalt standard solution (4.10.5.2) into a series of 100 ml volumetric flasks. Add 7 ml of nitric acid (4.2). 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.

4.10.6 Copper solutions

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

Weigh, to the nearest $\pm 0,0002$ g, approximately 1,0000 g copper metal (minimum purity 99,5 %) and dilute it in a covered 250 ml glass beaker with 10 ml nitric acid (4.3). 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.

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

Pipette 20,00 ml of the copper stock solution (4.10.6.1) into a 1000 ml volumetric flask. Add 20 ml of nitric acid (4.3), fill to the mark with water and mix well.

4.10.6.3 Copper calibration solutions, aqua regia

Pipette 5,00 ml, 10,00 ml, 20,00 ml, 30,00 ml and 40,00 ml of copper standard solution (4.10.6.2) into a series of 100 ml volumetric flasks. Add 21 ml of hydrochloric acid solution (4.1) and 7 ml of nitric acid (4.2). 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.

4.10.6.4 Copper calibration solutions, nitric acid

Pipette 5,00 ml, 10,00 ml, 20,00 ml, 30,00 ml and 40,00 ml of copper standard solution (4.10.6.2) into a series of 100 ml volumetric flasks. Add 7 ml of nitric acid (4.2). 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.

4.10.7 Iron solutions

4.10.7.1 Iron, stock solution corresponding to 1000 mg/l of iron

Weigh, to the nearest $\pm 0,0002$ g, approximately 1,0000 g iron metal (minimum purity 99,5 %) and dissolve it in a covered 250 ml glass beaker with 10 ml nitric acid (4.3). 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.

4.10.7.2 Iron, standard solution corresponding to 20 mg/l of iron

Pipette 20,00 ml of the copper stock solution (4.10.6.1) into a 1000 ml volumetric flask. Add 20 ml of nitric acid (4.3), fill to the mark with water and mix well.

4.10.7.3 Iron calibration solutions, aqua regia

Pipette 5,00 ml, 10,00 ml, 20,00 ml, 30,00 ml and 40,00 ml of iron standard solution (4.10.7.2) into a series of 100 ml volumetric flasks. Add 21 ml of hydrochloric acid solution (4.1) and 7 ml of nitric acid (4.2). Dilute to the mark with water and mix well.

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

4.10.7.4 Iron calibration solutions, nitric acid

Pipette 5,00 ml, 10,00 ml, 20,00 ml, 30,00 ml and 40,00 ml of iron standard solution (4.10.7.2) into a series of 100 ml volumetric flasks. Add 7 ml of nitric acid (4.2). Dilute to the mark with water and mix well.

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

4.10.8 Lead solutions

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

Weigh, to the nearest $\pm 0,0002$ g, approximately 1,0000 g lead metal (minimum purity 99,5 %) and dilute it in a covered 250 ml glass beaker with 10 ml nitric acid (4.3). 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.

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

Pipette 20,00 ml of the lead stock solution (4.10.8.1) into a 1000 ml volumetric flask. Add 20 ml of nitric acid (4.3), fill to the mark with water and mix well.

4.10.8.3 Lead calibration solutions, aqua regia

Pipette 5,00 ml, 10,00 ml, 20,00 ml, 30,00 ml and 40,00 ml of lead standard solution (4.10.8.2) into a series of 100 ml volumetric flasks. Add 21 ml of hydrochloric acid solution (4.1) and 7 ml of nitric acid (4.2). 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.

4.10.8.4 Lead calibration solutions, nitric acid

Pipette 5,00 ml, 10,00 ml, 20,00 ml, 30,00 ml and 40,00 ml of lead standard solution (4.10.8.2) into a series of 100 ml volumetric flasks. Add 7 ml of nitric acid (4.2). 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.

4.10.9 Manganese solutions

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

Clean manganese metal by transferring several grams of electrolytic manganese (minimum purity 99,5 %) and dissolve it in a covered 250 glass beaker containing about 150 ml dilute sulfuric acid (4.5). Stir and allow the manganese to settle for several minutes. Decant, wash several times with water and finally with acetone (4.9). Decant the surplus acetone, dry the metal for 2 minutes 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 hydrochloric acid (4.1) and 20 ml nitric acid (4.3). 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.

