

Sludge, treated biowaste and soil — Trace elements — Method by inductively coupled plasma - mass spectrometry (ICP MS)

Schlamm, behandelte Bio-Abfälle und Boden — Spuren Elementen — Methode mit induktiv gekoppeltes Plasma mit Massen- Spectrometer (ICP-MS)

Boue, bio déchet traité et sol — Éléments trace — Méthode de spectromètre de masse à source plasma (ICP-MS)

ICS:

Descriptors:

Document type: European Standard
Document subtype:
Document stage: Working Document
Document language: E

Contents

Page

Foreword.....	3
Introduction	4
1 Scope	5
2 Normative references	5
3 Terms and definitions	5
4 Symbols and abbreviations	6
5 Principle.....	6
6 Interferences	6
6.1 General.....	6
6.2 Spectral interferences	6
6.2.1 Isobaric elemental interferences.....	6
6.2.2 Isobaric molecular and doubly charged ion interferences	6
6.2.3 Non spectral interferences	7
7 Reagents.....	7
8 Apparatus	9
9 Procedure	11
9.1 Test sample	11
9.2 Test portion	11
9.3 Instrument set up.....	11
9.4 Calibration	11
9.4.1 Linear calibration function.....	11
9.4.2 Standard addition calibration	12
9.4.3 Determination of correction factors.....	12
9.4.4 Variable isotope ratio	12
9.5 Sample measurement.....	12
10 Calculation.....	13
11 Expression of results	13
12 Performacne characteristics	13
12.1 Blank	14
12.2 Continuing calibration verification	14
12.3 Internal standard response.....	14
12.4 Interference	14
12.5 Recovery	14
12.6 Precision.....	14
13 Test report	15
Annex A (informative) Selected isotopes, spectral interferences and detection limits for quadrupole ICP-MS instruments	16
Annex B (informative) Validation	23
Bibliography	35

Foreword

This document (BT/TF151 WI CSS99027) has been prepared by Technical Committee CEN/BT TF 151 "Horizontal standards in the field of Sludge, Biowaste and Soil", the secretariat of which is held by Danish Standards

This document is a working document.

The following TC's have been involved in the preparation of the standard:

This standard is applicable and validated for several types of matrices. The table below indicates which ones.

[table to be filled and amended by the standards writer]

Material	Validated	Document
Soil	<input type="checkbox"/>	[reference]
Sludge	<input type="checkbox"/>	
Biowaste	<input type="checkbox"/>	
Soil improvers	Not validated yet	

Introduction

This document is developed in the framework of the project 'Horizontal'. It is the result of a desk study "Determination of elements by ICP-OES and ICP-MS" in Phase I and "Trace elements with ICP-MS: ruggedness test" in Phase II and aims at evaluation of the latest developments in assessing measurement of trace elements in sludge, soil, treated biowaste and neighbouring fields. After an evaluation study, in which e.g. the ruggedness of the method was studied, a European wide validation of the draft standard has taken place. The results of the desk studies as well as the evaluation and validation studies have been subject to discussions with all parties concerned in CEN. The standard is part of a modular horizontal approach in which the standard belongs to the analytical step.

Until now test methods determining properties of materials were often prepared in Technical Committees (TCs) working on specific products or specific sectors. In those test methods often steps as sampling, extraction, release or other processing, analyses, etc were included. In this approach it was necessary to develop, edit and validate similar procedural steps over and over again for every material or product. Consequently this has resulted in duplication of work. To avoid such duplication of work for parts of a testing procedure references to parts of test methods from other TCs were introduced. However the following problems are often encountered while using references in this way: 1) The referenced parts are often not edited in a way that they could easily be referred to, 2) the referenced parts are often not validated for the other type of material and 3) the updates of such test standards on products might lead to inadequate references.

In the growing amount of product and sector oriented test methods it was recognised that many steps in test procedures are or could be used in test procedures for many products, materials and sectors. It was supposed that, by careful determination of these steps and selection of specific questions within these steps, elements of the test procedure could be described in a way that can be used for all materials and products or for all materials and products with certain specifications.

Based on this hypothesis a horizontal modular approach is being investigated and developed in the project 'Horizontal'. 'Horizontal' means that the methods can be used for a wide range of materials and products with certain properties. 'Modular' means that a test standard developed in this approach concerns a specific step in assessing a property and not the whole "chain of measurement" (from sampling to analyses). **A beneficial feature of this approach is that "modules" can be replaced by better ones without jeopardizing the standard "chain".**

The use of modular horizontal standards implies the drawing of test schemes as well. Before executing a test on a certain material or product to determine certain characteristics it is necessary to draw up a protocol in which the adequate modules are selected and together form the basis for the test procedure.

The modules that relates to this standard are specified in section XX Normative references.

An overview of modules and the manner, in which modules are selected will be worked out later, at which time proper reference in this standard will be provided.

1 Scope

This European Standards describes a horizontal method for the determination of the dissolved elements aluminum, antimony, arsenic, barium, beryllium, bismuth, boron, cadmium, cesium, calcium, cerium, chromium, cobalt, copper, dysprosium, erbium, europium, gadolinium, gallium, germanium, gold, hafnium, holmium, indium, iridium, iron, lanthanum, lead, lithium, lutetium, magnesium, manganese, mercury, molybdenum, neodymium, nickel, palladium, phosphorus, platinum, potassium, praseodymium, rubidium, rhenium, rhodium, ruthenium, samarium, scandium, selenium, silicon, silver, sodium, strontium, sulphur, terbium, tellurium, thorium, thallium, thulium, tin, titanium, tungsten, uranium, vanadium, yttrium, ytterbium, zinc, and zirconium in *aqua regia* and nitric acid digests of treated biowaste, soil, sludge and sediments.

The working range depends on the matrix and the interferences encountered.

In soil, sludge and biowaste, the limit of detection is between 0,1 mg/kg dry weight and 2,0 mg/kg dry weight for most elements (see Annex B).

Note: The limit of detection of most elements will be affected their natural abundance, ionization behavior and by blank contamination and this will depend predominantly on the laboratory air-handling facilities available.

The limit of detection will be higher in cases where the determination is likely to be interfered (see clause 4) or in case of memory effects (see i.e. clause 8.2 of ISO 17294-1).

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

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

CSS99034 Soil, sludge and treated biowaste – Guidance for sample pre-treatment

CSS99025A Soil, sludge and treated biowaste – Microwave digestion for the extraction of nitric acid soluble fraction of trace elements

CSS99025B Soil, sludge and treated biowaste – Digestion for the extraction of aqua regia soluble fraction of trace elements.

EN-ISO 17294-1, *Water quality — Application of inductively coupled plasma mass spectrometry (ICP-MS) — Part 1: General guidelines*.

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1

Instrumental limit of detection (IDL)

three times the repeatability standard deviation ($3 \times Sr$) calculated from multiple readings ($n > 8$) of a (matrix) solution within a single run

TC WI :2007 (E)

3.2 method detection limit (MDL)
three times the within laboratory reproducibility standard deviation ($3 \times S_w$) calculated from multiple measurements ($n > 8$) on different days of a solution with low analyte concentrations in a relevant matrix

4 Symbols and abbreviations

ICS: Interference check solution

5 Principle

This international standard describes the multi-elemental determination of analytes by ICP-MS in (diluted) nitric acid or aqua regia digests. The method measures ions produced by a radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol is transported by argon gas into the plasma. The ions produced by high temperatures of the plasma are entrained in the plasma gas and introduced, by means of an interface, into a mass spectrometer, sorted according to their mass-to-charge ratios and quantified with a detector (e.g. channel electron multiplier). Interferences must be assessed and valid corrections applied. Interference correction must include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix.

6 Interferences

6.1 General

Detailed information on spectral and non-spectral interferences is given in clause 6.1 of EN ISO 17294-1.

6.2 Spectral interferences

6.2.1 Isobaric elemental interferences

Isobaric elemental interferences are caused by isotopes of different elements of closely matched nominal mass-to-charge ratio and which cannot be separated due to an insufficient resolution of the mass spectrometer in use (e.g. ^{114}Cd and ^{114}Sn).

Element interferences from isobars may be corrected for taking into account the influence from the interfering element (see Table A.1). The isotopes used for correction shall be free of interference if possible. Correction options are often included in the instrument software. Common isobaric interferences are given in Table A.2.

