

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.

Table 1. Detection limit and optimum measurement range for direct determination.

| Element | Wavelength nm | Detection limit mg/l | Measurement range mg/l |
|-----------|------------------|-------------------------|---------------------------|
| Aluminium | 309,3 | 0,05 | 0,5 – 150 |
| Cadmium | 228,8 | 0,005 | 0,05 – 2 |
| Cobalt | 240,7 | 0,02 | 0,2 – 10 |
| Chromium | 357,9 | 0,01 | 0,1 – 10 |
| Copper | 324,8 | 0,005 | 0,05 – 10 |
| Iron | 248,3 | 0,03 | 0,3 – 10 |
| Manganese | 279,5 | 0,01 | 0,1 – 5 |
| Nickel | 232,0 | 0,02 | 0,2 – 10 |
| Lead | 217,0 | 0,05 | 0,5 – 20 |
| Vanadium | 318,4 | 0,05 | 0,5 – 10 |
| Zinc | 213,9 | 0,005 | 0,05 – 2 |

The optimum measurement range is corresponding to ten times the detection limit, and the upper limit for direct determination is corresponding to a concentration giving an absorbance about 1 abs/cm. For the determination of higher concentrations the sample has to be diluted.

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.

2 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 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. |
| EN xxx: 200y (Hor.) | Chemical analyses - Digestion of soil, sludge, biowaste and waste for the extraction of <i>aqua regia</i> soluble elements. |
| EN xxx: 200y (Hor.) | Chemical analyses - Digestion of soil, sludge, biowaste and waste for the extraction of nitric acid soluble fraction of trace elements. |
| EN-ISO 15587-1:2003 | Water Quality – Digestion for the determination of selected elements in water – Part 1: Aqua regia digestion. |
| EN-ISO 15587-1:2003 | Water Quality – Digestion for the determination of selected elements in water – Part 1: Nitric acid digestion. |

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 the standards given under clause 2, using the instrumental conditions given in table 2.

Table 2. 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 |
| 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 |
| 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 |
| Lead | 217,0 | 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 Interferences

Sample solutions of waste waters and digestions of sediments and soils, may contain large amounts of substances that may affect the results. Matrix effects may be overcome, partially or completely, by the use of a chemical modifier like lanthanum, the standard addition technique, and the use of background correction.

5 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.

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

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

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

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

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

Add 250 ml of nitric acid (5.3) to 500 ml of water in a 1000 ml volumetric flask and fill to the mark with water.

5.4 Aqua regia, diluted $\sim 1 + 3$

Dilute 210 ml of hydrochloric acid (5.1) and 70 ml of nitric acid (5.2) with about 500 ml of water in a 1000 ml volumetric flask, and dilute to the mark.

5.5 Stock solutions, 1000 mg/l

Both single-element stock solutions and multi-element stock solutions with adequate specification, stating the acid used and the preparation technique, are commercially available. These solutions are considered to be stable for more than one year, but in reference to guaranteed stability, the recommendations of the manufacturer should be considered.

Alternatively, the stock solutions may be prepared as indicated in table A1 in Annex A.

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 100 mg/l of element

Pipette 10,00 ml of the actual element stock solution (5.5) into a 100 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 10 mg/l of element

Pipette 10,00 ml of the element standard solution (5.6.1) into a 100 ml volumetric flask. Add 2 ml of nitric acid (5.3) or 2 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 range of concentrations to be determined, the optimum working range being indicated in table 1. 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 Blank calibration solutions

Prepare a blank calibration solution in the same way as the calibration solutions, but add no standard solution. Use a 100 ml volumetric flask. Add acid in correspondence to the samples that the solution will be analysed together with. Cool if necessary and dilute to volume with water.

5.9 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.

5.9.1 Blank solution without lanthanum, aqua regia

Dilute 210 ml of hydrochloric acid (5.1) and 70 ml of nitric acid (5.2) with 500 ml water in a 1000 ml volumetric flask and fill to the mark with water.

5.9.2 Blank solution without lanthanum, nitric acid

Dilute 210 ml of hydrochloric acid (5.1) and 70 ml of nitric acid (5.2) with 500 ml water in a 1000 ml volumetric flask and fill to the mark with water.

5.9.3 Blank solution with lanthanum, aqua regia

Dilute 210 ml of hydrochloric acid (5.1) and 70 ml of nitric acid (5.2) with 500 ml water in a 1000 ml volumetric flask. Add 100 ml lanthanum chloride solution (5.9) and fill to the mark with water.

5.9.4 Blank solution with lanthanum, nitric acid

Dilute 210 ml of hydrochloric acid (5.1) and 70 ml of nitric acid (5.2) with 500 ml water in a 1000 ml volumetric flask. Add 100 ml lanthanum chloride solution (5.9) and fill to the mark with water.