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

Pipette 20,00 ml of the manganese stock solution (4.10.9.1) into a 1000 ml volumetric flask. Add 20 ml of nitric acid (4.3), fill to the mark with water and mix well.

4.10.9.3 Manganese calibration solutions, aqua regia

Pipette 2,00 ml, 5,00 ml, 10,00 ml, 20,00 ml, 30,00 ml and 40,00 ml of manganese standard solution (4.10.9.2) into a series of 100 ml volumetric flasks. Add 21 ml of hydrochloric acid solution (4.1) and 7 ml of nitric acid (4.2). Dilute to the mark with water and mix well.

For measurement with an air acetylene flame, add 10 ml of lanthanum chloride solution (4.6) 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.

4.10.9.4 Manganese calibration solutions, nitric acid

Pipette 2,00 ml, 5,00 ml, 10,00 ml, 20,00 ml, 30,00 ml and 40,00 ml of manganese standard solution (4.10.9.2) into a series of 100 ml volumetric flasks. Add 7 ml of nitric acid (4.2). Dilute to the mark with water and mix well.

For measurement with an air acetylene flame, add 10 ml of lanthanum chloride solution (4.6) 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.

4.10.10 Molybdenum solutions

4.10.10.1 Molybdenum, stock solution corresponding to 1000 mg/l of molybdenum

Dissolve 1,840 g of ammonium heptamolybdate tetrahydrate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, in water, add 20 ml hydrochloric acid (4.1) and 20 ml nitric acid (4.3). Transfer to a 1000 ml volumetric flask and fill to the mark with water.

4.10.10.2 Molybdenum, standard solution corresponding to 20 mg/l of molybdenum

Pipette 20,00 ml of the molybdenum stock solution (4.10.10.1) into a 1000 ml volumetric flask. Add 20 ml of nitric acid (4.3), fill to the mark with water and mix well.

4.10.10.3 Molybdenum calibration solutions, aqua regia

Pipette 2,00 ml, 5,00 ml, 10,00 ml, 20,00 ml, 30,00 ml and 40,00 ml of molybdenum standard solution (4.10.10.2) into a series of 100 ml volumetric flasks. Add 21 ml of hydrochloric acid solution (4.1) and 7 ml of nitric acid (4.2). Dilute to the mark with water and mix well.

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.

4.10.9.4 Molybdenum calibration solutions, nitric acid

Pipette 2,00 ml, 5,00 ml, 10,00 ml, 20,00 ml, 30,00 ml and 40,00 ml of molybdenum standard solution (4.10.10.2) into a series of 100 ml volumetric flasks. Add 7 ml of nitric acid (4.2). Dilute to the mark with water and mix well.

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.

4.10.11 Nickel solutions

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

Weigh, to the nearest $\pm 0,0002$ g, approximately 1,0000 g nickel metal (minimum purity 99,5 %) and dilute it in a covered 250 ml glass beaker with 10 ml hydrochloric acid (4.1) and 10 ml nitric acid (4.3). 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.

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

Pipette 20,00 ml of the nickel stock solution (4.10.11.1) into a 1000 ml volumetric flask. Add 20 ml of nitric acid (4.3), fill to the mark with water and mix well.

4.10.11.3 Nickel calibration solutions, aqua regia

Pipette 5,00 ml, 10,00 ml, 20,00 ml, 30,00 ml and 40,00 ml of nickel standard solution (4.10.11.2) into a series of 100 ml volumetric flasks. Add 21 ml of hydrochloric acid solution (4.1) and 7 ml of nitric acid (4.2). 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.

4.10.11.4 Nickel calibration solutions, nitric acid

Pipette 5,00 ml, 10,00 ml, 20,00 ml, 30,00 ml and 40,00 ml of nickel standard solution (4.10.11.2) into a series of 100 ml volumetric flasks. Add 7 ml of nitric acid (4.2). 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.

4.10.12 Silver solutions

4.10.12.1 Silver, stock solution corresponding to 1000 mg/l of silver

Dissolve 1,574 g silver nitrate, AgNO_3 , in deionized water and add 10 ml nitric acid (4.3). Transfer to a 1000 ml volumetric flask and fill to the mark with water.

4.10.12.2 Silver, standard solution corresponding to 20 mg/l of silver

Pipette 20,00 ml of the silver stock solution (4.10.12.1) into a 1000 ml volumetric flask. Add 20 ml of nitric acid (4.3), fill to the mark with water and mix well.

