

**Soils, sludges, Sediments and treated bio-wastes — trace elements —
Method by inductively coupled plasma – Atomic Emissions spec-
trometry (ICP AES)**

Boden, Schlamm Sedimente und behandelte Bio-Abfälle — Spuren Elementen — Methode mit induktiv gekoppeltes Plasma mit Atomare Emission Spectrometer (ICP-AES)

Sols, boues, Sediment et bio déchets traités — Éléments trace — Méthode de spectromètre de émission atomique à source plasma (ICP-AES)

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Foreword

This document has been prepared in the framework of the project Horizontal.

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-AES and ICP-MS" in Phase I and "Trace elements with ICP-AES: 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 discussion with all parties concerned in CEN and selection of a number of test methods described in this study the standard has been developed further as an modular horizontal method and has been validated within in the project 'Horizontal'

1 SCOPE

This international standard specifies the method for the determination of 44 elements in water (e.g. drinking water, surface water, groundwater, wastewater and eluates) and *aqua regia* and nitric acid digests of water, eluates, industrial and organic wastes, soils, sludge's, sediments, and other solid wastes: aluminum, antimony, arsenic, barium, beryllium, bismuth, boron, cadmium, calcium, cerium, chromium, cobalt, copper, iron, lanthanum, lead, lithium, magnesium, manganese, mercury, molybdenum, neodymium, nickel, phosphorus, potassium, praseodymium, samarium, scandium, selenium, silica, silver, sodium, strontium, sulphur, tellurium, thallium, thorium, tin, titanium, tungsten, uranium, vanadium, zinc and zirconium.

Table 1 lists elements for which this method applies along with the recommended wavelength and typical instrumental detection limits for clean aqueous matrices.

2 NORMATIVE REFERENCES

The following normative documents contain provisions, which, through reference in this text, constitute provisions of <standard number>. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on <standard number> are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies.

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

<*Aqua regia* horizontal standard>. Digestion for the determination of selected elements. Part 1: *Aqua regia* digestion.

<Nitric acid horizontal standard>. Digestion for the determination of selected elements. Part 2: Nitric acid digestion.

3 Definitions

For the purposes of this **Error! Reference source not found.**, the following terms and definitions apply.

3.1 Instrumental limit of detection (IDL):

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

3.2 Method detection limit (MDL):

Three times the within laboratory reproducibility standard deviation ($3 * Sw$) calculated from multiple measurements ($n > 8$) on different days of a relevant matrix solution.

4 Symbols and abbreviations

4.1 ICS: Interference check solution

4.2 IEC: Interelement correction factor

5 PRINCIPLE

This method describes multi-elemental determinations by ICP-AES using sequential or simultaneous optical systems and axial or radial viewing of the plasma. The instrument measures characteristic emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the emission lines are monitored by photosensitive devices. Background correction is required for trace element determination. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. Additional interferences and matrix effects must be recognized and appropriate corrections made; tests for their presence are described.

Alternatively, users may choose multivariate calibration methods. In this case, point selections for background correction are superfluous since whole spectral regions are processed.

6 INTERFERENCES

Spectral interferences are caused by background emission from continuous or recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra.

Background emission and stray light can usually be compensated for by subtracting the background emission determined by measurements adjacent to the analyte wavelength peak. Spectral scans of samples or single element solutions in the analyte regions may indicate when alternate wavelengths are desirable because of severe spectral interference. These scans will also show whether the most appropriate estimate of the background emission is provided by an interpolation from measurements on both sides of the wavelength peak or by measured emission on only one side. The locations selected for the measurement of background intensity will be determined by the complexity of the spectrum adjacent to the wavelength peak. The locations used for routine measurement must be free of off-line spectral interference (inter-element or molecular) or adequately corrected to reflect the same change in background intensity as occurs at the wavelength peak.

Spectral overlaps may be avoided by using an alternate wavelength or can be compensated by equations that correct for inter-element contributions. Instruments that use equations for inter-element correction **require** the interfering elements be analyzed at the same time as the element of interest. When operative and uncorrected, interferences will produce false positive determinations and be reported as analyte concentrations. The interferences are listed in Table 1.

Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample or by using a peristaltic pump, by using an internal standard or by using a high solids nebulizer.

Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique, but if observed, can be minimized by careful selection of operating conditions (incident power, observation position, and so forth), by

buffering of the sample, by matrix matching, and by standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer and from the build up of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples. The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element must be estimated prior to analysis.

7 REAGENTS

7.1 General

For the determination of elements at trace and ultratrace 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.

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

7.2 Nitric acid, $\rho(\text{HNO}_3) = 1,4 \text{ g/ml}$.

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

7.3 Hydrochloric acid, $\rho(\text{HCl}) = 1,16 \text{ g/ml}$.

7.4 Hydrochloric acid, $c(\text{HCl}) = 0,2 \text{ mol/l}$.

7.5 Element stock solutions

Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cu, Fe, Hg, K, La, Li, Mg, Mn, Mo, Na, Nd, Ni, P, Pb, Pr, Si, Sb, Sc, Se, Sm, Sn, Sr, Te, Ti, Th, Tl, U, V, W, Zn, Zr, $\rho = 1\,000 \text{ mg/l}$ each.

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 $\rho = 1\,000 \text{ mg/l}$ 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 calibration 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, and Zr.

Multi-element standard solution A may contain the following elements:
Ag, Al, As, B, Ba, Be, Bi, Cd, Ce, Co, Cr, Cu, La, Li, Mn, Ni, Pb, Se, Sr, Tl, V, Zn.
Use nitric acid for stabilization of standard solution A.

Multi-element standard solution B may contain the following elements:
Mo, Sb, Sn, W, Zr.
Standard solution B needs hydrochloric acid for stabilization

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

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 – 7.5) 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 calibration solutions.

7.8 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.

7.9 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.

7.10 Calibration check solution

Prepare the calibration check solution in the same acid matrix using the same standards used for calibration at a upper concentration level.

7.11 Interference check solution (ICS)

If interference cannot be excluded (see Table 1) prepare the interference check solution to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. The choice of the concentration and interfering element are matrix dependent.

Avoid two or more interferents for an analyte in the same interference check solution.

Spike the sample with the analytes of interest, particularly those with known interferences at 0.5 to 1 mg/L. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary.

8 APPARATUS

8.1 Inductively coupled argon plasma emission spectrometer:

- Computer-controlled emission spectrometer with background correction.
- Radio-frequency generator
- Optional mass flow controller for argon nebulizer gas supply.
- Optional peristaltic pump.
- Optional auto sampler.
- Argon gas supply - high purity.

Note: The instruments for ICP-AES come in two different varieties i.e. axial or radial viewing or a combination of both. Axial viewing gives more signal intensity due to the increased observation path length of the normal analytical zone of the plasma. This will in most cases lead to a higher signal but an increase of interference relative to radial viewing is commonly observed for many elements. Most instruments however have special adaptations to overcome the excessive interference by radiation from the bullet zone and molecular region of the plasma. Especially for low UV (e.g. Pb, Zn, As, Cd, P, Se and S) the Signal to Background Ratio's are more or less the same for both types. Several instruments are equipped with dual view by using additional mirrors. This allows the choice by the operator to select the most suitable option but can give limitations use due to the lower light intensity and because of different torch design (longer neck), lead to faster blockage and decreased long term stability. For environmental samples axial viewing can be advantageous.

8.2 Volumetric flasks of suitable precision and accuracy.

8.3 Volumetric pipets of suitable precision and accuracy.

9 PROCEDURE

9.1 Test sample

The test sample is an acidified aqueous sample ($\text{pH} \leq 1$) free of particles or a particle free 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 for the test sample or may be diluted from the test sample 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. sulphide oxidation by hydrogen peroxide.

9.3 Set up of the procedure

Adjust the instrumental parameters of the ICP-AES system in accordance with the manufacturer's manual.

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

Check the sensitivity and the stability of the system.

Check the wavelength calibration as often as required by the manufacturer.

Select wavelengths for measurement (Table A.1) and for background subtraction (Clause 4). Alternatively, apply multivariate calibration procedures.

The use of an internal standard should be considered if the matrix is highly variable and matrix-matching is difficult.

Apply an element with a non-measurable concentration. Examples are scandium and yttrium.

Add the internal standard in measurable amounts to samples and calibration solutions.

Divide every analyte response by the internal standard response and use this ratio as the measurement signal.