6.2.2 Isobaric molecular and doubly charged ion interferences

Isobaric molecular and doubly-charged ion interferences in ICP-MS are caused by ions consisting of more than one atom or charge, respectively. Examples include $^{40}\text{Ar}^{35}\text{Cl}^+$ and $^{40}\text{Ca}^{35}\text{Cl}^+$ ion on the ^{75}As signal and $^{98}\text{Mo}^{16}\text{O}^+$ ions on the $^{114}\text{Cd}^+$ signal. Natural isotope abundances are available from the literature. However, the most precise coefficients for an instrument will be determined from the ratio of the net isotope signals observed for a standard solution.

The accuracy of these types of equations is based upon the constancy of the observed isotopic ratios for the interfering species. Corrections that presume a constant fraction of a molecular ion relative to the "parent" ion have not been found to be reliable, e.g., oxide levels can vary with operating conditions. If a correction for an oxide ion is based upon the ratio of parent-to-oxide ion intensities, the correction must be adjusted for the degree of oxide formation by the use of an appropriate oxide internal standard previously demonstrated to form a similar level of oxide as the interferent.

Other possibilities to correct for isobaric and doubly charged ion interferences are the use of an instrument with collision/reaction cell technology or high resolution ICP–MS.

The response of the analyte of interest shall be corrected for the contribution of isobaric molecular and doubly charged interferences if their impact can be higher than three times the instrumental detection limit or higher than half the lowest concentration to be reported.

6.2.3 Non spectral interferences

Physical interferences are associated with the sample nebulization and transport processes as well as with ion-transmission efficiencies. Nebulization and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement. Dissolved solids can deposit on the nebulizer tip of a pneumatic nebulizer and on the cones.

It is recommended to keep the level of total dissolved solids below 0,2% (2,000 mg/l) to minimize deposition of solids in the sample introduction system of the plasma torch. An internal standard can be used to correct for physical interferences if it is carefully matched to the analyte so that the two elements are similarly affected by matrix changes. Other possibilities to minimize non spectral interferences are matrix matching, particularly matching of the acid concentration, and standard addition.

When intolerable physical interferences are present in a sample, a significant suppression of the internal standard signals (to less than 30 % of the signals in the calibration solution) will be observed. Dilution of the sample (e.g. fivefold) will usually eliminate the problem.

7 Reagents

7.1 General

For the determination of elements at trace and ultra trace level, the reagents shall be of adequate purity. The concentration of the analyte or interfering substances in the reagents and the water should be negligible compared to the lowest concentration to be determined.

Preferably, nitric acid preservation and digestion should be applied in order to minimize interferences by polyatoms. Bi, Hg, Hf, Mo, Sn, Sb, Te, W and Zr may need hydrochloric acid for preservation and digestion.

7.2 Water

Use water according to Grade 1 of ISO 3696 for all sample preparations and dilutions.

7.3 Nitric acid, $c(\text{HNO}_3) = 16 \text{ mol/l}$.

NOTE Nitric acid is available both as $\rho(\text{HNO}_3) = 1,40 \text{ g/ml}$ ($w(\text{HNO}_3) = 650 \text{ g/kg}$) and $\rho(\text{HNO}_3) = 1,42 \text{ g/ml}$ ($w(\text{HNO}_3) = 690 \text{ g/kg}$). Both are suitable for use in this method provided the content of the analytes of interest is minimal.

7.4 Hydrochloric acid, $c(\text{HCl}) = 12 \text{ mol/l}$; $\rho \sim 1,18 \text{ g/ml}$.

7.5 Element stock solutions

Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, In, Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nd, Ni, P, Pb, Pd, Pr, Pt, Rb, Re, Rh, Ru, S, Sb, Sc, Se, Si, Sm, Sn, Sr, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr, $\rho = 1\ 000 \text{ mg/l}$ each.

TC WI :2007 (E)

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.

7.6 Anion stock solutions

Cl, P-PO₄, S-SO₄, ρ = 1 000 mg/l each.

Prepare these solutions from the respective acids. The solutions are as well 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.

7.7 Multi-element standard solutions

Depending on the scope, different multi-element standard solutions may be necessary. In general, when combining multi-element standard solutions, their chemical compatibility and the possible hydrolysis of the components shall be regarded. Care must be taken to prevent chemical reactions (e.g. precipitation).

The multi-element standard solutions are considered to be stable for several months, if stored in the dark. This does not apply to multi-element standard solutions that are prone to hydrolysis, in particular solutions of Bi, Mo, Sn, Sb, Te, W, Hf and Zr.

Multi-element standard solution A at the mg/l level may contain the following elements:

Ag, Al, As, B, Ba, Be, Bi, Cd, Ce, Co, Cr, Cs, Cu, La, Li, Mn, Ni, Pb, Rb, Sr, Th, Tl, U, V, Se, Zn.

Use nitric acid for stabilization of standard solution A.

Multi-element standard solution B at the mg/l level may contain the following elements:

Au, Mo, Sb, Sn, W, Zr

Standard solution B needs hydrochloric acid for stabilization.

Mercury standard solutions can be stabilized by adding 1 ppm Au in nitric acid or by adding hydrochloric acid (up to 0,6%).

NOTE When Au is to be used as modifier the instrument is not suitable for accurate Au determination.

Multi-element standard solutions with more elements are allowed provided that these solutions are stable.

7.8 Multi-element calibration solutions

Prepare in one or more steps calibration solutions at the highest concentration of interest. If more concentration levels are needed prepare those similarly.

Add acids (7.3 – 7.4) to match the acid concentration of samples closely.

If traceability of the values is not established check the validity by comparison with a (traceable) independent standard.

Check the stability of the diluted calibration solutions.

7.9 Internal standard solution

The choice of elements for the internal standard solution depends on the analytical problem. The solution of this/these internal standard(s) should cover the mass range of interest. The concentrations of the selected elements (used as internal standard) should be negligibly low in the digests of samples. The elements In, Lu, Re, Ge and Rh have been found suitable for this purpose.

Generally, a suitable concentration of the internal standard in samples and calibration solutions is 10 µg/l to 50 µg/l (or optimized to ± 50.000 – 100.000 counts/s). The use of a collision/reaction cell may require higher concentrations.

7.10 Calibration blank

Prepare the calibration blank by acidifying water (7.2) to the same concentrations of the acids found in the calibration solutions and samples.

7.11 Method blank

The method blank must contain all of the reagents in the same volumes as used in the processing of the samples. The method blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

7.12 Optimization solution

The optimization solution serves for mass calibration and for optimization of the instrumental settings, e.g. adjustment of maximal sensitivity with respect to minimal oxide formation rate and minimal formation of doubly charged ions. It should contain elements covering the total mass range, as well as elements prone to a high oxide formation rate or to the formation of doubly charged ions. The composition of the optimization depends on the elements of interest, instrument and manufacturer's recommendations. An optimization solution containing e.g. Mg, Cu, Rh, In, Ba, La, Ce, U and Pb is suitable. Li, Be and Bi are less suitable because they tend to cause memory effects at higher concentrations.

The mass concentrations of the elements used for optimization should allow count rates of more than 10^4 counts per second.

7.13 Interference check solution

The interference check solutions serve to determine the correction factors for the corresponding equations. High demands are made concerning the purity of the basic reagents due to the high mass concentrations.

Interference check solutions shall contain all the interferents of practical relevance given in Table A.1, at a concentration level at the same range as expected in the samples (see also 12.4).

Leaving out an interferent of Table A.1 is permitted if it can be demonstrated that its impact is negligible and lasting.

In extraordinary situations also the other interferents of Table A.1 shall be investigated for relevance.

NOTE An example of the composition of an interferent check solution is :
 $\rho(\text{Ca}) = 2500 \text{ mg/l}$; $\rho(\text{Cl}) = 2000 \text{ mg/l}$; $\rho(\text{P-PO}_4) = 500 \text{ mg/l}$ and $\rho(\text{S-SO}_4) = 500 \text{ mg/l}$ and for digests also $\rho(\text{C}) = 1000 \text{ mg/l}$; $\rho(\text{Fe}) = 500 \text{ mg/l}$; $\rho(\text{Na}) = 500 \text{ mg/l}$ and $\rho(\text{AL}) = 500 \text{ mg/l}$ [1].

8 Apparatus

8.1 General requirements

The stability of samples, measuring, and calibration solutions depends to a high degree on the container material. The material shall be checked according to the specific purpose. For the determination of elements in a very low concentration range (sub ppb), glass or polyvinyl chloride (PVC) should not be used. Instead, it is recommended to use perfluoroalkoxy (PFA), hexafluoroethene propene (FEP) or quartz containers, cleaned with diluted, high quality nitric acid or hot, concentrated nitric acid in a closed system. For the determination of elements in a higher concentration range, HDPE or PTFE containers are also allowed for the collection of

TC WI :2007 (E)

samples. Immediately before use, all glassware should be washed thoroughly with diluted nitric acid (e.g. $w(\text{HNO}_3) = 10\%$), and then rinsed several times with water (7.2).