4.10.12.3 Silver calibration solutions, aqua regia

Pipette 5,00 ml, 10,00 ml, 20,00 ml, 30,00 ml and 40,00 ml of silver standard solution (4.10.12.2) into a series of 100 ml volumetric flasks. Add 21 ml of hydrochloric acid solution (4.1) and 7 ml of nitric acid (4.2). Dilute to the mark with water and mix well.

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

4.10.12.4 Silver calibration solutions, nitric acid

Pipette 5,00 ml, 10,00 ml, 20,00 ml, 30,00 ml and 40,00 ml of silver standard solution (4.10.12.2) into a series of 100 ml volumetric flasks. Add 7 ml of nitric acid (4.2). Dilute to the mark with water and mix well.

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

4.10.13 Thallium solutions

4.10.13.1 Thallium, stock solution corresponding to 1000 mg/l of thallium

Dissolve 1,303 g thallium nitrate, $TlNO_3$, in deionized water and add 10 ml nitric acid (4.3). Transfer to a 1000 ml volumetric flask and fill to the mark with water.

4.10.13.2 Thallium, standard solution corresponding to 20 mg/l of thallium

Pipette 20,00 ml of the thallium stock solution (4.10.13.1) into a 1000 ml volumetric flask. Add 20 ml of nitric acid (4.3), fill to the mark with water and mix well.

4.10.13.3 Thallium calibration solutions, aqua regia

Pipette 5,00 ml, 10,00 ml, 20,00 ml, 30,00 ml and 40,00 ml of thallium standard solution (4.10.13.2) into a series of 100 ml volumetric flasks. Add 21 ml of hydrochloric acid solution (4.1) and 7 ml of nitric acid (4.2). Dilute to the mark with water and mix well.

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

4.10.13.4 Thallium calibration solutions, nitric acid

Pipette 5,00 ml, 10,00 ml, 20,00 ml, 30,00 ml and 40,00 ml of thallium standard solution (4.10.13.2) into a series of 100 ml volumetric flasks. Add 7 ml of nitric acid (4.2). Dilute to the mark with water and mix well.

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

4.10.14 Vanadium solutions

4.10.14.1 Vanadium, stock solution corresponding to 1000 mg/l of vanadium

Dissolve 1,000 g vanadium metal in a minimum volume of nitric acid (4.3). Transfer to a 1000 ml volumetric flask, add 10 ml nitric acid (4.2) and fill to the mark with water.

4.10.14.2 Vanadium, standard solution corresponding to 20 mg/l of vanadium

Pipette 20,00 ml of the vanadium stock solution (4.10.14.1) into a 1000 ml volumetric flask. Add 20 ml of nitric acid (4.3), fill to the mark with water and mix well.

4.10.14.3 Vanadium calibration solutions, aqua regia

Pipette 5,00 ml, 10,00 ml, 20,00 ml, 30,00 ml and 40,00 ml of vanadium standard solution (4.10.14.2) into a series of 100 ml volumetric flasks. Add 21 ml of hydrochloric acid solution (4.1) and 7 ml of nitric acid (4.2). Dilute to the mark with water and mix well.

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

4.10.14.4 Vanadium calibration solutions, nitric acid

Pipette 5,00 ml, 10,00 ml, 20,00 ml, 30,00 ml and 40,00 ml of vanadium standard solution (4.10.14.2) into a series of 100 ml volumetric flasks. Add 7 ml of nitric acid (4.2). Dilute to the mark with water and mix well.

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

4.10.15 Zinc solutions

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

Weigh, to the nearest $\pm 0,0002$ g, approximately 1,0000 g zinc metal (minimum purity 99,5 %) and dilute it in a covered 250 ml glass beaker with 40 ml nitric acid (4.3). 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.

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

Pipette 20,00 ml of the zinc stock solution (4.10.15.1) into a 1000 ml volumetric flask. Add 20 ml of nitric acid (4.3), fill to the mark with water and mix well.

4.10.15.3 Zinc calibration solutions, aqua regia

Pipette 1,00 ml, 2,00 ml, 4,00 ml, 6,00 ml, 8,00 ml and 10,00 ml of zinc standard solution (4.10.15.2) into a series of 100 ml volumetric flasks. Add 21 ml of hydrochloric acid solution (4.1) and 7 ml of nitric acid (4.2). 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.

