

## **Trace elements: ICP-MS Ruggedness test**

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## **Contents**

1.	<b>INTRODUCTION</b>	<b>6</b>
2.	<b>INSTRUMENTATION</b>	<b>8</b>
3.	<b>PROCEDURES</b>	<b>9</b>
4.	<b>RESULTS</b>	<b>11</b>
5.	<b>CONCLUSIONS</b>	
	<b>25</b>	
6.	<b>ANNEX</b>	<b>26</b>
7.	<b>REFERENCES</b>	<b>26</b>

## **LIST OF TABLES**

- |                 |  |
|-----------------|--|
| <b>Table 1</b>  | <b>Matrices applied in this study</b>                                  |
| <b>Table 2</b>  | <b>Elements under investigation</b>                                    |
| <b>Table 3</b>  | <b>Maximum matrix concentrations and the chosen ICS concentrations</b> |
| <b>Table 4</b>  | <b>Major and practical relevant interferences.</b>                     |
| <b>Table 5</b>  | <b>Matrix interference contribution on isotopes.</b>                   |
| <b>Table 6</b>  | <b>Instrumental detection limit</b>                                    |
| <b>Table 7</b>  | <b>Method detection limit</b>  |
| <b>Table 8</b>  | <b>Precision</b>   |
| <b>Table 9</b>  | <b>Spike recovery</b>  |
| <b>Table 10</b> | <b>Difference between original and fivefold-diluted samples.</b>       |

## **LIST OF FIGURES**

- |                 |                            |
|-----------------|----------------------------|
| <b>Figure 1</b> | <b>Aqua regia results</b>  |
| <b>Figure 2</b> | <b>Nitric acid results</b> |
| <b>Figure 3</b> | <b>Reaction cell</b>       |

## 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 1 for measurement of elements in soil, sludge and bio waste with ICP-MS can be used in practice. The results of this study show that the criteria for the limit of detection, precision and QC criteria can be met. Several comments on the text are formulated to improve the practical daily use like the criteria for interference correction and the control of the correction applied and stability check between the days

The main differences between the two digestion methods are the chlorine and carbon content. Measurements show that the influence of the chlorine on several elements is apparent but can be corrected for or can be eliminated by use of a reaction cell or by matrix matching. The carbon content of the digest with HNO<sub>3</sub> is 25 to 500% higher than Aqua Regia digests of the same sample. Several elements but especially Cr is affected by carbon interference. 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. Based on the highest concentrations found in the AR digest an ICS is proposed. and used for further test.

The maximum allowed contribution of interference is limited at three times the instrumental detection limit (IDL)(see 10.4 H19). In practice this is not a suitable criterion because the contribution of the interference depends on the concentration of the interfering component.

The doubly charged interference of Sn on Ni(60,61,62) must be added to the table 1 of the proposed standard.

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 has a median value of 0.075 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 isotopes the method detection limit (MDL<sub>R</sub>) is between 0.1 and 4 mg/kg (median value 0.15 mg/kg). In comparison to the IDL the MDL is on average 2-3 times higher.

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 **6.1%** and the median value is 5.1%.

The criterion for recovery of the spike (within 80 -120%) can be met in practice. The overall averaged recovery is 98,4%.

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 recovery (of the diluted to the undiluted result) is for a 5-fold dilution on average 105,5% with all within 80-120%.

## 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-MS 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\_MS 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].

For the determination of the Detection Limit (DL) a definition is given and the definition of NEN 7777 is used [7.4].

### 1.1 Scope

This study incorporates an ICP-MS quadrupole instrument with two different setups, a standard and a reaction cell mode. 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\_MS METHOD[7.2].

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

Table 1:

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

The project definition mentions 'common elements' in its scope. The elements selected for this study are listed 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.

Table 2:

Elements used in this study	CAS-number	Part of the scope of H-19 ICP-MS?
Arsenic (As)	7440-38-2	Yes
Cadmium (Cd)	7440-43-9	Yes
Chromium (Cr)	7440-47-3	Yes
Copper (Cu)	7440-50-8	Yes
Mercury (Hg)	7440-92-1	No
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
Tellurium (Te)	13494-80-9	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 ICP-MS in aqueous solutions in nitric acid or *aqua regia* digests. The method measures ions produced by a radio-frequency inductively coupled plasma. Element species present in a liquid are nebulized and the resulting aerosol is transported by argon into the plasma. The ions produced by the high temperature are retained in an argon flow and introduced, by means of an interface, into a mass spectrometer (quadrupole). The ions produced in the plasma are selected according to their mass-to-charge ratios and quantified with a channel electron multiplier. Interferences are assessed and valid corrections applied. Where applicable, interference corrections must include compensation for background ions, contributed by the plasma gas, reagents and constituents of the sample matrix.

## 1.3 Definitions

For this study the following definitions are applied.

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

Method limit of detection (MDL):  $3 * S_R$  (the within lab reproducibility standard deviation calculated from multiple measurements ( $n > 8$  days) of a matrix solution on different days).

## **2 INSTRUMENTATION**

The measurements will be performed with an ICP-MS quadrupole instrument with a standard mode and a reaction cell mode.

### **2.1 Apparatus.**

An Agilent 7500 CE:in standard mode & reaction mode is used according to the requirements stated in 6.2 of the proposed standard. Helium and Hydrogen are used as reaction gasses and a Babington type nebulizer. Chemstation software is used for data acquisition and reprocessing, a Cetac ASX 510 auto sampler for sample introduction. All samples are diluted tenfold, on-line, with peristaltic pumps programming.

ICP-MS has excellent multi element capability. The instrument has been set up in multi element mode for the elements listed in table 2 with the use of 5 internal standards (Li, Ge, Rh, In, Bi) which are added on line to all samples.

The instrument is tuned as required by the manufacturer.

### **2.2 Reagents**

All reagents used are of PA quality.

ICS solution: custom made CPI p/n 440-132073

Citric acid.monohydrate: Merck 100244.0500

Potassiumdihydrogenphosphate: Merck 1.04873.0250

Sodiumsulphate: Baker 313

Calciumchloride.dihydrate: Merck1.02382.1000

### **2.3 Standards**

BDH multi element Standard solutions (cat no 456422W and 456432B)

Perkin Elmer Tellurium standard solution (cat no N9300156)

Pure elemental standards (1000 mg/L): Merck

Pure elemental standards (1000 mg/L): Baker

### **3 PROCEDURES**

#### **3.1 Method development**

The method is developed according to guidelines given in the proposed standard [7.2]. A description of the method applied is given in Annex 6.1. For this study only isobaric elemental correction factors are applied when necessary. All samples are diluted tenfold before measurement by means of an on line dilution by peristaltic pump programming. This is necessary to prevent the fast deterioration of the cones of the interface caused by the high acid (Aqua regia) content.

#### **3.2 Interferences (from matrix)**

Digests from the matrices from table 1 are analyzed and relevant concentrations of the major matrix elements are determined.

For this purpose several available Certified Reference Materials are 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) control**

Based on the composition of relevant matrices and the proposed ICS content the composition of the ICS will be determined. The content of the ICS will be bases 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 (3 times the Instrumental DL).

Interferences which are investigated in this study:

- Isobaric elemental;
- Molecular and doubly charged ions.

Single element stock solutions are used to determine the major interferences for ICP-MS method. A series of standard solutions with concentrations between 10 and 10.000 mg/L (depending on the expected practical abundance in these matrices) will be measured in the standard, the helium and the hydrogen reaction mode. For this experiment standard solutions in diluted nitric acid are nebulized into the plasma and for all elements of interest the possible interferences are measured. The solutions are aspirated without prior dilution.

Non spectral interferences are not investigated in this study. To minimize the effects of these interferences the total solid concentration is kept below 0.2% and through matrix matching.

Day to day correction factors may not vary more than 20% therefore drift (within day and between day's) is also investigated. The ICS solution is analyzed several times within a day and on eight consecutive days. The variation in response is calculated.

#### **3.4 Detection Limit in matrix solution (ICS)**

The instrumental and method limit of detection limit are determined according to the definitions in 1.3. The content of the ICS used for this purpose depends on the result of ICS in 3.2 & 3.3. The obtained values are

expressed is solution concentration (mg/L or µg/L) of the digest. Therefore the detection limit is also expressed in mass concentration after recalculation with 1 gram soil to a end volume of 50 mL and 5 gram soil to 100 mL and 5 gram soil to 200 mL.

### **3.5 Precision**

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

### **3.6 Recovery of spike**

The recovery is determined by two methods by comparing a spiked matrix solution with the original solution and by comparing a fivefold diluted sample (CRM144R) with the undiluted value.

## 4 RESULTS

### 4.1 Interferences

Reference material is used for the 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; biowaste/garden waste.

The reference materials were digested with aqua regia and 10% nitric acid. The digests are analyzed to determine the matrix. The results are summarized in figure 1 for Aqua regia and figure 2 for Nitric acid.

Figure 1: Aqua regia results

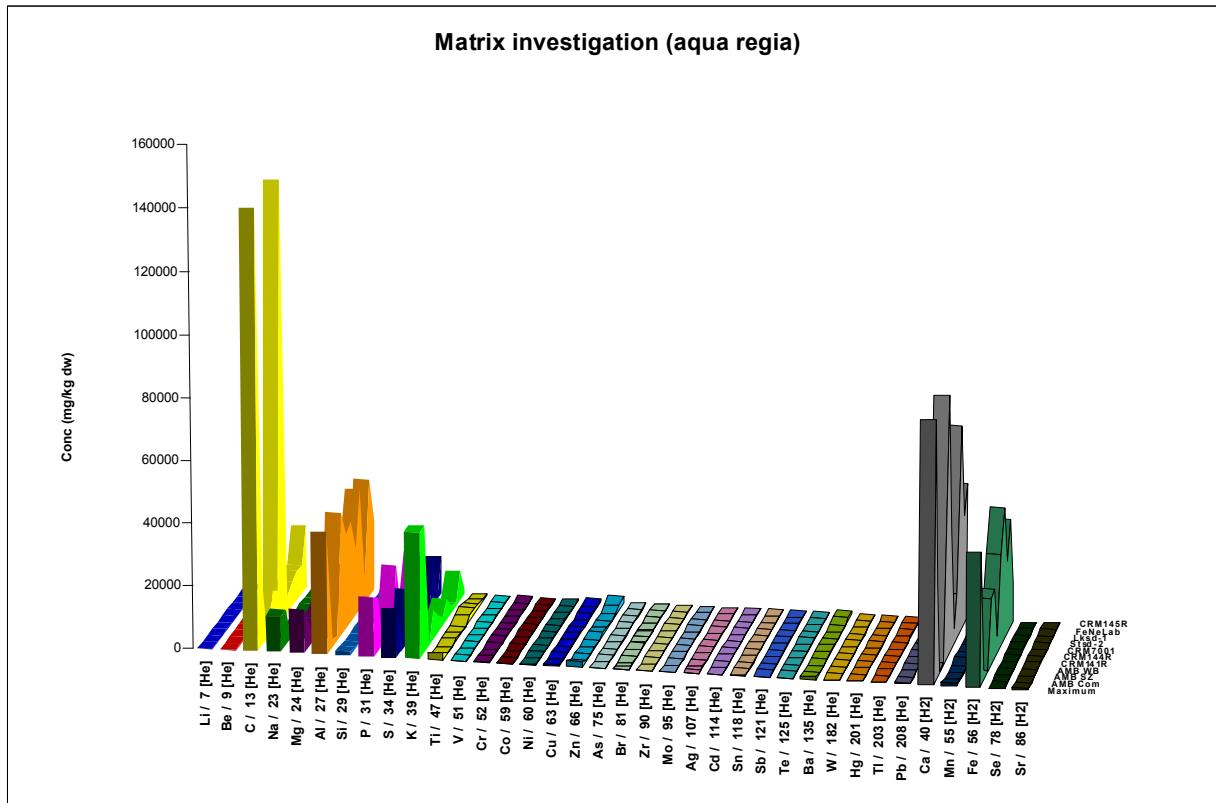
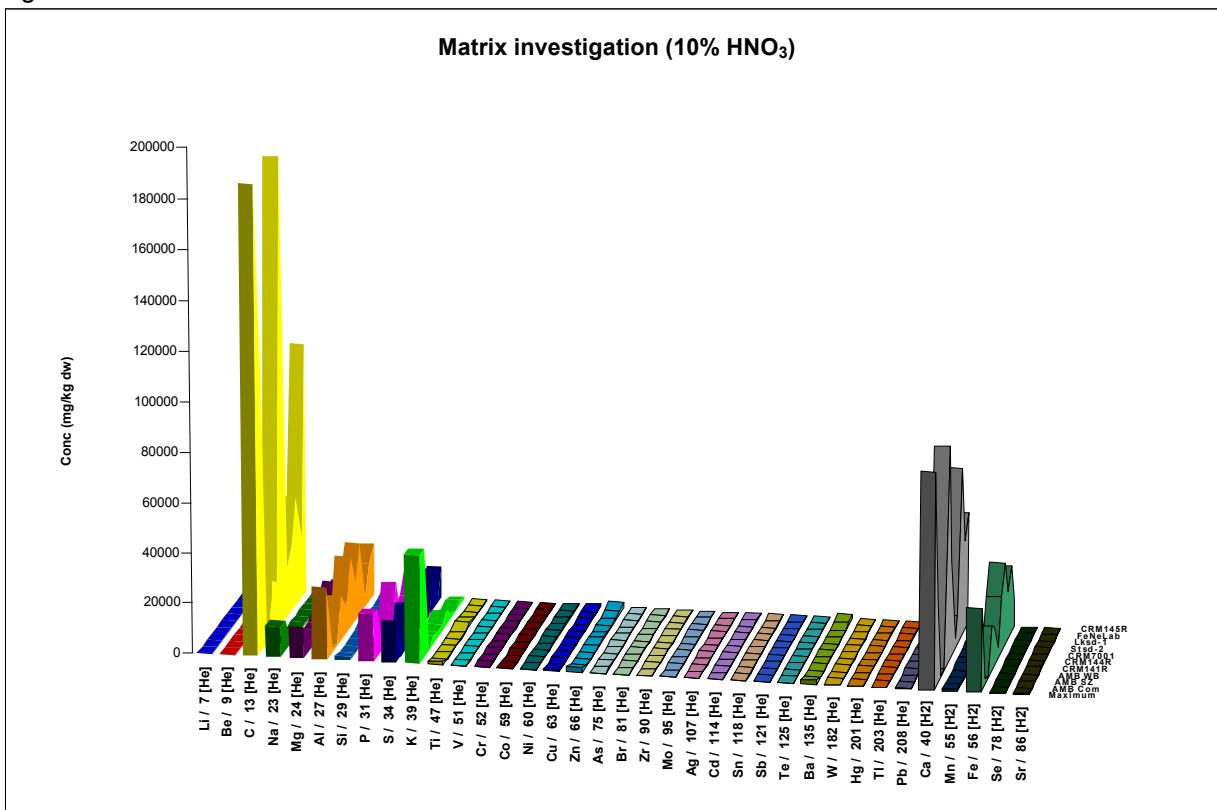


Figure 2: 1:1 Nitric acid results:



#### Discussion:

The major matrix elements from real samples are carbon, sodium, magnesium, aluminium, phosphorus, sulphur, potassium, calcium and iron. The contribution of chlorine is not expressed because of the fact that it is added during digestion and has to be overcome by matrix matching. Chlorine can interfere on V, Cr 53, As and Se77.

There is a remarkable difference between the aqua regia digests and the nitric acid digests of real samples for the element carbon. In all samples the carbon content in the nitric acid digest is 25 to 500% higher than on aqua regia. This can mean that the effect of the interference by carbon on specific elements (like ArC on Cr) is more severe.

Based on the results reported in table 3, the concentrations of the ICS are determined. This leads for this study to three ICS solutions with different elements and concentrations (ICS1, ICS2 and a mixture of ICS 1+2 (see table 3)).