The limit of detection of most elements will be affected by blank contamination and this will depend predominantly on the laboratory air-handling facilities available.

The use of piston pipettes is permitted and also enables the preparation of smaller volumes of calibration solutions. The application of dilutors is also allowed. Every charge of pipette tips and single-use plastics vessels shall be tested for impurities.

NOTE Dispensing of a volume of less than 50 μl by means of a pipet should be avoided.

For more detailed information on the instrumentation see clause 5 of ISO 17294-1.

8.2 Mass spectrometer

A mass spectrometer with inductively coupled plasma (ICP) suitable for multi-element and isotope analysis is required. The spectrometer should be capable of scanning a mass range from 5 m/z (AMU) to 240 m/z (AMU) with a resolution of at least 1 m_r/z peak width at 5% of peak height (m_r = relative mass of an atom species; z = charge number). The instrument may be fitted with a conventional or extended dynamic range detection system.

Quadrupole ICP-MS, high-resolution ICP-MS and collision/reaction cell ICP-MS instrumentation is fit for purpose.

8.3 Mass-flow controller

A mass-flow controller on the nebulizer gas supply is strongly recommended. Mass-flow controllers for the plasma gas and the auxiliary gas are preferred. A cooled spraychamber (cold water or Peltier) may be of benefit in reducing some types of interferences (e.g. from polyatomic oxide species).

NOTE The plasma is very sensitive to variations in the gas flow rate. For older instruments a flowrestrictor in combination with elevated pressure may be used for nebulizer flow adjustment but makes an internal standard obligatory.

8.4 Nebulizer with variable speed peristaltic pump

NOTE The speed of the pump shall not be too low and the number of rolls as high as possible to provide a stable signal.

8.5 Gas supply

Argon gas with high purity grade, i.e. > 99,99 %

Reaction gas: He, H₂ high purity (i.e. > 99.99 %)

8.6 Glassware

- Volumetric flasks;
- Erlenmeyer flasks;
- Pipettes.

8.7 Storage bottles for the stock, standard, calibration and sample solutions

Preferably made from perfluoroalkoxy (PFA) or hexafluoroethene propene (FEP). For the determination of elements in a higher concentration range (> sub ppb) glass, HDPE or PTFE bottles may be sufficient for the storage of samples.

9 Procedure

9.1 Test sample

The test sample is an acidified aqueous sample ($\text{pH} \leq 1$) free of particles or the digest obtained by *<Horizontal standard nitric acid digestion>* or *<Horizontal standard aqua regia digestion>*.

9.2 Test portion

The test portion may be directly obtained from the digest or may be diluted to accommodate the measurement range or to dilute the matrix. The acidity of the test portion must match the acidity of calibration solutions.

Ensure that all elements are present in a non-volatile form. Volatile species must be converted to non-volatile ones e.g. sulfide oxidation by hydrogen peroxide.

9.3 Instrument set up

Adjust the instrumental parameters of the ICP-MS system in accordance with the manufacturer's manual. A guideline for method and instrument set up is given in ISO 17294-1.

Define the isotopes and the need for corresponding corrections. See clause 6.3.2 of ISO 17294-1 for a method to determine these factors. Alternatively, apply multivariate calibration procedures.

Define the rinsing times depending on the length of the flow path; in the case of wide working range of analyte mass concentrations in the measuring solutions, allow longer rinsing periods.

The use of an internal standard is recommended. Add the internal standard solution (7.9) to the interference check solution (7.13), to all multi-element calibration solutions (7.8), to the blank calibration solutions (7.10), and to all measuring solutions. On-line dilution and mixing of the sample flow with internal standard solution by means of the peristaltic pump of the nebuliser is commonly used. In such case the calibration solutions are diluted the same way as the sample solutions.

The mass concentration of the reference-elements shall be the same in all solutions. A mass concentration of 10 $\mu\text{g/l}$ to 50 $\mu\text{g/l}$ (or optimized to $\pm 50.000 - 100.000$ counts/s) is often suitable.

About 30 min prior to measurement, adjust the instrument to working condition.

Before each series of measurement check the sensitivity and the stability of the system and minimize interference e.g. by using the optimization solution (7.12).

Check the resolution and the mass calibration as often as required by the manufacturer.

NOTE ICP-MS has excellent multi-element capability. Nevertheless it does not mean that all elements can be analyzed during one measurement run. The sensitivity of determination depends on numerous parameters (nebulizer flow, radio-frequency power, lens voltage, lens voltage mode etc.). The optimal instrument settings can not be reached for all elements at once.

9.4 Calibration

9.4.1 Linear calibration function

If more than two concentration levels, including zero, are used apply weighted linear regression to obtain the linear calibration function.

TC WI :2007 (E)

NOTE ICP-MS provides a large measurement range. The dispersion of blank measurements is usually much smaller than the dispersion at full scale. Ordinary linear regression assumes that the dispersion is constant over the entire range. As a consequence a much higher percentage of the calculated intercepts is out of the range expected from the spread of blanks: a non-zero blank value is calculated that is actually not there. Weighted linear regression forces the line through points of low dispersion, resulting in the expected intercept dispersion. Unfortunately, many data systems cannot handle weighted regression.

An alternative, but less efficient, approach is ordinary linear regression where the line is forced through the blank value or through zero.

The most inexpensive way however is a (single or multiple) two point calibration. If calibration lines are linear, as they are usually in ICP-MS, this procedure is valid and efficient.

If weighted linear regression is not possible apply linear regression forced through the blank value or through zero. In the latter case check regularly by running a blank whether the assumption on the absence of a blank value is justified.

NOTE Weighted linear regression is not suitable for lower element concentrations.

A two point calibration is allowed if the calibration function is linear, which usually is the case. Check regularly with a calibration solution of known dilution whether the assumption on linearity is justified.

Instead of one measurement per level more measurements can be performed to reduce the uncertainty of the calibration line.

9.4.2 Standard addition calibration

Add a known amount of standard solution (V_s) of the analyte and an equal amount of blank solution (V_b) to two separate but equal portions of the sample solution (or its dilution). Minimise dilution or correct for spike dilution. The added amount of standard solution should be between 0,4 and 2 times the expected sample mass concentration. Measure both solutions as a sample solution. Determine the 'measured spike concentration' as the difference in mass concentration between the two spiked sample portions. Use the ratio 'true spike concentration' versus 'measured spike concentration' as a correction factor for the initially measured concentration of the sample portion.

9.4.3 Determination of correction factors

The need for the use of correction factors is determined during method development. In order to evaluate and to update the correction factors, measure the interference check solutions (7.13) at regular intervals within a measuring cycle.

9.4.4 Variable isotope ratio

Take into account the possible discrepancies in the isotope composition between the calibration solutions and the measuring solutions (e.g. relevant for Li, Pb, U).

9.5 Sample measurement

Run one or more calibration solutions and a calibration blank.

Run the interference check solution(s) to establish interference correction or to check presence of interference.

Every 25 samples or less and at the beginning and end, run a calibration blank and a calibration check solution of an independent source (7.8).

Every (e.g.) 50 samples and at the end of a run, analyze an interference check solution (ICS).

Run all samples including one or more method blanks.

Run at least one post digestion spiked sample from the series to check recovery.

NOTE If standard addition calibration is applied to all samples leave out recovery check.

Some elements (for example Ag, B, Be, Hg, Li, Th) are rinsed very slowly from the sample inlet system. Check whether a high sample count rate has an effect on the next measurement result.

Whenever a unknown sample matrix is encountered check:

- matrix effects by running the spike sample;
- matrix effects by running a fivefold diluted sample;
- inter-element interference analysing a different isotope.

10 Calculation

Calculate the element concentration in the digested solid sample:

$$w = \frac{(\rho_1 - \rho_0) \times f_a \times 100}{m \times dw}$$

where:

ρ_1 is the concentration of the element in the test sample in $\mu\text{g/l}$;

ρ_0 is the concentration of the element in the blank in $\mu\text{g/l}$;

f_a is the dilution factor of the test portion;

w is the mass fraction of the element in the solid sample in $\mu\text{g/g}$ or mg/kg ;

V is the volume of the test sample (digest) in l;

m is the mass of the digested sample in g.

dw is the dry weight of the sample, in %.