4.10.15.4 Zinc calibration solutions, nitric acid

Pipette 1,00 ml, 2,00 ml, 4,00 ml, 6,00 ml, 8,00 ml and 10,00 ml of zinc standard solution (4.10.15.2) into a series of 100 ml volumetric flasks. Add 21 ml of hydrochloric acid solution (4.1) and 7 ml of nitric acid (4.2). 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.

5 Apparatus

5.1 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 hours, followed by rinsing with water before use. The nitric acid shall be replaced each week.

NOTE It has been found convenient to to keep separate sets of glass or plastic ware for the determinations given in this Horizontal Standard, in order to reduce the possibility of within-laboratory contamination. Similarly, it can be convenient to carry out the acid cleaning step overnight.

5.2 Atomic absorption spectrometer

This shall be equipped with a hollow cathod lamp or electrodeless discard lamp appropriate to the element of interest and operated at a 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 to 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.

6 Procedure

6.1 Test portion

The solid samples shall be extracted with aqua regia or nitric acid in accordance with ISO 11466 or ISO 15587-2, respectively.

6.2 Blank test

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

6.3 Preparation of calibration solutions

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

6.4 Calibration and determination

6.4.1 Set up the atomic absorption spectrometer according to the manufacturer's instructions at the appropriate wavelength using appropriate conditions (see table 1), and with the suitable background correction system in operation. Aspirate a calibration solution (4.10) 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 solution (4.8.1 or 4.8.2). After a delay of more than 10 seconds, 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 Horizontal Standard. However, users are reminded of NOTE 1 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.

6.5 Plotting the graph

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 (4.8.1 or 4.8.2)), in milligrams per litre, as abscissa, and the corresponding absorbance values as ordinate.

6.6 Determination of test portion

6.6.1 General

Aspirate the blank test solution (6.2) and the test portion (6.1) 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 6.4). 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 (4.7.1 or 4.7.2) accordingly. Particular elements might need special precautions (6.6.2).

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

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

6.6.2 Special factors

6.6.2.1 Chromium

For measurement with an air/acetylene flame, add 10 ml of lanthanum chloride solution (4.8.1 or 4.8.2) to the blank, each standard and sample flask.

NOTE The efficiency of the extraction of chromium from soils by aqua regia or nitric acid depends strongly on the nature of chromium compounds present, and the analytical signal is strongly affected by matrix elements (see table 1) in the extract.

6.6.2.2 Manganese

For measurement with an air/acetylene flame, add 10 ml of lanthanum chloride solution (4.8.1 or 4.8.2) to the blank, each standard and sample flask.

6.6.2.3 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.

7 Calculation

By reference to the calibration graph obtained, determine the concentration of the element corresponding to the absorbance of the test portion (6.1) and of the blank test solution (6.2). Calculate the content (w) of the element in the sample using the following equation:

$$w_{(M)} = (\bullet_1 - \bullet_0) \cdot f \cdot V/m$$

where

- $w_{(M)}$ is the mass fraction of the element M in the sample, in milligrams per kilogram;
- \bullet_1 is the concentration of the element, in milligrams per litre, corresponding to the absorbance of the diluted test portion (6.1);
- \bullet_0 is the concentration of the element, in milligrams per liter, corresponding to the absorbance of the blank test solution (6.2);
- f is the dilution factor of the diluted test portion (6.1), if applicable;

- V is the volume, in litres, of the test portion taken for the analysis, e.g. 0,1 litre 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.

8 Precision

An interlaboratory test has to be performed to yield precision data. Repeatability and reproducibility shall be calculated according to ISO 5725.1.

9 Expression of results

The measurement uncertainty reported for the results should reflect the results from the 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 on the statistics of the quality control procedures mentioned earlier, and the requirements of the analysis.

Example: $w(\text{Co}) = 8,5 \text{ mg/kg}$
 $w(\text{Co}) = 0,3 \text{ mg/kg}$

10 Test report

The test report shall contain the following information:

- a) a reference to this horizontal standard;
- b) a reference to the method used;
- c) complete identification of the sample;
- d) the results of the determination;
- e) any detail not specified in this horizontal standard or which are optional, as well as any factor which may have affected the results.