Table 3: Maximum matrix concentrations and the chosen ICS concentrations<sup>#</sup>:

ICS solution						
Element	A.R.	Max (mg/L)		ICS concentration (mg/L)		
		HNO3	ICS	ICS1	ICS2	ICS1+2
Li / 7 [He]	1	1				
Be / 9 [He]	0	0				
C / 13 [He]	293	1461	x		2000	1000
Na / 23 [He]	104	110	x	1000		500
Mg / 24 [He]	355	321	x	1000		500
Al / 27 [He]	988	728	x	1000		500
Si / 29 [He]	16	22				
P / 31 [He]	154	169	x		1000	500
S / 34 [He]	401	408	x		1000	500
K / 39 [He]	368	395	x	1000		500
Ti / 47 [He]	58	36				
V / 51 [He]	2	1				
Cr / 52 [He]	5	4				
Co / 59 [He]	0	0				
Ni / 60 [He]	2	2				
Cu / 63 [He]	5	5				
Zn / 66 [He]	25	25				
As / 75 [He]	1	1				
Br / 81 [He]	-1	-1				
Zr / 90 [He]	0	0				
Mo / 95 [He]	0	0				
Ag / 107 [He]	0	0				
Cd / 114 [He]	0	0				
Sn / 118 [He]	1	0				
Sb / 121 [He]	0	0				
Te / 125 [He]	0	0				
Ba / 135 [He]	21	20				
W / 182 [He]	0	0				
Hg / 201 [He]	0	0				
Tl / 203 [He]	0	0				
Pb / 208 [He]	7	7				
Ca / 40 [H2]	2095	2177	x	1000	4000	2500
Mn / 55 [H2]	26	25				
Fe / 56 [H2]	1075	847	x	1000		500
Se / 78 [H2]	0	0				
Sr / 86 [H2]	11	10				

# : results of the std mode are giving for example and are used as good indicative values.

The final concentration of Chloride (Cl) in the ICS is 2000 mg/L.

## 4.2 Major interferences in digest samples.

Single element stock solutions were used to determine the major interferences for ICP-MS methods. A series of 24 standard solutions were analyzed in the standard, the helium and the hydrogen mode. The 'undiluted' method was used, instead of the 'online tenfold-dilution soil' method. In table 4 the possible interferences listed in the proposed standard are summarized.

Table 4: Major and practical relevant interferences (see Horizontal 19 Annex 2 table 1):

Element	Mass	Interferences	
Mg	24 NaH	Ca++	Ti++
Mg	25 Ti++		
K	39 NaO		
Ca	43 AlO	Sr++	
Ca	44 CO2	Sr++	
Ti	47 PO	Zr++	
Ti	48 Ca	SO	Zr++
V	51 ClO		
Cr	52 ArC		
Cr	53 ClO		
Fe	57 CaOH		
Ni	58 Fe	NaCl	MnO2
Co	59 ArNa	CaO	MgCl
Ni	60 NaCl	CaO	Sn++
Ni	61 CaOH	ScO	Sn++
Ni	62 TiO	ScO	Sn++
Cu	63 ArNa	TiO	
Zn	64 ArMg	SO2	TiO
Cu	65 ArMg	SO2H	Ba++
Zn	66 SO2	TiO	
Zn	68 Ba++	ArSi	
As	75 ArCl		
Se	77 ArCl		
Se	78 ArCa		
Se	82 ArCa	BrH	
Ag	107 ZrO		
Cd	111 ZrO	MoO	
Cd	114 MoO	Sn	
Hg	200 WO		
Hg	201 WO		
Hg	202 WO		

In Annex 6.2 the results of the interference measurement are summarized for the standard and reaction mode. The blue marked cells are the expected isobaric interference according to table 4. The red marked cells are additional interferences that are noted yet included in the proposed standard.

Discussion: The doubly charged interference of Sn on Ni must be added to the table 1 of the proposed standard. The expected interferences are obvious. Se77 in combination with chlorine can not be determined without interference in standard mode but can be in the hydrogen reaction mode. The reaction cell is a powerful option to reduce the interferences.

The effect of the reaction cell is shown in figure 3.

The maximum allowed contribution of interference is limited to three times the instrumental detection limit (see 10.4 H19). This is in practice not a suitable criterion because the contribution of the interference depends on the concentration of the interfering component. When the concentration of the interfering component is known the contribution can be measured and calculated. Secondly, because of the multi element conditions there can be a great difference in instrumental detection limit and the required reporting limit. Than correction on the level of three times the IDL is not necessary. A fixed limit at 0,5 times the required reporting limit can be more adequate.

Note: Assume that the concentration for calcium in an interference check solution (ICS) is 200 mg/L. If the contribution on the interfered isotope (Ni60) is lower than three times the instrumental detection limit (or lower than 0.5\* the reporting limit or if the concentration of the interference in the sample is LOWER than 200 mg/L ) the interfered isotope (Ni60) can be reported. If the concentration of the interference on the interfered isotope is higher than 200 mg/L, Ni60 can NOT be reported.

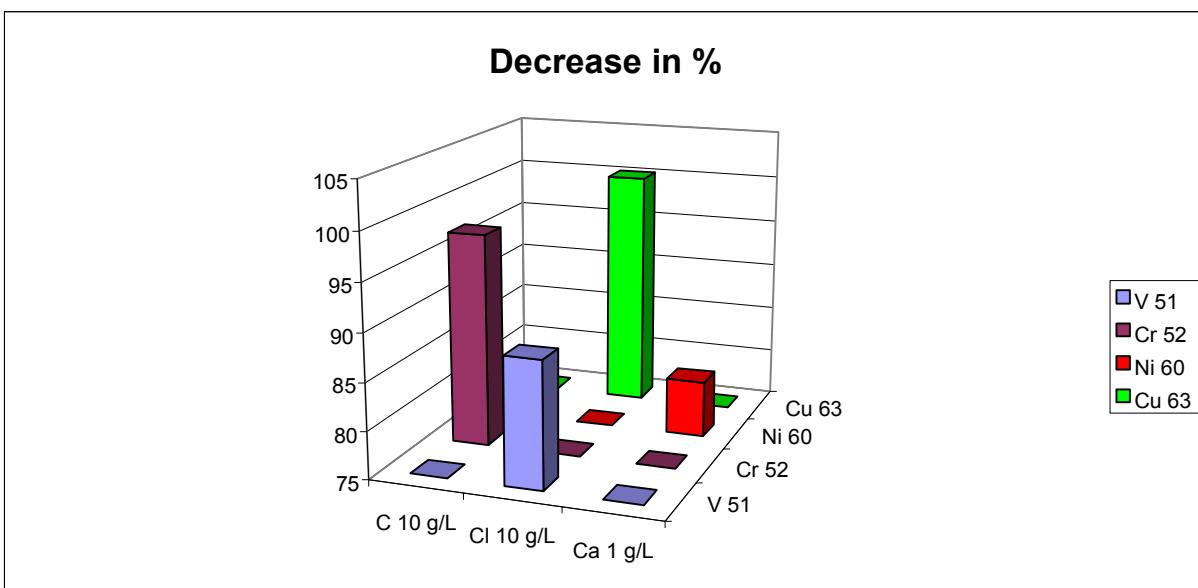
In this case the contribution of 1000 mg/L calcium solution on Ni60 is 2.2 µg/L; 0.5 \* the required report limit is 1.0 µg/L so the uncorrected Ni 60 can be reported up to (1.0/2.2\*1000=) 455 mg Ca /L. Above this value correction must be applied

Figure 3: Reaction cell

Element	Mass	Unit	Rep.limit	C 10 g/L			Cl 10 g/L			Ca 1 g/L		
				St-Mode	He-Mode	H2-mode	St-Mode	He-Mode	H2-mode	St-Mode	He-Mode	H2-mode
V	51	ug/L	2	x	x	x	15.41	1.81	7.69	x	x	x
Cr	52	ug/L	1	22.08	0.98	0.28	x	x	x	x	x	x
Ni	60	ug/L	2	x	x	x	x	x	x	2.19	0.56	2.78
Cu	63	ug/L	3	x	x	x	58.13	0.52	3.85	x	x	x

Element	Mass	Unit	Rep.limit	St-mode - He-mode			In- or decrease in %			Conc. inter < 50% rep.limit		
				C 10 g/L	Cl 10 g/L	Ca 1 g/L	C 10 g/L	Cl 10 g/L	Ca 1 g/L	C 10 g/L	Cl 10 g/L	Ca 1 g/L
V	51	ug/L	2	x	13.59	x	x	88.23	x	x	5516	x
Cr	52	ug/L	1	21.10	x	x	97.35	x	x	10698	x	x
Ni	60	ug/L	2	x	x	1.64	x	x	80.95	x	x	3404
Cu	63	ug/L	3	x	57.61	x	x	100.16	x	x	166113	x



#### 4.3 Interference corrections stability.

The interference contribution on the possible interfered isotope, measured in ICS solutions 1 and 2 using the standard mode and the reaction mode, are reported in table 5.

Table 5: Matrix interference contribution on interfered isotopes.

Interference								
	Inter. ?	Conc. appr.	Unit	Blank	ICS1	ICS2	ICS1-bl	ICS2-bl
Ti / 47 [He]	P31	1000	mg/L	-0.0010	-0.0023	0.0479		0.049
Ti / 48 [He]	Ca44	4000	mg/L	-0.0012	2.3530	9.2530		9.254
V / 51 [He]	Cl35	2000	mg/L	-0.0003	-0.0029	-0.0004		0.000
Cr / 52 [He]	C13	2000	mg/L	-0.0091	-0.0070	-0.0063		0.003
Cr / 53 [He]	Cl35	2000	mg/L	-0.0112	-0.0177	-0.0102		0.001
Ni / 58 [He]	<b>Fe54</b>	1000	mg/L	-0.0043	1.2710	-0.0029	1.275	
Co / 59 [He]	Ca44	4000	mg/L	-0.0001	0.0173	-0.0001		0.000
Ni / 60 [He]	Ca44	4000	mg/L	-0.0042	0.0095	-0.0029		0.001
Ni / 61 [He]	Ca44	4000	mg/L	-0.0060	0.0260	0.0593		0.065
Cu / 63 [He]	Na23	2600	mg/L	-0.0005	0.0019	0.0008		0.001
Zn / 64 [He]	S34	1000	mg/L	0.0003	0.0294	0.0075		0.007
As / 75 [He]	Cl35	2000	mg/L	0.0015	0.0170	0.0035		0.002
Se / 77 [He]	Cl35	2000	mg/L	-0.0148	-0.0228	0.0357		0.050
Ti / 47 [St]	P31	100	mg/L	-0.0012	-0.0012	0.2097		0.211
Ti / 48 [St]	Ca44	4000	mg/L	-0.0017	3.5450	13.9300		13.932
V / 51 [St]	Cl35	2000	mg/L	-0.0011	-0.0255	-0.0004		0.001
Cr / 52 [St]	C13	2000	mg/L	-0.0098	-0.0084	-0.0016		0.008
Cr / 53 [St]	Cl35	2000	mg/L	-0.0121	-0.0904	-0.0096		0.002
Ni / 58 [St]	<b>Fe54</b>	1000	mg/L	-0.0047	1.4070	0.0011	1.412	
Co / 59 [St]	Ca44	4000	mg/L	-0.0002	0.0178	0.0015		0.002
Ni / 60 [St]	Ca44	4000	mg/L	-0.0049	0.0108	0.0042		0.009
Ni / 61 [St]	Ca44	4000	mg/L	-0.0045	0.1356	0.4878		0.492
Cu / 63 [St]	Na23	2600	mg/L	-0.0005	0.0093	0.0204		0.021
Zn / 64 [St]	S34	1000	mg/L	0.0001	0.0352	0.0221		0.022
As / 75 [St]	Cl35	2000	mg/L	0.0035	-0.0221	0.0507		0.047
Se / 77 [St]	Cl35	2000	mg/L	-0.0178	-0.2976	0.3001		0.318

**Remark: Isobaric correction Ni58: -0.04825 x Fe54**

Note: For example chromium52 in standard mode is interfered by carbon (2000 mg/L). The concentration for Cr 52 in ICS2 minus blank is 0.008 mg/L. So the contribution of 2000 mg/L carbon on Cr52 is 0.008 mg/L.

#### Discussion:

The interference contribution on the possible interfered isotope is at a very low level, this is good for measurement but too low for stability experiments.

To examine the interference stability it's necessary to use higher concentration ICS concentrations. The interference solutions that were prepared and measured are:

- Reagent blank
- ICS1: see table 3.
- ICSa: 20.000 mg/L Calcium and 35.000 mg/L Chlorine (Calciumchloride dehydrate).
- ICSb: 100.000 mg/L Carbon (as Citric acid).
- ICSc: 10.000 mg/L Sulphur and 14.000 mg/L Sodium (Sodiumsulfate).
- ICSD: 10.000 mg/L Phosphorus (Potassium di-hydrogen phosphate).

The six interference solution where measured every 3 hours during 24 hours and also on 8 different days. The stability is reported in contribution concentration and interference correction factor on the interfered isotope.

See for results the graphs in annex 6.3.

In paragraph 10.4 Quality control of the proposed standard on ICP-MS [7.2], the criterion for change in correction factors is that the change may not be more than 20%.

Within a period of 24 hours the stability is for most isotopes within this range, but not on day to day basis. Some are out of range; the most important reason is that the contribution from the matrix (= interference) is almost on detection limit level. The day to day variation is strongly influenced by the changing of e.g. cones due to deterioration of these parts; this is a normal process which can not be overcome.

The contribution in reaction mode for the polyatomic interference is reduced significantly compared to the value in standard mode.

#### **4.4      Instrumental detection limit.**

The instrumental detection limit is determined with four solutions (reagent blank, ICS1, ICS2 and ICS1+2). The ICS solutions contain matrix and not the analytes themselves. See for matrix concentrations table 3.

Each solution is measured with 10 replicates. The standard deviation multiplied by 3 is the detection limit in the measuring value. The instrumental detection limit expressed in mass concentration depends on the amount of the soil that's digested and the end volume. Therefore the instrument detection limit expressed in mass content is calculated with 1 gram soil to a final solution of 50 mL, 5 gram to 100 mL and 5 gram to 200 mL. The results are summarized in table 6.

Discussion:

For almost all isotopes the instrumental detection limit is between 0,001 and 0.01 mg/L and 0.12 and 1.0 µg/L for Hg (**expressed in µg/L**). Isotopes i.e. Ni58 and Ni61 (in standard mode) are sometimes higher for heavy matrices, but the Ni58 and Ni61 isotopes are not the most important or the less interfered isotopes (which is i.e. Ni60).

The instrumental detection limit depends on the instrumental setup parameters like measuring time, dwell time etc. So for individual, optimized settings per element the instrumental detection limit may be better than the value listed in table 6. It is emphasized that the conditions in this study are based on robust multi element measurement. Compared with the background values for several of these elements in the Netherlands the limits are much lower.

The reaction cell can help to reduce interference and to lower the instrumental detection limit for example Ni61 in the standard mode is 5.3 mg/kg d.w. and in the helium mode 1.2 mg/kg d.w. (1 gram to 50 mL). The red coloured cells express high values for certain elements for a certain mode.