11 Expression of results

State as many significant figures as are acceptable according to the precision of the measuring values, but not more than three significant figures.

12 Performance characteristics

The performance of this analytical method has been verified in connection with the digestion methods for soil, sludge and treated biowaste using nitric acid and aqua regia. A separate validation of digests has not been carried out apart from the within lab variability in the ruggedness phase. The reproducibility is generally a factor 2 – 2.5 larger than the repeatability.

TC WI :2007 (E)

12.1 Blank

Result of the calibration blank check shall be less than 3 times the instrumental limit of detection or 0,5 times the lowest concentration to be reported.

12.2 Continuing calibration verification

Result of the calibration check standard shall not deviate more than 10 % otherwise recalibrate.

12.3 Internal standard response

The relative response of the internal standard in a sample shall be between 70 and 130 % of the response of the internal standard blank or calibration check solution. If not, clean the cones and recalibrate.

12.4 Interference

The contribution of corrected and uncorrected isobaric molecular and doubly charged shall not be higher than three times the instrumental detection limit in trace analysis or lower than halve the value of the lowest concentration to be reported.

In high matrix measurements the limit of detection of the analytes of interest should be determined in ICS containing relevant interferences.

NOTE Assume that the concentration for calcium in an interference check solution (ICS) based upon a relevant matrix is 200 mg/l. As long as the contribution of interference of Ca on the interfered isotope (Ni60) is lower than three times the instrumental detection limit or lower than 0,5 times the lowest concentration to be reported (and if the concentration of the interferent (Ca) in the test sample is LOWER than 200 mg/L) the concentration of the interfered isotope (Ni60) can be reported.

Assume that the contribution of interference by the same 200 mg/l calcium solution is e.g. 0,5 µg/l and the maximum allowed contribution is 1 µg/l (either 3* IDL or 0,5 * lowest concentration to be reported) than the maximum concentration of the interferent (Ca) in the test sample on the interfered isotope (Ni60) is 400 mg/l (= 1/0,5 * 200 mg/l assuming a linear relation). Otherwise Ni60 can NOT be reported prior to further investigation of the interference.

12.5 Recovery

Spike recovery shall be between 75 % and 125 % or difference between results for the original sample and the fivefold-diluted sample shall be less than 20 % when the concentration in fivefold-diluted sample is higher than three times the instrumental detection limit or twice the lowest concentration to be reported. Spike concentration should be within 0,4 and 2,5 times the analyte concentration.

12.6 Precision

The performance characteristics of the method data have been evaluated based on the repeatability results (Annex B) and the performance data of digests (see CSS99025 a and b). Table 2 gives typical values for repeatability and reproducibility limits that can be expected taking into consideration the different sensitivities of the different elements.

Table 2 — Typical values and observed ranges of the repeatability and reproducibility limits

<p>The reproducibility limit provides a determination of the differences (positive and negative) that can be found (with a 95 % statistical confidence) between a single test result obtained by a laboratory using its own facilities and another test result obtained by another laboratory using its own facilities, both test results being obtained under the following conditions : The tests are performed in accordance with all the requirements of the present standard and the two laboratory samples are obtained from the same primary field sample and prepared under identical procedures. Conversely, the repeatability limit refers to measurements obtained from the same laboratory, all other conditions being identical. The reproducibility limit and the repeatability limit do not cover sampling but cover all activities carried out on the laboratory sample including its preparation from the primary sample.</p>		
Results of the validation of the determination of elements in aqua regia extract from, sludge by Inductively coupled plasma – mass spectrometry (ICP MS) method	Typical value %	Observed range %
Repeatability limit, r	5	3 - 10
Reproducibility limit, R	10	6 - 20

NOTE 1. The above results refer to the difference that may be found between two test results performed on two laboratory samples obtained under the same conditions. In the case when reference is made to the dispersion of the values that could reasonably be attributed to the parameter being measured, the above typical reproducibility values and observed reproducibility ranges should be divided by $\sqrt{2}$ to obtain the corresponding typical dispersion limit and its observed range.

NOTE 2 The repeatability and reproducibility are at least better than the performance characteristics reported for the aqua regia and nitric acid digestion as specified in respectively BT_TF151_WI_CSS99025B_Aqua_regia digestion and BT_TF151_WI_CSS99025A_Nitric acid digestion.

13 Test report

The test report shall make reference to this international standard and contain the following details:

- a) Complete identification of the sample;
- b) Expression of results as indicated in clause 11;
- c) Sample pre-treatment, if appropriate;
- d) Any deviations from this method, and details of all circumstances which could have affected the result.

Annex A (informative)

Selected isotopes, spectral interferences and detection limits for quadrupole ICP-MS instruments

Table 1 — Selected isotopes, spectral interferences and detection limits for quadrupole ICP-MS instruments

Element	Isotope	Abundance (%)	Potential interferences		Interference with practical relevance	Best usable isotopes	
			Interelement	Polyatomic ions		Preference	Reason
Ag	107	51,8		ZrO YO	⁹¹ Zr ¹⁶ O	x	least interference
	109	48,2		ZrO ZrOH NbO			
Al	27	100		BeO BO CN HCN		x	
As	75	100	Sm ²⁺ Nd ²⁺	Eu ²⁺ ArCl CoO Ar ₂ H ArK CaO ₂ NaCAr CPO ₂ CaCl	⁴⁰ Ar ³⁵ Cl	x	
Au	197	100		HfO TaO		x	
B	10	19,9				x	free of interference, low background
	11	80,1		BH			
Ba	135	6,6					
	137	11,2				x	highest abundance, least interference
	138	71,7	La Ce		La, Ce		
Be	9	100				x	
Bi	209	100				x	
Ca	43	0,14	Sr ²⁺	MgO BO ₂ AlO CaH CNO CO ₂	Sr ²⁺	x	low background, least interference
	44	2,1	Sr ²⁺	CaH MgO AlO BO ₂ CNO SiO CO ₂ N ₂ O	Sr ²⁺ , ¹² C ¹⁶ O ₂	x	lowest det. limit
Cd	111	12,8		MoO MoOH ZrOH K ₂ O ₂ H	⁹⁴ Zr ¹⁶ O ¹ H, ⁹⁵ Mo ¹⁶ O		
	113	12,2	In	MoO ZrOH Ca ₂ O ₂ H Ar ₂ O ₂ H RuO	In, ⁹⁷ Mo ¹⁶ O	x	for high Sn

Element	Isotope	Abundance (%)	Potential interferences		Interference with practical relevance	Best usable isotopes	
			Interelement	Polyatomic ions		Preference	Reason
	114	28,7	Sn	MoO MoOH RuO	Sn, $^{98}\text{Mo}^{16}\text{O}$	x	lowest det. limit, least interference
Ce	140	88,5				x	
Co	59	100	Sn^{2+}	CaO CaOH MgCl ArNa ArOH ArF	$^{43}\text{Ca}^{16}\text{O}$	x	
Cr	52	83,8		SO ArO ArC ArN ClO HClO ClN ArNH	$^{40}\text{Ar}^{12}\text{C}$	x	for low C and high Cl
	53	9,5		HSO ArC HClO ClO ArOH ArN ArNH SO	$^{37}\text{Cl}^{16}\text{O}$	x	for high C and low Cl
Cs	133	100		RuO ₂		x	
Cu	63	69,2		TiO PO ₂ ArNa MgCl NaCa CaOH ArCNH NCCl COCl	$^{47}\text{Ti}^{16}\text{O}$, $^{40}\text{Ar}^{23}\text{Na}$	x	for low Na and Ti, lowest det. limit
	65	30,8	Ba^{2+}	TiO PO ₂ SO ₂ SO ₂ H ArMg CaOH ArN ₂ H S ₂ COCl	$^{49}\text{Ti}^{16}\text{O}$, $^{32}\text{S}^{16}\text{O}_2^1\text{H}$, $^{40}\text{Ar}^{25}\text{Mg}$	x	for medium Mg, S and Ti and high Na
Dy	163	24,9		NdO SmO		x	
Er	166	33,6		SmO NdO		x	
Eu	151	47,8		BaO			
	153	52,2		BaO		x	
Fe	54	5,8	Cr	HClO ArO ArN ArNH ArOH SO ClO	ArN Cr	x	abundance and background determine choice
	57	2,2		CaO ArO ArOH CaC CaN CaOH MgO ₂ ArF	$^{40}\text{Ar}^{16}\text{O}^1\text{H}$ $^{40}\text{Ca}^{16}\text{O}^1\text{H}$	x	
Ga	69	60,1	Ce^{2+} Ba^{2+} La^{2+}	ClO ₂ ArP VO ArS SO ₂ S ₂	Ba^{2+}		
	71	39,9	Nd^{2+} Ce^{2+}	ArP ClO ₂ ArCl SO ₂ ArS CrO		x	least interference
Gd	157	15,7		CeO PrO LaO BF		x	least interference
	158	24,8	Dy	CeO PrO NdO	Dy		

TC WI :2007 (E)

Element	Isotope	Abundance (%)	Potential interferences		Interference with practical relevance	Best usable isotopes	
			Interelement	Polyatomic ions		Preference	Reason
Ge	74	35,9	Se Sm2+ Nd2+	ArS Cl2 Ar2	Se	x	
Hf	178	27,3		GdO DyO ErO		x	
Hg	200	23,1		WO	184W16O		
	201	13,2		WO	184W17O	x	least interference of WO
	202	29,9		WO	186W16O		
Ho	165	100		SmO		x	
In	115	95,7	Sn	RuO	Sn	x	
Ir	193	62,7		HfO LuO		x	
K	39	93,3		ArH		x	
La	139	99,9				x	
Li	6	7,5					
	7	92,5				x	lowest det. limit
Lu	175	97,4	Hf	GdO TbO	Hf	x	
Mg	24	79,0	Ti2+ Ca2+	LiO NaH C2		x	lowest det. limit, least interference
	25	10,0	Ti2+	LiO BeO C2 C2H			
	26	11,0		BeO BO CN C2H2 C2H		x	for higher Mg concentrations
Mn	55	100		HClO ArN ClO NaS ArOH ArNH KO ArN ArO ArF	ArNH	x	
Mo	95	15,9		ArKO BrO			
	98	24,1	Ru	BrO K2O	Ru	x	lowest det. limit
Na	23	100	Ti2+ Ca2+	LiO		x	
Nd	146	17,2		BaO RuO3		x	
Ni	58	68,1	Fe	CaO ArO CaN NaCl MgS CaOH Si2 ArOH	Fe	x	for low Fe

Element	Isotope	Abundance (%)	Potential interferences		Interference with practical relevance	Best usable isotopes	
			Interelement	Polyatomic ions		Preference	Reason
	60	26,2	Sn ²⁺	CaO CaOH MgCl NaCl	44Ca16O	x	least interference
	61	1,1	Sn ²⁺	CaOH ScO	44Ca16O1H, 45Sc16O		
P	31	100		SiH NO NOH N ₂ H CO COH	NO	x	
Pb	206B)	24,1		PtO		x	Sum of 206, 207 and 208
	207B)	22,1		IrO		x	Sum of 206, 207 and 208
	208B)	52,4		PtO		x	Sum of 206, 207 and 208
Pd	105	22,3		YO ArCu			
	108	26,5	Cd	MoO ZrO	Cd	x	
Pr	141	100				x	
Pt	195	33,8		HfO		x	
Rb	85	72,2	Yb ²⁺ Er ²⁺			x	
Re	185	37,4		TmO ErO		x	least interference
	187	62,6	Os	TmO YbO	Os	x	highest abundance
Rh	103	100	Pb ²⁺	SrO ArCu RbO		x	
Ru	101	17,0		ArNi NiCl			
	102	31,6	Pd	SrO	Pd	x	lowest det. limit, least interference
S	34	4,2		O ₂ SH NOH O ₂ H	O ₂	x	
Sb	121	57,4		PdO		x	least interference
	123	47,6	Te	ZrO	Te		
Sc	45	100	Zr ²⁺	CO ₂ SiO BO ₂ AlO CaH CHO ₂ SiOH N ₂ OH	13C16O ₂ , 29Si16O	x	
Se	77	7,6	Sm ²⁺ Gd ²⁺	ArCl Ar ₂ H CaCl CFNO ₂	40Ar37Cl	x	for low Cl

TC WI :2007 (E)

Element	Isotope	Abundance (%)	Potential interferences		Interference with practical relevance	Best usable isotopes	
			Interelement	Polyatomic ions		Preference	Reason
	78	23,8	Kr Gd ²⁺ Dy ²⁺	Ar ₂ CaCl ArCa	38Ar40Ar	x	for high Cl and Br
	82	8,7	Kr Ho ²⁺ Er ²⁺ Dy ²⁺	Ar ₂ H BrH CCl ₂ SO ₃ Ar ₂ H ₂ ArCa	Kr, 81Br1H	x	for low Br
Si	29	4,7		CO N ₂ BO SiH AlH COH N ₂ H		x	
Sm	147	15,0		RuO ₃		x	
Sn	118	24,2	U ²⁺	MoO RuO PdO		x	least interference
	120	32,6	Te	RuO PdO	Te		
Sr	86	9,9	Kr Yb ²⁺	RbH			
	88	82,6	Yb ²⁺ Lu ²⁺			x	lowest det. limit, least interference
Tb	159	100		NdO PrO		x	
Te	125	7,1				x	least interference
Te	126	19,0	Xe	PdO	Xe	x	lowest det. limit
Th	232	100				x	
Ti	47	7,3	Zr ²⁺	NO ₂ PO SiO CCl SNH SiOH SN N ₂ NO ₂ H	31P16O	x	least interference
	48	73,8	Ca Zr ²⁺	ArC CCl SO NO ₂ PO SN NN ₂ C ₄	Ca, 32S16O		
	49	5,5		SOH	32S16O1H		
Tl	203	29,5		WO ReO WHO			
	205	70,5				x	lowest det. limit, least interference
Tm	169	100		EuO		x	
U	238	99,3				x	
V	51	99,8		HSO ClO ClN ArNH ArC ArN SN SO	35Cl16O	x	
W	182	26,3		HoO DyO ErO		x	least interference
	184	30,7	Os	ErO YbO	Os		

Element	Isotope	Abundance (%)	Potential interferences		Interference with practical relevance	Best usable isotopes	
			Inter-element	Polyatomic ions		Preference	Reason
Y	89	100				x	
Yb	172	21,9		DyO SmO GdO		x	least interference
	174	31,8	Hf	DyO GdO	Hf		
Zn	64	48,6	Ni	TiO CaO PO ₂ SO ₂ AlCl ₃ S ₂ PO ₂ H ArN ₂ ArMg	Ni,48Ti16O,32S16O ₂ , 40Ar24Mg		
	66	27,9	Ba ²⁺	TiO VO SO ₂ PCI FeC S ₂ SO ₂ H	50Ti16O, 34S16O ₂	x	for medium Ti ans S
	68	18,8	Ba ²⁺ Ce ²⁺	VO ClO ₂ SO ₂ TiO ArS FeN PCI FeC S ₂ ArN ₂ ArSi	Ba ²⁺ ,40Ar28Si	x	for low Ba and Si
Zr	90	51,5				x	

Table A2 — Examples of equations for isobaric overlay.

Element	Recommended isotope and inter-element correction
As	$^{75}\text{As} - 3,127(^{77}\text{Se} - 0,815^{82}\text{Se})$ or $^{75}\text{As} - 3,127(^{77}\text{Se} + 0,3220^{78}\text{Se})$
Ba	$^{138}\text{Ba} - 0,0009008^{139}\text{La} - 0,002825^{140}\text{Ce}$
Cd	$^{114}\text{Cd} - 0,02684^{118}\text{Sn}$
Ge	$^{74}\text{Ge} - 0,1385^{82}\text{Se}$
In	$^{115}\text{In} - 0,01486^{118}\text{Sn}$
Mo	$^{98}\text{Mo} - 0,1106^{101}\text{Ru}$
Ni	$^{58}\text{Ni} - 0,04825^{54}\text{Fe}$
Pb	$^{208}\text{Pb} + ^{207}\text{Pb} + ^{206}\text{Pb}$
Se	$^{82}\text{Se} - 1,009^{83}\text{Kr}$
Sn	$^{120}\text{Sn} - 0,01344^{125}\text{Te}$
V	$^{51}\text{V} - 3,127(^{53}\text{Cr} - 0,1134^{52}\text{Cr})$

TC WI :2007 (E)

W	¹⁸⁴ W - 0,001242 ¹⁸⁹ Os
---	---

Annex B (informative)

Validation

NOTE The data in Table B.1 are recorded with quadrupole mass spectrometer equipped with a reaction cell and the use of Helium [He] and Hydrogen [H₂] gas in reaction mode.

Table B.1 — Method Limit of detection

Method detection limit (in mg/kg dw) ^a				
Element	Blank	ICS1	ICS2	ICS1+2
	3 g	3 g	3 g	3 g
	100 ml	100 ml	100 ml	100 ml
Be / 9 [He]	0,06	0,05	0,05	0,06
V / 51 [He]	0,15	0,26	0,19	0,21
Cr / 52 [He]	0,16	0,13	0,13	0,13
Cr / 53 [He]	0,60	0,65	0,66	0,57
Ni / 58 [He]	0,12	4,82	0,09	3,01
Co / 59 [He]	0,06	0,05	0,04	0,03
Ni / 60 [He]	0,09	0,10	0,06	0,06
Ni / 61 [He]	0,31	0,53	1,15	0,77
Cu / 63 [He]	0,91	1,05	1,01	1,06
Zn / 64 [He]	0,21	0,21	0,14	0,16
Cu / 65 [He]	0,88	0,99	0,98	1,02
Zn / 66 [He]	0,21	0,18	0,18	0,19
Zn / 68 [He]	0,31	0,28	0,19	0,19
As / 75 [He]	0,12	0,15	0,09	0,07
Se / 77 [He]	1,67	1,24	0,83	1,69
Se / 78 [He]	1,27	1,05	1,41	1,44
Se / 82 [He]	0,71	0,67	0,55	0,63

TC WI :2007 (E)

Method detection limit (in mg/kg dw) ^a				
	Blank	ICS1	ICS2	ICS1+2
	3 g	3 g	3 g	3 g
Element	100 ml	100 ml	100 ml	100 ml
Mo / 95 [He]	0,19	0,54	0,51	0,60
Mo / 98 [He]	0,19	0,56	0,53	0,62
Cd / 111 [He]	0,06	0,05	0,05	0,04
Cd / 114 [He]	0,06	0,03	0,04	0,03
Sn / 118 [He]	0,13	0,10	0,07	0,09
Sn / 120 [He]	0,13	0,10	0,08	0,10
Sb / 121 [He]	0,07	0,09	0,07	0,09
Sb / 123 [He]	0,07	0,09	0,10	0,09
Te / 125 [He]	0,08	0,06	0,10	0,10
Te / 126 [He]	0,05	0,05	0,04	0,04
Ba / 135 [He]	0,12	0,09	0,10	0,06
Ba / 137 [He]	0,10	0,07	0,06	0,05
Hg / 200 [He]	0,01	0,01	0,01	0,01
Hg / 201 [He]	0,01	0,01	0,01	0,01
Hg / 202 [He]	0,01	0,01	0,01	0,01
Tl / 203 [He]	0,14	0,16	0,11	0,10
Tl / 205 [He]	0,16	0,16	0,11	0,09
Pb / 206 [He]	0,07	0,04	0,05	0,05
Pb / 207 [He]	0,08	0,04	0,06	0,06
Pb / 208 [He]	0,07	0,04	0,05	0,04
Se / 77 [H2]	0,34	0,56	0,60	0,70
Se / 78 [H2]	0,05	0,08	0,07	0,10
Be / 9 [St]	0,04	0,03	0,02	0,04
V / 51 [St]	0,77	1,68	0,96	1,23
Cr / 52 [St]	0,20	0,13	0,19	0,11

Method detection limit (in mg/kg dw) ^a				
Element	Blank	ICS1	ICS2	ICS1+2
	3 g	3 g	3 g	3 g
	100 ml	100 ml	100 ml	100 ml
Cr / 53 [St]	2,63	5,55	3,34	4,08
Ni / 58 [St]	0,13	11,48	0,08	5,75
Co / 59 [St]	0,05	0,04	0,03	0,04
Ni / 60 [St]	0,11	0,09	0,13	0,10
Ni / 61 [St]	0,37	2,09	8,83	6,36
Cu / 63 [St]	0,91	1,05	1,18	1,17
Zn / 64 [St]	0,17	0,22	0,37	0,25
Cu / 65 [St]	0,85	1,00	0,97	1,02
Zn / 66 [St]	0,20	0,19	0,20	0,14
Zn / 68 [St]	0,20	0,18	0,14	0,12
As / 75 [St]	0,57	1,81	1,32	1,32
Se / 77 [St]	5,07	11,93	9,32	8,46
Se / 78 [St]	2,05	4,46	5,34	5,19
Se / 82 [St]	0,34	0,21	0,37	0,26
Mo / 95 [St]	0,15	0,28	0,25	0,29
Mo / 98 [St]	0,16	0,27	0,26	0,32
Cd / 111 [St]	0,06	0,03	0,03	0,04
Cd / 114 [St]	0,04	0,02	0,02	0,02
Sn / 118 [St]	0,11	0,11	0,10	0,13
Sn / 120 [St]	0,11	0,10	0,08	0,11
Sb / 121 [St]	0,05	0,09	0,06	0,09
Sb / 123 [St]	0,05	0,10	0,07	0,08
Te / 125 [St]	0,05	0,03	0,03	0,02

TC WI :2007 (E)

Method detection limit (in mg/kg dw) ^a				
	Blank	ICS1	ICS2	ICS1+2
	3 g	3 g	3 g	3 g
Element	100 ml	100 ml	100 ml	100 ml
Te / 126 [St]	0,03	0,01	0,02	0,02
Ba / 135 [St]	0,10	0,05	0,06	0,04
Ba / 137 [St]	0,09	0,07	0,08	0,06
Hg / 200 [St]	0,02	0,01	0,02	0,01
Hg / 201 [St]	0,02	0,02	0,02	0,02
Hg / 202 [St]	0,02	0,01	0,01	0,01
Tl / 203 [St]	0,14	0,16	0,13	0,11
Tl / 205 [St]	0,14	0,14	0,12	0,11
Pb / 206 [St]	0,08	0,06	0,06	0,03
Pb / 207 [St]	0,07	0,04	0,04	0,03
Pb / 208 [St]	0,06	0,03	0,04	0,03
^a : Horizontal phase II: ICP-MS Ruggedness test Table 8 [1]				
Key:				
Component	ICS 1	ICS 2		
Aluminium	1 000 mg/l	-		
Iron	1 000 mg/l	-		
Potassium	2 000 mg/l	-		
Sodium	1 000 mg/l	-		
Phosphorus	-	1 000 mg/l		
Calcium	1 000 mg/l	4 000 mg/l		
Magnesium	1 000 mg/l	-		
Sulphur	-	1 000 mg/l		
Carbon	-	2 000 mg/l		
Chlorine	2 000 mg/l	2 000 mg/l		
Cl: can interfere on V, Cr 53, As, Se77				

Tabel B.2 — Measurement of precision (in VC_w %):

Element	Rep. limit Limit	1	2	3	4	5	6	7	8	9	10	Average
Be / 9 [He]	0,1	30,1	4,9	25,1	2,1	4,9	54,3	3,5	7,7	<r.l.	<r.l.	16,6
V / 51 [He]	1	6,2	7,9	5,3	7,4	4,7	6,4	4,1	5,1	10,7	10,9	6,9
Cr / 52 [He]	15	5,6	5,2	5,5	4,3	6,4	5,0	4,7	5,6	<r.l.	6,9	5,5
Cr / 53 [He]	15	5,9	5,0	9,0	4,3	5,7	5,3	4,6	5,8	<r.l.	8,4	6,0
Ni / 58 [He]	3	5,5	4,7	4,4	2,9	4,2	4,2	4,4	4,8	<r.l.	7,5	4,7
Co / 59 [He]	1	5,0	5,0	4,5	3,8	5,0	4,7	4,6	5,3	<r.l.	8,2	5,1
Ni / 60 [He]	3	5,4	5,3	5,0	3,9	5,4	4,6	4,5	5,4	<r.l.	7,2	5,2
Ni / 61 [He]	3	4,8	5,6	7,7	4,1	5,4	6,8	5,5	5,9	<r.l.	17,0	7,0
Cu / 63 [He]	5	4,4	4,5	4,6	3,7	5,1	3,9	4,3	5,2	<r.l.	6,4	4,7
Zn / 64 [He]	17	3,7	3,7	3,4	2,7	4,3	3,1	2,7	4,1	<r.l.	5,0	3,6
Cu / 65 [He]	5	4,5	4,8	4,7	4,1	5,5	4,0	4,6	5,5	<r.l.	7,0	5,0
Zn / 66 [He]	1	3,6	3,9	3,6	3,1	3,9	3,1	3,7	4,2	4,0	5,0	3,8
Zn / 68 [He]	17	3,5	3,9	3,4	3,0	4,0	3,3	3,4	4,2	<r.l.	4,4	3,7
As / 75 [He]	4	5,1	3,2	3,0	2,5	3,2	<r.l.	2,8	3,8	<r.l.	<r.l.	3,4
Se / 77 [He]	10	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.
Se / 78 [He]	10	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.
Se / 82 [He]	10	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.
Mo / 95 [He]	1.5	23,7	<r.l.	7,0	4,1	<r.l.	18,3	<r.l.	<r.l.	<r.l.	<r.l.	13,2
Mo / 98 [He]	1.5	22,8	<r.l.	7,5	4,6	<r.l.	18,6	<r.l.	<r.l.	<r.l.	<r.l.	13,4
Cd / 111 [He]	0.17	2,6	3,6	4,6	3,9	7,4	5,2	2,7	<r.l.	<r.l.	8,3	4,8
Cd / 114 [He]	0,17	5,0	4,0	3,8	5,0	8,1	4,9	3,6	<r.l.	<r.l.	8,2	5,3
Sn / 118 [He]	6	4,.1	5,4	<r.l.	<r.l.	11< r.l.	5,2	<r.l.	<r.l.	<r.l.	<r.l.	4,9
Sn / 120 [He]	6	4,1	5,3	<r.l.	<r.l.	<r.l.	5,3	<r.l.	<r.l.	<r.l.	<r.l.	4,9

TC WI :2007 (E)

Sb / 121 [He]	1	4,6	9,4	<r.l.	12,7	<r.l.	8,0	<r.l.	<r.l.	<r.l.	<r.l.	8,7
Sb / 123 [He]	1	4,7	8,5	<r.l.	13,4	<r.l.	7,3	<r.l.	<r.l.	<r.l.	<r.l.	8,5
Te / 125 [He]	10	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.
Te / 126 [He]	10	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.
Ba / 135 [He]	15	11,4	4,1	2,9	3,2	4,3	3,7	3,3	13,8	<r.l.	3,9	5,6
Ba / 137 [He]	15	13,0	4,8	3,8	4,3	5,8	4,5	4,2	15,9	<r.l.	4,9	6,8
Hg / 200 [He]	0,05	1,4	2,0	8,1	8,2	5,4	3,0	3,2	3,2	<r.l.	<r.l.	4,3
Hg / 201 [He]	0,05	3,0	1,9	10,1	<r.l.	9,8	2,9	4,7	3,4	<r.l.	<r.l.	5,1
Hg / 202 [He]	0,05	2,7	1,8	5,2	7,4	3,7	1,8	2,8	2,9	<r.l.	<r.l.	3,5
Tl / 203 [He]	3	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.
Tl / 205 [He]	3	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.
Pb / 206 [He]	13	2,5	2,3	1,5	2,7	2,3	2,8	1,8	<r.l.	<r.l.	6,7	2,8
Pb / 207 [He]	13	2,4	2,4	1,7	2,4	2,7	2,7	1,7	<r.l.	<r.l.	6,3	2,8
Pb / 208 [He]	13	3,6	2,2	1,5	2,6	2,5	2,6	1,7	<r.l.	<r.l.	6,1	2,9
Se / 77 [H2]	10	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.
Se / 78 [H2]	10	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.
Be / 9 [St]	0,1	21,5	2,9	15,6	2,2	3,9	25,8	3,3	4,1	<r.l.	<r.l.	9,9
V / 51 [St]	1	15,5	7,5	12,2	6,3	6,3	24,5	6,5	6,9	76,7	61,8	22,4
Cr / 52 [St]	15	5,0	6,6	6,2	5,0	4,5	7,6	5,4	5,4	<r.l.	6,7	5,8
Cr / 53 [St]	15	8,0	8,0	<r.l.	9,6	7,8	13,6	6,7	9,5	<r.l.	24,1	10,9
Ni / 58 [St]	3	5,2	6,2	5,1	5,1	5,4	4,9	4,9	4,7	<r.l.	7,3	5,4
Co / 59 [St]	1	5,6	6,3	5,5	4,7	5,1	4,7	4,6	5,0	<r.l.	6,0	5,3
Ni / 60 [St]	3	5,4	6,5	5,8	4,7	4,8	4,8	4,8	5,0	<r.l.	8,0	5,5
Ni / 61 [St]	3	5,9	7,0	12,0	4,9	4,8	10,8	6,2	5,7	<r.l.	18,6	8,4
Cu / 63 [St]	5	4,5	5,4	5,0	4,5	5,1	4,3	4,7	5,0	<r.l.	6,3	5,0
Zn / 64 [St]	17	2,1	3,5	2,7	2,6	5,7	2,7	2,7	3,2	<r.l.	3,5	3,2
Cu / 65 [St]	5	4,3	5,2	4,8	4,6	4,9	4,6	4,7	4,6	<r.l.	6,0	4,9
Zn / 66 [St]	1	2,1	3,2	3,4	2,4	2,8	2,9	2,4	2,5	3,3	3,3	2,8

Zn / 68 [St]	17	2,1	3,1	2,3	2,7	3,1	2,7	2,4	2,9	<r.l.	3,0	2,7
As / 75 [St]	4	58,6	5,1	6,1	5,0	9,9	<r.l.	16,0	7,8	<r.l.	<r.l.	15,5
Se / 77 [St]	10	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.
Se / 78 [St]	10	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.
Se / 82 [St]	10	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.
Mo / 95 [St]	1,5	14,3	<r.l.	4,6	3,3	<r.l.	10,9	12,7	14,2	<r.l.	<r.l.	10,0
Mo / 98 [St]	1,5	13,5	<r.l.	4,5	3,4	<r.l.	10,3	12,4	13,7	<r.l.	<r.l.	9,6
Cd / 111 [St]	0,17	4,5	1,7	3,5	3,0	6,3	4,1	1,6	<r.l.	<r.l.	3,5	3,5
Cd / 114 [St]	0,17	2,0	1,5	1,9	2,4	4,2	4,3	1,7	<r.l.	<r.l.	3,2	2,7
Sn / 118 [St]	6	2,5	1,5	<r.l.	<r.l.	<r.l.	3,2	<r.l.	<r.l.	<r.l.	<r.l.	2,4
Sn / 120 [St]	6	2,1	1,3	<r.l.	<r.l.	<r.l.	2,5	<r.l.	<r.l.	<r.l.	<r.l.	2,0
Sb / 121 [St]	1	3,0	5,4	<r.l.	11,4	<r.l.	4,8	<r.l.	<r.l.	<r.l.	<r.l.	6,1
Sb / 123 [St]	1	3,2	5,8	<r.l.	11,0	<r.l.	5,1	<r.l.	<r.l.	<r.l.	<r.l.	6,3
Te / 125 [St]	10	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.
Te / 126 [St]	10	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.
Ba / 135 [St]	15	9,5	1,8	1,5	2,4	2,8	2,5	2,2	13,1	<r.l.	2,2	4,2
Ba / 137 [St]	15	8,8	1,5	1,7	1,8	2,9	2,3	2,5	12,9	<r.l.	1,8	4,0
Hg / 200 [St]	0,05	2,5	3,7	14,2	20,1	7,2	4,8	4,2	4,7	<r.l.	<r.l.	7,7
Hg / 201 [St]	0,05	2,5	2,9	8,7	<r.l.	10,0	2,2	6,3	4,0	<r.l.	<r.l.	5,2
Hg / 202 [St]	0,05	4,1	4,5	7,8	11,3	7,5	4,2	7,9	4,6	<r.l.	<r.l.	6,5
Tl / 203 [St]	3	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.
Tl / 205 [St]	3	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.	<r.l.
Pb / 206 [St]	13	2,2	3,7	1,9	3,5	2,1	3,0	2,5	<r.l.	<r.l.	2,4	2,7
Pb / 207 [St]	13	2,0	3,4	1,8	3,2	2,0	2,8	2,3	<r.l.	<r.l.	2,2	2,5
Pb / 208 [St]	13	2,0	3,6	2,5	3,7	2,1	2,9	1,5	<r.l.	<r.l.	2,2	2,6
Average:												6,1

TC WI :2007 (E)

Key

1. CRM 145R: sewage sludge.
 2. FeNeLab: internal reference material, river clay.
 3. Lksd-1: lake sediment.
 4. Stsd-2: stream sediment.
 5. CRM 7001: light sandy soil.
 6. CRM 144R: sewage sludge from domestic origin.
 7. CRM 141R: Calcareous loam soil.
 8. AMB WB: internal reference material: lake sediment.
 9. AMB SZ: internal reference material: 'playground sand'.
 10. AMB Compost: internal reference material; biowaste/garden waste.
- Average: averaged precision of the 10 testsamples.

Annex C (informative)

Comparison of OES and MS analysis on the same extracts for different matrices in one lab - Comparison of a standard AR extract by MS and OES and comparison of individual AR extracts for different matrices by MS and OES by different labs.

There are different levels of comparison of OES and MS analysis. First there is the measurement by OES and MS on the same digest of different matrices within one lab (table C.1)

Table C.1 Comparison of the ratio of OES/MS for different matrices and different digestion methods within one lab

Matrix Digestion	Element	Compost 2		Sludge 1		Sludge 2		Soil 1		Soil 2		Digestion & Element
		Average Ratio OES/MS	Stdev Ratio OES/MS	Average Ratio OES/MS	Stdev Ratio OES/MS	Average Ratio OES/MS	Stdev Ratio OES/MS	Average Ratio OES/MS	Stdev Ratio OES/MS	Average Ratio OES/MS	Stdev Ratio OES/MS	Average
AR reflux	Pb	1.107	0.036	0.938	0.005	0.967	0.025	1.23	0.04	0.96	0.09	1.04
AR MW 115	Pb	0.940	0.032	1.023	0.011	0.920	0.022	1.04	0.13	0.83	0.02	0.95
AR MW 175	Pb	1.037	0.025	1.035	0.012	0.942	0.011	1.07	0.15	0.96	0.10	1.01
NA	Pb	1.244	0.135	1.070	0.029	0.943	0.093	1.16	0.02	0.94	0.03	1.07
AR reflux	Cr	1.07	0.03	0.81	0.01	1.11	0.03	1.15	0.02	1.07	0.01	1.04
AR MW 115	Cr	1.18	0.07	0.87	0.02	1.03	0.02	1.14	0.01	1.12	0.02	1.07
AR MW 175	Cr	1.15	0.04	0.90	0.01	0.99	0.01	1.05	0.01	1.09	0.01	1.03
NA	Cr	1.08	0.13	0.92	0.03	1.01	0.01	1.09	0.04	1.07	0.06	1.03
AR reflux	V	0.98	0.02	1.11	0.02	1.09	0.13	1.05	0.01	0.93	0.01	1.03
AR MW 115	V	1.19	0.01	1.25	0.03	1.05	0.02	1.03	0.01	0.93	0.01	1.09
AR MW 175	V	1.06	0.02	1.24	0.04	1.00	0.02	0.98	0.01	0.92	0.01	1.04
NA	V	1.04	0.08	1.29	0.03	1.02	0.02	1.06	0.02	0.92	0.02	1.06

TC WI :2007 (E)

AR reflux	Zn	1.24	0.04	1.05	0.01	1.12	0.02	1.08	0.02	0.88	0.01	1.07
AR MW 115	Zn	1.18	0.01	1.15	0.02	1.05	0.02	1.14	0.01	0.91	0.02	1.09
AR MW 175	Zn	1.16	0.03	1.18	0.02	1.06	0.01	1.18	0.01	0.95	0.01	1.11
NA	Zn	1.15	0.03	1.12	0.01	0.97	0.02	1.19	0.01	0.94	0.02	1.07
AR reflux	As	0.86	0.05	1.02	0.00	1.04	0.05	0.96	0.03	0.93	0.01	0.96
AR MW 115	As	0.83	0.10	1.05	0.03	1.01	0.04	1.01	0.05	0.95	0.01	0.97
AR MW 175	As	0.84	0.04	1.10	0.01	1.02	0.05	1.06	0.05	0.91	0.04	0.99
NA	As	0.78	0.06	1.06	0.02	0.90	0.02	1.05	0.04	0.97	0.03	0.95
AR reflux	Ni	1.15	0.02	1.04	0.01	1.14	0.07	1.11	0.01	1.21	0.01	1.13
AR MW 115	Ni	1.23	0.04	1.11	0.02	1.09	0.01	1.10	0.02	1.46	0.11	1.20
AR MW 175	Ni	1.21	0.09	1.15	0.02	1.07	0.01	1.11	0.02	1.53	0.03	1.21
NA	Ni	1.10	0.05	1.21	0.02	1.09	0.01	1.16	0.00	1.41	0.02	1.19
AR reflux	Co	1.18	0.03	0.96	0.01	1.27	0.01	1.24	0.01	1.07	0.01	1.14
AR MW 115	Co	1.39	0.10	1.00	0.00	1.21	0.01	1.24	0.01	1.03	0.04	1.18
AR MW 175	Co	1.36	0.04	1.04	0.01	1.22	0.00	1.21	0.12	1.16	0.02	1.20
NA	Co	1.36	0.05	1.08	0.01	1.10	0.02	1.19	0.15	1.05	0.02	1.16
	Matrix	Average	stdev	Average	stdev	Average	stdev	Average	stdev	Average	stdev	
		1.111	0.050	1.063	0.017	1.051	0.029	1.110	0.037	1.039	0.027	
										Overall average		1.075
										Overall st dev		0.13
										Var %		12.15

Conclusion 1: There appears to be a systematic difference between OES and MS

Conclusion 2: If labs can not be forced to use either MS or OES or both, this uncertainty has to be considered in the comparison of digestion methods

Conclusion 3: ICP OES/ MS difference is independent of the digestion method

Conclusion 4: ICP/MS difference seems element specific (e.g. As, Ni, Co)

Further more there is the comparison of analysis of the same extract from different matrices by OES and MS by different labs (Table C.2).

Table C.2 Comparison of ratios ICP OES/MS for the same digest for different matrices analysed by different labs

		Compost 2	Sewage Sludge 1	Soil 2	
Lab		Ratio OES/MS	Ratio OES/MS	Ratio OES/MS	
Cd	1	0.91	1.07		
	2	1.45	1.16	1.60	
	3	0.99	0.76	0.94	
	4	0.95	1.08	0.95	
	Avg	1.08	1.02	1.17	
	Stdev	0.25	0.17	0.38	
		23.62 %	17.11 %	32.28 %	
Labs		Compost 2	Sewage Sludge 1	Soil 1	
		Ratio OES/MS	Ratio OES/MS	Ratio OES/MS	
Cr	1	0.99		1.06	
	2	0.95	0.92	0.93	
	3	1.00	0.93	1.05	
	4	0.97	0.98	0.98	
	5	1.04	1.06	1.07	
	Avg	0.99	0.97	1.02	
	Stdev	0.03	0.06	0.06	
	3.53 %	6.28 %	6.23 %		
Labs		Compost 2	Sewage Sludge 1	Soil 1	
		Ratio OES/MS	Ratio OES/MS	Ratio OES/MS	
Cu	1	1.07	1.17	1.17	
	2	1.19	1.24	1.15	
	3	0.97	1.02	0.96	
	4	0.98	1.03	0.96	
	5		0.93	0.95	
	Avg	1.05	1.08	1.04	
	Stdev	0.10	0.13	0.11	
	9.9 %	11.6 %	10.84 %		

TC WI :2007 (E)

Finally, an aqua regia extract was circulated for analysis in parallel with the samples. The number of labs performing this step was limited.(Table C.3)

Table Table C.3 Within and between lab variability for an AR extract of sludge (no distinction between OES or MS).

Matrix	p	Mean (ug/l)	sr	sR	VCr	VCR	Outliers	No of test data	BD #
ICP Cd	8	10.4	0.8	0.9	7.2%	9.0%	0	19	0
ICP Co	7	72	2.3	19	3.2%	26%	0	15	0
ICP Cr	8	361	25	43.6	7.0%	12%	0	17	0
ICP Cu	9	1968	61	202	3.1%	10%	0	17	0
ICP Ni	9	258	7.2	29	2.8%	11%	0	18	0
ICP Pb	8	754	37	52	4.9%	7.0%	0	15	0
ICP Zn	9	6746	60	361	0.88%	5.4%	0	16	0

Bibliography

- [1] Veldhuizen, A (2006), *Ruggedness ICP-MS*; Desk study 19 phase II, Horizontal project.
- [2] Van de Wiel, Henk J. (2005), **Determination of elements by ICP OES and MS**; Desk study 19 Horizontal project
- [3] Janssen,E.; Koopmann,R. (2005) *Determination of total phosphorus, total nitrogen and nitrogen fractions; Desk study 1 in Project Horizontal*; www.ecn.nl/horizontal
- [4] EPA 6020, *Water and solid waste: Inductively coupled plasma - mass spectrometry*.