Define the rinsing times depending on the length of the flow; in the case of largely varying mass concentrations in the measuring solutions, allow for longer rinsing periods.

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.

NOTE ICP-AES provide 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-AES, 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 sample whether the assumption on the absence of a blank value is justified.

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 Non-linear calibration function

Alkali and alkaline earth metals may have non-linear response curves due to ionization and self-absorption effects.

Calculate the calibration function from weighted polynomial regression (second degree).

If this option is not possible use polynomial regression under the condition that the function is forced through the blank or through zero. In the latter case check regularly whether the assumption on the absence of a blank value is justified.

9.4.3 Standard addition calibration

Add a known amount of analyte to the known amount of the sample portion. Calculate the corresponding concentration change. Measure the difference in concentration between the original and the spiked sample portion. Use the ratio 'true spike concentration' versus 'measured spike concentration' as a correction factor for the initially measured concentration of the sample portion.

Minimise dilution or correct for spike dilution.

9.4.4 Inter-element correction

Investigate whether the interfering elements in Table 1 may results in measured values higher than three times the instrumental detection limit or 0.5 times the lowest concentration to be determined. If so, correct for interference.

Correction may be performed by:

- analysing one or more interferent check solutions (7.11),
- determining the ratio of supplied interferent concentration versus detected analyte concentration,
- using this ratio to calculate the interferent contribution from the measured interferent concentration of that specific test portion.

Factors that influence the mathematical IEC are:

- Peak setting (very strong influence);
- The assumption of linear response between analyte and interferent;
- Multiple overlap may not be present.

If sample composition strongly varies matrix matching may not be possible. Investigate the application of an internal standard to reduce the effect of the mismatch on analyte sensitivity (7.3). The internal standard method can be applied independently from the calibration procedure.

If the internal standard procedure insufficiently reduces matrix effects, apply standard addition calibration (7.4.3).

9.5 Sample measurement

Run one or more calibration solutions and calibration blanks.

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

Run all samples including one or more method blanks.

Every 25 samples or less and at the end, run a calibration blank and a calibration check solution.

Run at least one spiked sample (digest or aqueous sample) from the series to check recovery.

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

Whenever a new of usual sample matrix is encountered check:

- matrix effects by running the spike sample or
- matrix effects by running a fivefold diluted sample and
- inter-element interference analysing at a different wavelength.

10 CALCULATION

Calculate the element concentration in the aqueous sample:

$$\rho = (\rho_1 - \rho_0)f_d \cdot f_a$$

Calculate the element concentration in the digested solid sample:

$$w = (\rho_1 - \rho_0)f_a V \cdot 100 / (m \cdot dw)$$

where:

- ρ is the concentration of the element in the aqueous sample in mg/l;
- ρ_1 is the concentration of the element in the test sample in mg/l;
- ρ_0 is the concentration of the element in the blank in mg/l;

f_d	is the dilution factor due to digestion of an aqueous sample; in all other cases $f_d = 1$;
f_a	is the dilution factor of the test portion;
w	is the mass fraction of the element in the solid sample in mg/kg;
V	is the volume of the test sample (digest) in litres;
m	is the mass of the digested sample in kg.
dw	is the dry weight percentage of the sample.

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

12.1 Blank

Result of the calibration blank check shall be within 3 times the instrumental detection limit.

12.2 Sensitivity

Result of the calibration check standard shall not deviate more than 10% from previous measurement.

12.3 Interference

Magnitude of uncorrected background and spectral interference shall not be higher than three times the instrumental detection limit or 0.5 times the lowest concentration to be determined.

Successive values of a correction factor shall not differ more than 20%.

12.4 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 after dilution is higher than three times the instrumental detection limit or higher than twice the lowest concentration to be reported. Spike concentration should be within 0.4 and 2 times the analyte concentration.

12.5 Limit of detection

Table 1: Method Limit of detection:

MDL in matrix						
Element	wavelength			mg/L matrix solution	mg/kg dw (2.5g/100 mL)	Reference (informative)
Ag	328,1	atom	axial	0,003	0,10	-
Ag	338,3	atom	axial	0,002	0,09	
As	189,0	atom	axial	0,034	1,72	
As	193,7	atom	axial	0,072	2,88	4
As	197,2	atom	axial	0,066	2,64	
Ba	234,5	ion	rad	0,012	0,46	15
Ba	455,4	ion	rad	0,008	0,31	
Ba	493,4	ion	rad	0,007	0,36	
Be	234,9	atom	axial	0,003	0,12	
Be	313,0	ion	axial	0,003	0,10	0,1
Be	313,1	ion	axial	0,002	0,11	
Cd	214,4	atom	axial	0,003	0,12	0,17
Cd	226,5	ion	axial	0,004	0,17	
Cd	228,8	atom	axial	0,003	0,16	
Co	228,6	ion	axial	0,003	0,12	1
Co	230,8	ion	axial	0,003	0,12	
Co	238,9	ion	axial	0,025	1,27	
Cr	205,6	ion	axial	0,031	1,22	15
Cr	206,2	ion	axial	0,036	1,42	
Cr	267,7	ion	axial	0,031	1,53	
Cu	224,7	ion	axial	0,014	0,72	
Cu	324,7	atom	axial	0,015	0,62	5
Cu	327,4	atom	axial	0,018	0,71	
Mo	202,0	ion	axial	0,005	0,19	1,5
Mo	203,8	ion	axial	0,022	1,10	
Mo	204,6	ion	axial	0,015	0,59	
Ni	221,6	ion	axial	0,008	0,31	
Ni	231,6	ion	axial	0,008	0,31	3
Ni	233,0	atom	axial	0,019	0,94	
Pb	217,0	atom	axial	0,074	2,97	
Pb	220,3	ion	axial	0,019	0,77	13
Pb	283,3	atom	axial	0,085	4,25	
Sb	206,8	atom	axial	0,037	1,49	
Sb	217,6	atom	axial	0,028	1,12	
Se	196,0	atom	axial	0,080	3,19	
Sn	189,9	ion	axial	0,021	0,83	6
Sn	242,2	atom	axial	0,065	3,24	
Tl	190,8	ion	axial	0,033	1,31	0,3
Tl	351,9	atom	axial	0,014	0,69	
V	290,9	ion	rad	0,010	0,41	4
V	292,4	ion	rad	0,009	0,35	

MDL in matrix				mg/L matrix solution	mg/kg dw (2.5g/100 mL)	Reference (informative)
Element	wavelength					
V	310,2	ion	rad	0,003	0,16	
Zn	202,5	ion	rad	0,022	0,89	17
Zn	206,2	ion	rad	0,065	3,27	
Zn	213,8	atom	rad	0,029	1,15	

Content of the matrix solution

Component	Concentration
Aluminium	1200 mg/L
Iron	950 mg/L
Potassium	2000 mg/L
Sodium	230 mg/L
Phosphorus	150 mg/L
Calcium	1800 mg/L
Magnesium	320 mg/L
Sulphur	430 mg/L
Manganese	20 mg/L
Titanium	60 mg/L

12.6 Precision

Tabel 2: Measurement of precision (in VC_w %):

			CRM 145R	Fenelab	LKSD- 01	STSD- 02	CRM 7001	CRM 144R	CRM 141R	AMB sludge	AMB soil	AMB biowaste	Average
Ag	atom	Axial	10,5%					14,4%					12,5%
Al	atom	rad	5,0%	5,4%	6,9%	4,2%	6,0%	6,6%	7,2%	7,0%	6,9%	5,9%	6,1%
As	atom	axial	17,8%	9,9%	7,4%	10,2%	18,1%			19,0%			13,7%
Ba	ion	rad	18,5%	6,7%	6,5%	5,1%	5,4%	5,7%	6,4%	31,8%	6,9%	6,9%	10,0%
Be	ion	axial	9,3%	4,9%	14,1%	3,3%	5,4%	14,3%	3,6%	5,1%			7,5%
Ca	ion	rad	5,4%	4,9%	4,5%	3,6%	4,8%	6,6%	4,6%	6,7%	5,3%	4,1%	5,0%
Cd	atom	axial	7,5%	6,5%	17,2%			11,7%	3,6%				9,3%
Co	ion	axial	6,5%	5,4%	7,5%	8,5%	9,1%	4,9%	8,0%	8,1%		11,6%	7,7%
Co	ion	axial	IE C	7,2%	5,5%	9,4%	10,6%	11,8%	5,0%	8,7%	8,7%		8,4%
Cr	ion	axial		3,9%	3,2%	8,1%	5,4%	5,1%	4,2%	3,9%	5,8%	5,2%	5,0%
Cu	atom	axial		4,7%	8,2%	4,0%	4,6%	3,8%	5,5%	4,3%	5,9%	8,1%	5,4%
Fe	ion	rad		3,8%	1,6%	3,4%	3,0%	2,3%	4,0%	3,6%	2,6%	3,3%	2,9%
Mg	atom	rad		5,2%	3,7%	5,9%	4,4%	5,4%	5,1%	5,7%	7,1%	6,7%	5,5%
Mn	ion	rad		4,7%	5,5%	6,1%	7,7%	8,1%	7,4%	3,3%	14,7%	14,8%	8,8%
Mo	ion	axial		8,1%		5,4%	5,0%		15,8%				8,6%
Ni	ion	axial		3,8%	4,8%	6,3%	4,0%	5,0%	4,1%	5,4%	7,9%		5,2%
Ni	ion	axial	IE C	3,9%	6,1%		5,8%	6,7%	4,2%	5,9%	10,4%		6,1%
P	atom	axial		2,9%	3,0%	3,3%	4,0%	3,8%	2,8%	3,1%	5,3%	4,3%	3,6%
Pb	ion	axial		3,8%	4,7%	4,5%	3,5%	4,8%	6,2%	4,3%	5,8%	7,0%	4,9%
S	atom	axial		1,7%	4,4%	1,8%	5,3%	3,3%	1,6%	22,7%	4,1%	3,4%	5,4%
Sb	atom	axial		12,6%									12,6%
Se	atom	axial											
Sn	ion	axial		5,2%	3,3%			6,6%					5,0%
Ti	ion	rad		5,2%	3,4%	4,8%	3,3%	4,6%	5,0%	3,6%	3,8%	5,5%	4,5%
Tl	ion	axial											
V	ion	rad		7,1%	6,1%	3,9%	2,8%	3,5%	5,2%	3,0%	4,3%	8,6%	4,9%
Zn	ion	rad		5,4%	2,7%	3,8%	2,8%	4,0%	5,0%	4,9%	5,5%	5,4%	4,4%
Zn	ion	rad	IE C	5,4%	2,7%	3,8%	2,8%	4,0%	5,0%	4,9%	5,5%	5,4%	4,4%
Over all													6,8%

Legenda

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.
11. Average: averaged precision of the 10 testsamples.

13 TEST REPORT

The test report shall contain the following information:

- a reference to this standard
- a reference to the digestion method used
- a complete identification of the sample
- the results of the determination
- any deviation from the standard

**Annex A
Informative**

TABLE A.1: Recommended wavelengths, spectral interferences and estimated instrumental detection limits (in µg/L)

Element	Line (nm)	Interfering elements	Instrumental detection limit
Ag	328,068	Mn	7
	338,289	Cr, Ti	15
Al	308,215	Mn, V, Fe	50
	396,152	Mo, Cu	10
As	167,08	Fe	1
	193,696	Fe, Al, Mo	50
	197,197	Fe, Al, V	75
B	189,042	Al	
	208,959	Al, Mo	10
	249,678	Fe, Cr	5
Ba	249,773	Fe	5
	233,527	Fe, V	5
	455,403		1
Be	493,409		1
	313,042	V, Ti	2
	234,861	Fe	30
Bi	313,107		
	223,061	Cu	30
	306,772	Fe, V	75
Ca	315,887	Co	30
	317,933	Fe, V	20
	393,366		0,2
Cd	214,438	Fe	3
	226,502	Fe	3
	228,802	As, Fe, Co, Cs	3
Ce	394,275	Co, Mn, Mo, Nd, Rh	70
	413,380	Zn, Fe, Mg, Ni, Ti	50
Co	228,616	Ti	7
Cr	205,552	Fe, Mo	6
	267,716	Mn, V	7
	283,563	Fe, Mo	7
	284,325	Fe	7
Cu	324,754	Ti, Fe	5
	327,396		10
Fe	259,940		6
	238,20	Co	1
K	766,490	Mg, Ar	6
	769,90		
Hg	184,887		5
	194,164	V	5
La	333,749	?	10
	379,478	?	10
Li	460,286	Fe	
	670,784		6
Mg	279,079	Fe	30
	279,553		0,1
Mn	285,21	Fe	
	257,610	Fe, Mo, Cr	1
	293,306	Al, Fe	1
Mo	202,030	Al, Fe	8
	204,598		10
Na	588,995	Ar	70
	589,592	Ba	100
Na	330,237		