Table 6 : Instrumental detection limit:

Instrumental detection limit (in 3x Sdev)					Instrumental detection limit (in mg/kg dw)													
Element	Unit	Blank	ICSI	ICSI2	ICSI+2 (1:1)	Reporting Limit	1 gram -> 50 mL			5 gram -> 100 mL			5 gram -> 200 mL					
							Blank	ICSI	ICSI2	ICSI+2	Blank	ICSI	ICSI2	ICSI+2	Blank	ICSI	ICSI2	ICSI+2
Be / 9 [He]	µg/L	0.001	0.002	0.001	0.000	0.1	0.06	0.08	0.05	0.02	0.02	0.03	0.02	0.01	0.05	0.06	0.04	0.01
V / 51 [He]	µg/L	0.002	0.002	0.002	0.001	1	0.12	0.08	0.09	0.04	0.06	0.03	0.04	0.02	0.10	0.06	0.07	0.03
Cr / 52 [He]	µg/L	0.001	0.001	0.002	0.001	15	0.05	0.05	0.08	0.05	0.02	0.02	0.03	0.02	0.04	0.04	0.06	0.04
Cr / 53 [He]	µg/L	0.006	0.005	0.008	0.006	15	0.37	0.24	0.41	0.32	0.13	0.10	0.16	0.13	0.25	0.19	0.32	0.25
Ni / 58 [He]	µg/L	0.001	0.130	0.001	0.068	3	0.03	6.51	0.06	2.88	0.01	2.80	0.02	1.15	0.02	5.21	0.05	2.30
Co / 59 [He]	µg/L	0.001	0.001	0.000	0.001	1	0.03	0.05	0.02	0.05	0.01	0.02	0.01	0.02	0.02	0.04	0.01	0.04
Ni / 60 [He]	µg/L	0.001	0.002	0.001	0.002	3	0.05	0.11	0.05	0.08	0.02	0.04	0.02	0.03	0.04	0.08	0.04	0.06
Ni / 61 [He]	µg/L	0.015	0.014	0.024	0.023	3	0.75	0.71	1.22	1.13	0.30	0.28	0.49	0.45	0.60	0.56	0.97	0.90
Cu / 63 [He]	µg/L	0.002	0.002	0.005	0.002	5	0.09	0.11	0.27	0.11	0.04	0.04	0.11	0.04	0.07	0.08	0.22	0.08
In / 64 [He]	µg/L	0.002	0.004	0.003	0.003	17	0.08	0.21	0.17	0.14	0.03	0.08	0.07	0.05	0.06	0.17	0.13	0.11
Cu / 65 [He]	µg/L	0.002	0.002	0.007	0.003	5	0.08	0.09	0.33	0.14	0.04	0.04	0.13	0.05	0.07	0.07	0.26	0.11
In / 66 [He]	µg/L	0.003	0.005	0.003	0.005	17	0.17	0.26	0.15	0.23	0.07	0.10	0.06	0.09	0.13	0.20	0.12	0.18
In / 68 [He]	µg/L	0.006	0.006	0.006	0.004	17	0.28	0.41	0.32	0.18	0.11	0.16	0.13	0.07	0.23	0.32	0.25	0.14
As / 75 [He]	µg/L	0.003	0.004	0.003	0.004	4	0.15	0.18	0.15	0.20	0.06	0.07	0.06	0.08	0.12	0.14	0.12	0.16
Se / 82 [He]	µg/L	0.059	0.118	0.073	0.059	10	2.90	5.91	3.66	2.93	1.16	2.36	1.46	1.17	2.32	4.73	2.93	2.34
Mo / 95 [He]	µg/L	0.005	0.002	0.002	0.002	15	0.27	0.08	0.09	0.12	0.11	0.03	0.04	0.05	0.22	0.06	0.07	0.10
Mo / 98 [He]	µg/L	0.007	0.001	0.002	0.002	15	0.35	0.06	0.08	0.08	0.14	0.02	0.03	0.03	0.28	0.05	0.06	0.06
Cd / 111 [He]	µg/L	0.001	0.001	0.001	0.001	0.17	0.06	0.05	0.06	0.05	0.02	0.02	0.02	0.05	0.04	0.05	0.04	0.04
Cd / 114 [He]	µg/L	0.001	0.001	0.000	0.000	0.17	0.03	0.03	0.02	0.02	0.01	0.01	0.01	0.02	0.02	0.01	0.01	0.01
Sn / 118 [He]	µg/L	0.001	0.002	0.001	0.001	6	0.06	0.09	0.05	0.05	0.02	0.04	0.02	0.02	0.05	0.07	0.04	0.04
Sn / 120 [He]	µg/L	0.001	0.001	0.001	0.001	6	0.06	0.05	0.05	0.03	0.02	0.02	0.02	0.01	0.05	0.04	0.04	0.02
Sn / 121 [He]	µg/L	0.001	0.001	0.002	0.001	1	0.03	0.03	0.08	0.06	0.01	0.01	0.03	0.02	0.02	0.02	0.06	0.05
Sn / 123 [He]	µg/L	0.001	0.001	0.001	0.001	1	0.05	0.05	0.05	0.06	0.02	0.02	0.02	0.02	0.04	0.04	0.05	0.05
Tl / 125 [He]	µg/L	0.002	0.004	0.003	0.002	10	0.08	0.18	0.15	0.08	0.04	0.07	0.06	0.03	0.07	0.14	0.12	0.06
Tl / 126 [He]	µg/L	0.001	0.002	0.001	0.001	10	0.06	0.08	0.06	0.05	0.02	0.03	0.02	0.02	0.04	0.06	0.05	0.04
Tl / 135 [He]	µg/L	0.001	0.001	0.003	0.003	15	0.06	0.06	0.15	0.14	0.02	0.02	0.06	0.05	0.05	0.12	0.11	0.11
Ba / 137 [He]	µg/L	0.001	0.001	0.004	0.001	15	0.05	0.06	0.18	0.06	0.02	0.02	0.07	0.02	0.04	0.05	0.14	0.05
Hg / 200 [He]	µg/L	0.122	0.315	0.188	0.228	0.05	0.01	0.01	0.01	0.00	0.01	0.00	0.01	0.00	0.00	0.01	0.01	0.01
Hg / 201 [He]	µg/L	0.188	0.494	0.294	0.190	0.05	0.01	0.02	0.01	0.01	0.00	0.01	0.01	0.00	0.01	0.02	0.01	0.01
Hg / 202 [He]	µg/L	0.128	0.223	0.159	0.178	0.05	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.01
Tl / 203 [He]	µg/L	0.002	0.002	0.001	0.001	3	0.11	0.08	0.06	0.05	0.04	0.03	0.02	0.02	0.08	0.06	0.05	0.04
Tl / 205 [He]	µg/L	0.002	0.001	0.001	0.001	3	0.11	0.06	0.06	0.05	0.04	0.02	0.02	0.02	0.08	0.05	0.05	0.04
Pb / 206 [He]	µg/L	0.001	0.001	0.001	0.001	13	0.05	0.06	0.03	0.06	0.02	0.02	0.01	0.02	0.04	0.05	0.02	0.05
Pb / 207 [He]	µg/L	0.001	0.001	0.001	0.001	13	0.05	0.05	0.05	0.06	0.02	0.02	0.02	0.02	0.04	0.04	0.04	0.05
Pb / 208 [He]	µg/L	0.001	0.001	0.001	0.001	13	0.03	0.03	0.03	0.03	0.01	0.01	0.01	0.01	0.02	0.02	0.02	0.02
Se / 77 [H2]	µg/L	0.014	0.008	0.017	0.010	10	0.68	0.41	0.83	0.48	0.27	0.16	0.33	0.19	0.54	0.32	0.66	0.38
Se / 78 [H2]	µg/L	0.001	0.054	0.001	0.001	10	0.06	2.69	0.05	0.05	0.02	1.07	0.02	0.02	0.05	2.15	0.04	0.04
Ba / 9 [S1]	µg/L	0.001	0.002	0.000	0.000	0.1	0.03	0.08	0.02	0.02	0.01	0.03	0.01	0.02	0.06	0.01	0.01	0.01
V / 51 [S1]	µg/L	0.005	0.002	0.004	0.002	1	0.27	0.08	0.20	0.12	0.11	0.03	0.08	0.05	0.22	0.06	0.16	0.10
Cr / 52 [S1]	µg/L	0.001	0.001	0.002	0.001	15	0.05	0.06	0.08	0.05	0.02	0.02	0.03	0.02	0.04	0.05	0.06	0.04
Cr / 53 [S1]	µg/L	0.019	0.006	0.010	0.009	15	0.93	0.79	0.48	0.44	0.37	0.11	0.19	0.17	0.74	0.23	0.38	0.35
Ni / 58 [S1]	µg/L	0.001	0.158	0.001	0.119	3	0.03	7.89	0.05	5.93	0.01	3.16	0.02	2.37	0.02	6.31	0.04	4.74
Co / 59 [S1]	µg/L	0.000	0.002	0.001	0.001	1	0.02	0.08	0.03	0.05	0.01	0.03	0.01	0.02	0.06	0.02	0.02	0.04
Ni / 60 [S1]	µg/L	0.001	0.002	0.001	0.002	3	0.06	0.09	0.05	0.09	0.02	0.04	0.02	0.04	0.05	0.07	0.04	0.07
Ni / 61 [S1]	µg/L	0.017	0.019	0.106	0.031	3	0.87	0.89	5.31	1.56	0.36	0.37	2.12	0.62	0.70	0.74	4.25	1.25
Cu / 63 [S1]	µg/L	0.001	0.002	0.004	0.002	5	0.05	0.08	0.18	0.09	0.02	0.03	0.07	0.04	0.04	0.06	0.14	0.07
In / 64 [S1]	µg/L	0.001	0.005	0.003	0.004	17	0.06	0.24	0.14	0.20	0.02	0.10	0.05	0.08	0.05	0.19	0.11	0.16
Cu / 65 [S1]	µg/L	0.001	0.003	0.003	0.001	5	0.06	0.14	0.17	0.06	0.02	0.05	0.07	0.02	0.05	0.11	0.13	0.05
In / 66 [S1]	µg/L	0.002	0.005	0.002	0.004	17	0.08	0.23	0.12	0.20	0.04	0.09	0.05	0.08	0.07	0.18	0.10	0.16
In / 68 [S1]	µg/L	0.004	0.004	0.004	0.004	17	0.18	0.20	0.21	0.18	0.07	0.08	0.08	0.07	0.14	0.16	0.17	0.14
As / 75 [S1]	µg/L	0.006	0.006	0.003	0.008	4	0.32	0.29	0.17	0.42	0.13	0.11	0.07	0.17	0.25	0.23	0.13	0.34
Se / 77 [S1]	µg/L	0.035	0.034	0.050	0.057	10	1.76	1.68	2.52	2.84	0.70	0.67	1.01	1.13	1.40	1.34	2.02	2.77
Se / 78 [S1]	µg/L	0.053	0.054	0.056	0.052	10	2.67	2.69	2.79	2.61	1.07	1.07	1.12	1.04	2.14	2.15	2.23	2.09
Se / 82 [S1]	µg/L	0.008	0.012	0.008	0.011	10	0.42	0.52	0.41	0.56	0.17	0.25	0.16	0.22	0.34	0.49	0.32	0.44
Mo / 95 [S1]	µg/L	0.002	0.002	0.002	0.002	1.5	0.12	0.11	0.12	0.08	0.06	0.04	0.05	0.03	0.10	0.08	0.10	0.06
Mo / 98 [S1]	µg/L	0.007	0.002	0.001	0.001	1.5	0.35	0.08	0.05	0.03	0.14	0.03	0.02	0.01	0.28	0.06	0.04	0.02
Cd / 111 [S1]	µg/L</td																	

#### **4.5 Method detection limit.**

The method detection limit is determined with four matrix solutions (reagent blank, ICS1, ICS2 and ICS1+2). The ICS solutions contain matrix and not the analyte itself. See for matrix concentrations table 3.

Each solution is measured on eleven different days. The standard deviation multiplied by three is the detection limit expressed in the measuring value. The method detection limit expressed in mass concentration depends on the amount of the soil that has been digested and the end volume. Therefore the method detection limit expressed in mass content is calculated with 1 gram soil to a final solution of 50 mL, 5 gram to 100 mL and 5 gram to 200 mL. The results are summarized in table 7.

Discussion:

For the most isotopes the method detection limits are between 0.1 and 2 mg/kg except for the ones that are marked red. Isotopes Ni58 and Ni61 are sometimes higher than this limit, but the Ni58 and Ni61 isotopes are not the preferred or the less interfered isotope which is Ni60.

Isotope V51 and Se77 (in standard mode) are higher than the isotope V51 in reaction mode which has a much lower value. Isotope Se77 is not the main isotope in standard mode (Se82),

The reaction cell can help to lower the method detection limit for example Ni61 in standard mode is 13.2 mg/kg d.w. and in helium mode 1.7 mg/kg d.w. (1 gram to 50 mL).

#### **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 different materials were measured on eight different days. The reference materials, digested with aqua regia, were used.

The results are reported in table 8.

Discussion:

For most isotopes the precision is better than 10%, the average overall precision is 6.1%; the precision corrected for the red marked values in table 8 is on average 4.5%. The main reason for the high values (red marked) is that the concentrations are close to the reporting limit or method detection limit. For Be9(He), Mo, V51(St), Cr52(St), As75(St) the average precision is higher than 10%. The DL value for Be9 in the standard mode is deteriorated by 'scattering' in reaction mode. Therefore the method detection limit is lower in standard mode than in the reaction mode.

Table 7: Method detection limit:

Method detection limit (in mg/kg dw)													
Element	Rep. limit	Blank			ICS1			ICS2			ICS1+2		
		1 gram	5 gram	5 gram	1 gram	5 gram	5 gram	1 gram	5 gram	5 gram	1 gram	5 gram	5 gram
Element	Limit	50 mL	100 mL	200 mL	50 mL	100 mL	200 mL	50 mL	100 mL	200 mL	50 mL	100 mL	200 mL
Be / 9 [He]	0.1	0.09	0.03	0.07	0.07	0.03	0.06	0.08	0.03	0.06	0.09	0.03	0.07
V / 51 [He]	1	0.23	0.09	0.18	0.39	0.15	0.31	0.29	0.12	0.23	0.32	0.13	0.26
Cr / 52 [He]	15	0.25	0.10	0.20	0.20	0.08	0.16	0.20	0.08	0.16	0.20	0.08	0.16
Cr / 53 [He]	15	0.90	0.36	0.72	0.98	0.39	0.78	1.00	0.40	0.80	0.85	0.34	0.68
Ni / 58 [He]	3	0.18	0.07	0.14	7.24	2.89	5.79	0.13	0.05	0.10	4.51	1.80	3.61
Co / 59 [He]	1	0.09	0.03	0.07	0.08	0.03	0.06	0.06	0.02	0.05	0.04	0.02	0.03
Ni / 60 [He]	3	0.13	0.05	0.11	0.15	0.06	0.12	0.08	0.03	0.07	0.09	0.04	0.07
Ni / 61 [He]	3	0.47	0.19	0.37	0.79	0.32	0.63	1.72	0.69	1.38	1.16	0.46	0.93
Cu / 63 [He]	5	1.37	0.55	1.10	1.58	0.63	1.26	1.51	0.61	1.21	1.58	0.63	1.27
Zn / 64 [He]	17	0.31	0.12	0.25	0.31	0.13	0.25	0.22	0.09	0.17	0.23	0.09	0.19
Cu / 65 [He]	5	1.32	0.53	1.06	1.49	0.60	1.19	1.47	0.59	1.17	1.54	0.61	1.23
Zn / 66 [He]	1	0.32	0.13	0.26	0.27	0.11	0.21	0.26	0.11	0.21	0.29	0.12	0.23
Zn / 68 [He]	17	0.46	0.18	0.37	0.42	0.17	0.33	0.29	0.12	0.23	0.28	0.11	0.23
As / 75 [He]	4	0.17	0.07	0.14	0.23	0.09	0.18	0.13	0.05	0.11	0.11	0.04	0.09
Se / 77 [He]	10	2.51	1.00	2.01	1.87	0.75	1.49	1.25	0.50	1.00	2.54	1.01	2.03
Se / 78 [He]	10	1.91	0.76	1.53	1.57	0.63	1.26	2.12	0.85	1.69	2.17	0.87	1.73
Se / 82 [He]	10	1.07	0.43	0.86	1.00	0.40	0.80	0.83	0.33	0.66	0.95	0.38	0.76
Mo / 95 [He]	1.5	0.28	0.11	0.22	0.81	0.32	0.65	0.77	0.31	0.61	0.90	0.36	0.72
Mo / 98 [He]	1.5	0.28	0.11	0.23	0.84	0.33	0.67	0.80	0.32	0.64	0.93	0.37	0.74
Cd / 111 [He]	0.17	0.09	0.04	0.07	0.07	0.03	0.06	0.08	0.03	0.07	0.06	0.02	0.05
Cd / 114 [He]	0.17	0.08	0.03	0.07	0.05	0.02	0.04	0.07	0.03	0.05	0.04	0.02	0.03
Sn / 118 [He]	6	0.19	0.08	0.15	0.15	0.06	0.12	0.11	0.04	0.09	0.14	0.06	0.11
Sn / 120 [He]	6	0.19	0.08	0.15	0.14	0.06	0.11	0.12	0.05	0.09	0.14	0.06	0.11
Sb / 121 [He]	1	0.10	0.04	0.08	0.13	0.05	0.10	0.11	0.04	0.08	0.13	0.05	0.11
Sb / 123 [He]	1	0.10	0.04	0.08	0.13	0.05	0.11	0.16	0.06	0.13	0.14	0.06	0.11
Te / 125 [He]	10	0.12	0.05	0.09	0.09	0.04	0.08	0.14	0.06	0.12	0.15	0.06	0.12
Te / 126 [He]	10	0.08	0.03	0.06	0.08	0.03	0.06	0.05	0.02	0.04	0.06	0.02	0.05
Ba / 135 [He]	15	0.18	0.07	0.15	0.14	0.06	0.11	0.14	0.06	0.11	0.10	0.04	0.08
Ba / 137 [He]	15	0.15	0.06	0.12	0.11	0.04	0.09	0.09	0.04	0.07	0.08	0.03	0.06
Hg / 200 [He]	0.05	0.01	0.00	0.01	0.02	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01
Hg / 201 [He]	0.05	0.02	0.01	0.01	0.02	0.01	0.01	0.02	0.01	0.01	0.02	0.01	0.02
Hg / 202 [He]	0.05	0.01	0.00	0.01	0.02	0.01	0.01	0.01	0.00	0.01	0.01	0.00	0.01
Tl / 203 [He]	3	0.22	0.09	0.17	0.24	0.10	0.19	0.16	0.06	0.13	0.14	0.06	0.12
Tl / 205 [He]	3	0.25	0.10	0.20	0.24	0.10	0.19	0.17	0.07	0.13	0.13	0.05	0.10
Pb / 206 [He]	13	0.11	0.04	0.08	0.06	0.02	0.05	0.07	0.03	0.06	0.07	0.03	0.05
Pb / 207 [He]	13	0.12	0.05	0.09	0.06	0.02	0.05	0.10	0.04	0.08	0.09	0.04	0.07
Pb / 208 [He]	13	0.10	0.04	0.08	0.05	0.02	0.04	0.07	0.03	0.06	0.06	0.03	0.05
Se / 77 [H2]	10	0.50	0.20	0.40	0.84	0.34	0.68	0.91	0.36	0.73	1.04	0.42	0.83
Se / 78 [H2]	10	0.07	0.03	0.06	0.12	0.05	0.10	0.10	0.04	0.08	0.14	0.06	0.12
Be / 9 [St]	0.1	0.05	0.02	0.04	0.05	0.02	0.04	0.04	0.01	0.03	0.05	0.02	0.04
V / 51 [St]	1	1.16	0.46	0.93	2.52	1.01	2.01	1.44	0.58	1.15	1.84	0.74	1.47
Cr / 52 [St]	15	0.29	0.12	0.23	0.20	0.08	0.16	0.29	0.12	0.23	0.16	0.06	0.13
Cr / 53 [St]	15	3.95	1.58	3.16	8.32	3.33	6.66	5.01	2.00	4.01	6.12	2.45	4.90
Ni / 58 [St]	3	0.19	0.08	0.15	17.22	6.89	13.77	0.12	0.05	0.10	8.63	3.45	6.90
Co / 59 [St]	1	0.08	0.03	0.06	0.06	0.02	0.05	0.05	0.02	0.04	0.05	0.02	0.04
Ni / 60 [St]	3	0.17	0.07	0.14	0.14	0.05	0.11	0.20	0.08	0.16	0.14	0.06	0.11
Ni / 61 [St]	3	0.56	0.22	0.45	3.13	1.25	2.51	13.24	5.30	10.59	9.54	3.82	7.64
Cu / 63 [St]	5	1.36	0.54	1.09	1.58	0.63	1.26	1.77	0.71	1.42	1.75	0.70	1.40
Zn / 64 [St]	17	0.26	0.10	0.21	0.33	0.13	0.27	0.55	0.22	0.44	0.37	0.15	0.29
Cu / 65 [St]	5	1.28	0.51	1.03	1.50	0.60	1.20	1.45	0.58	1.16	1.54	0.61	1.23
Zn / 66 [St]	1	0.30	0.12	0.24	0.29	0.12	0.23	0.30	0.12	0.24	0.22	0.09	0.17
Zn / 68 [St]	17	0.30	0.12	0.24	0.27	0.11	0.21	0.20	0.08	0.16	0.18	0.07	0.15
As / 75 [St]	4	0.85	0.34	0.68	2.72	1.09	2.17	1.99	0.79	1.59	1.98	0.79	1.58
Se / 77 [St]	10	7.61	3.04	6.09	17.90	7.16	14.32	13.98	5.59	11.18	12.69	5.08	10.15
Se / 78 [St]	10	3.07	1.23	2.46	6.69	2.68	5.36	8.00	3.20	6.40	7.79	3.11	6.23
Se / 82 [St]	10	0.50	0.20	0.40	0.32	0.13	0.25	0.56	0.22	0.45	0.38	0.15	0.31
Mo / 95 [St]	1.5	0.22	0.09	0.18	0.41	0.17	0.33	0.37	0.15	0.30	0.44	0.18	0.35
Mo / 98 [St]	1.5	0.24	0.10	0.19	0.41	0.16	0.33	0.38	0.15	0.31	0.48	0.19	0.38
Cd / 111 [St]	0.17	0.09	0.04	0.07	0.04	0.02	0.03	0.04	0.02	0.04	0.06	0.02	0.05
Cd / 114 [St]	0.1	0.07	0.03	0.05	0.02	0.01	0.02	0.03	0.01	0.03	0.04	0.01	0.03
Sn / 118 [St]	6	0.17	0.07	0.13	0.17	0.07	0.13	0.16	0.06	0.12	0.20	0.08	0.16
Sn / 120 [St]	6	0.17	0.07	0.14	0.15	0.06	0.12	0.13	0.05	0.10	0.16	0.07	0.13
Sb / 121 [St]	1	0.07	0.03	0.06	0.13	0.05	0.10	0.10	0.04	0.08	0.14	0.05	0.11
Sb / 123 [St]	1	0.08	0.03	0.06	0.14	0.06	0.12	0.10	0.04	0.08	0.12	0.05	0.10
Te / 125 [St]	10	0.08	0.03	0.06	0.04	0.02	0.04	0.05	0.02	0.04	0.03	0.01	0.03
Te / 126 [St]	10	0.05	0.02	0.04	0.02	0.01	0.01	0.03	0.01	0.02	0.02	0.01	0.02
Ba / 135 [St]	15	0.15	0.06	0.12	0.08	0.03	0.06	0.09	0.04	0.07	0.06	0.02	0.04
Ba / 137 [St]	15	0.14	0.06	0.11	0.10	0.04	0.08	0.12	0.05	0.10	0.09	0.04	0.07
Hg / 200 [St]	0.05	0.03	0.01	0.02	0.02	0.01	0.01	0.03	0.01	0.02	0.02	0.01	0.02
Hg / 201 [St]	0.05	0.03	0.01	0.02	0.03	0.01	0.02	0.02	0.01	0.02	0.03	0.01	0.02
Hg / 202 [St]	0.05	0.02	0.01	0.02	0.01	0.00	0.01	0.02	0.01	0.01	0.02	0.01	0.02
Tl / 203 [St]	3	0.21	0.08	0.17	0.24	0.10	0.19	0.19	0.08	0.15	0.16	0.06	0.13
Tl / 205 [St]	3	0.21	0.09	0.17	0.22	0.09	0.17	0.17	0.07	0.14	0.16	0.06	0.13
Pb / 206 [St]	13	0.12	0.05	0.09	0.08	0.03	0.07	0.08	0.03	0.07	0.05	0.02	0.04
Pb / 207 [St]	13	0.11	0.04	0.09	0.07	0.03	0.05	0.06	0.02	0.05	0.05	0.02	0.04
Pb / 208 [St]	13	0.09	0.04	0.08	0.05	0.02	0.04	0.06	0.02	0.05	0.04	0.02	0.03

Table 8: Precision (in %):

Element	Rep. limit	CRM145R	1948469	LKSD-1	STSD	CRM7001	CRM144R	CRM141R	AMBWB	AMBSZ	AMBCOMPO	Average
	Limit											
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.	<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
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

#### **4.7 Recovery (spike and dilution).**

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

- Spiking of a multi element standard to a matrix solution (ICS1+2) and
- Measurements in the original sample and a fivefold diluted sample (CRM144R).

A multi element standard solution was spiked to ICS (1+2) with a solution concentration of 0,5 mg/L before dilution. This was also done with a reagent blank. The recovery of the spike to the ICS (1+2) solution was calculated against the spike to the reagent blank and the theoretical concentration.

The recovery after dilution was determined by a fivefold dilution of the digest before measurement.

The results of the addition are reported in table 9 and from the dilution experiment in table 10.

#### **Discussion**

Paragraph '10.5 Quality control' of the proposed standard on ICP-MS prescribes the criteria for the spike recovery which should be between 75% and 125%. With the method developed in this study all isotopes are well within that range. The overall average value of the recovery is 98,4%

Paragraph '10.5 Quality control' of the proposed standard on ICP-MS [7.2] prescribes the criteria for the difference between results in original sample and the fivefold-diluted sample which should be less than 20%. Differences for all isotopes are below 20%.

The overall average of the difference between diluted and undiluted is +5,5%.

Table 9: Spike recovery (in %):

Element	Unit	ICS1+2	ICS1+2 add	Addition measured		Recovery (%)	
				In blank	In matrix	Theoretical (ICS 1+2)	Measured Between 75-125%
Be / 9 [He]	mg/L	0.00	0.50	0.48	0.50	100.3	104.1
V / 51 [He]	mg/L	0.00	0.48	0.46	0.48	96.8	104.2
Cr / 52 [He]	mg/L	0.00	0.47	0.47	0.47	94.6	100.1
Cr / 53 [He]	mg/L	-0.02	0.50	0.52	0.51	103.0	99.5
Ni / 58 [He]	mg/L	0.38	0.85	0.47	0.46	92.9	98.8
Co / 59 [He]	mg/L	0.01	0.48	0.48	0.47	94.8	98.7
Ni / 60 [He]	mg/L	0.00	0.47	0.47	0.46	92.6	97.7
Ni / 61 [He]	mg/L	0.04	0.56	0.51	0.52	103.5	102.5
Cu / 63 [He]	mg/L	-0.03	0.42	0.45	0.45	89.8	99.8
Zn / 64 [He]	mg/L	0.02	0.46	0.47	0.45	89.1	93.9
Cu / 65 [He]	mg/L	-0.03	0.43	0.46	0.46	91.1	98.1
Zn / 66 [He]	mg/L	0.02	0.50	0.53	0.48	96.6	91.2
Zn / 68 [He]	mg/L	0.02	0.50	0.52	0.48	96.8	92.2
As / 75 [He]	mg/L	0.02	0.54	0.53	0.52	103.8	97.6
Se / 77 [He]	mg/L	0.00	0.46	0.51	0.46	92.4	90.7
Se / 78 [He]	mg/L	-0.02	0.49	0.52	0.51	102.1	97.9
Se / 82 [He]	mg/L	0.00	0.51	0.51	0.51	102.9	100.2
Mo / 95 [He]	mg/L	0.02	0.49	0.45	0.47	93.4	103.0
Mo / 98 [He]	mg/L	0.02	0.49	0.45	0.46	92.8	102.3
Cd / 111 [He]	mg/L	0.00	0.51	0.52	0.51	102.5	97.7
Cd / 114 [He]	mg/L	0.00	0.46	0.48	0.46	92.0	95.4
Sn / 118 [He]	mg/L	0.00	0.49	0.48	0.49	97.0	102.0
Sn / 120 [He]	mg/L	0.00	0.49	0.48	0.48	96.9	101.8
Sb / 121 [He]	mg/L	0.00	0.49	0.46	0.49	97.6	106.5
Sb / 123 [He]	mg/L	0.00	0.49	0.46	0.48	96.9	104.7
Te / 125 [He]	mg/L	0.02	0.00	0.00	-0.01	x	x
Te / 126 [He]	mg/L	0.01	0.00	0.00	-0.01	x	x
Ba / 135 [He]	mg/L	0.00	0.53	0.52	0.53	105.5	102.4
Ba / 137 [He]	mg/L	0.00	0.54	0.52	0.53	106.2	102.7
Hg / 200 [He]	μg/L	-0.50	-0.53	-0.13	-0.04	x	x
Hg / 201 [He]	μg/L	-0.58	-0.67	-0.29	-0.09	x	x
Hg / 202 [He]	μg/L	-0.52	-0.55	-0.15	-0.04	x	x
Tl / 203 [He]	mg/L	0.02	0.46	0.52	0.44	88.3	85.6
Tl / 205 [He]	mg/L	0.02	0.47	0.53	0.45	89.9	85.6
Pb / 206 [He]	mg/L	0.00	0.48	0.47	0.48	95.8	102.6
Pb / 207 [He]	mg/L	0.00	0.48	0.46	0.48	95.5	103.2
Pb / 208 [He]	mg/L	0.00	0.48	0.47	0.48	95.6	102.6
Se / 77 [H2]	mg/L	-0.01	0.48	0.51	0.49	97.6	95.4
Se / 78 [H2]	mg/L	0.00	0.48	0.53	0.48	95.8	90.6
Be / 9 [St]	mg/L	0.00	0.46	0.46	0.46	92.4	100.9
V / 51 [St]	mg/L	-0.01	0.47	0.47	0.48	96.4	102.6
Cr / 52 [St]	mg/L	0.00	0.48	0.48	0.48	96.3	99.6
Cr / 53 [St]	mg/L	-0.05	0.46	0.51	0.51	102.8	101.3
Ni / 58 [St]	mg/L	0.85	1.36	0.48	0.51	101.7	105.8
Co / 59 [St]	mg/L	0.01	0.48	0.48	0.47	93.7	97.4
Ni / 60 [St]	mg/L	0.01	0.46	0.47	0.45	90.3	95.4
Ni / 61 [St]	mg/L	0.22	0.72	0.52	0.50	100.4	95.8
Cu / 63 [St]	mg/L	-0.02	0.44	0.45	0.45	90.9	101.2
Zn / 64 [St]	mg/L	0.03	0.46	0.48	0.44	87.3	90.5
Cu / 65 [St]	mg/L	-0.02	0.42	0.45	0.45	89.4	99.1
Zn / 66 [St]	mg/L	0.02	0.47	0.50	0.45	89.7	90.6
Zn / 68 [St]	mg/L	0.02	0.48	0.52	0.46	92.3	88.7
As / 75 [St]	mg/L	0.01	0.48	0.48	0.47	93.8	97.3
Se / 77 [St]	mg/L	-0.04	0.44	0.48	0.48	95.3	100.3
Se / 78 [St]	mg/L	-0.09	0.42	0.52	0.51	101.2	96.7
Se / 82 [St]	mg/L	0.00	0.48	0.50	0.47	94.9	94.6
Mo / 95 [St]	mg/L	0.03	0.49	0.46	0.46	92.6	100.8
Mo / 98 [St]	mg/L	0.03	0.49	0.46	0.46	91.7	100.2
Cd / 111 [St]	mg/L	0.00	0.46	0.47	0.46	91.4	96.5
Cd / 114 [St]	mg/L	0.00	0.46	0.48	0.46	91.0	95.1
Sn / 118 [St]	mg/L	0.00	0.47	0.47	0.47	93.4	99.3
Sn / 120 [St]	mg/L	0.00	0.48	0.48	0.48	95.0	98.7
Sb / 121 [St]	mg/L	0.00	0.48	0.46	0.48	95.6	102.9
Sb / 123 [St]	mg/L	0.00	0.48	0.46	0.47	94.6	102.9
Te / 125 [St]	mg/L	0.01	0.00	0.00	0.00	x	x
Te / 126 [St]	mg/L	0.01	0.00	0.00	-0.01	x	x
Ba / 135 [St]	mg/L	0.01	0.53	0.51	0.52	104.5	102.9
Ba / 137 [St]	mg/L	0.00	0.48	0.47	0.47	94.2	100.1
Hg / 200 [St]	μg/L	-0.48	-0.51	-0.12	-0.03	x	x
Hg / 201 [St]	μg/L	-0.31	-0.40	-0.06	-0.09	x	x
Hg / 202 [St]	μg/L	-0.53	-0.72	-0.15	-0.19	x	x
Tl / 203 [St]	mg/L	0.02	0.47	0.49	0.45	89.2	90.6
Tl / 205 [St]	mg/L	0.02	0.48	0.50	0.46	91.3	91.0
Pb / 206 [St]	mg/L	0.00	0.47	0.46	0.47	94.2	102.3
Pb / 207 [St]	mg/L	0.00	0.48	0.46	0.47	94.9	102.6
Pb / 208 [St]	mg/L	0.00	0.48	0.46	0.48	95.1	102.3

Table 10: Difference between original and fivefold-diluted sample:

Element	Rep. limit Limit (mg/kg)	Unit	CRM144R (undiluted)	CRM144R (5x diluted)	Difference < 20%
Be / 9 [He]	0.1	mg/kgds	0.2	0.1	< r.l.
V / 51 [He]	1	mg/kgds	15.7	14.0	11.6
Cr / 52 [He]	15	mg/kgds	101.4	105.1	3.5
Cr / 53 [He]	15	mg/kgds	109.4	109.7	0.3
Ni / 58 [He]	3	mg/kgds	51.3	54.4	5.7
Co / 59 [He]	1	mg/kgds	15.1	15.2	0.5
Ni / 60 [He]	3	mg/kgds	47.3	47.8	1.1
Ni / 61 [He]	3	mg/kgds	55.9	51.0	9.7
Cu / 63 [He]	5	mg/kgds	305.4	297.6	2.6
Zn / 64 [He]	17	mg/kgds	944.5	947.2	0.3
Cu / 65 [He]	5	mg/kgds	308.7	302.3	2.1
Zn / 66 [He]	1	mg/kgds	1054.0	1085.0	2.9
Zn / 68 [He]	17	mg/kgds	1049.0	1090.0	3.8
As / 75 [He]	4	mg/kgds	4.1	4.8	< r.l.
Se / 77 [He]	10	mg/kgds	1.1	-9.9	< r.l.
Se / 78 [He]	10	mg/kgds	-0.3	-13.9	< r.l.
Se / 82 [He]	10	mg/kgds	1.1	0.9	< r.l.
Mo / 95 [He]	1.5	mg/kgds	5.6	-9.9	< r.l.
Mo / 98 [He]	1.5	mg/kgds	5.6	-9.8	< r.l.
Cd / 111 [He]	0.17	mg/kgds	2.0	2.1	4.2
Cd / 114 [He]	0.17	mg/kgds	1.8	1.5	17.5
Sn / 118 [He]	6	mg/kgds	43.4	42.8	1.4
Sn / 120 [He]	6	mg/kgds	43.2	43.9	1.6
Sb / 121 [He]	1	mg/kgds	3.5	2.9	< r.l.
Sb / 123 [He]	1	mg/kgds	3.4	3.2	< r.l.
Te / 125 [He]	10	mg/kgds	0.2	1.0	< r.l.
Te / 126 [He]	10	mg/kgds	0.1	0.5	< r.l.
Ba / 135 [He]	15	mg/kgds	438.3	435.3	0.7
Ba / 137 [He]	15	mg/kgds	434.6	444.3	2.2
Hg / 200 [He]	0.05	mg/kgds	3.1	3.4	8.6
Hg / 201 [He]	0.05	mg/kgds	3.0	3.2	5.9
Hg / 202 [He]	0.05	mg/kgds	3.1	3.6	12.2
Tl / 203 [He]	3	mg/kgds	1.3	4.8	< r.l.
Tl / 205 [He]	3	mg/kgds	1.3	4.7	< r.l.
Pb / 206 [He]	13	mg/kgds	95.4	103.7	8.0
Pb / 207 [He]	13	mg/kgds	96.7	106.6	9.3
Pb / 208 [He]	13	mg/kgds	96.0	105.2	8.8
Se / 77 [H2]	10	mg/kgds	0.3	-8.4	< r.l.
Se / 78 [H2]	10	mg/kgds	1.7	0.1	< r.l.
Be / 9 [St]	0.1	mg/kgds	0.1	-0.3	< r.l.
V / 51 [St]	1	mg/kgds	15.9	17.6	9.8
Cr / 52 [St]	15	mg/kgds	104.0	108.3	4.0
Cr / 53 [St]	15	mg/kgds	109.8	120.5	8.9
Ni / 58 [St]	3	mg/kgds	51.1	52.5	2.7
Co / 59 [St]	1	mg/kgds	15.2	15.2	0.1
Ni / 60 [St]	3	mg/kgds	46.6	46.9	0.6
Ni / 61 [St]	3	mg/kgds	67.6	70.2	3.7
Cu / 63 [St]	5	mg/kgds	339.7	294.1	15.5
Zn / 64 [St]	17	mg/kgds	1027.0	953.3	7.7
Cu / 65 [St]	5	mg/kgds	304.8	296.2	2.9
Zn / 66 [St]	1	mg/kgds	1058.0	1026.0	3.1
Zn / 68 [St]	17	mg/kgds	1030.0	1057.0	2.6
As / 75 [St]	4	mg/kgds	2.3	0.7	< r.l.
Se / 77 [St]	10	mg/kgds	-9.1	-19.9	< r.l.
Se / 78 [St]	10	mg/kgds	-12.4	-36.9	< r.l.
Se / 82 [St]	10	mg/kgds	1.5	0.6	< r.l.
Mo / 95 [St]	1.5	mg/kgds	6.6	-2.1	< r.l.
Mo / 98 [St]	1.5	mg/kgds	6.3	-2.6	< r.l.
Cd / 111 [St]	0.17	mg/kgds	1.8	1.5	19.6
Cd / 114 [St]	0.17	mg/kgds	1.8	1.5	18.5
Sn / 118 [St]	6	mg/kgds	42.2	41.8	1.0
Sn / 120 [St]	6	mg/kgds	42.9	42.4	1.3
Sb / 121 [St]	1	mg/kgds	3.2	2.4	< r.l.
Sb / 123 [St]	1	mg/kgds	3.0	2.2	< r.l.
Te / 125 [St]	10	mg/kgds	0.1	0.3	< r.l.
Te / 126 [St]	10	mg/kgds	0.1	0.3	< r.l.
Ba / 135 [St]	15	mg/kgds	430.5	448.1	3.9
Ba / 137 [St]	15	mg/kgds	389.8	405.7	3.9
Hg / 200 [St]	0.05	mg/kgds	3.1	3.0	3.4
Hg / 201 [St]	0.05	mg/kgds	3.5	4.0	11.9
Hg / 202 [St]	0.05	mg/kgds	3.4	3.5	2.0
Tl / 203 [St]	3	mg/kgds	1.4	5.3	< r.l.
Tl / 205 [St]	3	mg/kgds	1.5	5.4	< r.l.
Pb / 206 [St]	13	mg/kgds	99.5	103.3	3.7
Pb / 207 [St]	13	mg/kgds	102.8	106.8	3.7
Pb / 208 [St]	13	mg/kgds	101.4	105.2	3.6

## **5 CONCLUSIONS**

The ICP MS method described in the proposed standard can be used for measurements in digest of soil, sludge and bio waste. The results of this study show that the criteria for the limit of detection, precision and QC criteria can be met. Several comments on the text are formulated to improve the practical daily use like the criteria for interference correction and the control of the correction applied and stability check between the days

The main differences between the two digestion methods are the chlorine and carbon content. Measurements show that the influence of the chlorine on several elements is apparent but can be corrected for or can be eliminated by use of a reaction cell or by matrix matching. The carbon content of the digest with HNO<sub>3</sub> is 25 to 500% higher than Aqua Regia digests of the same sample. Several elements but especially Cr is affected by carbon interference.

The maximum allowed contribution of interference is limited at three times the instrumental detection limit (see 10.4 H19). This is in practice not a suitable criterion because the contribution of the interference depends on the concentration of the interfering component.

The doubly charged interference of Sn on Ni(60,61,62) must be added to the table 1 of the proposed standard.

The proposed standard doesn't give a definition of the way the instrumental detection limit has to be determined. An other option is proposed in comment 1 & 4.

Proposals for text changes:

Comment 1:

10.4: Interference: The magnitude depends on the concentration level of the interference check solution (5.13). If the concentration level of the ICS is two times higher, the contribution on the interfered isotope will also be two times higher. A statement about the concentration of the ICS in the quality control is therefore necessary.

Proposed text:

"The contribution of corrected and uncorrected isobaric molecular and doubly charged interferences from the maximum concentration interferences shall not be higher than three times the instrumental detection limit or lower than halve the value of the reporting limit."

Comment 2:

10.4: Interference: Successive values of a correction factor shall not differ more than 20%. It's possible, after changing cones, that the correction factor differ more than 20% on a day to day basis. A statement on the correction factor difference is therefore necessary.

Proposed text (this can be omitted if comment 1 is accepted because it is than included in the control procedure):

"Successive values of a correction factor shall not differ more than 20% within one sequence."

Comment 3:

Checking of the difference in correction factor is difficult during a sequence. Checking the contribution (in mg/L or µg/L) of corrected interferences from the interference check solution within one sequence can be considered.

7.5 Sample measurement: proposed additional text:

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

Comment 4:

10.5 Spike recovery: Differences between results for the original sample and the five-fold diluted sample shall be less than 20% is only possible if the concentration in the five-fold diluted sample is higher than

the three times the instrumental detection limit (or higher than the reporting limit). A statement about the concentration levels in the five-fold diluted sample is therefore necessary.

Proposed text:

10.5 Spike 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 the reporting limit."

## 6 ANNEX

- 6.1 Method description.
- 6.2 Interference measurement.
- 6.3 Interference correction stability.

## 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-MS method: "Determination of dissolved elements by inductively coupled plasma mass spectrometry (ICP-MS), Horizontal Desk study 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

**TOPLEVEL PARAMETERS****Method Information For: D:\ICPCHEM\1\METHODS\ISIS.M****Method Sections To Run:**

( ) Save Copy of Method With Data  
( ) Pre-Run Cmd/Macro =  
 Data Acquisition  
 Data Analysis  
( ) Post-Run Cmd/Macro =

**Method Comments:**

Alle isotopen met alle tunefiles

**END OF TOPLEVEL PARAMETERS****-----  
Acquisition Parameter Summary  
-----****Acquisition Mode : Spectrum Analysis (Multi Tune)****Number of Masses : 74****===== << Step 1 >> =====**

Mass	Element	Det.Mode	Integration Time [sec]	/Point	/Mass
220		Auto	0.10000	0.30000	

**===== << Step 2 >> =====**

Mass	Element	Det.Mode	Integration Time [sec]	/Point	/Mass
6	Li	Auto	0.50000	1.50000	
7	Li	Auto	0.10000	0.30000	
9	Be	Auto	0.50000	1.50000	
13	C	Auto	0.01000	0.03000	
23	Na	Auto	0.10000	0.30000	
24	Mg	Auto	0.10000	0.30000	
26	Mg	Auto	0.10000	0.30000	
27	Al	Auto	0.10000	0.30000	
28- 30	Si	Auto	0.10000	0.30000	
31	P	Auto	0.10000	0.30000	
34	S	Auto	0.10000	0.30000	
35	Cl	Auto	0.01000	0.03000	
39	K	Auto	0.10000	0.30000	
44	Ca	Auto	0.10000	0.30000	
45	Sc	Auto	0.10000	0.30000	
47- 48	Ti	Auto	0.10000	0.30000	
51	V	Auto	0.10000	0.30000	
52- 53	Cr	Auto	0.10000	0.30000	
54	Fe	Auto	0.10000	0.30000	
55	Mn	Auto	0.10000	0.30000	
58	Ni	Auto	0.10000	0.30000	
59	Co	Auto	0.10000	0.30000	
60- 61	Ni	Auto	0.10000	0.30000	
63	Cu	Auto	0.10000	0.30000	
64	Zn	Auto	0.10000	0.30000	
65	Cu	Auto	0.10000	0.30000	
66	Zn	Auto	0.10000	0.30000	

68	Zn	Auto	0.10000	0.30000
74	Ge	Auto	0.10000	0.30000
75	As	Auto	0.10000	0.30000
77- 78	Se	Auto	0.10000	0.30000
81	Br	Auto	0.10000	0.30000
82	Se	Auto	0.10000	0.30000
86	Sr	Auto	0.10000	0.30000
88	Sr	Auto	0.10000	0.30000
90	Zr	Auto	0.10000	0.30000
95	Mo	Auto	0.10000	0.30000
98	Mo	Auto	0.10000	0.30000
101	(Mo)	Auto	0.10000	0.30000
103	Rh	Auto	0.10000	0.30000
106		Auto	0.10000	0.30000
107	Ag	Auto	0.10000	0.30000
108		Auto	0.10000	0.30000
109	Ag	Auto	0.10000	0.30000
111	Cd	Auto	0.10000	0.30000
114	Cd	Auto	0.10000	0.30000
115	In	Auto	0.10000	0.30000
118	Sn	Auto	0.10000	0.30000
120	Sn	Auto	0.10000	0.30000
121	Sb	Auto	0.10000	0.30000
123	Sb	Auto	0.10000	0.30000
125-126	Te	Auto	0.10000	0.30000
135	Ba	Auto	0.10000	0.30000
137	Ba	Auto	0.10000	0.30000
182	W	Auto	0.10000	0.30000
200-202	Hg	Auto	0.50000	1.50000
203	Tl	Auto	0.10000	0.30000
205	Tl	Auto	0.10000	0.30000
206-208	Pb	Auto	0.10000	0.30000
209	Bi	Auto	0.10000	0.30000

===== << Step 3 >> =====

Mass	Element	Det.Mode	Integration Time [sec]	
			/Point	/Mass
40	Ca	Auto	0.10000	0.30000
44	Ca	Auto	0.10000	0.30000
45	Sc	Auto	0.10000	0.30000
55	Mn	Auto	0.10000	0.30000
56	Fe	Auto	0.10000	0.30000
74	Ge	Auto	0.10000	0.30000
77- 78	Se	Auto	0.50000	1.50000
86	Sr	Auto	0.10000	0.30000
88	Sr	Auto	0.10000	0.30000
103	Rh	Auto	0.10000	0.30000
115	In	Auto	0.10000	0.30000
209	Bi	Auto	0.10000	0.30000

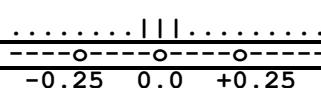
===== << Step 4 >> =====

Mass	Element	Det.Mode	Integration Time [sec]	
			/Point	/Mass
6- 7	Li	Auto	0.10000	0.30000
9	Be	Auto	0.10000	0.30000
13	C	Auto	0.10000	0.30000
23	Na	Auto	0.10000	0.30000
24	Mg	Auto	0.10000	0.30000
26	Mg	Auto	0.10000	0.30000
27	Al	Auto	0.10000	0.30000
31	P	Auto	0.10000	0.30000
34	S	Auto	0.10000	0.30000
35	Cl	Auto	0.10000	0.30000
39	K	Auto	0.10000	0.30000
44	Ca	Auto	0.10000	0.30000
45	Sc	Auto	0.10000	0.30000
47- 48	Ti	Auto	0.10000	0.30000

51	V	Auto	0.10000	0.30000
52-	53 Cr	Auto	0.10000	0.30000
54	Fe	Auto	0.10000	0.30000
55	Mn	Auto	0.10000	0.30000
58	Ni	Auto	0.10000	0.30000
59	Co	Auto	0.10000	0.30000
60-	61 Ni	Auto	0.10000	0.30000
63	Cu	Auto	0.10000	0.30000
64	Zn	Auto	0.10000	0.30000
65	Cu	Auto	0.10000	0.30000
66	Zn	Auto	0.10000	0.30000
68	Zn	Auto	0.10000	0.30000
74	Ge	Auto	0.10000	0.30000
75	As	Auto	0.10000	0.30000
77-	78 Se	Auto	0.10000	0.30000
81	Br	Auto	0.10000	0.30000
82	Se	Auto	0.10000	0.30000
86	Sr	Auto	0.10000	0.30000
88	Sr	Auto	0.10000	0.30000
90	Zr	Auto	0.10000	0.30000
95	Mo	Auto	0.10000	0.30000
98	Mo	Auto	0.10000	0.30000
101	(Mo)	Auto	0.10000	0.30000
103	Rh	Auto	0.10000	0.30000
106		Auto	0.10000	0.30000
107	Ag	Auto	0.10000	0.30000
108		Auto	0.10000	0.30000
109	Ag	Auto	0.10000	0.30000
111	Cd	Auto	0.10000	0.30000
114	Cd	Auto	0.10000	0.30000
115	In	Auto	0.10000	0.30000
118	Sn	Auto	0.10000	0.30000
120	Sn	Auto	0.10000	0.30000
121	Sb	Auto	0.10000	0.30000
123	Sb	Auto	0.10000	0.30000
125-126	Te	Auto	0.10000	0.30000
135	Ba	Auto	0.10000	0.30000
137	Ba	Auto	0.10000	0.30000
182	W	Auto	0.10000	0.30000
200-202	Hg	Auto	0.10000	0.30000
203	Tl	Auto	0.10000	0.30000
205	Tl	Auto	0.10000	0.30000
206-208	Pb	Auto	0.10000	0.30000
209	Bi	Auto	0.10000	0.30000