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 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 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.

6.2 Atomic absorption spectrometer

This shall be equipped with a hollow cathod lamp or electrodeless discharge 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.

7 Procedure

7.1 Test portion

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

7.2 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.

7.3 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 in the appendix. Calibration solutions shall be prepared on the day of use.

7.4 Calibration and determination

7.4.1 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 (4.9.1 or 4.9.2, alternatively 4.93 or 4.94 when lanthanum is added to the test solution). 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.

7.5 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 (4.9.1 or 4.9.2, alternatively 4.93 or 4.94)), in milligrams per litre, as abscissa, and the corresponding absorbance values as ordinate.

7.6 Determination of test portion

7.6.1 General

Aspirate the blank test solution (7.2) and the test portion (7.1) 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 7.4). 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 (4.9.1 or 4.9.2, alternatively 4.93 or 4.94) accordingly. Particular elements might need special precautions (7.6.2).

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.

7.6.2 Special factors

7.6.2.1 Chromium

For measurement with an air/acetylene flame, add 10 ml of lanthanum chloride solution (4.9.3 or 4.9.4) 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.

7.6.2.2 Manganese

For measurement with an air/acetylene flame, add 10 ml of lanthanum chloride solution (4.9.3 or 4.9.4) to the blank, each standard and sample flask.

7.6.2.3 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.

8 Calculation

By reference to the calibration graph obtained, determine the concentration of the element corresponding to the absorbance of the test portion (7.1) and of the blank test solution (7.2). Calculate the content (w) of the element in the sample using the following equation:

$$w_{(M)} = (\rho_1 - \rho_0).f.V/m$$

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 (7.1);
- ρ_0 is the concentration of the element, in milligrams per liter, corresponding to the absorbance of the blank test solution (7.2);
- f is the dilution factor of the diluted test portion (7.1), if applicable;
- V is the volume, in litres, of the test portion taken for the analysis;

m is the mass of the sample, in kilograms, corrected for water content;

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.

11 Performance characteristics of the method

An interlaboratory test has to be performed to yield precision data.

Annex A (Informative)

Preparation of stock solutions, 1000 mg/l

The following procedures for preparation of stock solutions are taken from U.S. Environmental Protection Agency, Method 200.9 – Determination of Trace Elements by Stabilized Temperature Graphite Furnace Atomic Absorption, Rev. 2.2, 1994, and Method 200.7 - Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry, Rev. 4.4, 1994 (V). All salts should be dried for one hour at 105 °C, unless otherwise is specified.

Table A.1 – Amount of metals and metal salts for preparation of stock solutions

| Element | Compound | Formulae | Amount, g |
|---------|--------------------|-----------------------------------|-----------|
| Al | Metal | Al | 1,000 |
| Cd | Metal ^a | Cd | 1,000 |
| Co | Metal ^a | Co | 1,000 |
| Cr | Chromium trioxide | CrO ₃ | 1,923 |
| Cu | Metal ^b | Cu | 1,000 |
| Fe | Metal | Fe | 1,000 |
| Mn | Electrolytic metal | Mn | 1,000 |
| Ni | Metal | Ni | 1,000 |
| Pb | Lead nitrate | Pb(NO ₃) ₂ | 1,599 |
| V | Metal ^a | V | 1,000 |
| Zn | Metal | Zn | 1,000 |

^a Acid cleaned with (1 + 9) HNO₃. ^b Acid cleaned with (1 + 1) HCl.

Al stock solution: Weigh, to the nearest ± 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.

Cd, Co, Cu, and V stock solution: Dissolve the metal in 50 ml (1 + 1) HNO₃ with heating if necessary to effect dissolution. Cool and dilute to volume with water in a 1000 ml volumetric flask.

Cr stock solution: Dissolve the metal compound in 120 ml (1 + 5) HNO₃. Dilute to volume with water in a 1000 ml volumetric flask.

Fe stock solution: Weigh, to the nearest ± 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. 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.

Mn stock solution: 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. Stir and allow the manganese to settle for several minutes. Decant, wash several times with water and finally with acetone. Decant the surplus acetone, dry the metal for 2 minutes at 105 °C and cool in a desiccator.

Weigh, to the nearest ± 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 and 20 ml nitric

acid. 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.

Ni stock solution: Dissolve the metal in 20 ml hot concentrated HNO₃. Cool and dilute to volume with water in a 1000 ml volumetric flask.

Pb stock solution: Dissolve the metal compound in minimum amount of (1 + 1) HNO₃. Add 20 ml (1 + 1) HNO₃ and dilute to volume with water in a 1000 ml volumetric flask.

Zn stock solution: 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. 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.