**Annex B
Validation**

Element	Line (nm)	Interfering elements	Instrumental detection limit
Nd	406,109	Sm,Pr	100
	430,358	Pr,V	75
Ni	231,604	Co,Fe	25
Ni	231,997	Cr	5
P	178,287	I	15
	213,618	Cu, Fe, Mo, Zn	7
	214,914	Cu, Al, Mg	7
	177,428	Cu	
Pb	220,353	Al, Co, Ti	40
	283,306		
Pr	390,844	Ce,U	40
	417,939	Cr,CeV,Fe,Sm,Nd	40
S	182,036	Cr, Mo	15
	180,669	Ca	13
Sb	206,833	Cr, Mg, Co, Mn	30
	217,581	Nb, V, W	40
Sc	357,635	Ce	0,3
	361,384	Ce,W	0,3
Se	196,026	Ti	75
	203,985	Cr, Mn, Sb	100
Si	251,611		10
	212,412		15
	288,158		30
Sm	359,260	?	40
	388,529	?	80
Sn	235,848	Mo, Co	100
	240,170	Fe	100
	283,998	Cr	100
	189,980		25
Sr	407,771		0,3
	421,552		0,3
	460,733		70
Te	214,281	V,Sc,Re	40
	225,902	W	100
Ti	334,941	Ca, Cr, Si	4
	336,121		5
	337,280		7
	368,520	Co, Cr	10
Tl	190,807	W	100
	190,794	Co	100
U	385,957	Fe, V,Sc,Sm,Pr,Th	10
	409,013		10
V	290,882	Fe, Mo	8
	292,402	Fe, Mo, Cr,Ti	8
	310,230	Ni	7
	311,071	Fe, Mn, Ti, Cr	10
W	207,911		30
	209,860		40
	239,709		60
	222,589	Cu	60
	202,998		75
Zn	206,191	Cr	6
	213,856	Cu, Ni, Fe	7
Zr	343,823		10
	354,262		7
	339,198		7

Inter element correction

Depending of the matrix of the samples that are to be determined the possible interference should be investigated for each individual instrument. Single element stock solutions should be used to determine the major interferences for ICP AES method. From these single element stock solutions a series of nine standard solutions with a concentration of 200 mg/L of the interfering elements can be made and measured. An example for environmental samples within the scope of this standard is given below.

Group I	Interferent standard I	V, Al, Ba, Ca, Ce
	Interferent standard II	La, Cu, Cd, Co, Cr
	Interferent standard III	Fe, Mo, Nd, Ti, Zn
	Interferent standard IV	Ni, S, As, Mg, Mn

Group II	Interferent standard V	V, Ti, Cu
	Interferent standard VI	Fe, Cr, Nd
	Interferent standard VII	Mn, Mo
	Interferent standard VIII	Ni, Zn, Nd
	Interferent standard IX	La, Ce

Standard solutions in diluted nitric acid are aspirated into the plasma and for all line of the elements of interest the possible interference is measured. The Inter-Element-Correction-factors (IEC) are calculated from these measurements.

IEC = *Apparent Analyte concentration / Interferent concentration*

Applying the IEC:

*Corrected Analyte concentration = measured Analyte concentration – (measured Interferent concentration * IEC)*

The conditions for applying an IEC are:

- Peak setting and selection must be stable and/or reproducible;
- Assuming linear response of interferent on analyte;
- No multiple overlap is allowed.

Beside the measurement of the IEC the background correction profile should be optimized by measuring the ICS solution followed by evaluation of the interference by other lines caused by elements present in the ICS.

Non spectral interferences (like physical, chemical and memory effects) are not investigated in this study. The effect of these interferences is minimized by the use of an internal standard and through matrix matching.

**Annex B
Validation**

To be added later

Bibliography

1. Horizontal Desk study 19; may 2004. "Determination of elements by ICP-AES and ICP-MS", Henk J. van de Wiel.
2. Standard Horizontal ICP-AES method: "Determination of dissolved elements by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), Horizontal Deskstudy 19; may 2004 (WP6).