=====

Number of Points per Mass : 3



Number of repetition : 3

Total Acquisition Time : 498 [sec]

Tune	Stabilization		
Step	Tune File	Time[sec]	Date Updated
<hr/>			
1	he start.u	5	Mar 02 2005 03:33 pm
2	he mode.u	180	Mar 02 2005 03:33 pm
3	h2 mode.u	30	Mar 02 2005 03:33 pm
4	st mode.u	30	Mar 02 2005 03:33 pm

(X) Return to First Tune Step

ISIS Peristaltic Pump Program

**--- Before Acquisition ---**Uptake Speed : 0.60 rpsUptake Time : 20 secStabilization Time(Undiluted) : 20 secStabilization Time(Diluted) : 20 sec**--- After Acquisition (Probe Rinse) ---**Rinse Speed : 0.60 rpsRinse Time(Sample) : 5 secRinse Time(STD) : 5 sec**--- After Acquisition (Rinse) ---**Rinse Vial : 1Uptake Speed : 0.60 rpsUptake Time : 20 secStabilization Speed : 0.10 rpsStabilization Time : 30 sec**Set Auto Dilution**Dilution Factor : 10Correction : OFFStd Element : ---Online ISTD Element : ---Tune Step : ---Dilute All Samples : ON

---

**DATA ANALYSIS PARAMETERS**

---

**Correction**

- Subtract Background  
 Interference Correction

**Quantitation Report**( ) Quantitation Report : SummaryDestination :(X) Screen( ) Printer( ) File =( ) Custom Report( ) Update Custom Database**QC Report**( ) QC Report : Recalculate then Print**SemiQuant Report (Tune Step 1)**( ) SemiQuant Report : Detailed (Text Only)Destination :(X) Screen( ) Printer( ) File =( ) Custom Report( ) Update Custom Database**Isotope Report**( ) Isotope Ratio Report (Tune Step 1): Isotope RatioDestination :

(X) Screen  
( ) Printer  
( ) File =

( ) Isotope Dilution Report (Tune Step 1): Summary

Destination :  
(X) Screen  
( ) Printer  
( ) File =

Interference Equation

Mass      Equation

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6 :	(6)*1 - (7)*0.0821
54 :	(54)*1 - (52)*0.028226
58 :	(58)*1 - (54)*0.04825
98 :	(98)*1 - (101)*0.110588
111 :	(111)*1 - (108)*1.073 + (106)*0.764
114 :	(114)*1 - (118)*0.026826
120 :	(120)*1 - (125)*0.013447
123 :	(123)*1 - (125)*0.127189
208 :	(208)*1 + (206)*1 + (207)*1

Calibration

Calibration File : D:\ICPCHEM\1\CALIB\ISIS.C

Auto Dilution Check Parameters

Check Auto Dilution Factor : OFF  
Control Limit : ---  
Action on Failure : ---  
Report Destination : ---

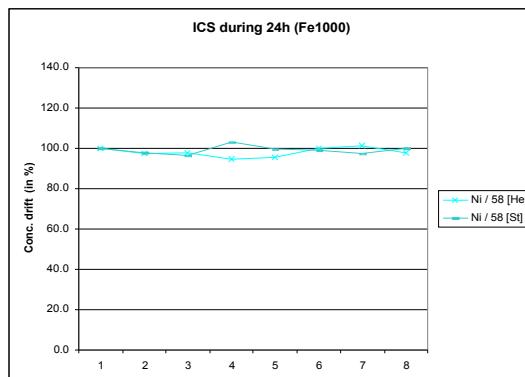
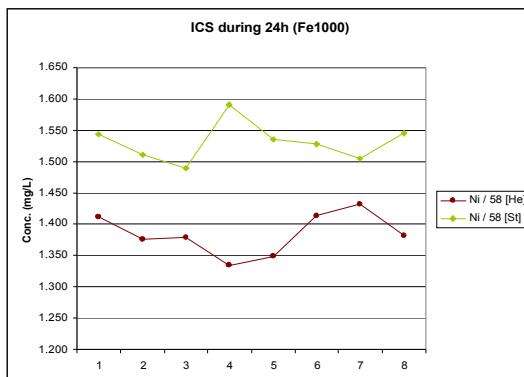
## Result in standard mode

Result in H2 mode		Mass Unit	Replimit	Al 1000 mol	Fe 1000 mol	Ni 1000 mol	K 1000 mol	Ca 1000 mol	Mo 1000 mol	P 500 mol	S 500 mol	C 10 mol	Cl 10 mol	Zr 10 mol	W 0.1 mol	Ba 10 mol	Co 10 mol	Mo 10 mol	Mn 10 mol	Tl 10 mol	Br 10 mol	Ba 10 mol	Sc 10 mol	V 10 mol	Si 10 mol	Cr 10 mol	Sn 10 mol
Co	5 mol	1	0.00	0.00	0.00	0.00	-0.01	0.00	-0.01	0.00	0.00	-0.01	0.02	0.01	0.01	-0.01	0.00	0.01	0.00	0.02	1000.00	1.71	1.34	1.01	0.74	0.60	
B	10 mol	10	5.62	3.58	0.07	-0.22	-0.60	-1.07	-1.82	-1.73	3.59	-1.84	-4.09	-4.41	-4.58	-4.85	-4.78	-4.48	-4.58	272.73	-3.48	-3.89	-4.58	-4.47	-4.38		
B	11 mol	10	7.78	4.89	-0.59	0.12	-0.82	-0.93	-1.82	-2.04	5.05	-2.21	-4.75	-5.41	-5.44	-5.53	-5.81	-5.72	-5.83	-5.78	-4.51	-5.77	-5.77	-5.62	-5.71	-5.84	
C	13 mol	n.v.t.	13.13	9.20	12.41	30.75	39.05	40.43	20.84	30.53	1050.03	25.50	12.86	17.58	17.05	9.36	10.44	11.88	7.98	11.78	36.65	B27	15.21	4.51	5.44	5.21	
Na	23 mol	5.8	0.18	0.05	678.83	2.81	0.80	0.36	0.31	0.26	0.26	1.21	2.81	1.65	1.17	1.05	0.87	0.81	0.81	3.77	0.78	0.71	126.63	0.80	0.64	1.00	
Mg	24 mol	0.4	0.02	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.06	0.07	0.06	0.06	0.06	0.06	0.06	0.05	0.05	0.05	0.05	0.04	0.03	0.02	
Mg	25 mol	0.4	0.03	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.06	0.07	0.06	0.06	0.06	0.06	0.06	0.05	0.05	0.05	0.05	0.04	0.03	0.03	
Mg	26 mol	0.4	0.03	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.06	0.07	0.06	0.06	0.06	0.06	0.06	0.05	0.05	0.05	0.05	0.04	0.03	0.03	
Al	27 mol	0.4	970.00	0.13	0.11	0.04	0.04	0.04	0.03	0.02	0.03	0.04	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	
Si	28 mol	n.v.t.	0.05	0.05	0.05	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	
P	31 mol	0.00	0.02	0.07	0.10	0.26	0.51	0.26	195.42	0.15	0.16	0.17	0.17	0.17	0.18	0.18	0.14	0.11	0.06	0.07	2.00	0.06	0.04	0.03	0.03		
S	34 mol	1	-1.85	3.04	6.24	18.87	28.15	30.88	14.37	188.88	17.11	23.32	18.80	20.81	21.38	18.90	15.74	13.84	10.87	8.67	8.10	8.15	5.80	4.87	6.08	6.27	
Cl	35 mol	n.v.t.	5386.00	7580.00	575.20	233.90	212.30	69.40	110.40	292.10	9.00	552.00	257.90	135.10	85.70	24.00	16.00	15.00	5.00	-24.00	-31.00	-25.00	-38.00	-46.00	-53.00	97.20	
K	39 mol	0.5	8.91	12.93	U/U	955.35	1.13	0.28	234.15	452.25	0.32	83.90	0.69	0.38	0.28	0.20	0.19	0.17	0.12	0.11	0.10	0.09	0.10	0.06	0.05	0.05	
Ca	40 mol	0.4	0.14	0.11	0.03	0.15	94.01	0.20	0.08	0.18	0.09	0.14	0.08	0.06	0.05	0.07	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.05	0.04		
Ca	43 mol	0.4	0.17	0.11	0.05	0.07	694.52	0.23	0.08	0.14	0.11	0.14	0.08	0.07	0.06	0.06	0.06	0.06	0.06	0.07	0.07	0.05	0.04	6.54	0.05		
Ca	44 mol	0.4	0.17	0.11	0.07	0.08	99.22	0.21	0.07	0.12	0.08	0.14	0.06	0.06	0.07	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.05	0.04	3.58		
Li	47 mol	50	0.67	31.00	0.68	0.44	0.20	0.15	24.83	0.37	1.26	0.28	10.92	0.24	0.25	0.16	0.18	0.13	1043.00	3.11	1.48	1.28	1.72	0.75	0.81		
Ag	49 mol	50	1.55	30.18	0.22	0.24	49/U/U	0.87	1.28	1.00	1.26	0.26	0.21	0.21	0.20	0.26	0.26	0.26	0.26	0.26	1.36	1.02	0.98	0.98	0.98		
V	51 mol	2	4.82	33.07	0.88	0.14	0.05	0.80	0.80	0.40	0.20	0.80	0.87	0.86	0.84	0.16	0.07	0.22	0.16	0.08	0.08	0.08	0.08	0.08	0.08		
Cr	52 mol	1	4.58	21.34	0.42	0.35	0.83	0.71	0.18	0.17	0.24	3.20	0.11	0.07	0.12	0.24	0.26	0.35	0.35	0.32	0.31	0.33	0.32	0.31	0.30		
Cr	53 mol	1	19.63	35.02	2.16	0.98	1.05	2.39	1.33	1.81	1.25	257.3	2.50	2.08	0.84	0.10	0.11	0.28	0.18	0.03	0.31	0.11	0.01	0.20	0.17	0.22	
Fe	54 mol	0.05	0.02	975.00	0.01	0.17	0.08	0.05	0.05	0.04	0.03	0.05	0.04	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.02	0.02	0.03	
Mn	55 mol	0.01	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
Fe	56 mol	0.05	0.01	503.50	0.15	0.08	0.05	0.05	0.04	0.04	0.03	0.03	0.04	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.02	0.02	0.02	
Fe	57 mol	0.05	0.01	981.40	0.18	0.08	2.49	0.05	0.04	0.03	0.04	0.03	0.04	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.02	0.02	0.02	
Ni	58 mol	2	1.58	5484.07	1.15	0.85	0.70	0.66	0.68	0.17	0.18	1.44	0.93	0.24	0.20	0.14	0.21	0.18	0.25	0.17	0.12	0.12	0.11	0.14	0.11	0.71	
Co	59 mol	1	0.05	11.48	0.04	0.03	1.18	0.07	0.02	0.02	0.03	0.16	0.04	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	
Ni	60 mol	2	1.54	15.24	0.33	0.55	1.73	0.84	0.00	0.10	1.27	1.08	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	
Ni	61 mol	2	2.84	16.54	3.37	2.89	655.98	1.49	1.77	3.00	2.01	10.89	2.69	0.85	3.22	16.20	1.02	1.81	1.91	1.28	1.52	454.55	1.06	1.40	1.01	11.10	
Ni	62 mol	2	2.40	15.00	163.37	15.53	0.83	0.20	0.51	0.20	1.30	15.87	1.24	0.80	0.13	0.45	0.13	0.18	0.12	0.61	84.38	0.25	0.60	0.22	28.80		
Cu	63 mol	3	1.81	4.36	25.13	2.51	0.46	1.14	0.12	-0.15	0.47	3.65	-0.27	-0.31	-0.47	-0.50	-0.41	-0.45	0.07	-0.52	-0.48	-0.43	-0.53	-0.46	-0.43	2.58	
Zn	64 mol	5	3.43	4.36	0.68	4.14	1.16	9.70	0.19	0.58	2.22	1.42	0.36	-0.02	-0.02	-0.02	-0.02	-0.02	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	0.08	
Cu	65 mol	3	1.87	4.60	0.10	0.85	3.77	1.13	0.17	0.78	0.70	0.36	-0.32	-0.28	-0.28	-0.42	-0.37	-0.30	1.01	-0.40	-0.38	-0.38	-0.40	-0.38	-0.38	-0.35	
Zn	66 mol	5	3.59	4.52	0.72	4.72	1.55	0.51	0.48	0.48	1.52	0.85	0.07	0.17	0.14	0.35	0.04	0.57	0.15	0.27	0.26	0.26	0.26	0.26	0.26	0.26	
Zn	67 mol	5	3.85	4.35	0.57	4.28	0.88	0.87	0.03	0.11	2.08	0.22	-0.32	-0.22	-0.22	-0.22	-0.22	-0.22	-0.22	-0.22	-0.22	-0.22	-0.22	-0.22	-0.22	-0.21	
As	75 mol	3	0.25	0.78	0.08	0.02	0.18	0.22	0.17	0.10	0.05	0.24	0.00	0.04	0.08	0.00	0.02	0.00	0.01	0.01	0.04	0.02	0.02	0.02	0.11		
Se	77 mol	0.8	0.22	0.94	-0.02	0.28	1.05	0.23	0.12	0.20	0.05	1.00	0.13	-0.12	-0.01	0.15	-0.08	-0.08	-0.18	-0.14	0.01	-0.07	-0.10	-0.26	-0.19		
Se	78 mol	0.8	0.10	0.11	0.19	1.35	U/U	0.06	0.20	0.09	0.22	0.07	0.06	0.10	0.06	0.07	0.06	0.10	0.06	0.04	0.04	0.07	0.08	0.12			
Fr	79 mol	n.v.t.	0.42	0.24	0.01	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
Se	80 mol	0.8	10.31	8.01	0.38	0.44	0.15	0.16	0.24	0.22	5.27	0.20	0.06	0.07	0.06	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
Se	81 mol	n.v.t.	0.43	0.24	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
Se	82 mol	0.8	53.33	30.24	1.48	1.15	0.68	0.43	0.21	0.20	0.35	1.13	0.46	0.20	0.17	0.07	0.02	0.02	134.24	45.00	16.24	7.00	3.55				

