

Trace elements: ICP-AES Ruggedness test

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Acknowledgement

This work has been carried out with financial support from EU DG Environment and JRC (Ispra) and the following EU Member States: UK, Germany, France, Italy, Spain, Nordic countries, The Netherlands, Denmark and Austria.

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SUMMARY

The present report covers the activity for HORIZONTAL-INORG, Work package 6 , Ruggedness test for a horizontal European standard for Determination of elements by ICP-AES and ICP-MS in soil, sludge and biowaste.

The main purpose of this study is: "Investigation of the major interferences to common elements and digested samples of matrices and digests in question are investigated for the ICP-AES method. Emphasis is given to interferences corrections and quality control criteria related to interferences and matrix effects".

The method described in the standard identified during the desk study carried out in Phase I for measurement of elements in soil, sludge and bio waste with ICP-AES can be used in practice. The measurements in this study show that the limit of detection is within the expected range, precision is less than 10% at levels above 5 times IDL and the QC criteria can be met.

Several comments on the text are formulated to improve the practical use.

The reference materials were digested with aqua regia and 1:1 nitric acid as prescribed in the proposed Horizontal standard on digestion [7.3]. The digests are analyzed to determine the matrix. The major matrix elements from real samples are sodium, magnesium, aluminium, phosphorus, sulphur, potassium, calcium and iron. There is, except for the concentrations, not a remarkable difference between the Aqua Regia digests and the nitric acid digests of real sample for the elements that are reported. ICP-MS data shows a higher carbon concentration in the nitric acid digests. Based on the highest concentrations found in the AR digest an ICS is proposed. and used for further test.

The proposed standard doesn't give a definition of the way the instrumental detection limit has to be determined. The IDL is determined in a reagent blank under repeatability conditions. The IDL in nitric acid digest has a median value of 0.0041 mg/L (0.16 mg/kg) and in AR digest 0.0046mg/L(0.18 mg/kg). A better way is to determine the MDL under repeatability or reproducibility conditions in a matrix solution containing relevant concentration of the interferents.

For the most elements the method detection limit (MDL) is between 0.1 and 4 mg/kg (median value 0.015 mg/L or 0.71 mg/kg). In comparison to the IDL the MDL is 2-3 times and for the interfered lines in some case 10 times higher.

The two criteria for applying an IEC can be misinterpreted and are not very practical. In this study the criterion "absolute contribution is more than 3 time the DL" is used. The IDL is determined in a pure standard solution which leads to very low, not practically relevant values. Therefore the use of the MDL has more relevance. This value should be used as criteria for applying the IEC correction or halve the lowest concentration to be reported.

The IEC is determined with pure standard solutions at a certain chosen concentration. The choice is relevant and matrix dependent.

The 5 % rule is not applicable during the interferences measurement but only applies in real samples where matrix is present. In practice during IEC measurements with pure standards, the need for an IEC is determined and will always be applied in real sample measurement. The 5% rule is only practical in relatively high concentration levels.

The stability of the IEC must be investigated during validation and checked during routine measurement on a more frequent base in case of a difference of more than 20% from the previous determination.

The precision is for most elements better than 10%, except for those elements where the concentration is at a low (<5 times DL) level. The average overall precision is **6.8%** and the median value is **5.5%**.

The criterion for recovery of the spike within the limits of 80 -120% is can be met in practice.

The recovery criterion after dilution is only applicable for those samples that contain high concentrations of the elements of interest. For lower concentrations and subsequent measurement close to the DL, dilution of the sample is not recommended as a QC criterion. De ratio between the diluted and undiluted results is for a 3-fold dilution on average.1.02 +/- 0.06 (6.1%).

1 INTRODUCTION

The main objective of the Horizontal program is the development of horizontal and harmonized European standards in the fields of the analysis of sewage sludge, soil, contaminated soil and treated bio-wastes to facilitate regulation of these major streams in the light of the different uses and disposal options that are governed by EU Directives.

The goal of this study is [from 7.1]:

“Investigation of the major interferences to common elements and digested samples of matrices and digests in question are investigated for the ICP-AES method. Emphasis is given to interferences corrections and quality control criteria related to interferences and matrix effects. “

The study is based on the Horizontal WP6 -19 document: “Determination of elements by ICP-AES and ICP-MS”, may 2004 by Henk J. van de Wiel, Annex 2: STANDARD HORIZONTAL ICP_AES METHOD[7.2].

Within Horizontal there are two proposed methods for digestion of samples. As both methods are being developed in a concurrent study, this study is carried out in Aqua Regia and nitric acid digests according to the digestion described in Horizontal WP6 – 18 (may 2004)[7.3].

A ‘work’ definition for the determination of the Instrumental Detection Limit (IDL) is defined and the definition for MDL of a Dutch standard (NEN 7777) is used [7.4].

1.1 Scope

The experimental work in this study will be performed on a PE Optima 4300 DV instrument. The set up for the determination of the DL and the interferences are based on routine multi-element conditions and according to the settings proposed by the STANDARD HORIZONTAL ICP_AES METHOD[7.2].

The matrices under investigation in this study are digests from the matrices which are stated in table 1.

Table 1:

Matrices used in this study	In of the scope of H-19 ICP-AES?
Soil	Yes
Sludge	Yes
(treated) Bio waste	Yes

The project description mentions ‘common elements’ in its scope. The elements selected for this study are given in table 2. Besides these elements the matrix elements which can be expected in environmental samples, like Al, Ca, Mg, Fe, C, Na and K are also part of the scope but not part of the QC and related interferences investigations.

Table 2:

Elements used in this study	CAS-number	Part of the scope of H-19 ICP-AES?
Arsenic (As)	7440-38-2	Yes
Cadmium (Cd)	7440-43-9	Yes
Chromium (Cr)	7440-47-3	Yes
Copper (Cu)	7440-50-8	Yes
Lead (Pb)	7440-47-3	Yes

Nickel (Ni)	7440-02-0	Yes
Zinc (Zn)	7440-66-5	Yes
Antimony (Sb)	7440-36-0	Yes
Barium (Ba)	7440-39-3	Yes
Beryllium (Be)	7440-41-7	Yes
Cobalt (Co)	7440-43-7	Yes
Molybdenum (Mo)	7440-98-7	Yes
Selenium (Se)	7440-49-2	Yes
Silver (Ag)	7440-22-4	Yes
Thallium (Tl)	7440-28-0	Yes
Tin (Sn)	7440-31-5	Yes
Vanadium (V)	7440-62-2	Yes

1.2 Summary of method

The method describes the multi-elemental determination of elements by simultaneous optical ICP-AES with axial or radial viewing of the plasma in aqueous and nitric or *aqua regia* digests. 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 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 background correction measurement would be actually degrading 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.

1.3 Definitions

For this study the following definitions are applied.

Instrumental limit of detection (IDL): $3 * S_r$ (the standard deviation calculated from multiple readings ($n=10$) of a blank within a single run).

Method limit of detection (MDL): $3 * S_r$ (the standard deviation calculated from multiple measurements ($n > 8$) of a matrix solution with low analyte concentration).

2 INSTRUMENTATION

A Perkin Elmer Optima 4300 DV (where DV stands for Dual View (=axial and radial)) instrument is used for this study.

2.1 Apparatus.

A Perkin Elmer Optima 4300 DV with a PE sharp cone spray is used according to the requirements stated in 6.2 of the proposed standard. Acquisition software is used for data acquisition and reprocessing and a Cetac AS93 Plus autosampler for sample introduction.

The instrument has been set up in multi element mode for the elements given in table 2.

The instrument is tuned as required by the manufacturer.

A Multiwave 3000 microwave (Anton Paar, Austria) with HF100 digestion vessels is used for digestion.

2.2 Reagents

All reagents used are of "PA" or "Baker analyzed" quality.

2.3 Standards

BDH multi element Standard solution (cat no 456422 W)

Pure element standards (Baker "Instra Analyzed" and Perkin Elmer "Pure") $C_{\text{element}} = [1000 \text{ mg/L}]$.

Three internal standards(Y, Rh, In) are used which are added to all solutions.

3 PROCEDURES

3.1 Method development

A method will be developed for multi element measurement of the elements given in table 1 and matrix elements in accordance with the manufacturer's manual. As the instrument is Dual View both directions will be part of the method although not all will be useful. The wavelength for measurement and background subtraction will be determined.

A wavelength check and calibration is part of the daily performance test. The adjustment of the wavelength is performed by the service engineer during PM.

3.2 Interferences (from matrix)

Digests from the matrices specified in table 1 will be analyzed and relevant concentrations of the major matrix elements determined.

For this purpose several available Certified Reference Materials will be digested in aqua regia and nitric acid and analyzed with the method developed in 3.1:

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.

3.3 Interference Check Solution (ICS)

Based on the composition of relevant matrices and the proposed ICS [7.] content the composition of the ICS will be determined. The content of the ICS will be based upon the levels obtained at 3.2.

The (potentially) interfering elements (see table 1 [7.3]) are quantified and checked against the criterion stated in the proposed standard (less than 5% impact on the measured value or 3 times the Instrumental DL).

Interferences which are investigated in this study:

- Spectral overlap;
- Background and stray light.

3.4 IEC correction

Single element stock solutions are 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 will be made and measured in 5 separate consecutive runs. The successive values of the correction factor shall not differ more than 20%.

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

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

Beside the measurement of the IEC the background correction profile is 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.

The following internal standards and their emission lines are examined:

Yttrium	371.030 (ion line)
Rhodium	343.489 (atom line)
Rhodium	233.477 (ion line)
Indium	230.606 (ion line)
Indium	303.936 (atom line)

3.5 Detection Limit in matrix solution (ICS)

The instrumental and method limit of detection are determined according to the definitions in 1.3. The content of the ICS used for this purpose depends on the results of ICS in 3.2 & 3.3. The obtained values are expressed as solution concentration (mg/L) of the digest. Therefore the detection limit is also expressed in mass concentration after recalculation with an amount of 2.5g soil, filled to the end volume of 100 mL.

3.6 Precision

Within the scope of this study the precision is defined as the relative standard deviation of the reproducibility of digests of relevant samples. Digests of the CRM's are measured on different days. The within laboratory reproducibility standard deviation (S_w) is calculated.

3.7 Recovery of spike

The recovery is investigated with two different methods which are both mentioned in the proposed standard. The first is a spike to a matrix solution (ICS) and the second is the ratio of measurements of the original sample and a diluted sample. The post-digestion spike recovery shall be between 80 and 120% or the difference between results for non-diluted and the fivefold diluted sample shall be less than 20%.

4 RESULTS

4.1 Method development

The method is developed according to guidelines given in the proposed standard [7.2]. For a description of the method applied see annex 6.1:

Table 3: Emission wavelength overview

Element	view	Emission wavelength (nm)		
Ag, Silver	Axial	328.068	338.289	243.778
As, Arsenic	Axial	193.696	197.197	188.979 ¹
Ba, Barium	Radial	233.527	455.403	493.409
Be, Beryllium	Axial	313.042	234.861	313.107
Cd, Cadmium	Axial	214.438	226.502	228.802
Co, Cobalt	Axial	228.616	230.780	238.892
Cr, Chrome	Axial	205.552	206.149	267.703
Cu, Copper	Axial	324.754	327.396	224.700
Mo, Molybdenum	Axial	202.030	204.598	203.839
Ni, Nickel	Axial	231.604	221.647	232.003
Pb, Lead	Axial	220.353	216.999	283.301
Sb, Antimony	Axial	206.833	217.581	231.146
Se, Selenium	Axial	196.026	203.985	
Sn, Tin	Axial	189.927 ¹	235.484 ²	242.165
Tl, Thallium ³	Axial	190.801	276.787	351.924
V, Vanadium	Radial	290.880	292.402	310.230
Zn, Zink	Radial	202.548	213.856	206.191

Remarks:

- (1) The in the Standard Horizontal method ICP-AES [4.1] given emission wavelength for Arsenic of 189.042 nm is not available on the Optima 4300 DV. There is a chance that the available wavelength at 188.979 is the same. The establishment of emission wavelengths happened in the past by using spectrophotometers with a much lower resolution than the modern ones.
- (2) In the Standard Horizontal method ICP-AES [4.1] there is an emission wavelength mentioned for tin of 235.848 nm which is incorrect and should be 234.484 nm.
- (3) The mentioned emission wavelength for thallium in Standard Horizontal method ICP-AES [4.1] of 190.864 nm is not available on the Optima 4300 DV.

4.2 Interferences

The reference materials used in this investigation of the major matrix interferences.

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; bio waste/garden waste.

The reference materials were digested with aqua regia and 1:1 nitric acid as prescribed in the proposed Horizontal standard on digestion [7.3]. The digests are analyzed to determine the matrix. The results are summarized in figure 1 Aqua regia and figure 2 for Nitric acid.

Figure 1: Aqua regia results

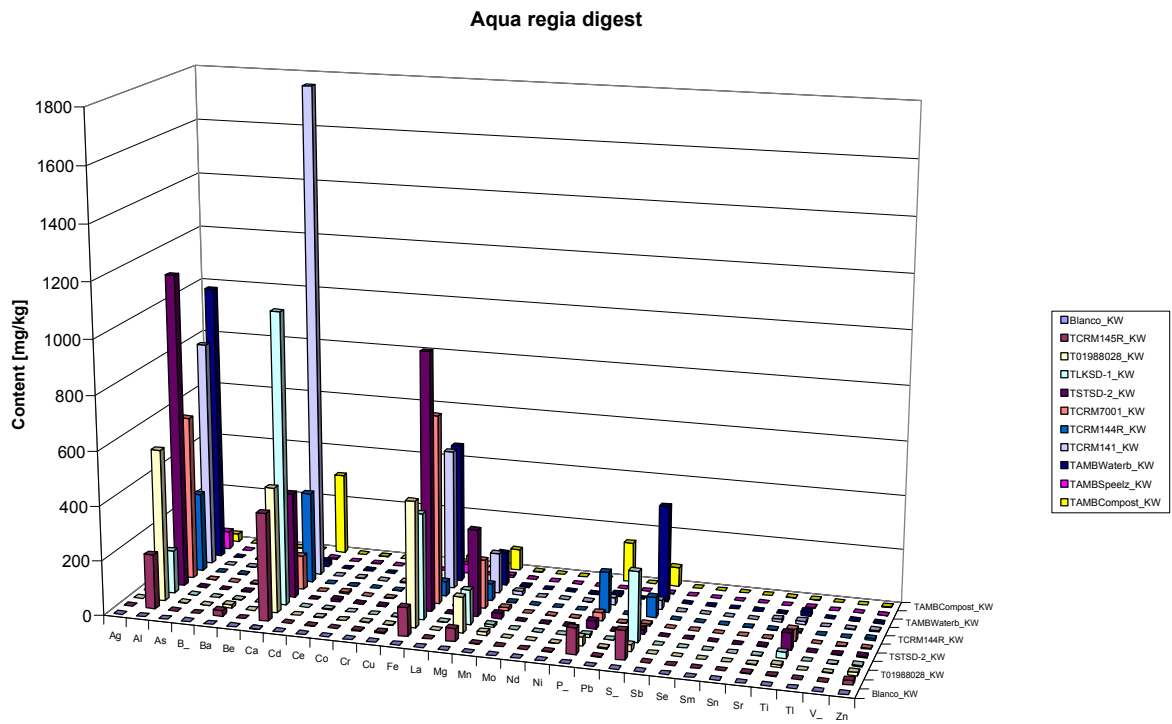
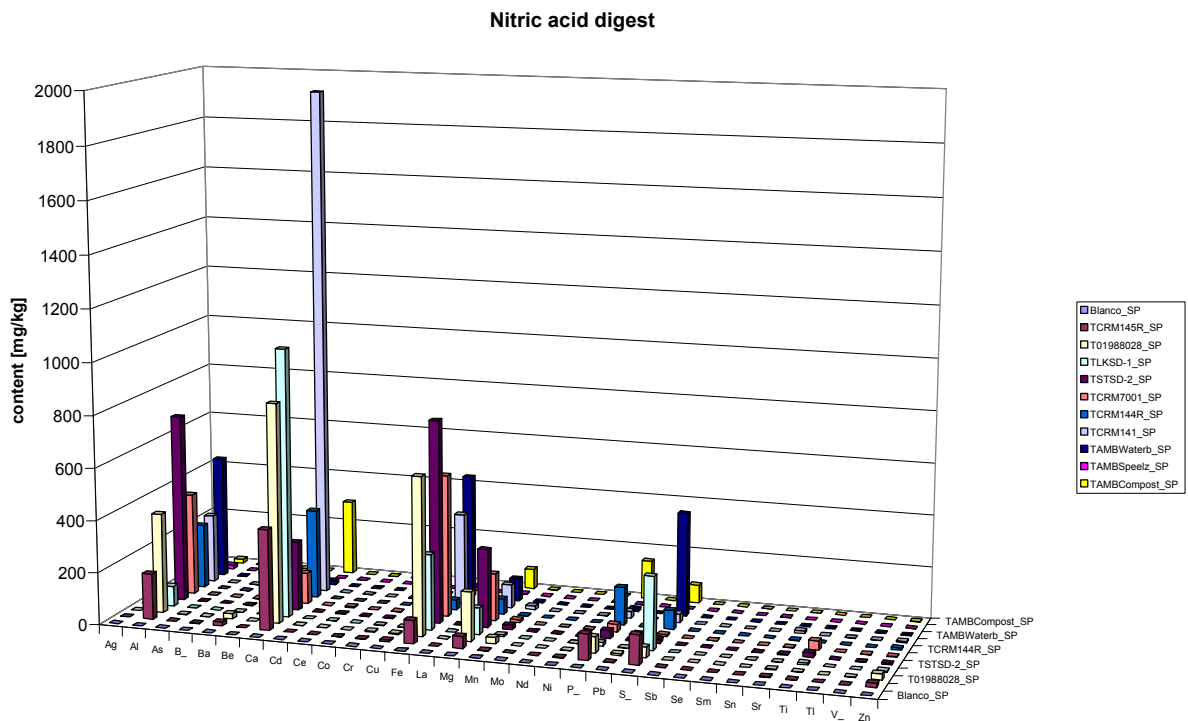


Figure 2: 1:1 Nitric acid results:



Discussion:

The major matrix elements from real samples are sodium, magnesium, aluminium, phosphorus, sulphur,

potassium, calcium and iron. There is not a remarkable difference between the Aqua regia digests and the nitric acid digests of real sample for the elements that are reported. ICP-MS data shows a higher carbon concentration in the nitric acid digests. The sodium result has been determined by ICP MS.

4.3 ICS solution

Based on the results reported in figure 1 and 2, the concentration for the ICS is determined.

Table 4: Maximum ICS concentration:

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

Discussion: In the note at 7.4.3. Of the proposed standard these elements are called ubiquitous elements together with Cr and V; the latter are not found in the samples used here. The concentrations in the table are the highest concentrations found in the samples. The outcome of the measurements in this study reflects therefore a worst case situation.

For control purposes the ICS is suitable but not for quantification of the interference correction factor.

4.4 Major interferences in standard solutions (IEC).

Selected element stock solutions were used to determine the major spectral interferences for ICP AES methods. A series of nine standard solutions were measured in axial and radial view. The Inter-Element Correction (IEC) factors were calculated and are summarized in annex 6.2 and visualized in figure 3. The criteria for the use of an IEC are :

- more than 5% impact on the measured value or
- a contribution more than 3-times the Instrumental DL.

A summary of the IEC factors used in this study is reported in table 5. An IEC is used for those lines that have a contribution of more than 3 times the IDL.

Table 5: IEC application .

Analyte	λ (nm)*	Interferent	IEC factor (%)
Co	228.607	Ti	0.14
Ni	231.600	Fe	0.035
Zn	202.541	Cu	0.65
Pb	216.992	Fe	0.054
V	292.391	Ti	0.14
Zn	213.849	Ca	0.0074
Co	238.882	Fe	0.085
Cu	224.693	Fe	0.070
Ni	231.997	Cr	2.6
Pb	283.297	Fe	0.16

Sn	242.16	Fe	-0.19
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* minor differences between the wavelength stated in table 1 of the proposed standard and this table can occur due to small adjustments of the detector used.

Based on the evaluation of the background profile, the spectral lines given below prove to be not useful due to interference mainly caused by spectral overlap by element present in the matrix solution ICS:

Silver	243.778 nm
Antimony	231.146 nm
Selenium	203.985 nm
Tin	235.484 nm
Thallium	276.787 nm

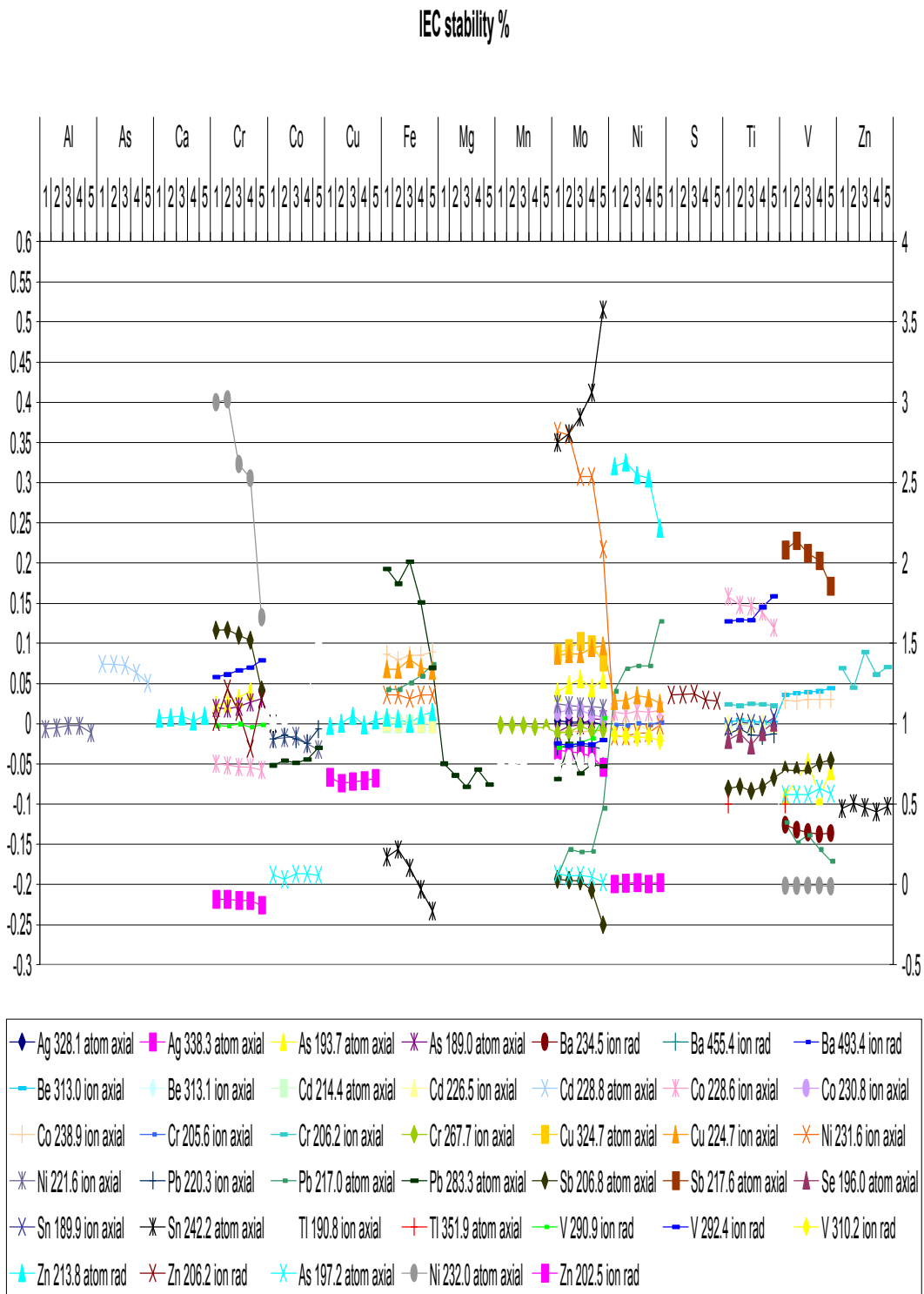
Discussion: The two criterions for applying an IEC are totally different and not very practical. Here the criterion "absolute contribution more than 3 time the MDL" is used. The IDL is determined in a pure standard solution which leads to very low, not practically relevant values. Therefore the use of the MDL or even reporting limit ($= k * MDL$; where $k = 2, 3, ?$) has more relevance. The IEC is determined with pure standard solutions at a certain chosen concentration. The choice of the concentration is relevant and matrix dependent. If, for example, a concentration of 200mg/L is used for IEC determination and there is no observed contribution higher than 3 times the DL, but samples contain a higher concentration than 200 mg/L, there might be a contribution of the interference that may not be ignored.

The 5 % rule is not applicable during the interferences measurement but only in real samples where matrix is present. In practice, IEC measurements with pure element standard solutions are measured to determine the need for an IEC and afterwards the IEC's will always be used in real sample measurement. The 5% rule is only practical in relatively high concentration levels.

4.4.1 Interference correction stability.

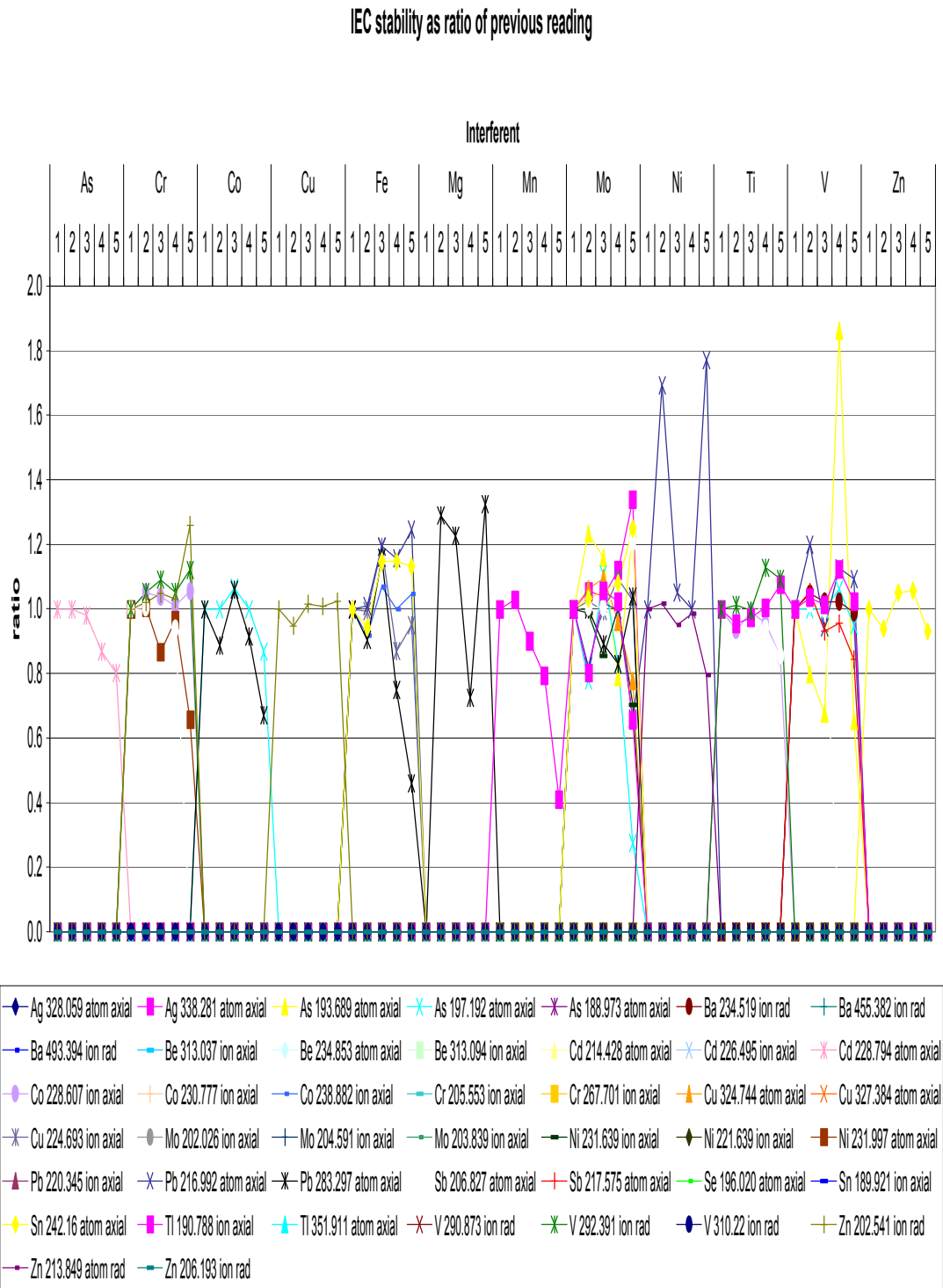
The interference correction stability is determined by measuring 5 consecutive runs and calculated as the ratio between two runs. The results for the elements of interest are reported in figure 3.

Figure 3: Interference Correction stability.



Note: At the top of the graph are the interfering elements and the 5 consecutive measurements; if an interference has been measured then the element of interest can be found in the legend. The lines As 197.2, Ni 232.0 and Zn 202.5 are linked to the right hand scale.

Figure 4: IEC stability as a ratio of the previous reading.



Discussion: Several elements in figure 3 show sloping curves, most of them are atom lines in axial view. This looks like a specific effect related to the axial view angle of several specific elements, probably a drift caused by thermal effects or system contamination although for the same spectral line, different stability curves are found (see line Sn 242.2 axial atom for Fe, Mo and Zn). Factors that influence the Inter Element (mathematical) Correction factors are:

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

Many instruments have additional methods for peak setting and recognition like ie. Multi Spectral fitting (MSF). In that case the peak setting is based on the peak profile and not on the fixed wavelength.

Further investigation of this phenomenon has to take place in cooperation with the supplier of the instrument.

For most elements the stability of the IEC is good and within the 20% deviation from the previous measurement; this is not always achievable at low values of the IEC.

The standard should contain a statement or note in case of a deviation more than 20% the IEC should be determined on a more frequent (daily?) basis.

4.5 Detection limit.

4.5.1 Instrumental Detection limit.

The instrumental detection limit is determined with a reagent blank solution that was obtained at 3.2.

Each solution is measured with 10 replicates. The standard deviation multiplied by 3 is the detection limit in solution concentration (mg/L). The instrumental detection limit expressed in mass concentration depends on the amount of the soil that's digested and the end volume. The results are summarized in table 6.

Table 6 : Instrumental detection limit:

IDL in reagent blanc				aqua regia mg/L	nitric acid mg/L
Ag	243.778	ion	axial	0.0147	0.0120
Ag	328.059	atom	axial	0.0007	0.0004
Ag	338.281	atom	axial	0.0019	0.0021
As	188.973	atom	axial	0.0126	0.0146
As	193.689	atom	axial	0.0143	0.0228
As	197.192	atom	axial	0.0296	0.0280
Ba	234.519	ion	Rad	0.0177	0.0395
Ba	455.382	ion	Rad	0.0011	0.0007
Ba	493.394	ion	Rad	0.0011	0.0006
Be	234.853	atom	axial	0.0003	0.0004
Be	313.037	ion	axial	0.0002	0.0003
Be	313.094	ion	axial	0.0002	0.0003
Cd	214.428	atom	axial	0.0004	0.0006
Cd	226.495	ion	axial	0.0011	0.0006
Cd	228.794	atom	axial	0.0007	0.0008
Co	228.607	ion	axial	0.0015	0.0022
Co	230.777	ion	axial	0.0012	0.0021
Co	238.882	ion	axial	0.0014	0.0013
Cr	205.553	ion	axial	0.0035	0.0029
Cr	206.152	ion	axial	0.0045	0.0024
Cr	267.701	ion	axial	0.0045	0.0027
Cu	224.693	ion	axial	0.0052	0.0041

Cu	324.744	atom	axial	0.0041	0.0031
Cu	327.384	atom	axial	0.0048	0.0035
Mo	202.026	ion	axial	0.0038	0.0036
Mo	203.839	ion	axial	0.0085	0.0078
Mo	204.591	ion	axial	0.0043	0.0098
Ni	221.639	ion	axial	0.0069	0.0037
Ni	231.600	ion	axial	0.0035	0.0024
Ni	231.997	atom	axial	0.0046	0.0055
Pb	216.992	atom	axial	0.0319	0.0105
Pb	220.345	ion	axial	0.0082	0.0059
Pb	283.297	atom	axial	0.0391	0.0258
Sb	206.827	atom	axial	0.0105	0.0127
Sb	217.575	atom	axial	0.0122	0.0215
Se	196.020	atom	axial	0.0412	0.0354
Sn	189.921	ion	axial	0.0099	0.0101
Sn	242.16	atom	axial	0.0507	0.0332
Tl	190.788	ion	axial	0.0149	0.0102
Tl	351.911	atom	axial	0.0316	0.0152
V	290.873	ion	rad	0.0155	0.0099
V	310.22	ion	rad	0.0043	0.0042
Zn	202.541	ion	rad	0.0822	0.1074
Zn	206.193	ion	rad	0.1643	0.1602

Discussion: The IDL's are within the expected concentration range and in good comparison with the IDL proposed in the standard. There is a good comparison of the IDL for aqua regia and nitric acid. The method for determination of the instrument detection limit is not clear and should for reason of comparison be part of the standard.

Method detection limit

The method detection limit is measured with a matrix solution (ICS). The ICS solution contains matrix and a low concentration (5 µg/L) of the analyte itself. See for matrix concentrations table 1.

Each solution is measured 10 times. The standard deviation multiplied by 3 is the detection limit in the unit mg/L. The method detection limit expressed in mass concentration depends on the amount of the soil that's digested and the end volume. Therefore the method detection limit expressed in mass content is calculated with 2.5 gram to 100 mL. The results are summarized in table 7.

Discussion: For the most elements the method detection limit is between 0.1 and 4 mg/kg. In comparison to the IDL the MDL is 2-3 times and in some case 10 times higher. The method for determination of the instrument detection limit is not clear and should for reason of comparison be part of the standard.

Table 7: Method detection limit:

MDL in matrix				mg/L matrix solution	mg/kg dw (2.5g/100 mL)	Reference (NL) (informative)
Element	wavelength					
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	
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	

4.6 Precision

The reference materials used for investigation of the precision (expressed as within lab reproducibility) are the same as used in 4.1. The selected materials were measured on eight different days.

The reference materials digested with aqua regia were used in this case. The results are reported in table 8. The red marked values are greater than 10%. See annex 6.5 for an overview of the concentration levels of the measured samples.

Discussion:

The precision is for most elements better than 10%, except for those elements where the concentration is at a low (<5 times DL) level. This corresponds in nearly all cases with the (red) marked values in table 8. The averaged overall precision is **6.8%**.

4.7 Recovery (spike and dilution).

The recovery is investigated with both methods prescribed in the proposed standard:

- addition of a multi element standard to a matrix solution (ICS) and
- measurements in the original sample and 2-3 times diluted samples.

A multi element standard solution was added to ICS with a solution concentration of 0.5 and 5 mg/L. This was also done to a reagent blank. The recovery of the spike to the ICS solution was calculated against the addition to the reagent blank and the theoretical concentration.

The recovery after dilution was determined by manual dilution of the digest before measurement. The standard proposes a dilution by 5 times but because of the low concentration of the elements of interest in the digests, a 2-3 time dilution was used here.

The results of the addition are reported in table 9. The results from the dilution experiment in annex [6.3]. The overall recovery ratio after 2-fold dilution is 1.03 +/- 0.05(5.1%) and for 3-fold dilution 1.02 +/- 0.06(6.1%) which is well within the required 20%.

Discussion: Nearly all recoveries of the spike are within the limits of 80 -120% except for Ni at low level (respectively 79.1 and 74.8%) and Zn. For Zn there is not a clear explanation for the slight deviation of the 80 % criteria but might be caused by a contamination of the blank addition because the recovery is low for all lines at all view directions.

Although the dilution factor is 2-3 fold all the recovery values are within the limits for those elements that have a remaining concentration after dilution above 5 times DL. The recovery criterion (after digestion) is only applicable for those samples that contain high concentrations of the elements of interest. For lower concentrations and subsequent measurement close to the DL, dilution of the sample is not recommended for QC purposes.

Table 8: Precision (in %):

			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%
			IE										
Co	ion	axial	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%	1,6%
Mg	atom	rad		5,2%	3,7%	5,9%	4,4%	5,4%	5,1%	5,7%	7,1%	6,7%	5,9%
Mn	ion	rad		4,7%	5,5%	6,1%	7,7%	8,1%	7,4%	3,3%	14,7%	14,8%	15,4%
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%
			IE										
Ni	ion	axial	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%
			IE										
Zn	ion	rad	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%

Table 9: Spike recovery (in %):

	Ag	As	Ba	Be	Cd	Cd	Co	Cr	Cu	Mo	Ni	Ni	Pb	Sb	Se	Sn	Tl	Tl	V	
	328.1	193.7	234.5	313.0	214.4	214.4	228.6	205.6	324.7	202.0	231.6	231.6	220.3	206.8	196.0	189.9	190.8	190.8	290.9	
	atom	atom	ion	ion	atom	atom	ion	ion	atom	ion	ion	ion	ion	atom	atom	ion	ion	ion	ion	
	axial	axial	rad	axial	axial	radial	axial	axial	axial	axial	axial	radial	axial	axial	axial	axial	axial	radial	rad	
Spike level (mg/L)	0.25	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
recovery corrected *(%)	97.4	90.7	81.9	93.1	78.4	85.0	83.0	88.6	108.4	92.5	80.9	79.1	82.5	93.6	107.2	90.1	74.8	63.3	94.1	
Spike level (mg/L)	2.5	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
recovery corrected *(%)	108.3	104.9	101.2	89.3	87.9	92.9	91.0	102.0	119.9	103.7	90.6	95.1	92.7	100.9	107.2	102.4	86.2	94.0	104.1	
	Ag	As	Ba	Be	Cd		Co	Cr	Cu	Mo	Ni		Pb	Sb					V	
	338.3	197.2	455.4	234.9	226.5		230.8	206.2	327.4	204.6	221.6		217.0	217.6					292.4	
	atom	atom	ion	Atom	ion		ion	ion	atom	ion	ion		atom	atom					ion	
	axial	axial	rad	axial	axial		axial	axial	axial	axial	axial		axial	axial					rad	
Spike level (mg/L)	0.25	0.50	0.50	0.50	0.50		0.50	0.50	0.50	0.50	0.50		0.50	0.50					0.50	
recovery corrected *(%)	96.1	87.1	86.4	91.2	85.9		84.7	87.6	111.0	91.5	87.2		92.5	88.8					93.5	
Spike level (mg/L)	2.5	5.00	5.00	5.00	5.00		5.00	5.00	5.00	5.00	5.00		5.00	5.00					5.00	
recovery corrected *(%)	109.9	109.6	105.7	102.0	92.7		92.4	97.9	118.4	100.4	97.9		105.1	102.3					104.5	

	Ag	As	Ba	Be	Cd	Co	Cr	Cu	Mo	Ni	Pb	Sb	Sn	Tl	V	Zn	Zn
	243.8	189.0	493.4	313.1	228.8	238.9	267.7	224.7	203.8	233.0	283.3	231.2	242.2	351.9	310.2	206.2	206.2
	ion	Atom	ion	ion	atom	ion	ion	ion	ion	atom	atom	atom	atom	atom	ion	ion	ion
	axial	Axial	rad	axial	axial	axial	axial	axial	axial	axial	axial	axial	axial	axial	rad	rad	axial
spike level (mg/L)	0.25	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
recovery corrected *(%)	82.4	101.3	87.6	92.0	88.1	84.3	84.2	81.8	94.2	91.4	98.4	95.6	89.0	107.6	97.2	77.5	79.3
spike level (mg/L)	2.5	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
recovery corrected *(%)	97.6	108.1	107.2	90.2	96.2	97.4	96.4	97.7	102.2	107.4	119.1	103.5	101.6	116.3	104.2	96.0	92.9

Recovery corrected*:
corrected recovery for internal standard Yttrium 371.019
nm

5 CONCLUSIONS

The method described in the proposed standard for measurement of elements in soil, sludge and bio waste with ICP-AES can be used in practice. The measurements in this study show that the limit of detection is within the expected range, precision is less than 10% at levels above 5 times IDL and the QC criteria can be met.

Several comments on the text are formulated to improve the practical daily use.

For the most elements the method detection limit is between 0.1 and 4 mg/kg. In comparison to the IDL the MDL is 2-3 times and in some case 10 times higher.

The proposed standard doesn't give a definition of the way the instrumental detection limit has to be determined. The IDL is determined in a reagent blank under repeatability conditions. A better way is to determine the MDL under repeatability or reproducibility conditions in a matrix solution..

The two criteria for applying an IEC can be misinterpreted and are not very practical. In this study the criterion "absolute contribution is more than 3 time the DL" is used. The IDL is determined in a pure standard solution which leads to very low, not practically relevant values. Therefore the use of the MDL has more relevance. This value multiplied by K (k= 1, 2, 3 or....) should be used as criteria for applying the IEC correction.

The IEC is determined with pure standard solutions at a certain chosen concentration. The choice is relevant and matrix dependent.

The 5 % rule is not applicable during the interferences measurement but only applies in real samples where matrix is present. In practice during IEC measurements with pure standards, the need for an IEC is determined and will always be applied in real sample measurement. The 5% rule is only practical in relatively high concentration levels.

The stability of the IEC must be investigated and determined on a more frequent base in case of a difference of more than 20% from the previous determination.

The precision is for most elements better than 10%, except for those elements where the concentration is at a low (<5 times DL) level. The average overall precision is **6.8%**.

The criterion for recovery of the spike within the limits of 80 -120% is can be met in practice..

The recovery criterion after dilution is only applicable for those samples that contain high concentrations of the elements of interest. For lower concentrations and subsequent measurement close to the DL, dilution of the sample is not recommended as a QC criterion.

6 ANNEX

- 6.1 Method description.
- 6.2 IEC application overview.
- 6.3 Results dilution experiment
- 6.4 Interference table
- 6.5 Precision data overview

7 REFERENCES

- 7.1 Horizontal Desk study 19; may 2004. "Determination of elements by ICP-AES and ICP-MS", Henk J. van de Wiel.
- 7.2 Standard Horizontal ICP-AES method: "Determination of dissolved elements by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), Horizontal Deskstudy 19; may 2004 (WP6).
- 7.3 Horizontal Desk study 18; may 2004 (WP6)." Digestion of solid matrices."
- 7.4 NEN 7777: Prestatiekenmerken van meetmethoden; 2004.

Annex 6.1 : Method description

Instrument: Perkin Elmer Optima 4300 DV ICP-AES spectrometer.

Nebulizer: Perkin Elmer Sharp cone spray Nebulizer.

Plasma conditions:

Plasma flow: Argon 15 L/min.

Auxiliary flow: Argon 0.1 L/min

Nebulizer flow: Argon 0.7 L/min

Power: 1400 Watt

View height radial measurement: 14.0 mm

Spectrometer:

Resolution: high

Purge gas: Nitrogen

Replicates: 3

Read time: auto (min. Time: 1 sec. / max. Time 5 sec)

Sampler:

Rinse: 35s

Delay: 240s

Annex 6.2 : IEC application

		Ag	As	Ba	Be	Cd	Co	Cr	Cu	Mo	Ni	Pb	Sb	Se	Sn	Ti	V	Zn	
		328.059	193.689	234.519	313.037	214.428	228.607	205.553	324.744	202.026	231.639	220.345	206.827	196.020	189.921	190.788	290.873	202.541	
		atom	Atom	ion	ion	atom	ion	ion	atom	ion	ion	ion	atom	atom	ion	ion	ion	ion	
		axial	Axial	rad	axial	axial	axial	axial	axial	axial	axial	axial	axial	axial	axial	axial	rad	rad	
MDL matrix solution	mg/L	0.003	0.072	0.012	0.003	0.003	0.003	0.031	0.015	0.005	0.008	0.019	0.037	0.080	0.021	0.033	0.010	0.022	
	mg/kg (2.5g/100 mL)	0.10	2.88	0.46	0.10	0.12	0.12	1.22	0.62	0.19	0.31	0.77	1.49	3.19	0.83	1.31	0.41	0.89	
	3*DL	0.30	8.65	1.39	0.31	0.35	0.35	3.67	1.85	0.58	0.94	2.31	4.46	9.57	2.49	3.93	1.24	2.67	
interfering element	highest conc in matrix (mg/kg)																		
Cr	300		0.038	=IEC			-	0.054					0.098						-0.1
			-					-					-						-
Cu	700																		0.65
																			IEC
Fe	38000										0.035								
											IEC								
Mn	1000																		-
																			0.041
																			-
Ti	2400							0.14					0.078	0.014					0.117
								IEC					-	-					-
													-	-					-
V	80		0.071	-0.13	0.039								0.054						0.077
			-	-	-								-						-

Annex 6.2 : IEC application

		Ag	As	Ba	Be	Cd	Co	Cr	Cu	Mo	Ni	Pb	Sb	V	Zn
		338.281	197.192	455.382	234.853	226.495	230.777	206.152	327.384	204.591	221.639	216.992	217.575	292.391	213.849
		atom	atom	ion	atom	ion	ion	ion	atom	ion	ion	atom	atom	ion	atom
		axial	axial	rad	axial	axial	axial	axial	axial	axial	axial	axial	axial	rad	rad
MDL matrix solution	mg/L	0.002	0.066	0.008	0.003	0.004	0.003	0.036	0.018	0.015	0.008	0.074	0.028	0.009	0.029
	mg/kg (2.5g/100 mL)	0.09	2.64	0.31	0.12	0.17	0.12	1.42	0.71	0.59	0.31	2.97	1.12	0.35	1.15
	3*DL	0.28	7.91	0.92	0.36	0.50	0.35	4.27	2.12	1.77	0.92	8.91	3.35	1.05	3.44
Al	45000										- 0.0057 IEC				
Ca	75000														0.0074 IEC
Cr	300												0.067		
Fe	38000					0.0012						0.054 IEC			0.0078
Ti	2400					-		0.023						0.138 IEC	
V	80		0.57									-0.15	0.21		
Zn	2000		-					0.067				-	-		
								-							

Annex 6.2 : IEC application

		As	Ba	Be	Cd	Co	Cr	Cu	Mo	Ni	Pb	Sn	Tl	V	Zn	
		188.973	493.394	313.094	228.794	238.882	267.701	224.693	203.839	232.997	283.297	242.16	351.911	310.22	206.193	
		atom	ion	ion	atom	ion	ion	ion	ion	atom	atom	atom	atom	ion	ion	
		axial	rad	axial	axial	axial	axial	axial	axial	axial	axial	axial	axial	rad	rad	
MDL matrix solution	mg/L	0.034	0.007	0.002	0.003	0.025	0.031	0.014	0.022	0.019	0.085	0.065	0.014	0.003	0.065	
	mg/kg (2.5g/100 mL)	1.72	0.36	0.11	0.16	1.27	1.53	0.72	1.10	0.94	4.25	3.24	0.69	0.16	3.27	
	3*DL	5.16	1.09	0.34	0.49	3.82	4.58	2.17	3.31	2.81	12.76	9.71	2.07	0.47	9.80	
As	50				0.067											
Cr	300	0.023								2.6 IEC						0.012
Fe	38000					0.085 IEC		0.0705 IEC			0.16 IEC	-0.19 IEC				
Mg	13000										-0.065					
S	16000															0.034
V	80					0.029										
Zn	2000															
												0.103				

Annex 6.3 Dilution experiment

			Ag	Al	As	B	Ba	Be	Ca	Cd	Ce	Co	Co	Cr	Cu	Fe	In	Mg	Mn	
			328.1	396.1	193.7	208.9	234.5	313.0	317.9	214.4	401.2	228.6	228.6	205.6	324.7	238.2	230.6	285.2	257.6	
			atom	atom	atom	atom	ion	ion	ion	atom	ion	ion	ion	ion	atom	ion	ion	atom	ion	
			axial	rad	axial	axial	rad	axial	rad	axial	rad	axial	axial	axial	axial	rad	axial	rad	rad	
dilution			IEC(Ti)																	
blank digest	aqua regia	2																		0.96
blank digest	nitric acid	2																		0.96
CRM145R	aqua regia	2	1.00	1.05			1.01		1.02	1.02		0.99	0.99	1.00	1.00	1.04	0.88	1.03	1.01	
CRM145R	nitric acid	2	1.00	0.99			0.99		0.99	1.01		1.02	1.02	1.03	0.98	1.01	0.96	0.99	1.01	
LKSD-1	aqua regia	2		1.02	1.12			1.03		1.10	1.07	1.03	1.07	1.07	1.05	1.02	1.08	1.05	1.06	1.07
LKSD-1	nitric acid	2		0.98	0.98			1.01		1.03		0.81	1.00	1.00		0.95	1.02	0.98	0.99	1.01
STSD-2	aqua regia	2		0.98	1.07			1.00	1.01	1.01		1.00	1.04	1.04	1.02	0.97	1.07	1.04	1.06	1.00
STSD-2	nitric acid	2		0.99			1.01	0.98	1.02		1.01	1.02	1.02	1.00	0.93	1.05	0.96	1.04	1.02	
CRM7001	aqua regia	2		1.03			1.02	1.03	1.04		1.01	1.01	1.00	0.98	1.00	1.07	1.02	1.06	1.05	
CRM7001	nitric acid	2		0.97			1.00		0.97		0.98	1.04	1.06	1.02	0.95	0.99	0.95	0.99	0.98	
CRM144R	aqua regia	2	1.01	1.04			1.08	1.04	1.00	0.94		1.01	1.01	1.00	0.98	1.00	0.99	1.02	0.99	
CRM144R	nitric acid	2	1.01	0.98			1.15	1.01	1.01	0.99		1.04	1.04	1.04	0.97	1.05	0.95	0.99	1.01	
CRM141R	aqua regia	2		1.02			1.05	1.04	1.05	1.06	1.06	0.96	1.06	1.06	1.03	0.99	1.06	1.00	1.04	1.04
CRM141R	nitric acid	2		0.98			1.03	1.04	1.07			1.06	1.06	1.02	0.99	1.04	1.04	1.01	1.03	
AMB sludge	aqua regia	2		1.02			1.03	1.01			1.00	1.03	1.03	1.02	0.99	1.05	0.98	1.03	1.05	
AMB sludge	nitric acid	2		0.97			1.00	1.04				0.99	0.99	0.98	0.93	1.03	0.95	1.01	1.04	
AMB soil	aqua regia	2		0.89			0.96	0.96								0.91	0.95	0.94		
AMB soil	nitric acid	2		0.96												0.96	0.95	0.97		
AMB biowaste	aqua regia	2		1.02			1.01		0.95			1.09		1.02	0.98	1.03	0.98	1.02	0.98	
AMB biowaste	nitric acid	2		0.98			1.00	1.02						1.05	0.96	1.07	0.97	1.01	1.01	
			1.00	0.99	1.06	1.09	1.01	1.02	1.02	1.02	0.98	1.03	1.03	1.02	0.97	1.03	0.98	1.01	1.02	
			0.006	0.037	0.067	0.051	0.020	0.031	0.037	0.048	0.071	0.028	0.027	0.023	0.024	0.044	0.040	0.033	0.027	
			0.6%	3.8%	6.4%	4.7%	2.0%	3.0%	3.7%	4.7%	7.3%	2.7%	2.6%	2.3%	2.5%	4.3%	4.1%	3.3%	2.6%	

Annex 6.3 Dilution experiment

			Mo	Ni	Ni	P	Pb	Rh	S	Sb	Sn	Sr	Ti	Tl	V	W	Y	Zn	Zn	
			202.0	231.6	231.6	177.4	220.3	233.5	180.7	206.8	189.9	407.8	336.1	190.8	290.9	207.9	371.0	202.5	202.5	
			ion	ion	ion	atom	ion	ion	atom	atom	ion	ion	ion	ion	ion	ion	ion	ion	ion	
			axial	axial	axial	axial	axial	axial	axial	axial	axial	rad	rad	axial	rad	axial	rad	rad	rad	
dilution			IEC(Fe)																	
blank digest	aqua regia	2						0.96										0.95		
blank digest	nitric acid	2						0.97										0.93		
CRM145R	aqua regia	2	1.12	1.02	1.02	1.07	1.02	0.98	1.08	1.07	1.04	1.03	1.04		1.02	1.00	0.97	1.00	1.00	
CRM145R	nitric acid	2	1.27	1.01	1.01	1.03	1.04	0.98	1.07			1.01	1.00		1.04	1.32	0.97	1.00	1.00	
LKSD-1	aqua regia	2	1.00	1.04		1.05	1.07	1.04	1.09			1.08	1.06		1.06	1.14	0.98	1.09	1.09	
LKSD-1	nitric acid	2	1.11	1.01		0.99	1.00	1.00	1.02			0.99	1.00		0.99	0.91	0.94	1.05	1.05	
STSD-2	aqua regia	2	1.02	1.04		1.03	1.05	1.04	1.05			0.99	1.01		1.00	0.97	0.90	1.02	1.02	
STSD-2	nitric acid	2	0.98	1.01		1.02	1.04	0.97	1.01			1.00	1.01		1.00	1.32	0.94	1.06	1.06	
CRM7001	aqua regia	2		0.99		1.02	0.99	1.03	1.01				1.03		1.00	1.14	0.96	1.05	1.05	
CRM7001	nitric acid	2		1.01		1.03	0.98	0.96	1.03				0.96		1.00	1.00	0.88	1.06	1.06	
CRM144R	aqua regia	2	1.25	1.00		1.06	0.98	1.01	1.08		0.98	0.99	1.02		1.03	1.03	0.96	1.00	1.00	
CRM144R	nitric acid	2	1.17	0.98		1.07	1.02	0.98	1.07			0.98			1.10	1.33	0.91	1.03	1.03	
CRM141R	aqua regia	2	1.07	1.06	1.06	1.07	1.05	1.01	1.04			1.03	1.04		1.05	1.00	0.92	1.08	1.09	
CRM141R	nitric acid	2		1.04	1.04	1.04	1.03	1.05	1.02			1.00			1.01	1.07	0.95	1.05	1.05	
AMB sludge	aqua regia	2	1.00	1.03		1.03	1.05	0.96	1.09				1.03		1.01		0.94		1.02	
AMB sludge	nitric acid	2		0.99		0.96	1.01	0.93	1.00				1.00		1.01		0.91		1.01	
AMB soil	aqua regia	2						0.96					0.94				0.92			
AMB soil	nitric acid	2						0.97									0.93			
AMB																				
biowaste	aqua regia	2	1.10	1.00		1.05	0.92	1.01	1.00			1.03	1.00		1.06	2.59	0.99	1.00	1.00	
AMB																				
biowaste	nitric acid	2	1.49	0.81		1.06	0.97	0.98	1.01			0.99			0.96	2.06	0.93	1.13	1.13	overall
			1.13	1.00	1.03	1.04	1.01	0.99	1.04	1.07	1.01	1.01	1.01		1.02	1.28	0.94	1.04	1.04	1.03
			0.148	0.056	0.024	0.030	0.038	0.033	0.033		0.042	0.027	0.030		0.036	0.476	0.027	0.041	0.039	0.05
			13.0%	5.6%	2.4%	2.9%	3.8%	3.3%	3.2%	0.0%	4.2%	2.7%	3.0%		3.5%	37.2%	2.8%	3.9%	3.8%	5.1%

Annex 6.3 Dilution experiment

			Ag	Al	As	B	Ba	Be	Ca	Cd	Ce	Co	Co	Cr	Cu	Fe	In	Mg	Mn
			328.1	396.1	193.7	208.9	234.5	313.0	317.9	214.4	401.2	228.6	228.6	205.6	324.7	238.2	230.6	285.2	257.6
			atom	atom	atom	atom	ion	ion	ion	atom	ion	ion	ion	ion	atom	ion	ion	atom	ion
			axial	rad	axial	axial	rad	axial	rad	axial	rad	axial	axial	axial	axial	rad	axial	rad	rad
			IEC(Ti)																
blank digest	aqua regia	3																	1.06
blank digest	nitric acid	3																	1.04
CRM145R	aqua regia	3	0.98	1.00			1.00		0.97	1.01		1.12	1.13	0.98	0.98	0.99	0.99	0.98	1.00
CRM145R	nitric acid	3	0.90	0.96			0.95		0.97	0.98		1.05	1.06	0.98	0.94	0.99	1.06	0.97	0.98
LKSD-1	aqua regia	3		1.02	1.19		1.03		1.09	1.03	0.96	1.03	1.03	1.05	0.98	1.07	1.19	1.05	1.06
LKSD-1	nitric acid	3		0.96	1.05		1.01		1.01		0.86	1.03	1.03		0.91	0.99	1.10	0.98	0.99
STSD-2	aqua regia	3		0.97	0.96		1.00	1.02	1.01		0.99	1.05	1.06	1.01	0.96	1.09	1.16	1.07	1.01
STSD-2	nitric acid	3		0.98			1.01	1.01	1.01		0.98	1.03	1.04	1.01	0.94	1.05	1.11	1.03	1.01
CRM7001	aqua regia	3		1.04			1.02	1.03	1.04		1.00	1.02	1.01	0.99	0.96	1.08	1.08	1.06	1.05
CRM7001	nitric acid	3		0.98			1.00		1.01		1.01	0.98	0.99	0.99	0.94	1.01	1.03	1.00	0.99
CRM144R	aqua regia	3	1.03	1.05		1.00	1.02		0.97	0.91		0.97	0.97	1.01	0.95	1.00	1.09	0.99	0.96
CRM144R	nitric acid	3	1.00	0.97		1.13	0.98		0.98	0.96		1.04	1.04	1.04	0.95	1.00	1.06	0.99	0.96
CRM141R	aqua regia	3		1.05		1.10	1.08	1.06	1.09	1.08	0.91	1.08	1.08	1.05	0.99	1.07	1.18	1.06	1.04
CRM141R	nitric acid	3		0.96			1.02		1.05	1.04		1.05	1.05	0.99	0.98	1.04	1.14	0.99	1.02
AMB sludge	aqua regia	3		1.01			1.04		1.03		1.03	1.04	1.04	1.01	0.95	1.05	1.11	1.04	1.04
AMB sludge	nitric acid	3		0.98			0.97		1.00			0.96	0.96	0.99	0.91	1.02	1.06	0.99	1.02
AMB soil	aqua regia	3		0.88			0.80		0.97							0.91	1.07	0.94	
AMB soil	nitric acid	3		0.94												0.94	1.04	0.95	
AMB biowaste	aqua regia	3		0.97			0.95		0.92			1.18		1.02	0.92	1.01	1.10	0.99	0.96
AMB biowaste	nitric acid	3		0.96			0.96		1.02					1.00	0.91	1.03	1.08	1.02	0.98
			0.98	0.98	1.06	1.08	0.99	1.03	1.01	1.00	0.97	1.04	1.04	1.01	0.95	1.02	1.09	1.01	1.00
			0.058	0.041	0.116	0.068	0.060	0.023	0.044	0.056	0.057	0.054	0.043	0.024	0.026	0.048	0.050	0.038	0.034
			5.9%	4.2%	10.9%	6.3%	6.0%	2.2%	4.4%	5.6%	5.9%	5.2%	4.2%	2.4%	2.7%	4.7%	4.6%	3.8%	3.4%

Annex 6.3 Dilution experiment

			Mo	Ni	Ni	P	Pb	Rh	S	Sb	Sn	Sr	Ti	Ti	V	W	Y	Zn	Zn	
			202.0	231.6	231.6	177.4	220.3	233.5	180.7	206.8	189.9	407.8	336.1	190.8	290.9	207.9	371.0	202.5	202.5	
			ion	ion	ion	atom	ion	ion	atom	atom	ion	ion	ion	ion	ion	ion	ion	ion	ion	
			axial	axial	axial	axial	axial	axial	axial	axial	axial	rad	rad	axial	rad	axial	rad	rad	rad	
			IEC(Fe)																	
blank digest	aqua regia	3						1.06										1.04		
blank digest	nitric acid	3						1.05										1.03		
CRM145R	aqua regia	3	1.13	1.00	1.00	1.06	0.99	1.09	1.07	0.97	0.93	0.98	1.02		1.02	0.98	1.02	1.01	1.01	
CRM145R	nitric acid	3	1.31	0.98	0.97	1.01	0.98	1.08	1.01			0.98	0.95		1.06	1.16	1.05	0.97	0.97	
LKSD-1	aqua regia	3	1.25	1.01		1.04	1.06	1.13	1.08			1.06	1.04		1.04	1.31	1.07	1.07	1.07	
LKSD-1	nitric acid	3	1.15	0.99		0.98	1.00	1.11	0.99			0.98	0.98		0.99	1.11	1.03	0.99	0.99	
STSD-2	aqua regia	3	0.97	1.05		1.07	1.05	1.18	1.05			1.00	1.01		1.01	1.09	0.97	1.06	1.06	
STSD-2	nitric acid	3	0.95	1.00		1.02	0.99	1.13	1.01			0.99	1.00		0.97	1.32	1.01	1.06	1.06	
CRM7001	aqua regia	3		1.00		1.04	0.99	1.08	1.03				1.03		1.01	0.81	1.05	1.04	1.04	
CRM7001	nitric acid	3		0.99		1.03	0.97	1.07	0.98				0.96		1.00	0.95	0.97	1.11	1.11	
CRM144R	aqua regia	3	1.08	1.00		1.08	0.92	1.12	1.09		1.07	0.98	0.99		0.99	1.11	1.05	0.98	0.98	
CRM144R	nitric acid	3	1.12	0.96		1.02	0.94	1.05	1.01			0.97			1.01	1.23	1.02	0.97	0.97	
CRM141R	aqua regia	3	1.19	1.08	1.08	1.11	1.05	1.17	1.05			1.06	1.05		1.06	1.15	1.02	1.09	1.09	
CRM141R	nitric acid	3		1.02	1.01	1.01	0.98	1.15	0.99			1.00			1.00	1.05	1.01	1.08	1.08	
AMB sludge	aqua regia	3	1.08	1.04		1.05	0.94	1.07	1.10				1.02		1.02		1.03		1.14	
AMB sludge	nitric acid	3		0.97		0.95	0.89	1.04	0.99				0.99		0.97		1.01		1.02	
AMB soil	aqua regia	3						1.08					0.95				1.03			
AMB soil	nitric acid	3						1.07									1.02			
AMB biowaste	aqua regia	3	1.53	1.06		1.06	0.92	1.14	0.99			0.99	0.98		0.98	1.87	1.05	1.00	1.00	
AMB biowaste	nitric acid	3	1.92	0.78		1.01	0.93	1.06	0.96			1.00			1.08	0.64	1.03	1.02	1.02	
			1.22	1.00	1.02	1.03	0.98	1.10	1.03	0.97	1.00	1.00	1.00		1.01	1.13	1.03	1.03	1.04	1.02
			0.269	0.065	0.045	0.039	0.050	0.041	0.043		0.098	0.031	0.033		0.034	0.282	0.025	0.047	0.051	0.06
			22.0%	6.5%	4.4%	3.8%	5.2%	3.7%	4.2%	0.0%	9.8%	3.1%	3.3%		3.3%	25.0%	2.4%	4.6%	5.0%	6.1%

Annex 6.4 Interference table

Elements which are often used as internal standards (Sc, Rh, In and Y) are also mentioned in this scheme.

Experiments are performed on an Optima 4300DV spectrometer (Perkin Elmer)

Element	λ (nm)	Spectral overlap		Background shift		Low resolution: potential interference	
		Interfering element	Description of interference	Interfering element	Description of interference	Interfering element	Description of interference
Ag	328.059	Mn	Partial overlap				
		Rh	Partial overlap				
		Y	Partial overlap				
Ag	338.281	Ti	Partial overlap				
As	193.689	Cr	Partial overlap				
		V	Partial overlap				
		Mo	Partial overlap				
As	197.192	V	Line overlap				
		Mo	Partial overlap				
As	188.973	Mo	Partial overlap				
		Cr	Partial overlap				
Ba	233.519	V	Partial overlap				
		Rh	Line overlap				
Ba	493.394	-					
Ba	455.382	-					
Be	313.037	Ti	Partial overlap				
Be	313.094	Ti	Partial overlap				
Be	234.853	Fe	Partial overlap				
		Ti	Partial overlap				
Cd	214.428	Fe	Partial overlap				
Cd	228.794	As	Partial overlap				
		Sc	Partial overlap				
		Ni	Partial overlap				
Cd	226.495	Fe	Line overlap				
		Ti	Partial overlap				
Co	228.607	Ni	Line overlap				
		Ti	Line overlap				

Annex 6.4 Interference table

		Cr	Partial overlap				
		Fe	Line overlap (?)				
Co	230.777	Ni	Partial overlap				
		Mo	Partial overlap				
Co	238.882	Fe	Partial overlap				
		V	Line overlap				
		Ni	Line overlap (?)				
Cr	205.553	Ni	Partial overlap				
		Mo	Partial overlap				
Cr	206.152	Zn	Partial overlap				
Cr	267.701	Mo	Partial overlap				
		Mn	Partial overlap				
Cu	324.744	Y	Partial overlap				
Cu	327.384	Ti	Partial overlap				
		Sc	Partial overlap				
Cu	224.693	Ti	Line overlap				
		Fe	Partial overlap				
		Mo	Partial overlap				
Mo	202.026	-					
Mo	204.591	-					
Mo	203.839	-					
Ni	231.596	-					
Ni	231.997	Cr	Line overlap				
		V	Partial overlap				
		Mn	Partial overlap				
		Mo	Partial overlap				
Pb	220.345	Co	Partial overlap				
		Ti	Partial overlap				
Pb	216.992	Fe	Partial overlap				
		Mo	Partial overlap				
		Sb	Partial overlap				
		V	Partial				

Annex 6.4 Interference table

			overlap				
		Ni	Partial overlap				
Pb	283.297	Fe	Line overlap				
Sb	217.575	V	Line overlap				
		W	Line overlap				
Sb	206.827	Ti	Partial overlap				
		Mo	Partial overlap				
Sb#	231.138#	Co	Partial overlap				
		Ni	Partial overlap				
		Mo	Partial overlap				
		Fe	Partial overlap				
Se	196.020	Ti	Line overlap				
Se#	203.985#	Cr	Partial overlap				
Sn	189.921	Ti	Partial overlap				
Sn#	235.476#	Fe	Partial overlap				
Sn	242.160	Mo	Partial overlap				
		Fe	Partial overlap				
Tl	351.911	V	Partial overlap				
		Ti	Partial overlap				
		Ce	Partial overlap				
Tl	190.788	V	Partial overlap				
		Co	Partial overlap				
Tl#	276.780#	Mn	Partial overlap				
		V	Partial overlap				
		Mg	Partial overlap				
		Cr	Partial overlap				
V	290.873	Mo	Partial overlap				
		Cr	Partial overlap				
V	292.391	Ti	Partial overlap				
		Rh	Partial overlap				
		Co	Partial				

Annex 6.4 Interference table

			overlap				
		Cr	Partial overlap				
		Mo	Partial overlap				
V	310.220	Ni	Partial overlap				Strong background
		Ca	Partial overlap				
Zn	202.541	Cu	Line overlap				
		Cr	Partial overlap				
		Ni	Partial overlap				
Zn	206.193	Cr	Partial overlap				
Zn	213.849	Ni	Line overlap				
		Fe	Line overlap				
		Cu	Partial overlap				
		Ca	Partial overlap				

Annex 6.5 Precision data overview

				CRM145R	Fenelab 19848469	LKSD-01	STSD-02	CRM7001	CRM144R	CRM141R	AMB sludge	AMB soil	AMB biowaste
			Unit	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw
Ag	328.1	atom	axial	13.2	1.9	-0.2	-0.8	0.1	9.0	0.0	-0.2	-0.1	-0.3
Al	396.1	atom	rad	23566	39807	8748	44058	22863	34454	34655	41834	2426	3102
As	193.7	atom	axial	10.7	47.4	35.5	38.0	13.0	6.3	8.3	19.0	0.7	1.7
Ba	234.5	ion	rad	1068	764	102	136	122	373	163	81	9	59
Be	313.0	ion	axial	0.4	1.9	0.2	3.0	1.1	0.2	1.3	1.0	0.1	0.1
Ca	317.9	ion	rad	45205	33493	64924	15627	5043	41522	73550	884	158	31408
Cd	214.4	atom	axial	3.3	7.7	1.3	0.8	0.3	1.7	10.8	0.1	0.0	0.6
Co	228.6	ion	axial	5.0	18.5	10.0	18.4	10.5	13.6	8.4	9.8	0.8	1.4
Co	228.6	ion	axial	IEC	4.6	17.5	8.1	15.0	8.1	13.2	7.8	0.7	1.2
Cr	205.6	ion	axial	319	209	20	65	81	99	146	67	8	60
Cu	324.7	atom	axial	686	165	47	49	31	302	47	35	1.5	46
Fe	238.2	ion	rad	12681	32208	23106	37592	27388	6384	20470	20793	1245	3742
Mg	285.2	atom	rad	5711	9570	7726	13087	7292	7576	5962	4886	320	8245
Mn	257.6	ion	rad	142	944	566	775	456	190	557	112	12	158
Mo	202.0	ion	axial	10.1	1.5	9.9	11.7	1.6	8.6	2.5	2.2	0.1	3.4
Ni	231.6	ion	axial	227.8	55.7	14.2	49.0	33.4	43.5	79.0	27.3	2.6	4.8
Ni	231.6	ion	axial	IEC	223.3	44.5	6.1	35.8	23.8	41.2	71.8	20.0	3.5
P	177.4	atom	axial	11933	2422	697	1247	1201	18428	1054	409	14	15586
Pb	220.3	ion	axial	265.5	279.7	81.7	63.4	27.5	100.7	45.2	10.9	1.7	24.9
S	180.7	atom	axial	12966	1509	15992	594	265	9509	1058	14542	12	7395
Sb	206.8	atom	axial	13.3	1.8	0.7	1.4	1.1	2.6	0.2	1.5	0.3	1.0
Se	196.0	atom	axial	8.0	2.0	1.1	-0.1	0.3	3.7	0.2	1.3	0.5	0.1
Sn	189.9	ion	axial	60.1	22.4	0.9	0.4	3.3	40.5	4.1	5.6	-0.4	0.0
Ti	336.1	ion	rad	294	717	1357	2436	1714	345	462	627	75	182
Tl	190.8	ion	axial	-0.6	-0.2	-2.3	-4.5	-3.3	0.1	-0.9	-0.3	-0.2	-0.7
V	290.9	ion	rad	31	74	37	72	52	17	62	57	3	9
Zn	202.5	ion	rad	1941	923	295	202	102	860	209	46	4	179
Zn	202.5	ion	rad	IEC	1937	922	294	201	101	858	209	46	178