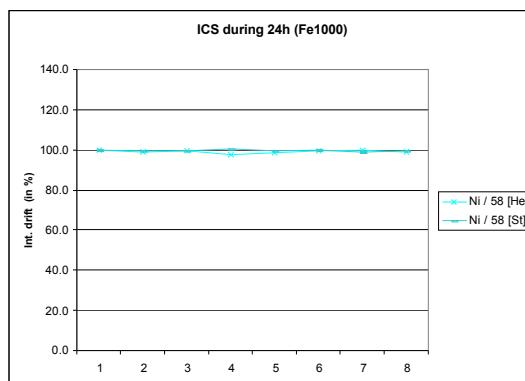
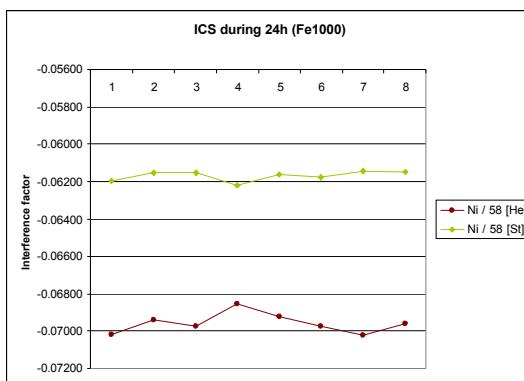
Result in He mode		Unit	Replimit	Al 1000 mol	Fe 1000 mol	Na 1000 mol	K 1000 mol	Ca 1000 mol	Mg 1000 mol	P 500 mol	S 500 mol	C 10 mol	Cl 10 mol	Zr 10 mol	W 0.1 mol	Ba 10 mol	Co 10 mol	Mo 10 mol	Mn 10 mol	Tl 10 mol	Br 10 mol	Be 10 mol	Sc 10 mol	Si 10 mol	V 10 mol	Cr 10 mol	Sn 10 mol				
<b>Co</b>		8 ug/L	1	0.02	-0.03	-0.01	0.00	-0.03	-0.02	-0.01	0.03	0.01	-0.04	-0.01	0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	12026.58	2.15	1.35	1.05	0.32	0.83			
<b>B</b>		10 ug/L	10	8.47	5.04	-1.81	1.77	1.78	1.88	-1.32	-3.18	7.78	-1.05	-7.88	-9.41	-9.58	-6.08	-5.97	-7.01	-9.88	-5.84	-5.82	-7.58	8.74	-8.81	-8.15	-8.02				
<b>B</b>		11 ug/L	10	8.01	5.26	0.57	1.77	2.23	1.58	-0.92	-1.88	12.23	0.08	-4.30	-4.72	-4.75	-5.32	-5.88	-5.13	-5.53	-5.28	-5.42	-5.08	-5.67	-5.23	-5.25					
<b>C</b>		13 mol/L	n.v.t.	16.34	2.81	14.85	32.28	40.77	228.03	39.85	34.90	9269.73	40.86	18.74	23.42	18.48	11.42	18.05	19.30	14.83	16.02	35.37	21.34	28.40	3.05	13.95	11.39				
<b>Na</b>		23 mol/L	n.v.t.	0.16	0.08	1047.03	3.78	1.06	0.46	0.36	0.28	0.33	1	3.63	1.83	1.61	1.36	1.14	1.04	0.90	4.17	0.84	0.82	136.83	0.71	0.84	0.81				
<b>Mg</b>		24 mol/L	0.4	0.02	0.04	0.00	0.00	1288.00	0.14	0.10	0.05	0.07	0.06	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.06	0.06	0.05	0.04	0.04	0.04				
<b>Mg</b>		25 mol/L	0.1	0.02	0.04	0.00	0.00	1305.00	0.14	0.10	0.05	0.07	0.06	0.07	0.07	0.06	0.07	0.07	0.06	0.06	0.06	0.06	0.06	0.05	0.04	0.04	0.04				
<b>Al</b>		27 mol/L	0.1	844.50	0.35	0.08	0.08	0.05	0.04	0.03	0.03	0.03	0.05	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.02	0.02	0.02				
<b>Si</b>		28 mol/L	n.v.t.	0.25	0.30	0.61	1.41	1.82	1.25	1.16	2.19	2.06	0.74	1.10	1.27	0.92	0.72	0.78	1.23	1.11	1.26	1.08	10.55	0.20	1.01	0.44					
<b>P</b>		31 mol/L	n.v.t.	0.01	0.01	0.02	0.04	0.04	0.05	223.28	0.08	0.06	0.04	0.04	0.03	0.03	0.03	0.03	0.03	0.02	0.02	0.02	0.02	0.02	0.01	0.01					
<b>S</b>		34 mol/L	1	-0.31	2.45	3.83	6.44	9.85	14.48	8.62	734.81	6.78	10.38	5.10	5.54	6.16	3.85	3.12	2.77	2.94	2.50	2.78	2.36	1.81	2.27						
<b>Cl</b>		35 mol/L	n.v.t.	1369.10	217.10	124.08	39.00	37.50	19.30	13.30	12.50	2.30	1876.10	4.00	11.10	11.20	-1.20	-1.20	-1.20	-1.20	-1.20	-1.20	-1.20	-1.20	-1.20	-1.20	-1.20				
<b>K</b>		39 mol/L	n.v.t.	0.06	0.10	U11	1209.97	2.01	0.47	261.97	549.57	0.55	2.07	0.48	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38			
<b>Ca</b>		40 mol/L	0.1																												
<b>Ca</b>		43 mol/L	0.1	0.32	0.11	0.11	0.45	1153.02	0.37	0.23	0.26	0.15	0.28	0.19	0.14	0.18	0.13	0.15	0.12	0.13	0.14	0.10	0.12	0.08	37.14	0.12					
<b>Ca</b>		44 mol/L	0.1	0.11	0.11	0.12	1184.04	0.40	0.23	0.30	0.38	0.37	0.20	0.18	0.18	0.17	0.16	0.11	0.10	0.12	0.10	0.09	0.07	19.27	0.06						
<b>Li</b>		47 mol/L	50	0.81	33.15	-0.02	0.14	0.00	0.33	9.47	-0.03	1.27	0.13	125.10	0.49	0.11	0.10	4.00	0.12	1209.90	3.26	2.26	1.88	1.31	1.05	0.94	0.80				
<b>Li</b>		48 mol/L	50	1.17	31.05	0.18	0.18	0.01	0.83	0.43	1.74	0.89	0.40	1.57	0.21	0.20	0.23	0.20	0.20	1172.07	3.98	2.44	1.88	1.45	1.02	0.92	0.85				
<b>V</b>		61 mol/L	2	0.94	22.08	0.17	0.07	0.01	0.16	0.11	0.11	0.10	1.81	0.24	0.17	0.15	0.07	0.05	0.08	0.02	0.02	0.04	0.04	10460.11	2.50	1.44					
<b>Cr</b>		52 mol/L	1	2.59	19.54	0.26	0.50	0.80	0.87	0.33	0.08	0.98	0.31	-0.23	-0.34	-0.35	-0.36	-0.36	-0.36	-0.36	-0.36	-0.36	-0.36	-0.36	-0.36	-0.36	-0.36				
<b>Cr</b>		53 mol/L	1	4.82	22.73	0.62	0.87	0.80	1.25	0.57	0.28	0.51	0.70	0.12	0.01	0.05	0.34	-0.26	-0.27	-0.36	-0.21	-0.44	-0.38	-0.35	-0.36	-0.36	-0.36	-0.36			
<b>Fe</b>		54 mol/L	0.05	0.02	689.90	0.16	0.14	0.08	0.07	0.06	0.05	0.04	0.05	0.06	0.04	0.04	0.04	0.06	0.04	0.04	0.04	0.04	0.04	0.04	0.03	0.03	0.03				
<b>Mn</b>		55 mol/L	0.01	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00					
<b>Fe</b>		56 mol/L	0.05	0.00	285.30	0.05	0.04	0.02	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01				
<b>Fe</b>		57 mol/L	0.05	0.01	685.70	0.15	0.13	0.53	0.05	0.05	0.04	0.03	0.04	0.05	0.04	0.04	0.04	0.06	0.04	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03				
<b>Ni</b>		58 mol/L	2	1.87	1023.13	0.44	0.82	0.26	0.68	0.02	0.17	1.47	0.84	0.05	0.01	0.01	0.05	0.02	0.02	0.05	0.03	0.03	0.04	0.02	0.05	0.47					
<b>Co</b>		59 mol/L	1	0.04	12.13	0.03	0.04	0.08	0.05	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01				
<b>Ni</b>		60 mol/L	2	1.85	18.23	0.30	0.54	0.86	0.01	0.12	1.47	0.65	0.02	0.01	0.02	0.16	0.05	0.02	0.03	0.05	0.04	0.02	0.05	0.02	0.02	0.02	2.23				
<b>Ni</b>		61 mol/L	2	1.51	20.10	0.32	0.75	26.88	0.89	0.00	0.20	1.27	0.84	0.05	0.03	0.03	0.04	0.02	0.02	0.03	0.05	0.04	0.02	0.02	0.02	0.02	7.72				
<b>Ni</b>		62 mol/L	2	1.80	18.11	1.17	1.44	0.35	0.37	-0.01	0.21	1.25	0.90	0.13	-0.03	-0.02	0.01	0.06	0.17	1.75	0.08	0.03	0.26	0.02	0.01	0.01	0.01	0.01	0.01		
<b>Cu</b>		63 mol/L	3	2.08	4.82	0.15	0.55	0.84	1.49	0.57	-0.14	0.46	0.52	-0.56	-0.51	-0.65	-0.72	-0.59	0.83	0.56	-0.57	-0.56	-0.72	4.74	-0.61	-0.60	-0.62				
<b>Zn</b>		64 mol/L	5	3.18	5.13	0.73	5.16	1.87	11.32	0.43	0.88	2.83	1.92	0.75	0.23	0.24	0.16	0.16	0.15	0.21	0.32	0.18	0.16	0.16	0.16	0.16	0.16	0.16	0.16		
<b>Cu</b>		65 mol/L	3	2.02	4.90	0.48	0.72	0.81	1.45	0.45	0.00	0.72	0.81	-0.35	-0.36	-0.37	-0.51	-0.38	-0.35	0.16	0.48	-0.43	-0.34	-0.35	-0.46	-0.46	-0.46	-0.46			
<b>Zn</b>		66 mol/L	5	3.06	4.21	0.76	5.37	1.50	11.72	0.32	0.89	2.73	1.51	0.77	-0.08	-0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08			
<b>Zn</b>		68 mol/L	5	3.26	4.53	1.17	5.05	1.85	11.01	0.88	0.82	2.74	1.86	0.85	0.03	0.03	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08		
<b>As</b>		75 mol/L	3	0.57	1.38	0.20	0.08	0.11	0.30	0.33	0.08	0.04	1.17	0.12	0.15	0.08	0.08	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04		
<b>Se</b>		77 mol/L	0.8	5.08	10.49	1.78	0.93	1.18	1.84	0.91	1.37	1.36	12.49	1.81	1.48	1.07	1.10	0.88	0.78	0.84	0.81	0.84	0.85	0.88	0.89	0.87	0.87	0.87	0.87		
<b>Se</b>		78 mol/L	0.9	1.82	3.39	3.07	4.38	8.45	7.02	9.03	8.89	8.91	4.20	4.59	3.65	3.90	3.28	3.41	3.61	3.60	3.60	3.60	3.60								

**Graphs ICS1:**

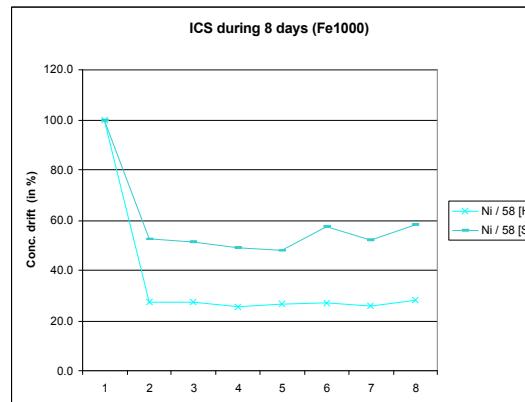
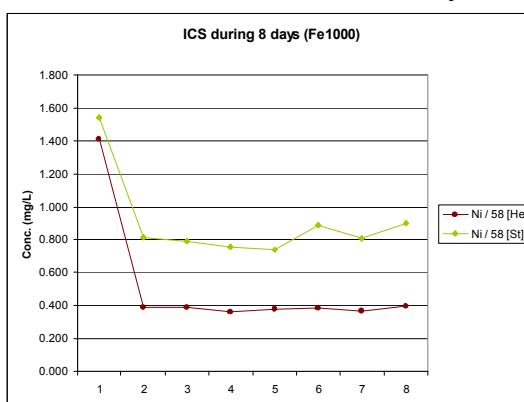
Contribution concentration 24hours:



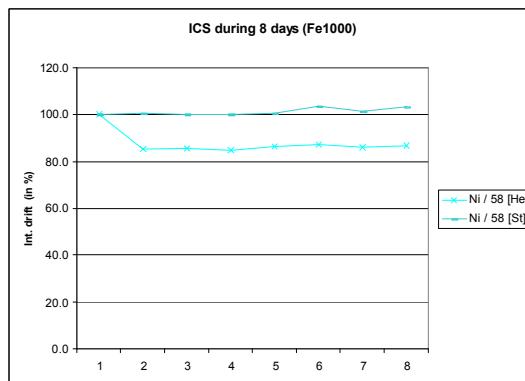
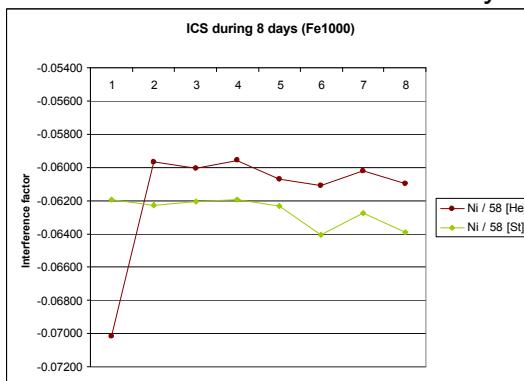
Interference correction factor 24hours:



Contribution concentration 8 days:

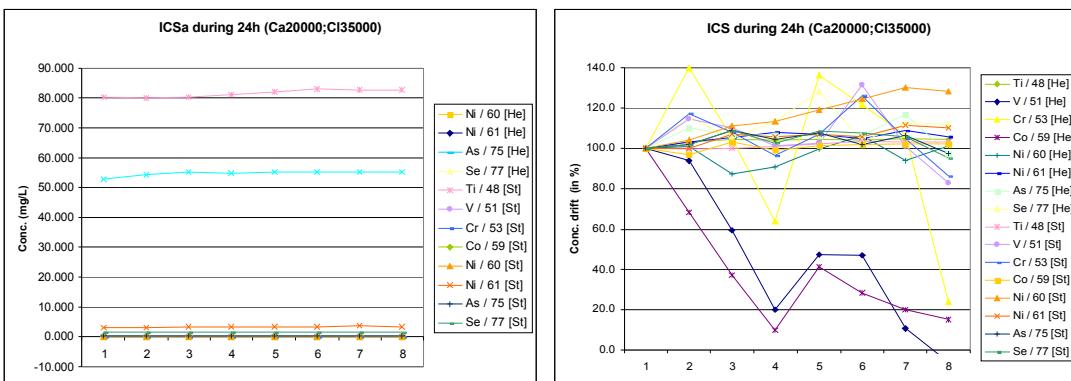


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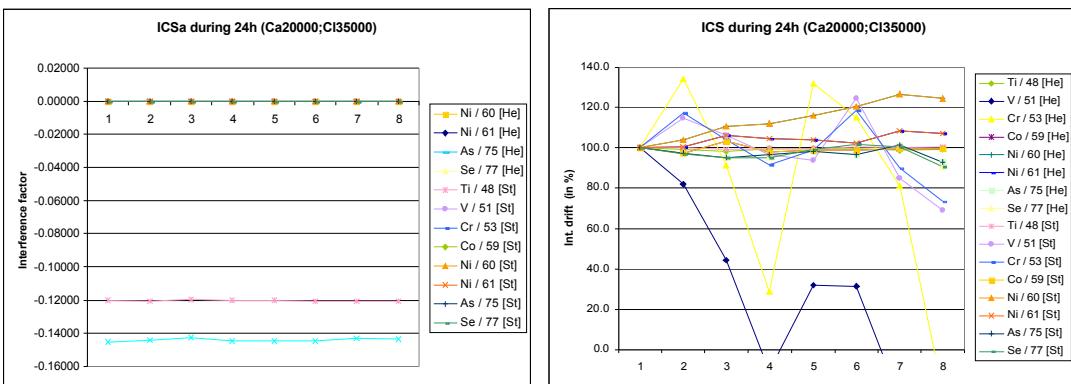


**Graphs ICSa:**

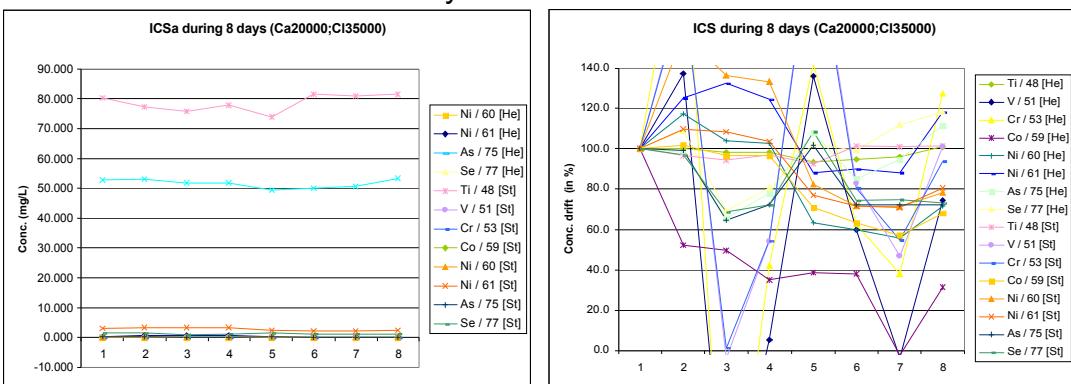
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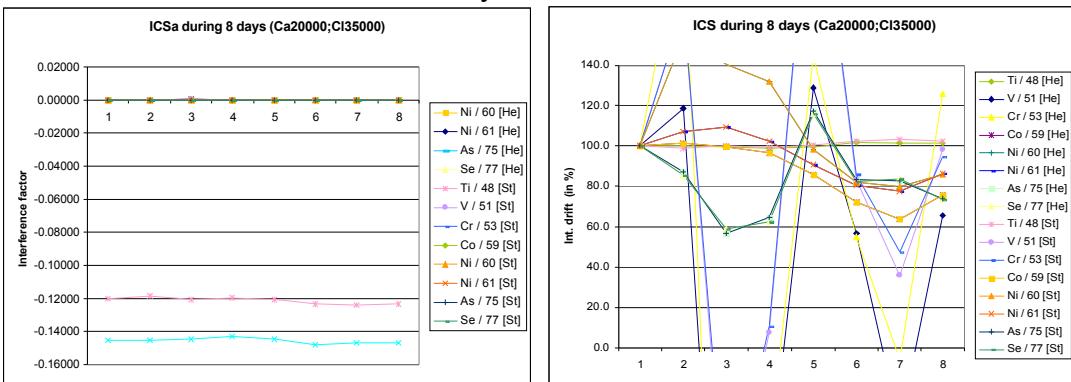
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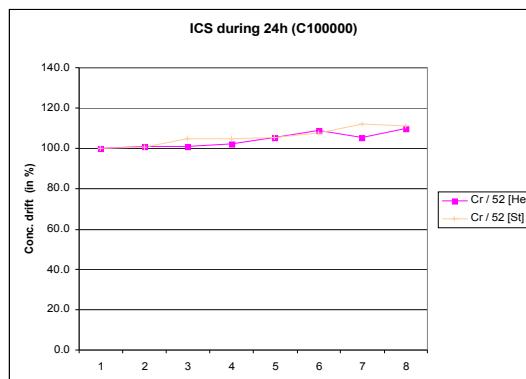
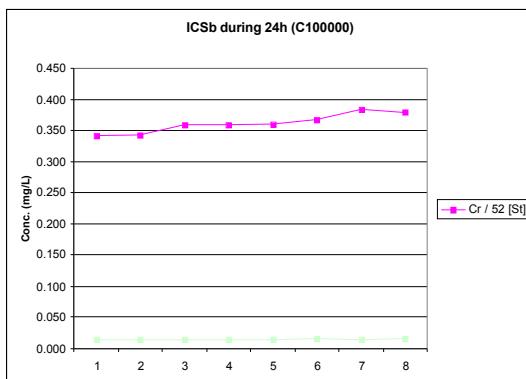


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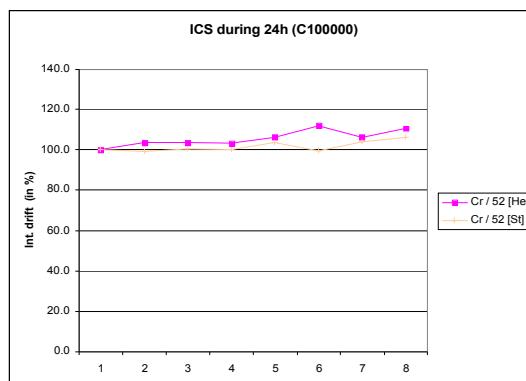
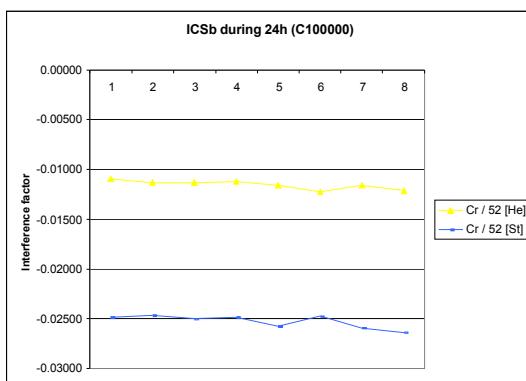


**Graphs ICSb:**

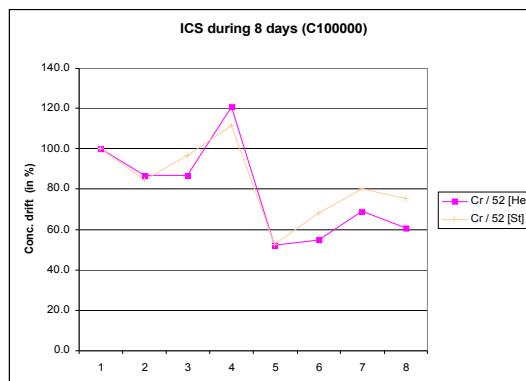
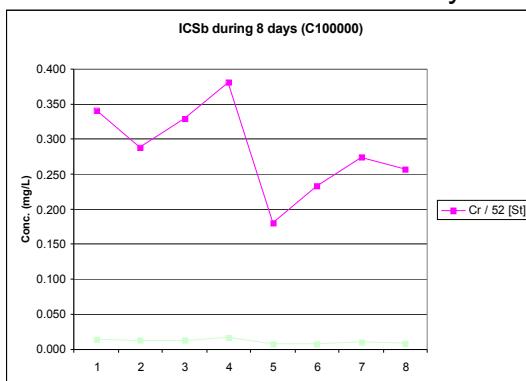
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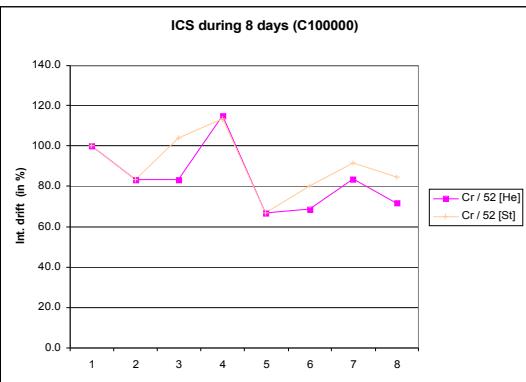
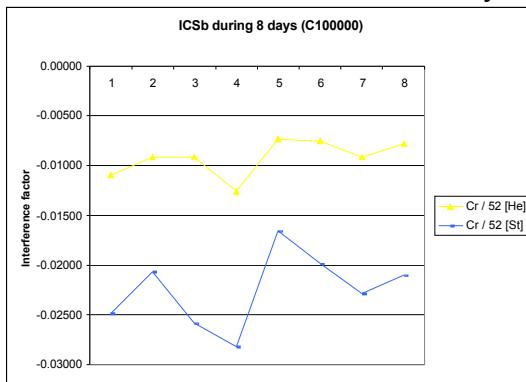
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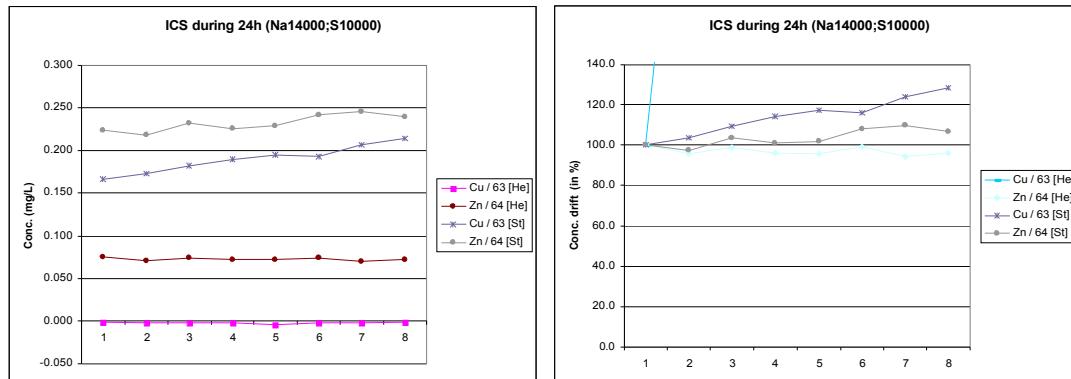
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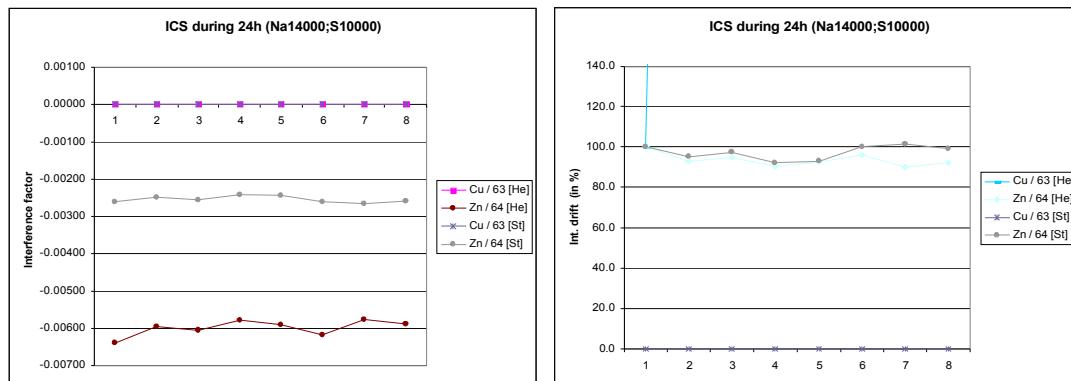
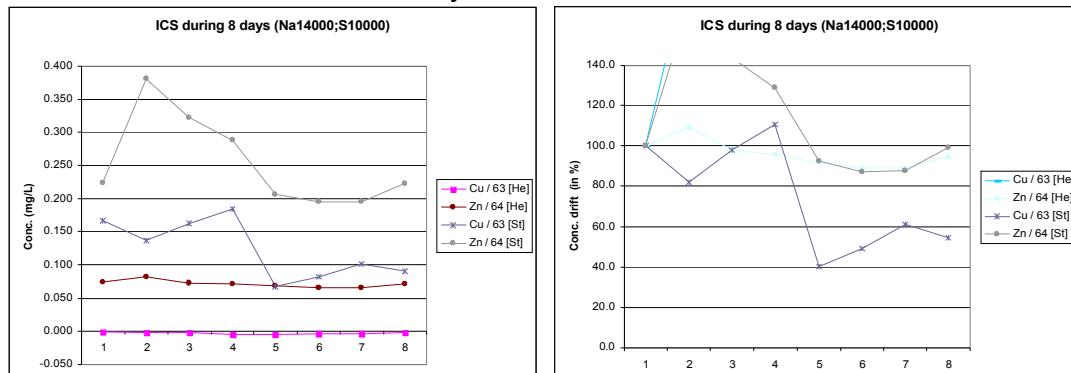
Interference correction factor 8 days:

**Graphs ICSc:**

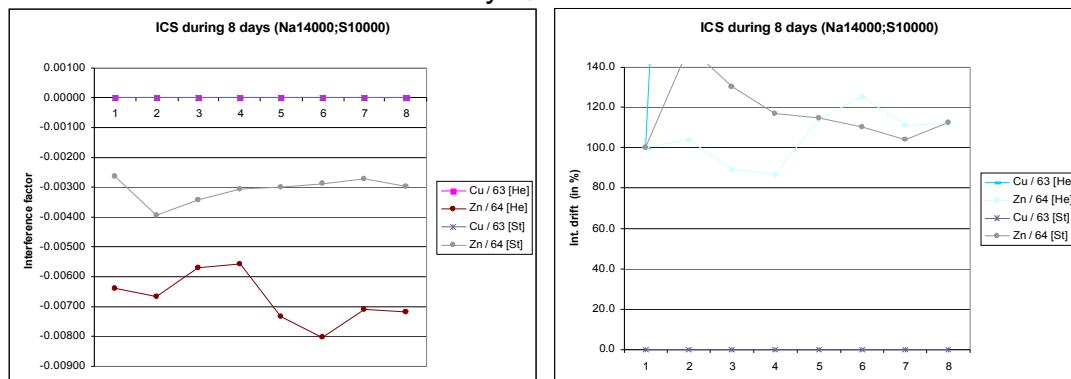
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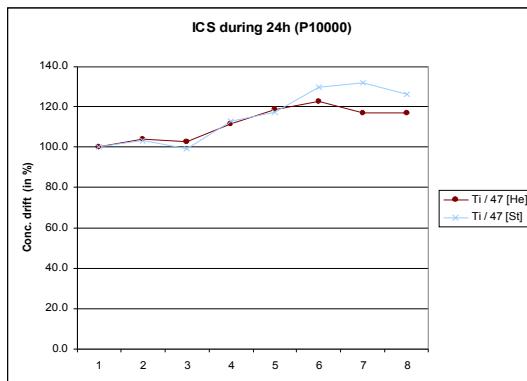
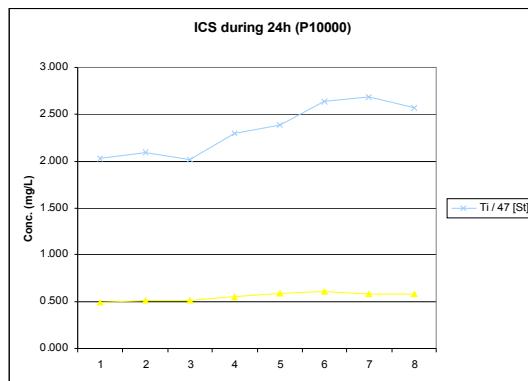
**Interference correction factor 24hours**

(Sodium saturated in standard mode so there is no correction calculated on Cu63).

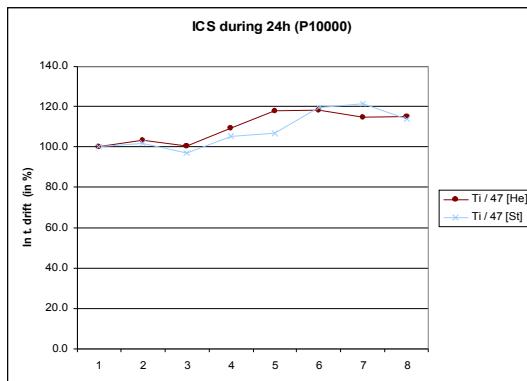
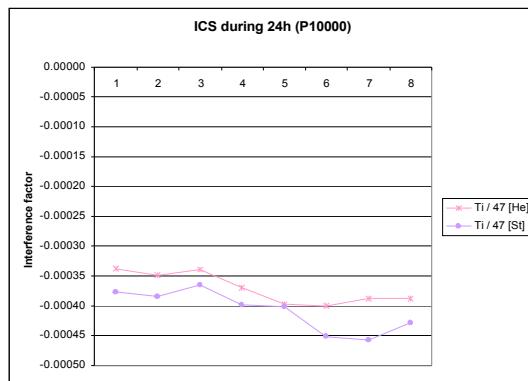
**Contribution concentration 8 days:****Interference correction factor 8 days**

(Sodium saturated in standard mode so there is no correction calculated on Cu63).

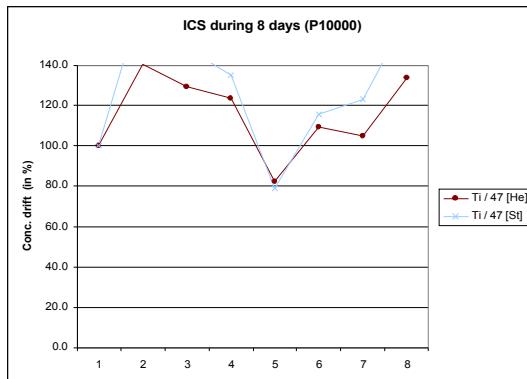
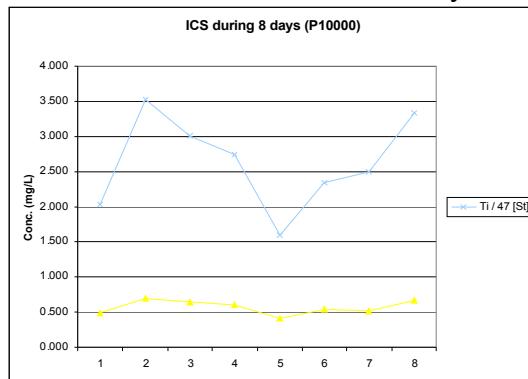
**Graphs ICSd:****Contribution concentration 24hours:**



### Interference correction factor 24hours:



### Contribution concentration 8 days:



### Interference correction factor 8 days:

