Distribution: General

Final report

Evaluation of different microwave digestion procedures for soil and waste samples

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Study accomplished under the authority of the Public Waste Agency of Flanders (OVAM)
2015/SCT/R/0026

January 2015

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SAMENVATTING

De ontsluiting van vaste monsters (bodem en afval) is zonder twijfel een cruciale stap bij de bepaling van elementen. In Vlaanderen was de van toepassing zijnde methode, beschreven in CMA/2/II/A.3 versie februari 2010 (ministerieel goedgekeurd bij besluit van 18 januari 2012), gebaseerd op de Europese norm NBN EN 13656, die verwijst naar een vermogen gecontroleerde microgolf ontsluiting met behulp van HF:HNO_3:HCl. Momenteel worden eveneens temperatuur gecontroleerde microgolf ontsluitingen toegepast en daarom werd op vraag van de erkende laboratoria de CMA methode in februari 2013 aangepast. Een verwijzing naar een temperatuur gecontroleerde ontsluiting werd opgenomen gebaseerd op de procedure beschreven in de horizontale Europese norm NBN EN 16174. Toch waren geen vergelijkbare validatiegegevens beschikbaar met HF:HNO_3:HCl ontsluiting met beide ontsluitingsmethoden. Bijkomend werd door de erkende laboratoria gevraagd om de huidige tijdrovende tweestaps ontsluitingsmethode verder te vereenvoudigen. Als alternatief zou een éénstaps ontsluitingsmethode met HBF_4 kunnen worden toegepast.

In deze studie werden een aantal alternatieve ontsluitingsmethoden geëvalueerd om de procedure te vereenvoudigen enerzijds en de toepasbaarheid van de procedure uit te breiden naar verschillende soorten microgolf systemen anderzijds om alzo elementen in bodem- en afvalmonsters te bepalen. In dit kader werden de volgende aspecten onderzocht:

1. Evaluatie van een éénstaps ontsluiting (met HBF_4) ter vervanging van de tweestaps ontsluiting met HF + H_3BO_3 ('HF-power')
   Deze procedure houdt een éénstaps ontsluiting in, met behoud van hetzelfde vermogen van ontsluiting van de silicaat matrix, met HBF_4 (vervanging HF met H_3BO_3). Bovendien geniet het gebruik van HBF_4 om veiligheidsredenen de voorkeur boven HF.
2. Evaluatie van temperatuur gecontroleerde microgolf systemen als aanvulling op de vermogen gecontroleerde microgolf systemen
   De HBF_4 ontsluiting met vermogen gecontroleerde microgolfoven ('HBF_4 power') werd vergeleken met de temperatuur gecontroleerde ontsluiting ('HBF_4 temp').

Evaluatie van 10 bodemmonsters

Voor de 8 VLAREBO elementen (As, Cd, Cr, Cu, Pb, Ni, Zn en Hg) komen de resultaten bekomen met de alternatieve methoden ('HBF_4 power' en 'HBF_4 temp') overeen met deze van de referentiemethode ('HF-power'). Hogere meetspreidingen worden soms waargenomen bij monsters met een lagere concentratie. Er is echter geen indicatie van een systematische fout bij toepassing van de alternatieve methoden vergeleken met de referentiemethode. In paragraaf 5.1 op pagina 99 wordt weergegeven dat een totale meetspreiding van minder dan 20% wordt bekomen bij toepassing van de verschillende ontsluitingsmethoden. Deze meetspreiding kan men ook verwachten bij duplometingen indien enkel de referentiemethode wordt toegepast. Testen en analysen uitgevoerd bij een aantal erkende laboratoria bevestigen de inzetbaarheid van de geëvalueerde alternatieve methoden ter vervanging van de tijdrovende referentiemethode.

Voor de andere sporenelementen (Sb, Ba, Co, Mn, Mo, Se, Sn en V) kan dezelfde conclusie worden geformuleerd. Regelmatig worden lage concentraties van deze elementen gemeten resulterend in een hogere meetspreiding, maar niettemin kan worden gesteld dat vergelijkbare resultaten worden verkregen met de 3 ontsluitingsmethoden.

Voor de hoofdelementen (Na, Mg, Al, K, Ca, Ti, Mn en Fe) wordt een goede overeenkomst waargenomen tussen de resultaten van de alternatieve methoden en de referentiemethode,

behalve voor Ti. Vooral de Ti resultaten verkregen met de 'HBF$_4$ power' methode zijn aanzienlijk lager dan met de referentiemethode 'HF-power’.

Evaluatie van 10 afvalmonsters (waarvan 6 uit de validatiestudie van EN 13656)

Voor de VLAREMA 4bis-elementen (As, Cd, Cr, Cu, Pb, Ni, Zn, Hg, Sb, Ba, Co, Mo, Se, Sn en V) worden vergelijkbare resultaten verkregen met de alternatieve methoden en de referentiemethode. In paragraaf 5.1 op pagina 99 wordt weergegeven dat een totale meetspreiding van minder dan 20% wordt bekomen bij toepassing van de verschillende ontsluitingsmethoden. Deze meetspreiding kan men ook verwachten bij duplometingen indien enkel de referentiemethode wordt toegepast. Bijkomend dient opgemerkt te worden dat voor de bepaling van Ba de ontsluitingsprocedure kritisch kan zijn en een invloed kan hebben op het verkregen resultaat (operationeel gedefinieerd). Bij de bepaling van dit element dient bijzondere aandacht besteed te worden aan de ontsluitingsprocedure. Dit effect werd eveneens vastgesteld tijdens de validatiestudie van EN 13656 in 1999. Testen en analysen uitgevoerd bij een aantal erkende laboratoria bevestigen de inzetbaarheid van de geëvalueerde alternatieve methoden ter vervanging van de tijdrovende referentiemethode.

Voor de hoofdelementen (Na, Mg, Al, K, Ca, Ti, Mn en Fe) kan dezelfde conclusie worden geformuleerd als voor de bodemmonsters. Een goede overeenkomst wordt waargenomen tussen de resultaten van de alternatieve methoden en de referentiemethode, behalve voor Ti.

Op basis van de verkregen resultaten kan de CMA methode CMA/2/II/A.3 worden aangepast. Allereerst wordt de procedure van de temperatuur gecontroleerde microgolf ontsluiting, zoals reeds in de CMA werkwijze beschreven, bevestigd. Ten tweede kan de éénstaps ontsluiting met HBF$_4$ als zuur ontsluitingsreagens in combinatie met HNO$_3$ en HCl worden toegevoegd.

SUMMARY

The digestion of solid samples (soils and waste) is without doubt a critical step in the determination of elements. In Flanders (Northern part of Belgium), the applicable method described in CMA/2/II/A.3 (Ministerial approved version of January 18, 2012) was based on the European Standard NBN EN 13656[1], which refers to a power-controlled microwave oven digestion using HF:HNO_3:HCl. Besides that also temperature controlled microwave oven digestions are applied and therefore, on the request of the recognized laboratories, the CMA method was adapted in February 2013. A reference to a temperature controlled digestion was included, based on the procedure described in the Horizontal European Standard NBN EN 16174[4]. Nevertheless no comparable validation data were available using the HF:HNO_3:HCl digestion with both digestion techniques. In addition, the recognized laboratories requested for further simplification of the current time consuming two-step digestion method. As alternative an one step digestion using HBF_4 might be introduced.

In this study some alternative digestion methods were evaluated to simplify the current procedure on one hand and to extend the applicability of the procedure to different types of micro wave instruments on the other for the determination of elements in soil and waste samples. In this framework the following aspects were considered:

1. *Evaluation of an one-step digestion (HBF_4) as replacement for the two-steps digestion with HF + H_3BO_3 ('HF power')*
   The procedure involves a one-step digestion, while maintaining the same power of digestion of the silicate matrix, by using HBF_4 (replacing HF with H_3BO_3). In addition, the use of HBF_4 is for safety reasons preferred over HF.
2. *Evaluation of temperature controlled microwave systems as an addition to power controlled microwave systems*
   The HBF_4 digestion using power controlled microwave oven ('HBF_4 power') was compared versus temperature controlled digestion ('HBF_4 temp').

Evaluation of 10 soil samples

For the 8 VLAREBO[1] elements (As, Cd, Cr, Cu, Pb, Ni, Zn and Hg) the results obtained with the alternative methods ('HBF_4 power' and 'HBF_4 temp'), corresponds with the results of the reference method ('HF power'). Higher measurements deviations are sometimes observed on samples with lower concentration levels. But there is no indication of a systematic error when applying the alternative methods with respect to the reference method. In paragraph 5.1 on page 99 it is shown that the overall measurement variation is situated in a range of < 20% if different digestion procedures are applied, which can also be expected from replicate/duplo analyses determined with the reference method only. Tests and analyses carried out by a few recognized laboratories confirm the applicability of the evaluated alternative methods to replace the time-consuming reference method.

For the other trace elements (Sb, Ba, Co, Mn, Mo, Se, Sn and V) the same conclusion can be formulated. Often low concentrations of these elements are measured resulting in a higher measurement deviation, but nevertheless it can be stated that comparable results are obtained with the 3 digestion methods.

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[1] Flemish regulation on soil remediation and protection regulations

For the major elements (Na, Mg, Al, K, Ca, Ti, Mn and Fe) a good correspondence is observed between the results of the alternative methods and the reference method, except for Ti. Especially the results obtained with the 'HBF_4 power' method are significantly lower than with the reference method 'HF power'.

Evaluation of 10 waste samples (of which 6 from the validation study of EN 13656)

For the VLAREMA 4bis[2] elements (As, Cd, Cr, Cu, Pb, Ni, Zn, Hg, Sb, Ba, Co, Mo, Se, Sn and V) comparable results are obtained with the alternative methods and the reference method. In paragraph 5.1 on page 99 it is shown that the overall measurement variation is situated in a range of < 20% if different digestion procedures are applied, which can also be expected from replicate/duplo analyses determined with the reference method only. Moreover, for the determination of Ba it is observed that the digestion procedure can be critical and can have an influence on the obtained results (operational defined). Special attention needs to be given to the digestion procedure for the determination of this element. This effect is no surprise as it was also established during the validation trial of EN 13656 in 1999. Tests and analyses carried out by a few recognized laboratories confirm the applicability of the evaluated alternative methods to replace the time-consuming reference method.

For the major elements (Na, Mg, Al, K, Ca, Ti, Mn and Fe) the same conclusion can be formulated as for the soil samples. A good correspondence is observed between the results of the alternative methods and the reference method, except for Ti. Especially the results obtained with the 'HBF_4 power' method are significantly lower than with the reference method 'HF power'.

Based on the obtained results the CMA method CMA/2/II/A.3 can be adapted. First of all, the procedure for a temperature controlled microwave oven digestion, as already described in the CMA method, is confirmed. Secondly, the one step digestion using HBF_4 as acid digestion reagent in combination with HNO_3 and HCl can be added.

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[2] Flemish regulation on sustainable management of material cycles and waste – draft dec 2013

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CHAPTER 1 INTRODUCTION

The digestion of solid samples (soils and waste) is without doubt a critical step in the determination of elements. In Flanders (Belgium), soil and waste samples are digested using an acid mixture of HF:HNO_3:HCl, according to NBN EN 13656[1] (Characterization of waste – Microwave assisted digestion with hydrofluoric (HF), nitric (HNO_3) and hydrochloric (HCl) acid mixture for subsequent determination of elements).

In 2009, a study was commissioned by the Public Waste Agency of Flanders (OVAM) to look for alternative and/or fast digestion methods for the determination of elements (VITO report 2009/MANT/R/010[2]). The study confirmed that the use of different temperature and pressure settings and combinations of acids during the destruction may lead to differences in recovery (mainly for the elements Ni and Cr, this was strongly pronounced) and therefore, none of the proposals were retained.

The applicable method described in CMA/2/II/A.3[3] (Ministerial approved version of January 18, 2012) is based on the European Standard NBN EN 13656, which refers to a power-controlled microwave oven digestion using HF:HNO_3:HCl. Besides that also temperature controlled microwave oven digestions are applied and therefore, on the request of the recognized laboratories, the CMA method was adapted in 2013. A reference to a temperature controlled digestion was included, based on the procedure described in the Horizontal European Standard NBN EN 16174[4] (Sludge, treated biowaste and soil – Digestion of aqua regia soluble fractions of elements). Nevertheless no comparable validation data were available using the HF:HNO_3:HCl digestion with both digestion techniques.

In addition, the recognized laboratories requested for further simplification of the current two-step method of digestion. In the current method the digestion for solids involves a two-step procedure. At first, 0.2 to 0.5 g of the sample is weighed into the digestion flask and 6 ml of HCl, 2 ml of HNO_3 and 2 ml of HF is added. After running the digestion microwave program, the containers are cooled. Then, 22 ml of a solution of boric acid (H_3BO_3) is added, one closes the containers back and they are warmed up again. The second step is necessary in order to resolve possible fluoride precipitate into solution and to complex the excess of HF as BF_4^-.

Refering to the issues above to simplify the procedure and to extend the applicable instruments, the following alternative/rapid digestion methods are evaluated for the determination of elements:

1. *Evaluation of an alternative acid (one-step digestion) as replacement for two-steps digestion with HF + H_3BO_3*
   This involves a one-step digestion, while maintaining the same power of digestion of the silicate matrix, by using HBF_4 (replacing HF with H_3BO_3). In addition, the use of HBF_4 is for safety reasons preferred over HF.
2. *Evaluation of temperature controlled microwave systems as an addition to power controlled microwave systems*
   Comparison of the CMA/2/II/A.3 procedure using power controlled microwave oven versus temperature controlled digestion.

This digestion methods for the determination of elements will be tested in various samples (soil and waste samples) and reference materials.

CHAPTER 2 SELECTION OF HBF_4 ACID

2.1. SELECTION OF HBF_4 ACID

The purity of the acid HBF_4 is one of the critical factors in order to obtain correct results. From different vendors 4 commercially available concentrated HBF_4 solutions were verified for their blank values. The selected HBF_4 solutions were from:

Blank 1: Chemlab	CL00.2009.025 (batchnumber 19.0840811.5)	380 g HBF_4/kg
Blank 2: Sigma	207-934-25g (batchnumber SHBC8208V)	48 wt% in water
Blank 3: Alfa Aesar	L14037 (batchnumber 10175822)	50 wt%
Blank 4: Alfa aesar	11484 (batchnumber J26Y027)	48 wt%

In a digestion vessel 6 ml of HCl (Suprapur), 2 ml of HNO_3 (Suprapur) and 2 ml of HBF_4 was added. The following digestion program was applied:

Time (min)	Power (W)
2	250
2	0
5	250
5	400
5	500

From each HBF_4 solution duplicate blank digestions were conducted to verify the blank values. The concentration of the elements Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Ti, Tl, V and Zn in these blank digestion solutions were determined by ICP-AES. In this case the elements were calibrated in 6% HCl and 2% HNO_3.

The results (Table 1) showed that the blank digestion solution produced from the HBF_4 solution of Chemlab (ultra pure) (blank 1) contained the lowest concentrations of the different elements to be determined. Therefore, this HBF_4 solution was used to perform the further measurements. All elements were calibrated using matrix matched standards (including 6% HCl, 2% HNO_3 and 2% HBF_4).

It should be noted that the blank value might be batch dependent. Verification of the used batch should be performed by the lab itself.

Table 1 Results of the blank values for different HBF_4 solutions

	Blanco1A	RSD	Blanco1B	RSD	Blanco2A	RSD	Blanco2B	RSD	Blanco3A	RSD	Blanco3B	RSD	Blanco4A	RSD	Blanco4B	RSD
	µg/l	%	µg/l	%	µg/l	%	µg/l	%	µg/l	%	µg/l	%	µg/l	%	µg/l	%
As 188.979 Axiaal	30	0,1	29	2,2	89	1,0	89	1,1	169	0,5	169	0,4	91	0,3	92	0,0
Ba 455.403 Axiaal	0,1	1,5	0,1	9,8	1,3	1,0	1,3	0,4	0,7	4,6	0,6	3,5	0,6	3,3	0,6	1,6
Be 313.107 Axiaal	0,2	19	0,1	1,3	0,1	23	0,1	1,2	0,2	35	0,1	0,3	0,1	6,2	0,1	15,2
Cd 214.438 Axiaal	0,4	9,2	0,4	7,2	0,7	4,4	0,7	2,2	0,7	1,0	0,7	3,3	0,8	2,7	0,7	0,1
Co 228.616 Axiaal	-2,9	2,9	-2,9	4,0	-5,4	0,7	-5,4	0,9	-5,7	2,2	-5,6	0,0	-6,0	0,1	-6,0	0,7
Cr 205.552 Axiaal	0,2	9,1	0,3	17	14	0,2	14	0,2	0,5	27	0,4	27	-0,1	193	-0,3	39
Mn 257.610 Axiaal	0,9	18	2,4	7,7	213	1,1	212	0,9	10	1,1	10	0,9	8,5	0,9	8	0
Mo 202.030 Axiaal	2,8	38	0,5	31	0,5	71	0,5	20	1,9	5,8	1,5	19	0,1	193	0,2	66
Ni 231.604 Axiaal	0,3	9,0	0,1	156	7,4	1,1	7,5	0,6	389	0,2	386	0,0	8,8	0,9	8,6	1,1
Pb 220.353 Axiaal	-1,5	37	-3,5	25	-7,3	0,8	-8,4	7,6	-8,4	5,7	-8,5	11	-8,1	4,1	-8,7	7,1
Sb 206.833 Axiaal	42	3,6	44	1,1	69	0,0	69	0,1	70	1,5	71	0,1	75	2,3	74	1,4
Se 196.026 Axiaal	-13	4,3	-10	12	-19	15	-19	1,7	-22	4,4	-22	4,4	-24	6,6	-24	0,6
Sn 189.933 Axiaal	9,2	1,0	9,2	5,6	17	0,4	17	3,5	17	2,8	17	1,7	18	2,2	18	1,0
Sr 407.771 Radiaal	0,2	35	-0,1	9,5	25	0,2	25	0,3	18	0,3	18	0,5	29	0,6	29	0,5
Ti 334.941 Axiaal	0,3	11	-0,3	0,5	-0,1	16	-0,1	43	3,2	0,6	3,2	0,7	0,8	4,0	0,8	0,7
Tl 190.800 Axiaal	8,3	20	6,3	26	9,6	17	12,1	11,9	12	9,5	12	3,0	11	16,5	12	3,9
V 292.402 Axiaal	0,8	11	0,7	11	1,6	7,5	1,6	1,0	1,6	1,6	1,6	3,4	1,7	3,0	1,8	6,1
Na 589.592 Radiaal	67	3,8	41	4,1	1129	1,8	1131	1,7	916	3,0	927	1,1	141	8,0	146	1,2
K 766.491 Radiaal	-48	41	-56	64	84	5,6	145	29	32	311	5,2	490	-94	53,6	-76	28,5
Ca 317.933 Radiaal	-15	11,7	-22	6,3	338	0,3	332	1,0	416	0,2	410	0,2	666	1,6	675	0,7
Mg 279.079 Radiaal	25	44	21	17	163	2,5	149	6,7	219	0,6	212	19	147	6,7	140	9,3
Fe 259.940 Axiaal	1,3	8,0	2,6	8,1	111	0,5	110	0,2	183	0,0	185	0,2	271	0,2	273	1,1
Al 396.152 Axiaal	164	0,4	-10	7,4	5,5	14	5,4	6,3	44	0,8	40	2,6	8,1	3,6	16,3	1,6
Cu 324.754 Axiaal	-1,5	26,2	-2,1	12	-1,3	17	-1,1	4,2	4,5	2,9	4,4	4,7	-0,7	61,8	-0,9	34,3
Zn 213.856 Axiaal	-1,4	45,7	-3,3	0,7	-0,7	5,7	-1,2	2,4	-2,4	16	-1,8	3,4	-2,9	2,8	-3,1	1,5

CHAPTER 3 DIGESTION OF SOIL SAMPLES

3.1. INTRODUCTION

In Flanders, soil and waste samples are digested using the same digestion method with HF:HNO_3:HCl. In case a soil sample is contaminated with several elements, it might be considered as a waste sample. Using the same digestion method, the obtained results can be verified towards the legislative values of soils as well as of waste.

Untill now soil samples were digested using an acid mixture of HF:HNO_3:HCl and a power controlled microwave digestion oven, according to the procedure describe in NBN EN 13656.
In this study the following two items were evaluated:

1. *Evaluation of an alternative acid (one-step digestion) as replacement for two-steps digestion with HF + H_3BO_3*
   This involves a one-step digestion, while maintaining the same power of digestion of the silicate matrix, by using HBF_4 (replacing HF with H_3BO_3). In addition, the use of HBF_4 is for safety reasons preferred over HF.
2. *Evaluation of temperature controlled microwave systems as an addition to power controlled microwave systems*
   Comparison of the CMA/2/II/A.3 procedure using power controlled microwave oven versus temperature controlled digestion. The evaluation was performed using the HBF_4 acid digestion.

3.2. SELECTED SOIL SAMPLES

The 10 selected soil samples were samples collected in Flanders (Belgium). All these samples were dried at 105°C and fine ground with the planetary ball mill (according to EN 13656 < 250 µm). As control samples a round robin soil sample (SETOC 701) – QC1 - , distributed by Wageningen, and a certified soil samples (NIST 2711) – QC 2 – were included in the analytical process.

3.3. DESCRIPTION DIGESTION PROCEDURE AND ICP-AES/CV-AFS MEASUREMENTS

All digestions were performed using an Anton Paar microwave system (Multiwave 3000). The system is equipped with an immersing temperature probe with integrated pressure sensor which is positioned in one reference vessel and infrared sensors are located underneath the rotor to simultaneously measure the temperature and pressure of each vessel. The system is capable of performing digestions using a power controlled or a temperature controlled microwave programme.

The digested solutions were analysed with ICP-AES[c] (Perkin Elmer, Optima 3000) for the determination of the elements. The calibration was set-up with matrix-matched standards fot both axial and radial view. After digestion a dilution of at least a factor of 5 was applied, except for the

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[c] Inductively coupled plasma atomic emission spectrometry

determination of element concentrations nearby the reporting limit. As internal standard Rh was used and the suppression of the internal standard was for all samples limited to maximum 10%. Data obtained in axial view were Rh corrected, while no Rh correction was applied on data measured in radial view.

Mercury was determined with CV-AFS[d] (Leeman, HYDRA AF Automated Hg-analyzer).

3.3.1. DIGESTION WITH HF:HNO_3:HCL AND POWER CONTROLLED MICROWAVE DIGESTION (HF POWER)

About 0.5 g of sample was weighed into the vessel. Then the following acids were separately added: 6 ml HCl, 2 ml HNO_3 and 2 ml HF. The digestion vessel was placed into the microwave unit (8 positions) and the following digestion process was applied:

	Time (min)	Power (W)
Stap 1	2	250
Stap 2	2	0
Stap 3	5	250
Stap 4	5	400
Stap 5	5	500

At the end of the programme the vessels were cooled down to room temperature. Subsequently, 22 ml of 4% m/m of boric acid was added and the vessels were placed in the microwave unit applying the following process:

Time (min)	Power (W)
3	300

After cooling the digested solution was transferred to a volumetric flask and filled up to 100 ml with ultrapure water.

Each batch contains 1 blank, 1 control sample (QC1 or QC2), 5 samples and 1 duplo sample.

3.3.2. DIGESTION WITH HBF_4 AND POWER CONTROLLED MICROWAVE DIGESTION (HBF_4 POWER)

About 0.5 g of sample was weighed into the vessel. Then the following acids were separately added: 6 ml HCl, 2 ml HNO_3 and 2 ml HBF_4 and the following digestion process was applied:

Time (min)	Power (W)
2	250
2	0
5	250
5	400
5	500

After cooling the digested solution was transferred to a volumetric flask and filled up to 100 ml with ultrapure water.

Each batch contains 1 blank, 1 control sample (QC1 or QC2), 5 samples and 1 duplo sample.

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[d] Cold vapour atomic fluorescence spectrometry

3.3.3. DIGESTION WITH HBF_4 AND TEMPERATURE CONTROLLED MICROWAVE DIGESTION (HBF_4 TEMP)

About 0.5 g of sample was weighed into the vessel. The acids 6 ml HCl, 2 ml HNO_3 and 2 ml HBF_4 were separately added. The digestion vessel was placed into the microwave unit (8 positions) and the temperature was raised with a heating rate of 15°C min^{-1} to 175°C and remained at 175°C for 10 minutes. After cooling the digested solution was transferred to a volumetric flask and filled up to 100 ml with ultrapure water.

Each batch contains 1 blank, 1 control sample (QC1 or QC2), 5 samples and 1 duplo sample.

3.4. EVALUATION OF THE DIGESTION PROCESS

As the system is equipped with an immersing temperature probe with integrated pressure sensor in the first reference vessel and infrared sensors to measure the temperature of each vessel, it was interesting to follow up the digestion profiles during the complete cycle.

In Figure 1 and Figure 2 the digestion profiles of the soil samples using HF:HNO_3:HCl (run 1 and run 2, respectively) with a power controlled program are shown. The temperature in vessel 1, monitored with the probe, raised up to 160-165°C when reaching the full power of 500 W. The temperature profiles, monitored with the IR sensor, looks quite similar (except the one of the blank samples, which has a lower maximum temperature).

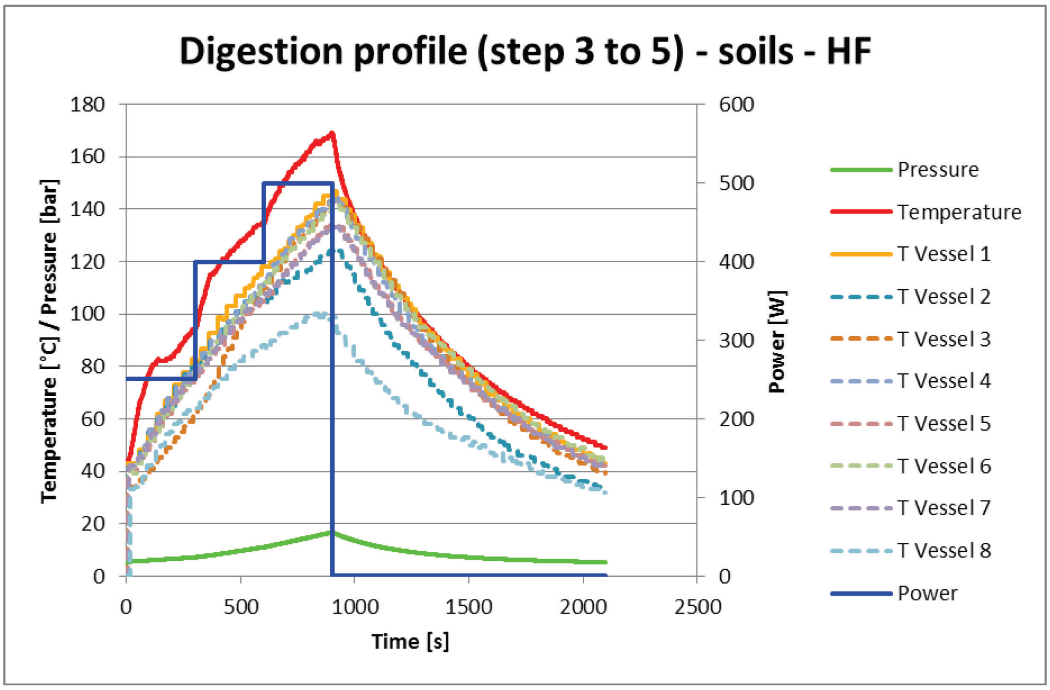

Figure 1 Digestion profile of the soil samples using HF:HNO_3:HCl (run 1) – power controlled program

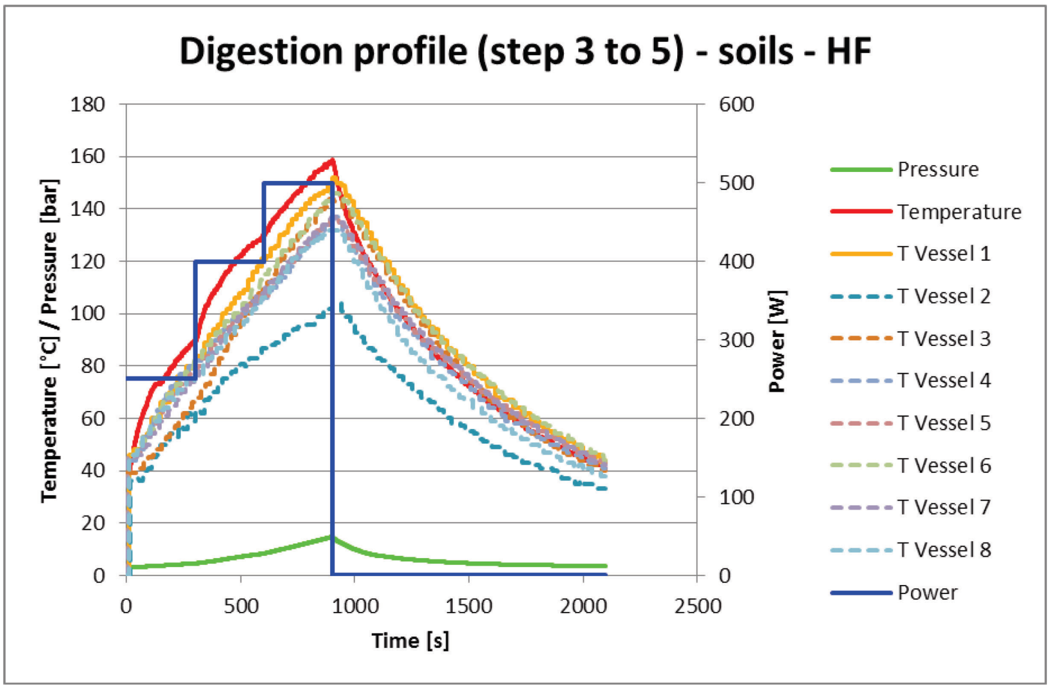

Figure 2 Digestion profile of the soil samples using HF:HNO_3:HCl (run 2) – power controlled program

In Figure 3 and Figure 4 the digestion profiles of the soil samples using HBF_4 (run 1 and run 2, respectively) with a power controlled program are shown. The temperature in vessel 1, monitored with the probe, raised up to 120-150°C when reaching the full power of 500 W. The temperature profiles, monitored with the IR sensor, looks quite similar.

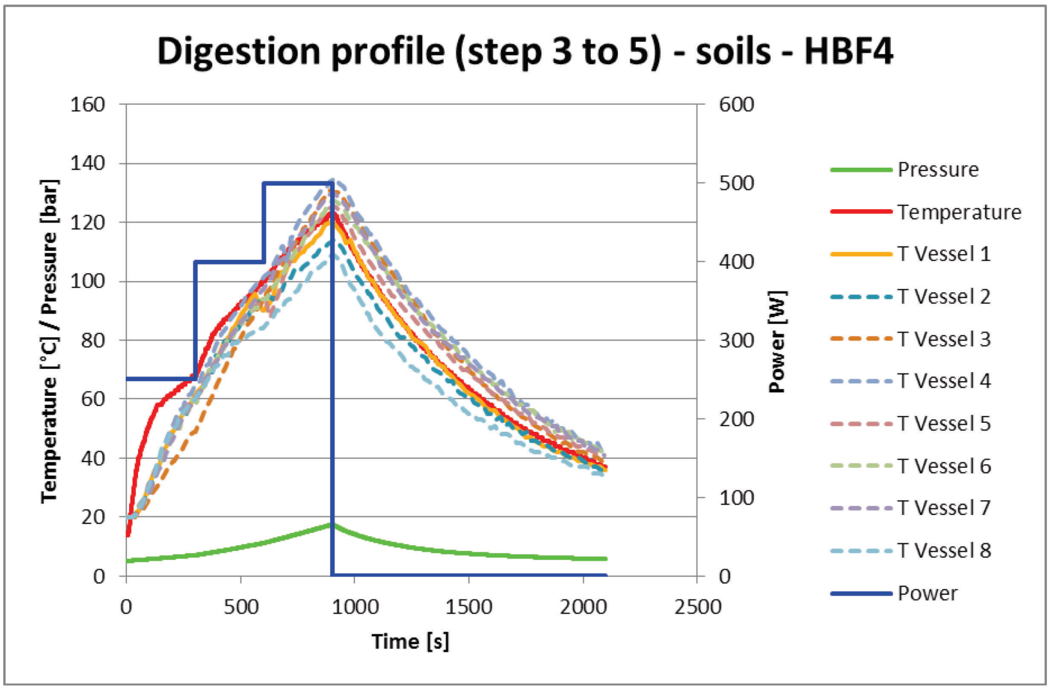

Figure 3 Digestion profile of the soil samples using HBF_4 (run 1) – power controlled program

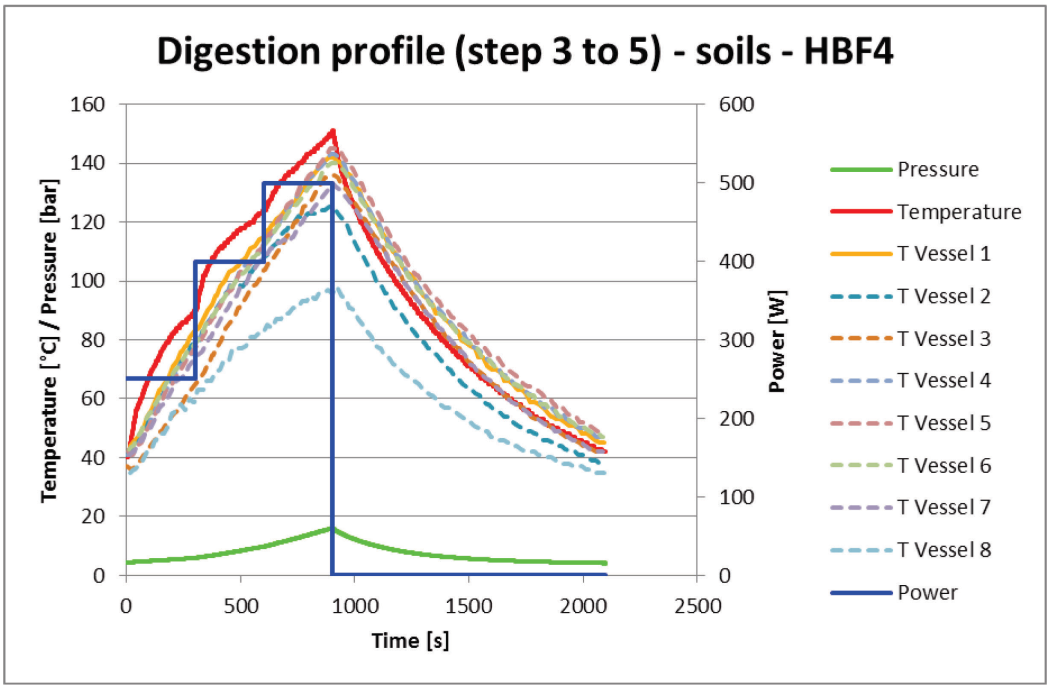

Figure 4 Digestion profile of the soil samples using HBF_4 (run 2) – power controlled program

In Figure 5 the digestion profiles of the soil samples using HBF_4 (run 1) with a temperature controlled program are shown. The temperature is raised up to 175°C, which can be verified with the probe in vessel 1. All the IR measurement shows comparable profiles with temperatures up to 160-175°C (except the one of the blank samples, which has a lower maximum temperature). The power increased up to about 750 W when reaching the max. temperature of 175°C and then drops further to about 400 W. Also the pressure remains below 20 bar.

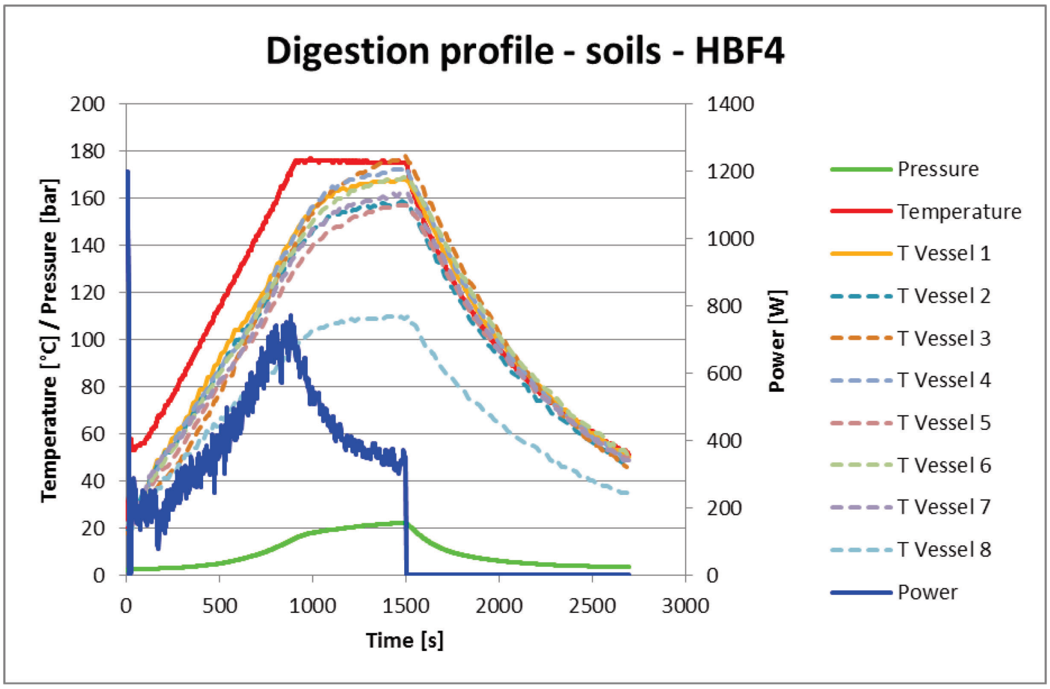

Figure 5 Digestion profile of the soil samples using HBF_4 (run 1) – temperature controlled program

3.5. RESULTS OF THE VLAREBO ELEMENTS

According to the Flemish regulation on soil remediation and protection regulations (VLAREBO) 8 elements are defined as critical contaminants (towards human and environmental toxicity): As, Cd, Cr, Cu, Pb, Ni, Zn and Hg. Therefore, these elements are of major interest to determine in soils.

In the following paragraphs the results obtained with the different digestion procedures are presented per element. Duplicate samples (including digestion) are marked with ‘b’. The reference method is always indicated as ‘HF power’, while the alternative methods are indicated as ‘HBF_4 power’ and HBF_4 temp’. Note that the evaluation is based on the comparison of single measurement results.

An overview of all elements is presented in paragraph 3.9 on page 41.

The individual results for all samples, parameters and digestions are compiled in Annex A.

3.5.1. ELEMENT ARSENIC

In Figure 6 the As results of the different soil samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the As results with the 3 digestion methods was calculated per sample and are presented in Figure 7. From all samples analysed the CV_R is situated below 20% and in most cases below 10%. The pooled CV_R of the 14 samples (including duplicate and QC samples) amounted 6.3%. The high CV_R was obtained on the QC sample with a concentration level of less than 10 mg/kg dm.

When calculating the % difference between the reference method (HF:HNO_3:HCl, power controlled digestion) and the 2 alternative methods ($HBF_{4,}$ power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively 6.5 and 4.4% difference is observed (see Figure 8).

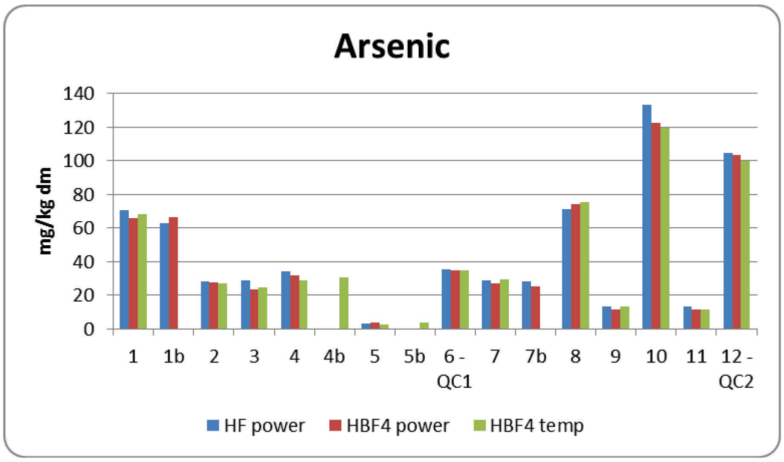

Figure 6 As results of the soil samples using the 3 digestion methods

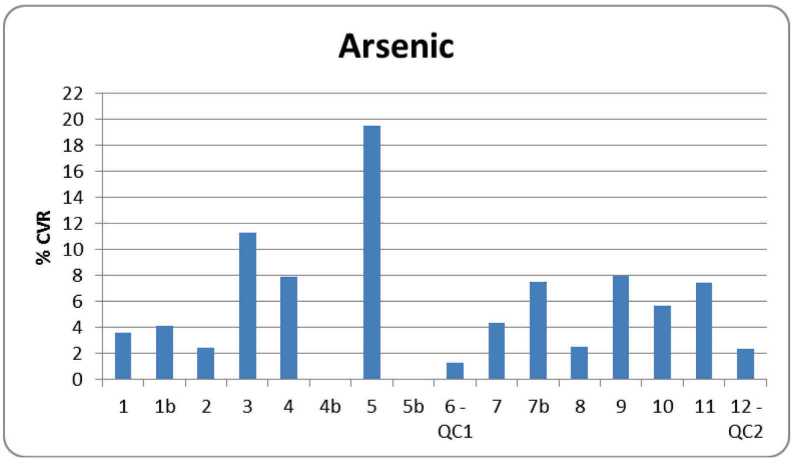

Figure 7 % CV_R of the 3 As results by sample

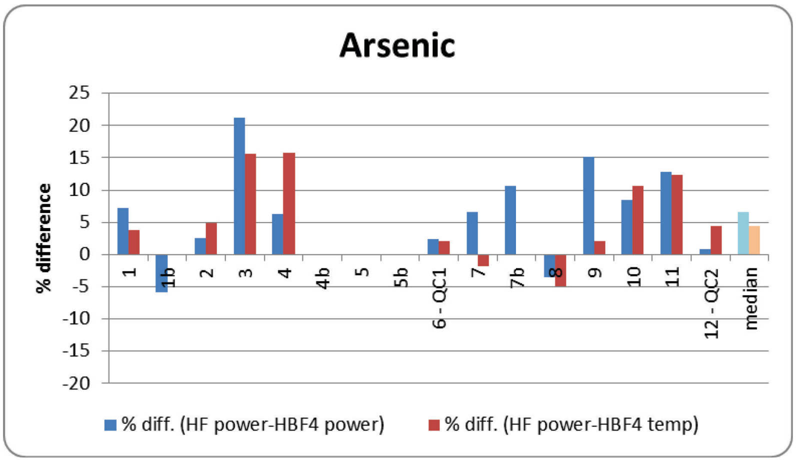

Figure 8 Difference between the reference method for As and the 2 alternative methods

3.5.2. ELEMENT CADMIUM

In Figure 9 the Cd results of the different soil samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the Cd results with the 3 digestion methods was calculated per sample and are presented in Figure 10. From all samples analysed the CV_R is situated below 10%. The pooled CV_R of the 12 samples (including duplicate and QC samples) amounted 3.9%.

When calculating the % difference between the reference method (HF:HNO_3:HCl, power controlled digestion) and the 2 alternative methods (HBF_4, power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively -3.2 and 1.0% difference is observed (see Figure 11).

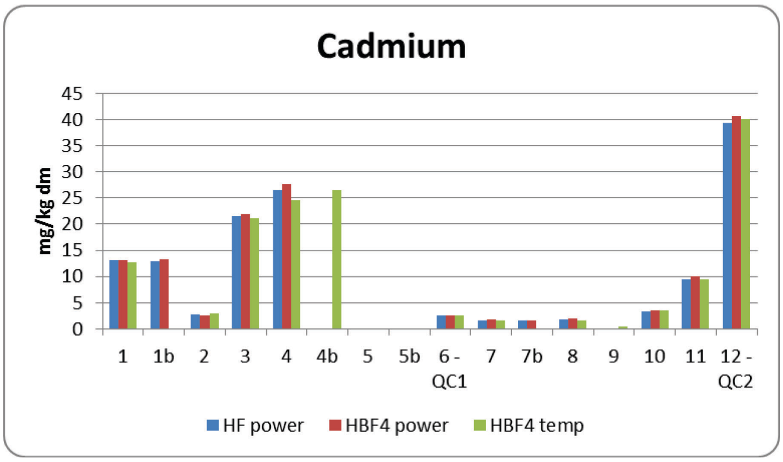

Figure 9 Cd results of the soil samples using the 3 digestion methods

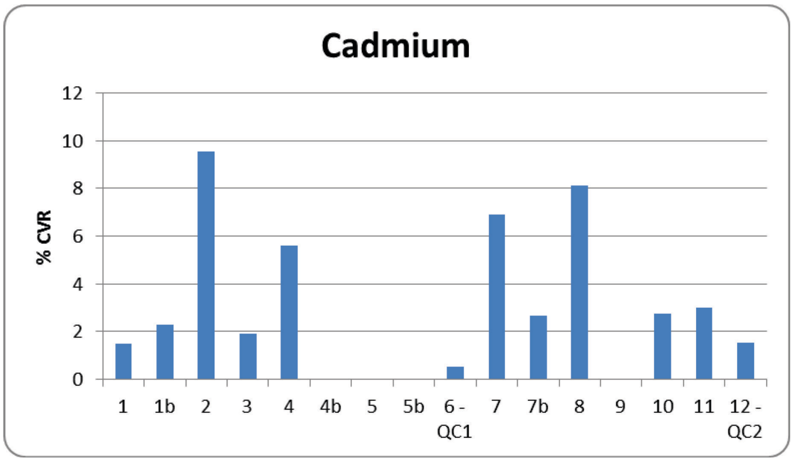

Figure 10 % CV_R of the 3 Cd results by sample

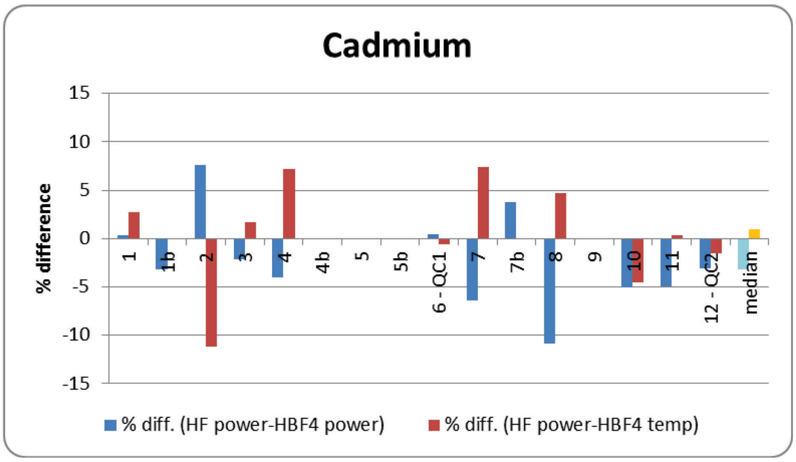

Figure 11 Difference between the reference method for Cd and the 2 alternative methods

3.5.3. ELEMENT CHROMIUM

In Figure 12 the Cr results of the different soil samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the Cr results with the 3 digestion methods was calculated per sample and are presented in Figure 13. From all samples analysed the CV_R is situated below 10%. The pooled CV_R of the 14 samples (including duplicate and QC samples) amounted 4.1%.

When calculating the % difference between the reference method ($HF:HNO_3:HCl$, power controlled digestion) and the 2 alternative methods (HBF_4, power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively 2.6 and -1.5% difference is observed (see Figure 14).

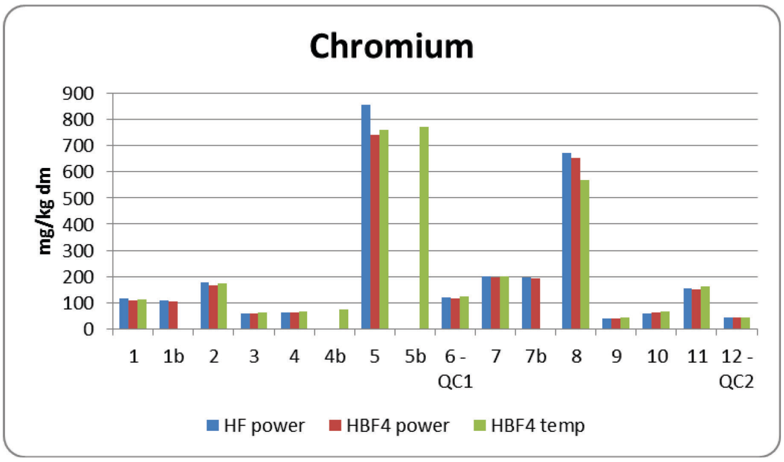

Figure 12 Cr results of the soil samples using the 3 digestion methods

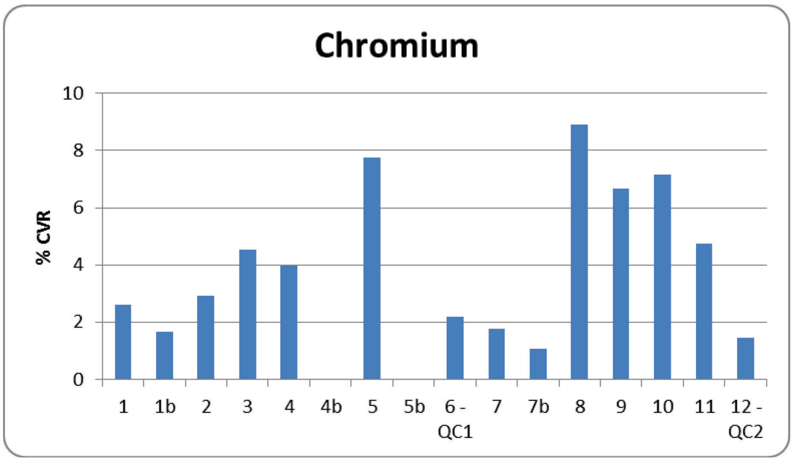

Figure 13 % CV_R of the 3 Cr results by sample

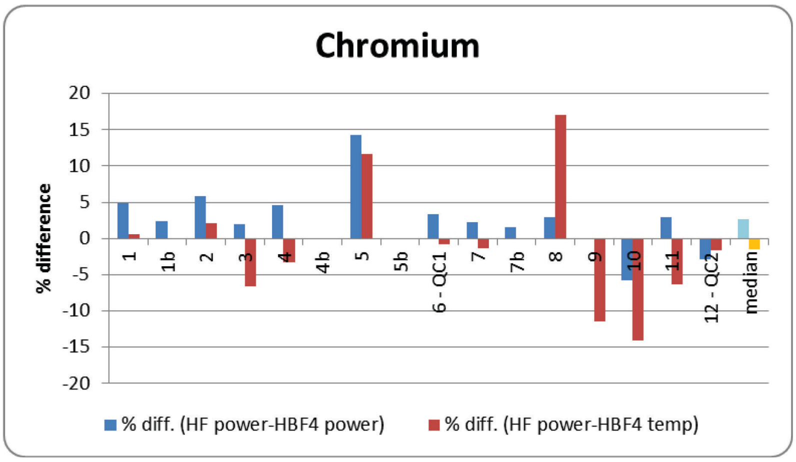

Figure 14 Difference between the reference method for Cr and the 2 alternative methods

3.5.4. ELEMENT CUPPER

In Figure 15 the Cu results of the different soil samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the Cu results with the 3 digestion methods was calculated per sample and are presented in Figure 16. From all samples analysed the CV_R is situated below 12%. The pooled CV_R of the 14 samples (including duplicate and QC samples) amounted 4.7%.

When calculating the % difference between the reference method ($HF:HNO_3:HCl$, power controlled digestion) and the 2 alternative methods (HBF_4, power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively 3.2 and 1.7% difference is observed (see Figure 17).

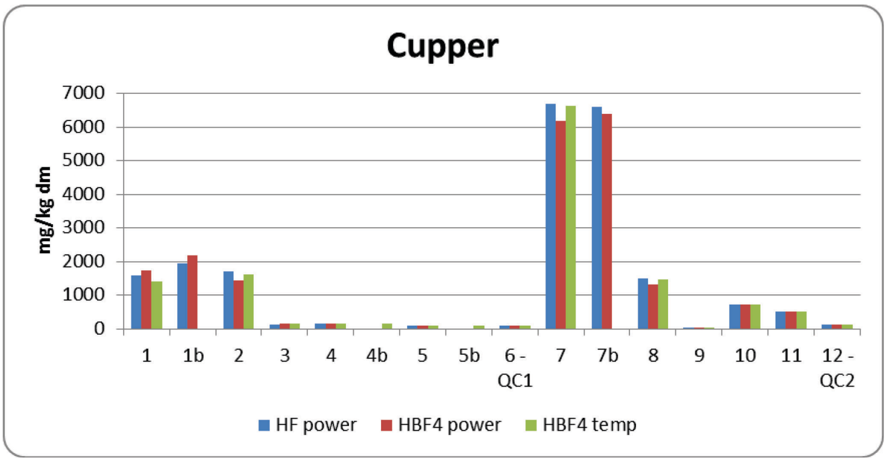

Figure 15 Cu results of the soil samples using the 3 digestion methods

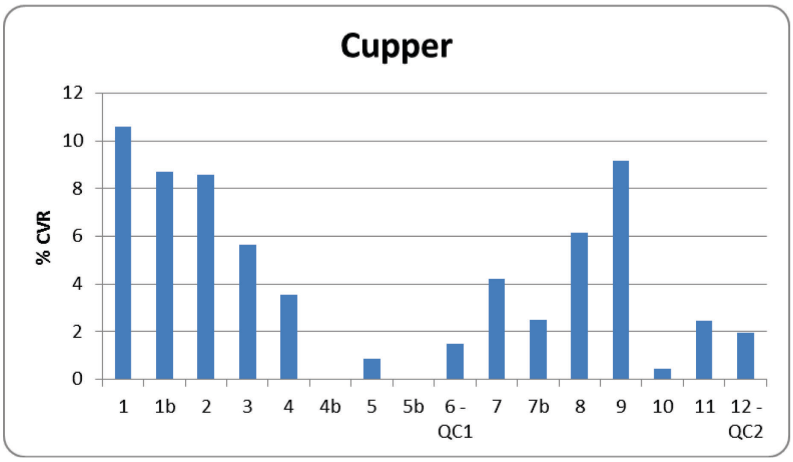

Figure 16 % CV_R of the 3 Cu results by sample

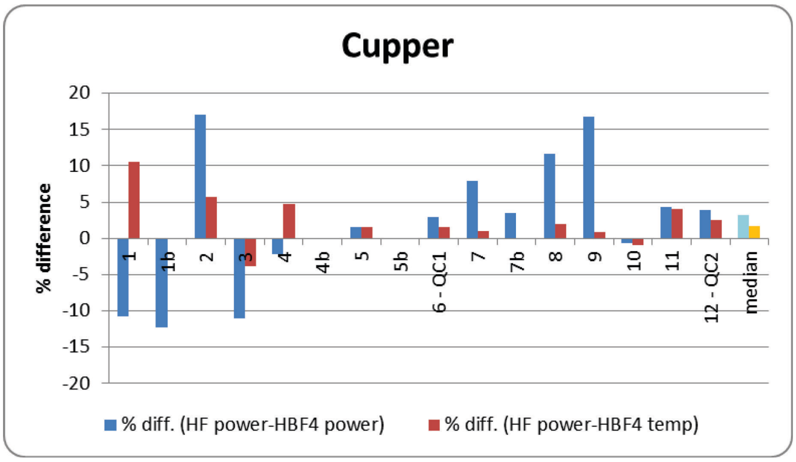

Figure 17 Difference between the reference method for Cu and the 2 alternative methods

3.5.5. ELEMENT LEAD

In Figure 18 the Pb results of the different soil samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the Pb results with the 3 digestion methods was calculated per sample and are presented in Figure 19. From all samples analysed the CV_R is situated below 15%. In most cases even below 6%. The pooled CV_R of the 14 samples (including duplicate and QC samples) amounted 4.7%.

When calculating the % difference between the reference method ($HF:HNO_3:HCl$, power controlled digestion) and the 2 alternative methods (HBF_4, power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively -3.2 and -2.3% difference is observed (see Figure 20). The highest difference (24%) was observed on a sample with a low concentration of less than 10 mg/kg dm.

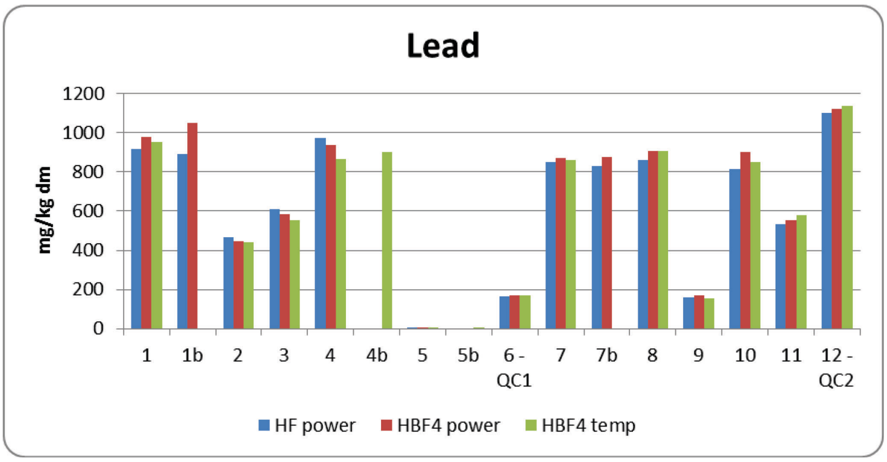

Figure 18 Pb results of the soil samples using the 3 digestion methods

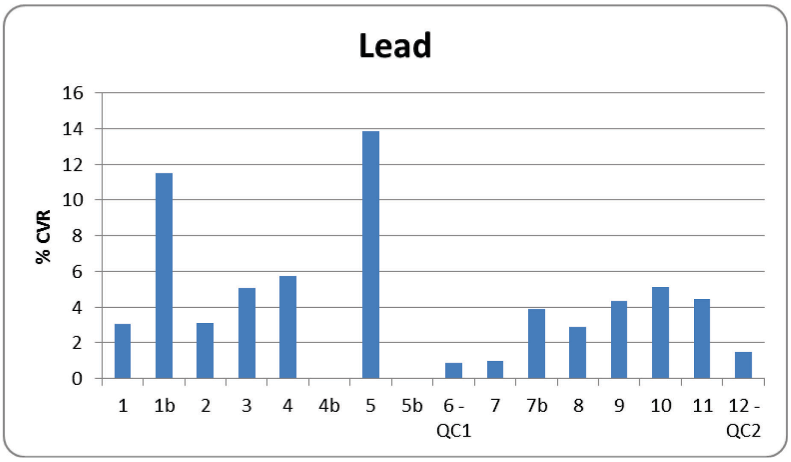

Figure 19 % CV$_R$ of the 3 Pb results by sample

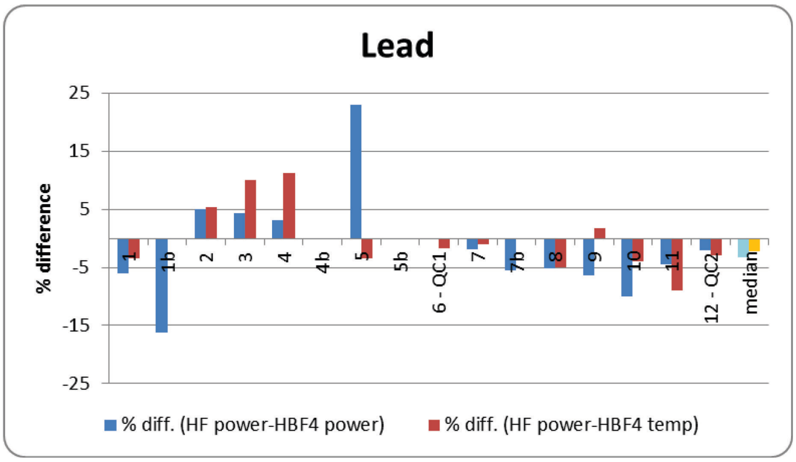

Figure 20 Difference between the reference method for Pb and the 2 alternative methods

3.5.6. ELEMENT NICKEL

In Figure 21 the Ni results of the different soil samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the Ni results with the 3 digestion methods was calculated per sample and are presented in Figure 22. From all samples analysed the CV_R is situated below 18%. In most cases even below 6%. The pooled CV_R of the 14 samples (including duplicate and QC samples) amounted 4.7%.

When calculating the % difference between the reference method ($HF:HNO_3:HCl$, power controlled digestion) and the 2 alternative methods (HBF_4, power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively -3.5 and 1.3% difference is observed (see Figure 23).

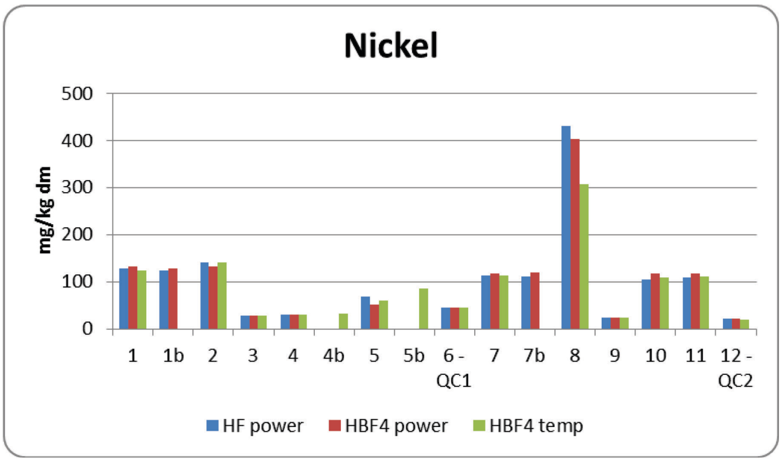

Figure 21 Ni results of the soil samples using the 3 digestion methods

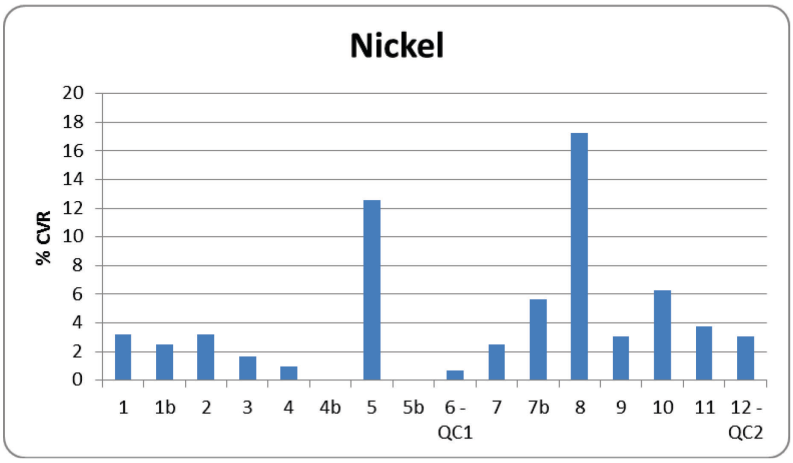

Figure 22 % CV_R of the 3 Ni results by sample

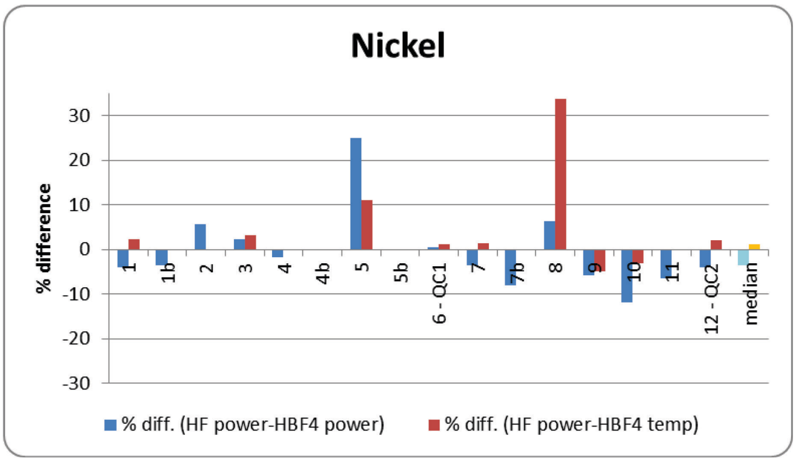

Figure 23 Difference between the reference method for Ni and the 2 alternative methods

3.5.7. ELEMENT ZINC

In Figure 24 the Zn results of the different soil samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the Zn results with the 3 digestion methods was calculated per sample and are presented in Figure 25. From all samples analysed the CV_R is situated below 10%. The pooled CV_R of the 14 samples (including duplicate and QC samples) amounted 3.1%.

When calculating the % difference between the reference method ($HF:HNO_3:HCl$, power controlled digestion) and the 2 alternative methods (HBF_4, power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively -2.1 and -0.6% difference is observed (see Figure 26).

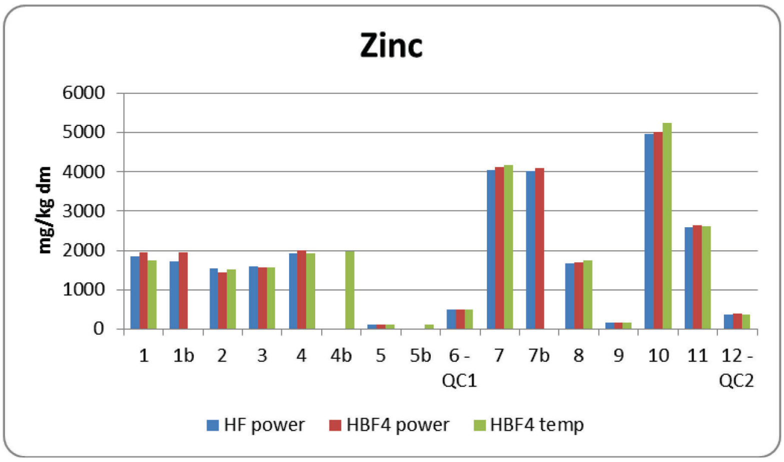

Figure 24 Zn results of the soil samples using the 3 digestion methods

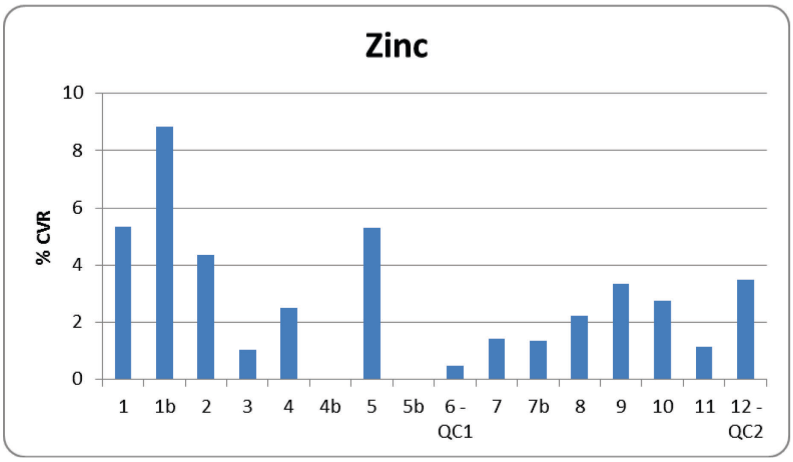

Figure 25 % CV_R of the 3 Zn results by sample

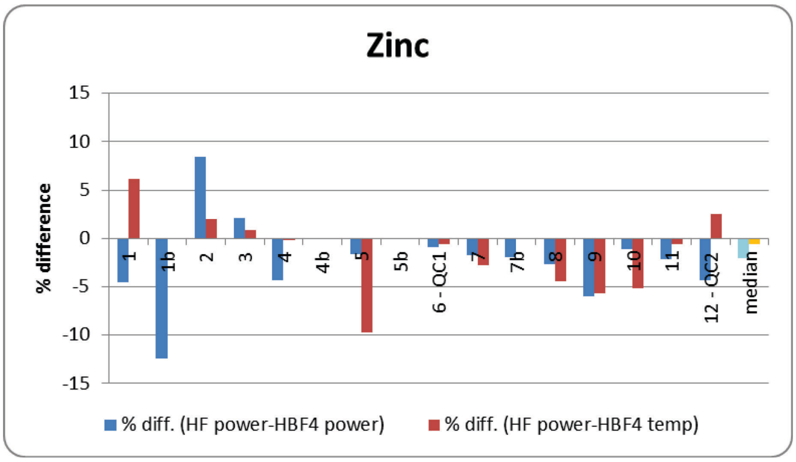

Figure 26 Difference between the reference method for Zn and the 2 alternative methods

3.5.8. ELEMENT MERCURY

In Figure 27 the Hg results of the different soil samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the Hg results with the 3 digestion methods was calculated per sample and are presented in Figure 28. From all samples analysed the CV_R is situated below 10%. The pooled CV_R of the 13 samples (including duplicate and QC samples) amounted 4.5%.

When calculating the % difference between the reference method ($HF:HNO_3:HCl$, power controlled digestion) and the 2 alternative methods (HBF_4, power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively 3.8 and 4.5% difference is observed (see Figure 29).

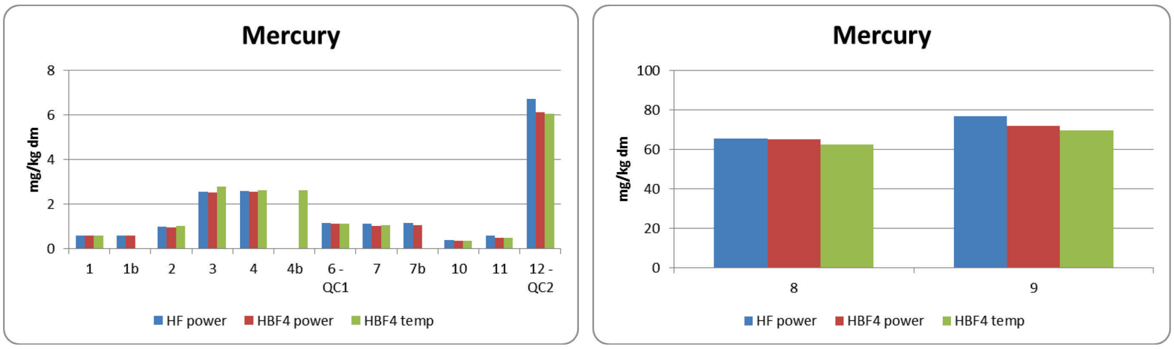

Figure 27 Hg results of the soil samples using the 3 digestion methods

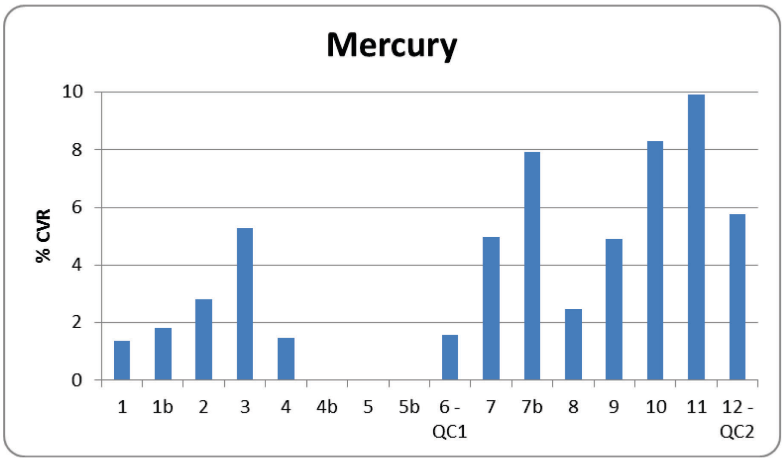

Figure 28 % CV_R of the 3 Hg results by sample

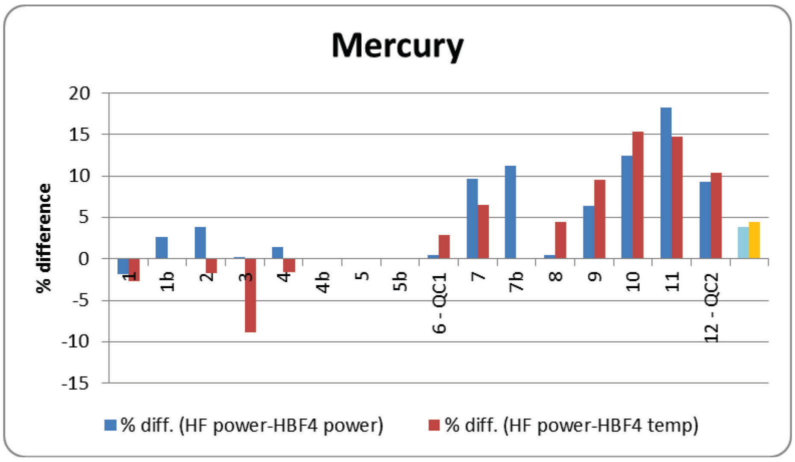

Figure 29 Difference between the reference method for Hg and the 2 alternative methods

3.6. RESULTS OF THE OTHER TRACE ELEMENTS

3.6.1. ELEMENT ANTIMONY

In Figure 30 the Sb results of the different soil samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the Sb results with the 3 digestion methods was calculated per sample and are presented in Figure 31. From all samples analysed, except for sample 5, the CV_R is situated below 20%. For sample 5 it amounts 50%, which is attributed to the relative low concentration of Sb present in the sample. The pooled CV_R of the 14 samples (including duplicate and QC samples) amounted 13%.

When calculating the % difference between the reference method (HF:HNO_3:HCl, power controlled digestion) and the 2 alternative methods ($HBF_{4,}$ power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively 2.3 and 3.0% difference is observed (see Figure 32). The highest differences are observed on the samples with concentration levels of less than 10 mg/kg dm.

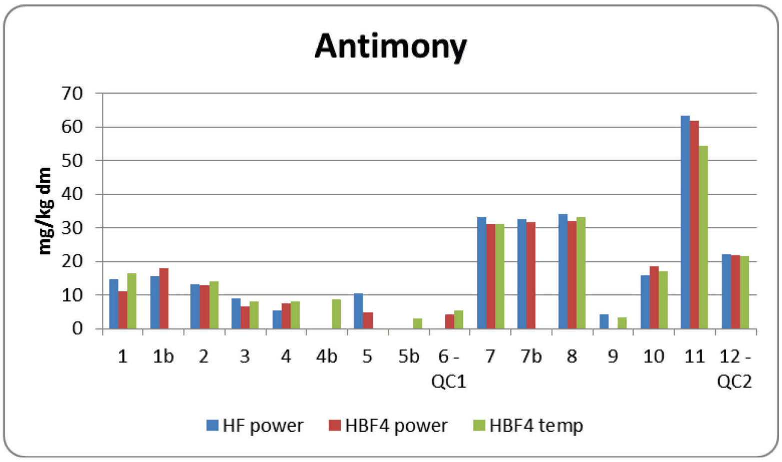

Figure 30 Sb results of the soil samples using the 3 digestion methods

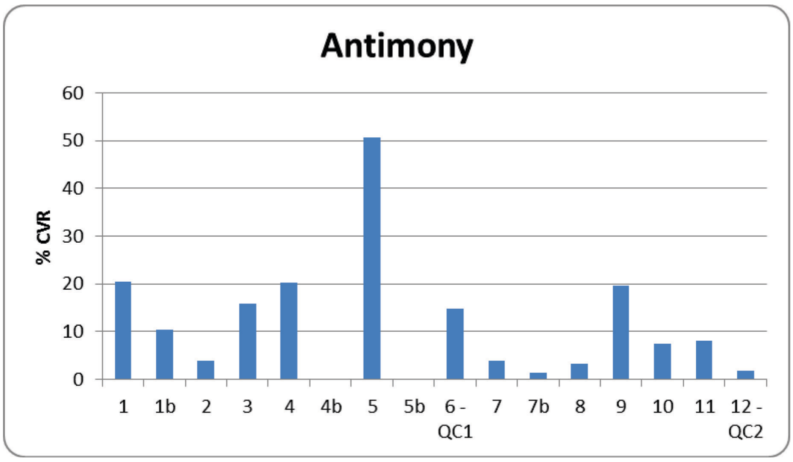

Figure 31 % CV_R of the 3 Sb results by sample

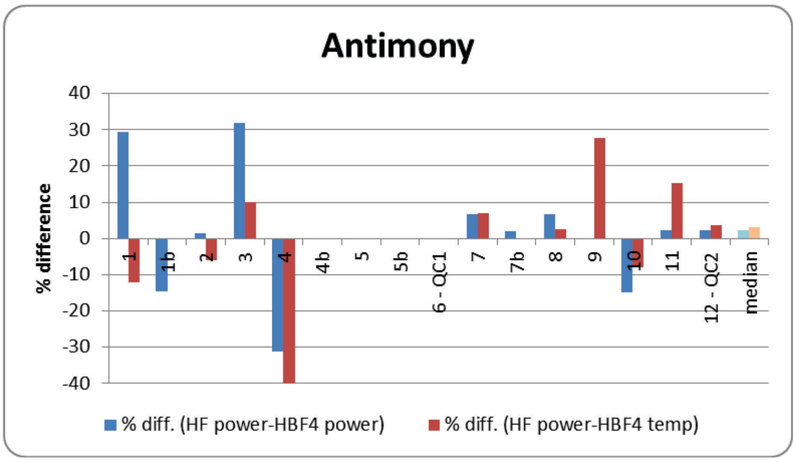

Figure 32 Difference between the reference method for Sb and the 2 alternative methods

3.6.2. ELEMENT BARIUM

In Figure 33 the Ba results of the different soil samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the Ba results with the 3 digestion methods was calculated per sample and are presented in Figure 34. From all samples analysed the CV_R is situated below 8%. The pooled CV_R of the 14 samples (including duplicate and QC samples) amounted 3.6%.

When calculating the % difference between the reference method ($HF:HNO_3:HCl$, power controlled digestion) and the 2 alternative methods (HBF_4, power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively 0.0 and 0.9% difference is observed (see Figure 35).

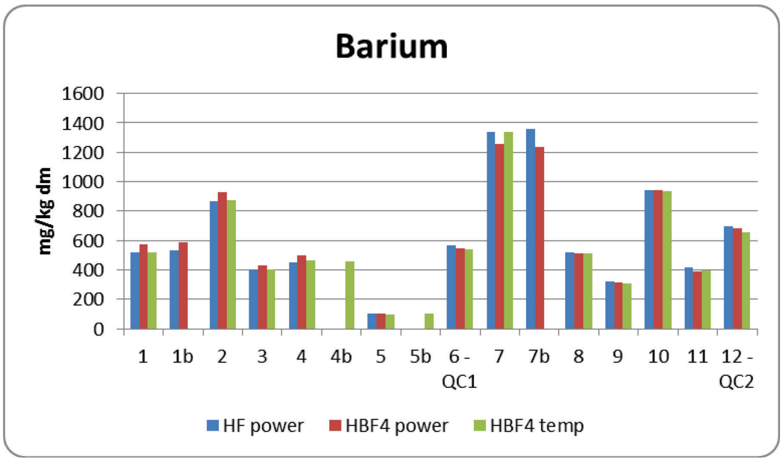

Figure 33 Ba results of the soil samples using the 3 digestion methods

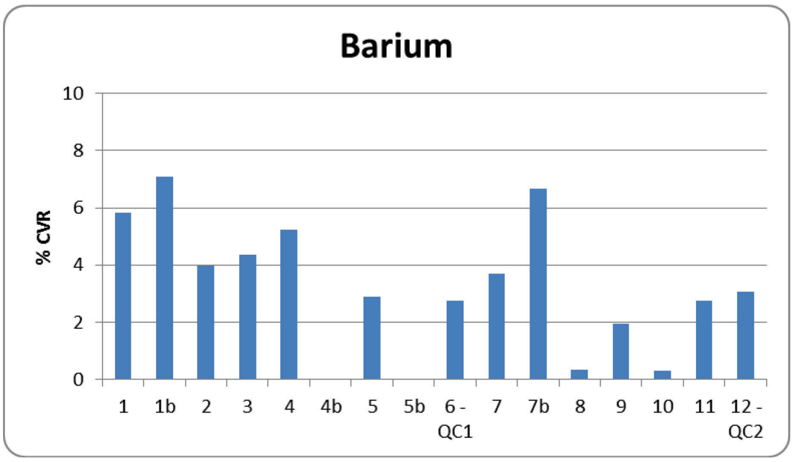

Figure 34 % CV_R of the 3 Ba results by sample

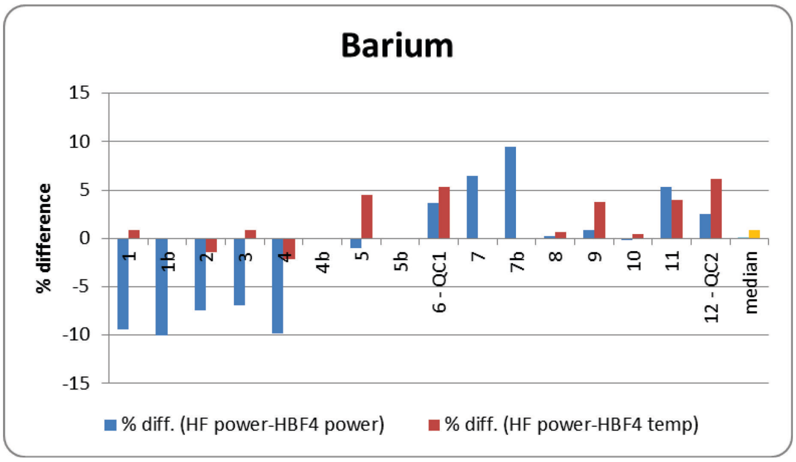

Figure 35 Difference between the reference method for Ba and the 2 alternative methods

3.6.3. ELEMENT COBALT

In Figure 36 the Co results of the different soil samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the Co results with the 3 digestion methods was calculated per sample and are presented in Figure 37. From all samples analysed the CV_R is situated below 18%. The highest deviation is observed on the sample with a concentration of less than 10 mg/kg dm. Samples with a higher concentration above 10 mg/kg dm have a CV_R of less than 10%. The pooled CV_R of the 14 samples (including duplicate and QC samples) amounted 5.0%.

When calculating the % difference between the reference method ($HF:HNO_3:HCl$, power controlled digestion) and the 2 alternative methods ($HBF_{4,}$ power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively -1.0 and -3.4% difference is observed (see Figure 38).

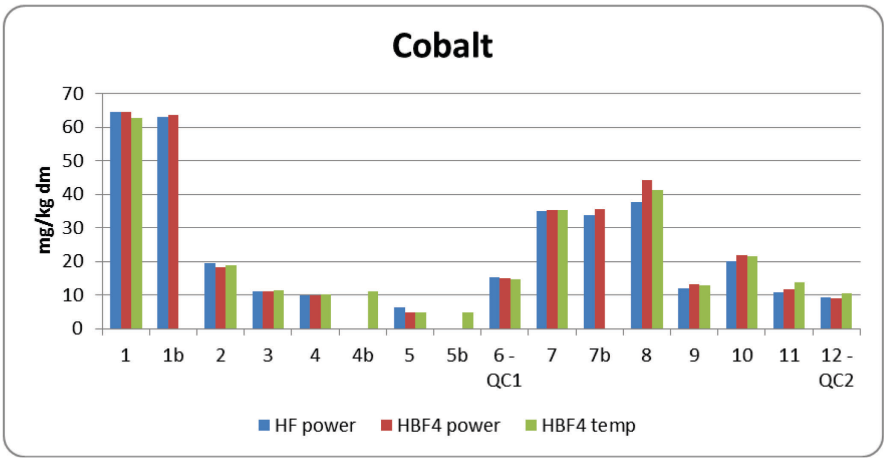

Figure 36 Co results of the soil samples using the 3 digestion methods

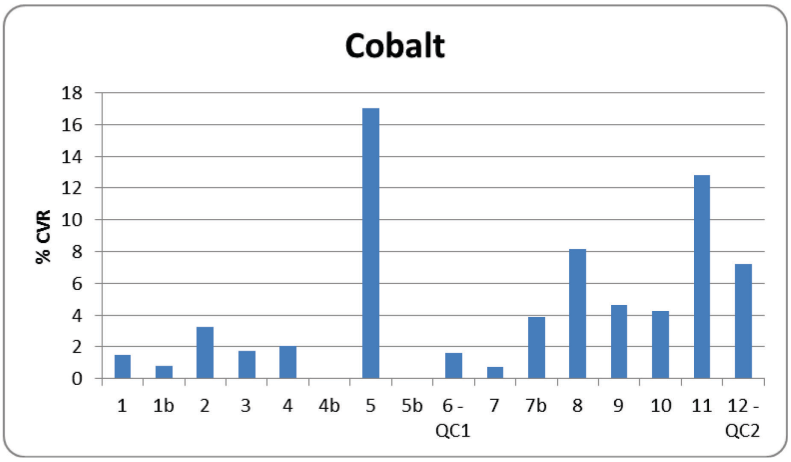

Figure 37 % CV$_R$ of the 3 Co results by sample

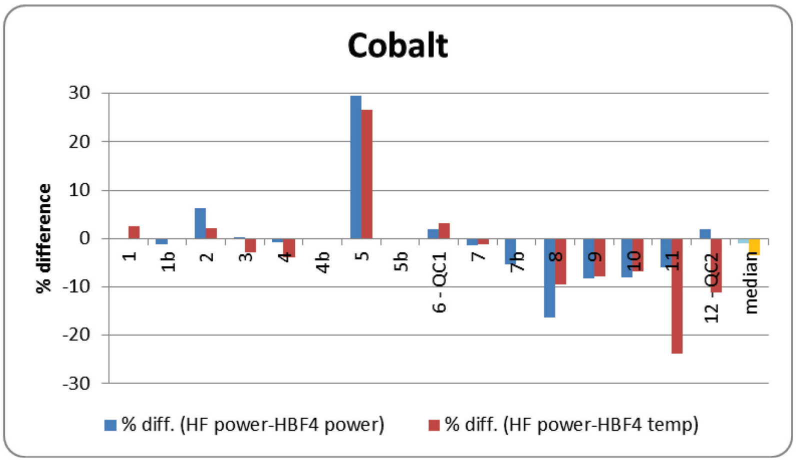

Figure 38 Difference between the reference method for Co and the 2 alternative methods

3.6.4. ELEMENT MOLYBDENUM

In Figure 39 the Mo results of the different soil samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the Mo results with the 3 digestion methods was calculated per sample and are presented in Figure 40. From all samples analysed the CV_R is situated below 25%. The highest deviations are observed on samples 2, 3 and 4 with a concentration of Mo below 10 mg/kg dm. The pooled CV_R of the 13 samples (including duplicate and QC samples) amounted 7.9%.

When calculating the % difference between the reference method ($HF:HNO_3:HCl$, power controlled digestion) and the 2 alternative methods (HBF_4, power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively 4.1 and 3.3% difference is observed (see Figure 41).

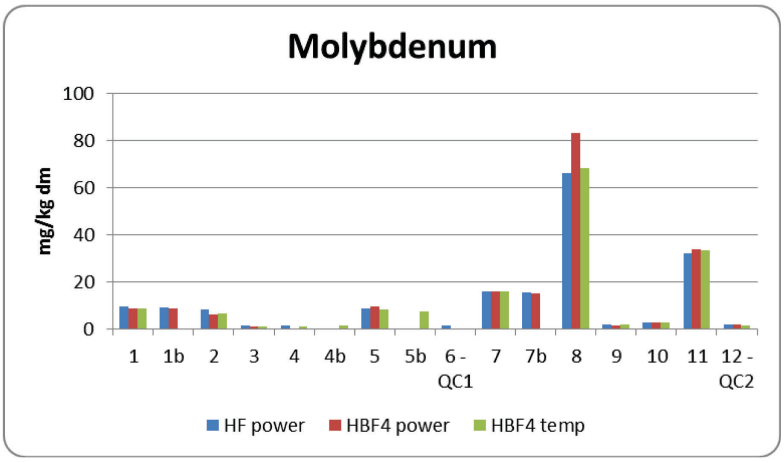

Figure 39 Mo results of the soil samples using the 3 digestion methods

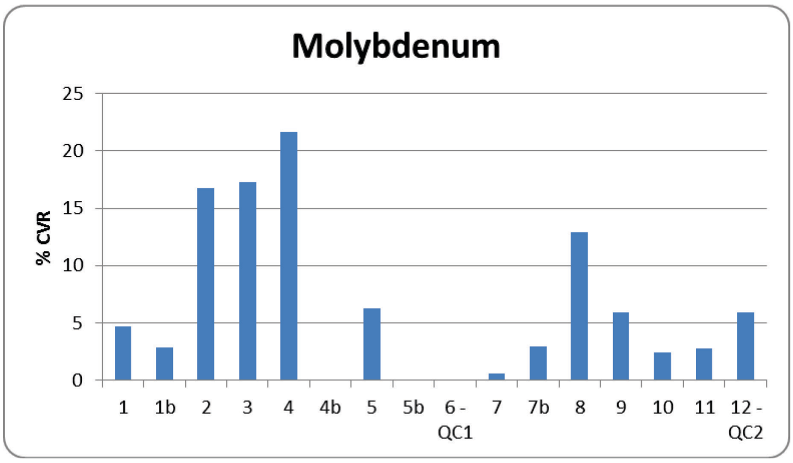

Figure 40 % CV_R of the 3 Mo results by sample

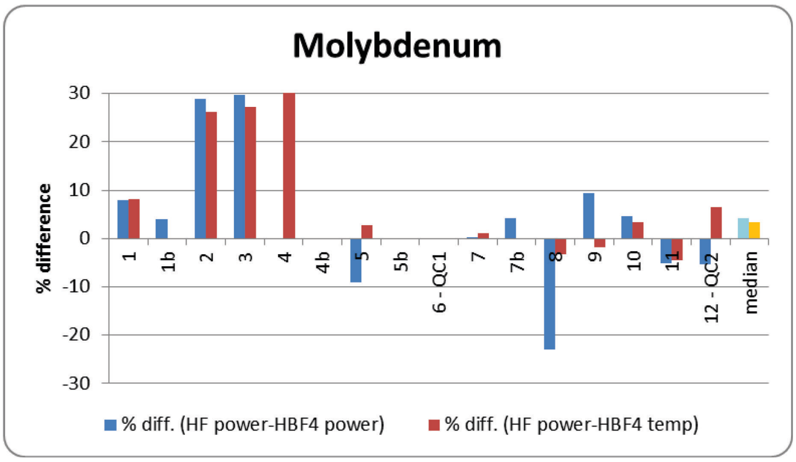

Figure 41 Difference between the reference method for Mo and the 2 alternative methods

3.6.5. ELEMENT TIN

In Figure 42 the Sn results of the different soil samples and the quality control (QC) samples are presented.

The coefficient of variation (CV_R) of the Sn results with the 3 digestion methods was calculated per sample and are presented in Figure 43. From all samples analysed the CV_R is situated below 60%. In most case even less than 10%. The highest deviation is observed for sample 1 and sample 1b, with a lower Sn value for the reference method compared to the alternative methods. The pooled CV_R of the 12 samples (including duplicate and QC samples) amounted 13 %.

When calculating the % difference between the reference method ($HF:HNO_3:HCl$, power controlled digestion) and the 2 alternative methods (HBF_4, power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively -5.5 and 0.3% difference is observed (see Figure 44).

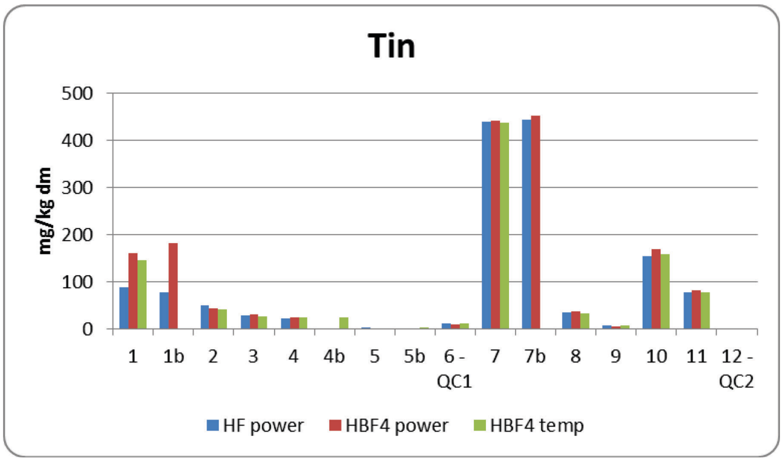

Figure 42 Sn results of the soil samples using the 3 digestion methods

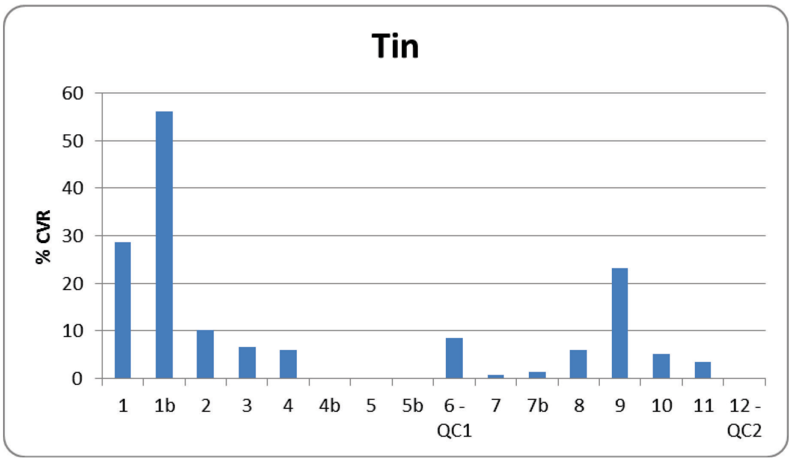

Figure 43 % CV_R of the 3 Sn results by sample

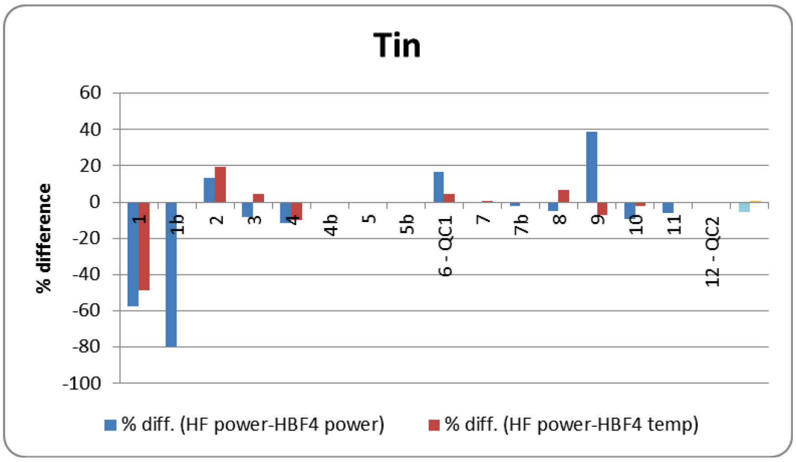

Figure 44 Difference between the reference method for Sn and the 2 alternative methods

3.6.6. ELEMENT VANADIUM

In Figure 45 the V results of the different soil samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the V results with the 3 digestion methods was calculated per sample and are presented in Figure 46. From all samples analysed the CV_R is situated below 6%. The pooled CV_R of the 14 samples (including duplicate and QC samples) amounted 2.5%.

When calculating the % difference between the reference method ($HF:HNO_3:HCl$, power controlled digestion) and the 2 alternative methods (HBF_4, power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively -2.9 and -0.6% difference is observed (see Figure 47).

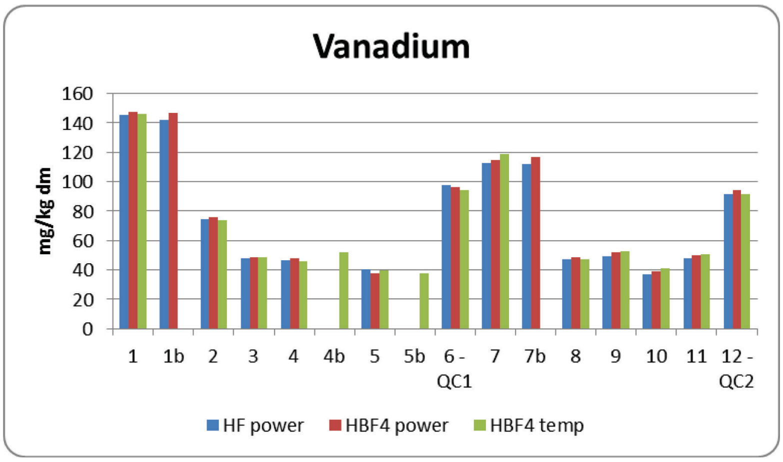

Figure 45 V results of the soil samples using the 3 digestion methods

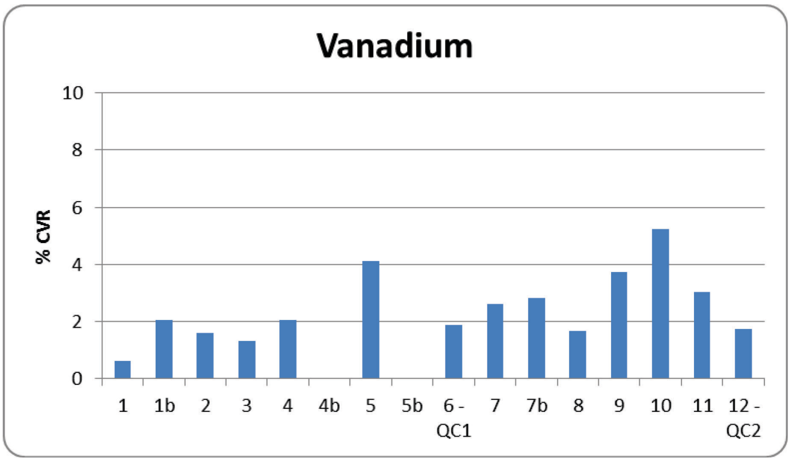

Figure 46 % CV_R of the 3 V results by sample

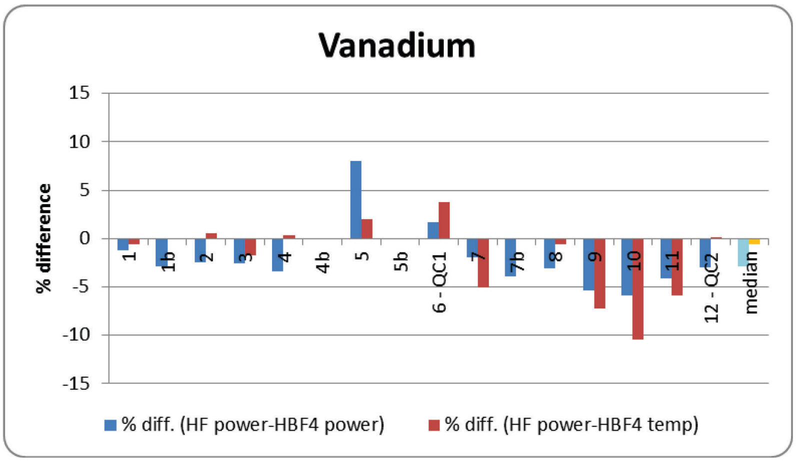

Figure 47 Difference between the reference method for V and the 2 alternative methods

3.7. RESULTS OF MAJOR ELEMENTS

3.7.1. ELEMENT SODIUM

In Figure 48 the Na results of the different soil samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the Na results with the 3 digestion methods was calculated per sample and are presented in Figure 49. From all samples analysed the CV_R is situated below 4%. The pooled CV_R of the 14 samples (including duplicate and QC samples) amounted 2.1%.

When calculating the % difference between the reference method ($HF:HNO_3:HCl$, power controlled digestion) and the 2 alternative methods ($HBF_{4,}$ power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively -1.1 and 2.0% difference is observed (see Figure 50).

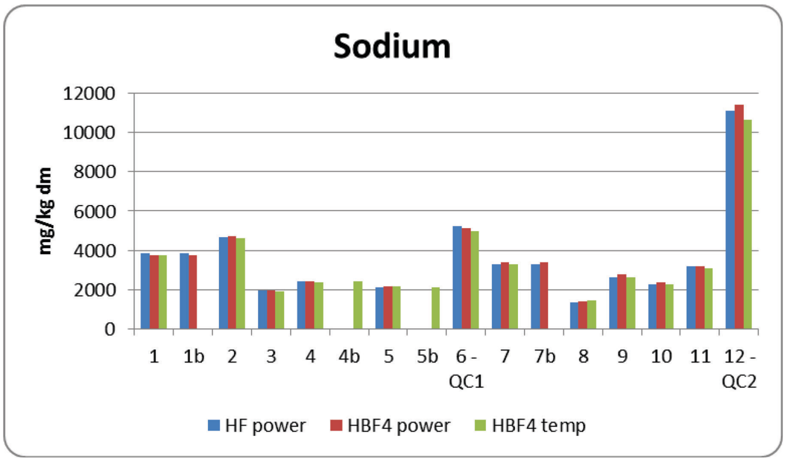

Figure 48 Na results of the soil samples using the 3 digestion methods

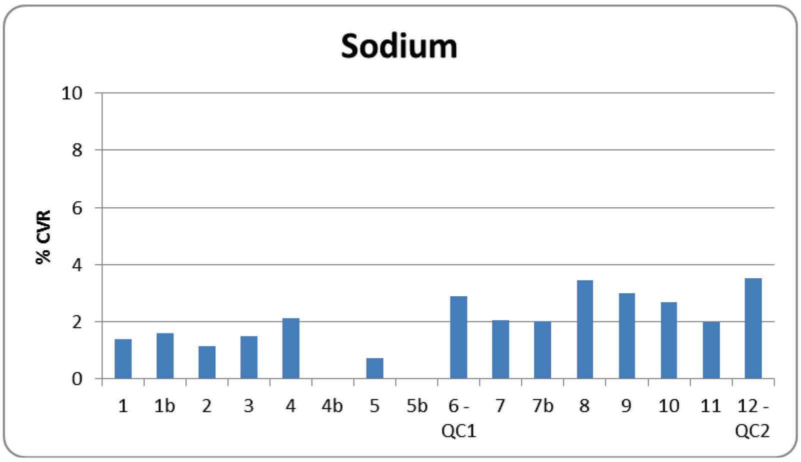

Figure 49 % CV_R of the 3 Na results by sample

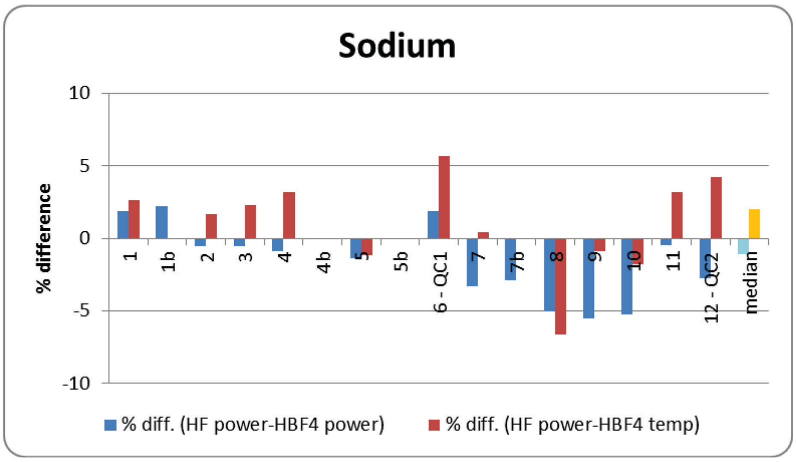

Figure 50 Difference between the reference method for Na and the 2 alternative methods

3.7.2. ELEMENT MAGNESIUM

In Figure 51 the Mg results of the different soil samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the Mg results with the 3 digestion methods was calculated per sample and are presented in Figure 52. From all samples analysed the CV_R is situated below 10%. The pooled CV_R of the 14 samples (including duplicate and QC samples) amounted 5.2%.

When calculating the % difference between the reference method (HF:HNO_3:HCl, power controlled digestion) and the 2 alternative methods (HBF_4, power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively -4.9 and 1.5% difference is observed (see Figure 53).

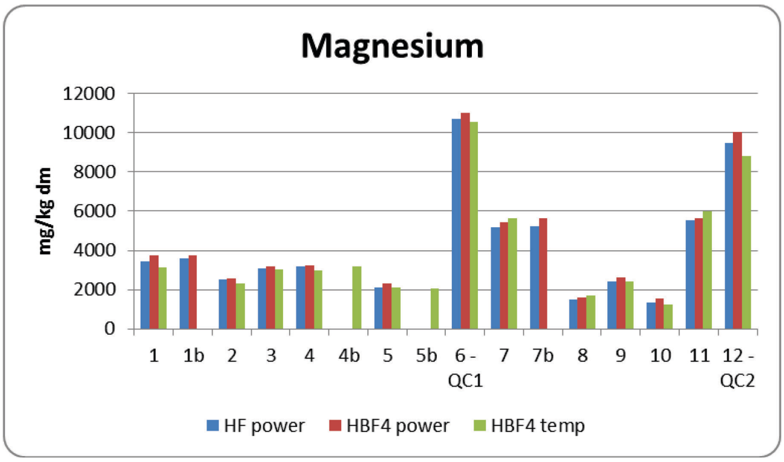

Figure 51 Mg results of the soil samples using the 3 digestion methods

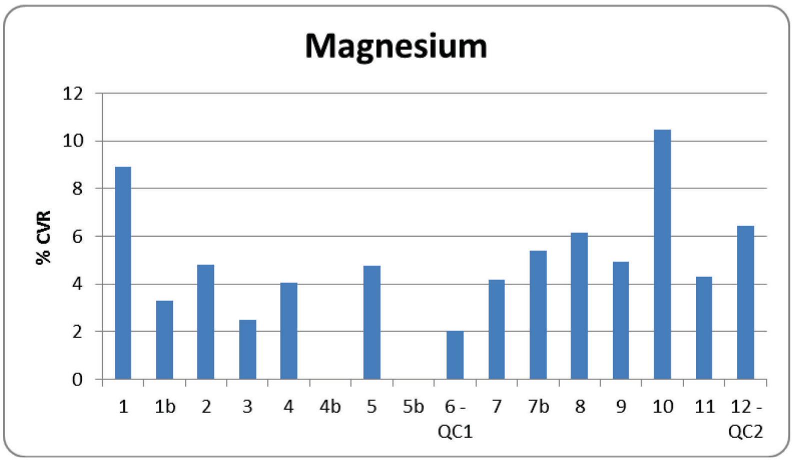

Figure 52 % CV_R of the 3 Mg results by sample

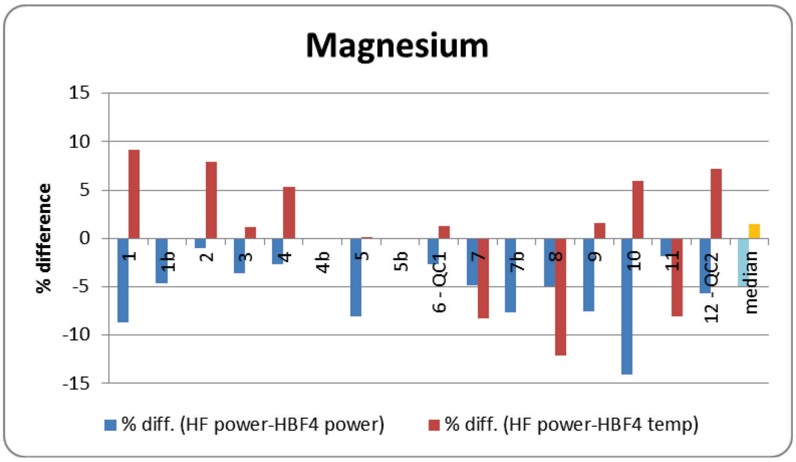

Figure 53 Difference between the reference method for Mg and the 2 alternative methods

3.7.3. ELEMENT ALUMINIUM

In Figure 54 the Al results of the different soil samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the Al results with the 3 digestion methods was calculated per sample and are presented in Figure 55. From all samples analysed the CV_R is situated below 12%. The pooled CV_R of the 14 samples (including duplicate and QC samples) amounted 6.5%.

When calculating the % difference between the reference method ($HF:HNO_3:HCl$, power controlled digestion) and the 2 alternative methods (HBF_4, power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively 0.3 and 6.9% difference is observed (see Figure 56).

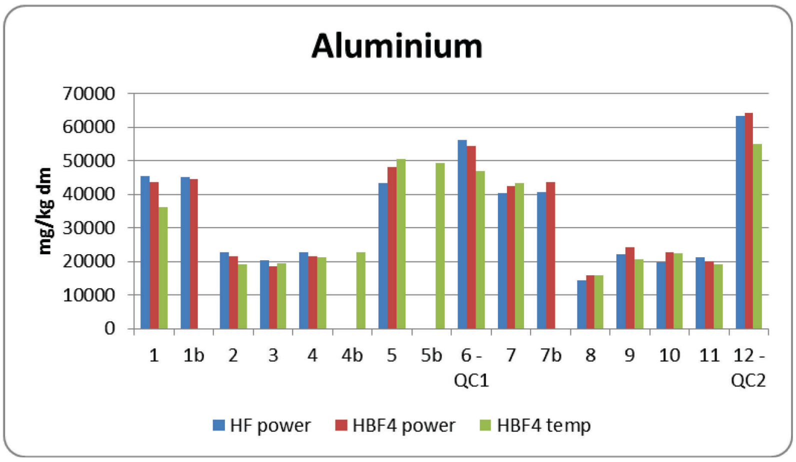

Figure 54 Al results of the soil samples using the 3 digestion methods

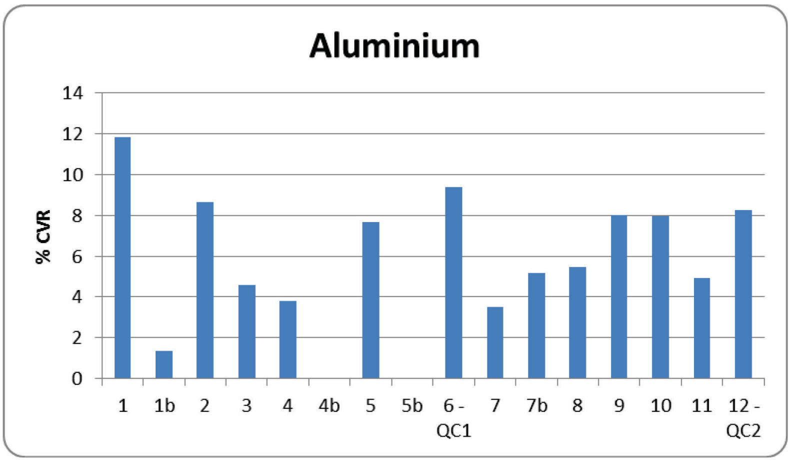

Figure 55 % CV$_R$ of the 3 Al results by sample

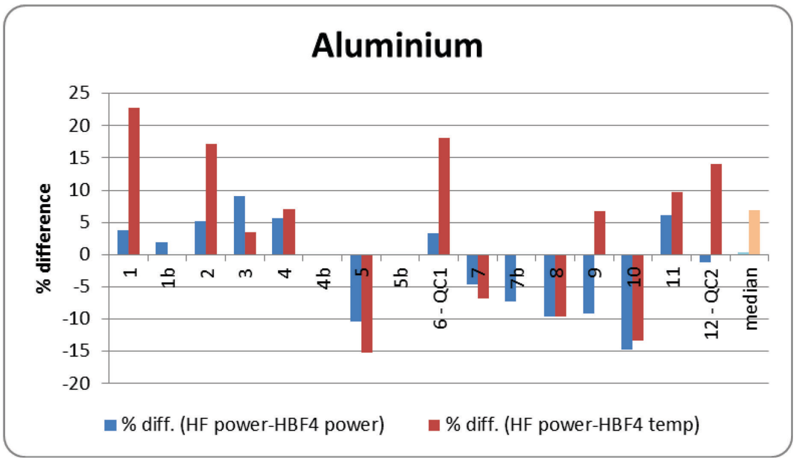

Figure 56 Difference between the reference method for Al and the 2 alternative methods

3.7.4. ELEMENT POTASSIUM

In Figure 57 the K results of the different soil samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the K results with the 3 digestion methods was calculated per sample and are presented in Figure 58. From all samples analysed the CV_R is situated below 9%. The pooled CV_R of the 14 samples (including duplicate and QC samples) amounted 3.9%.

When calculating the % difference between the reference method ($HF:HNO_3:HCl$, power controlled digestion) and the 2 alternative methods (HBF_4, power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively -1.7 and 2.8% difference is observed (see Figure 59).

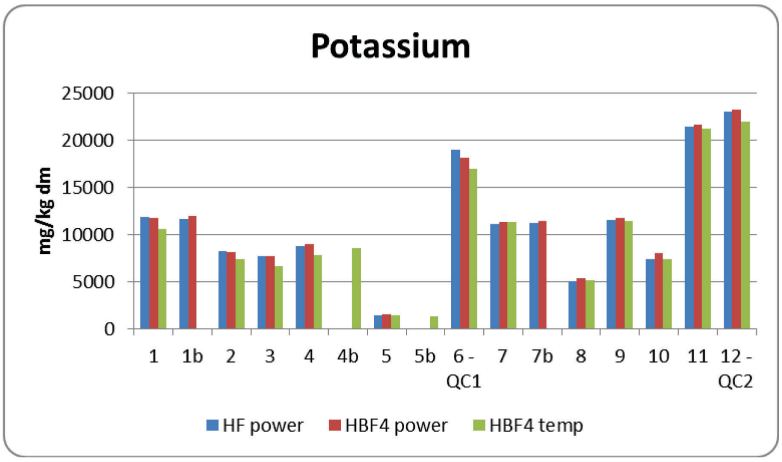

Figure 57 K results of the soil samples using the 3 digestion methods

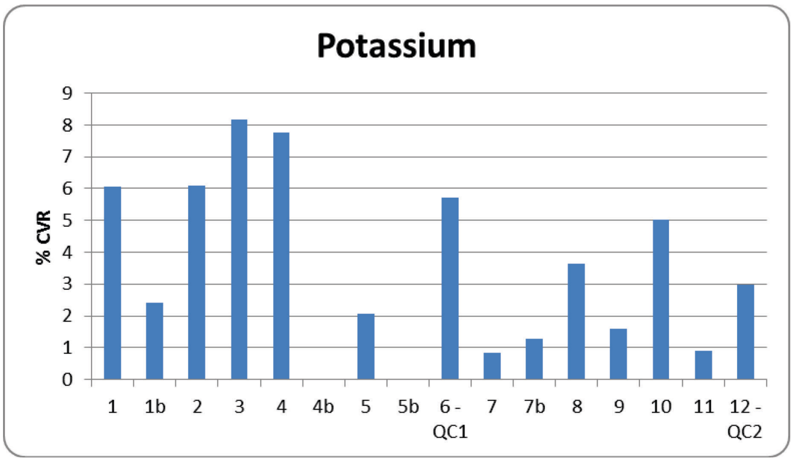

Figure 58 % CV_R of the 3 K results by sample

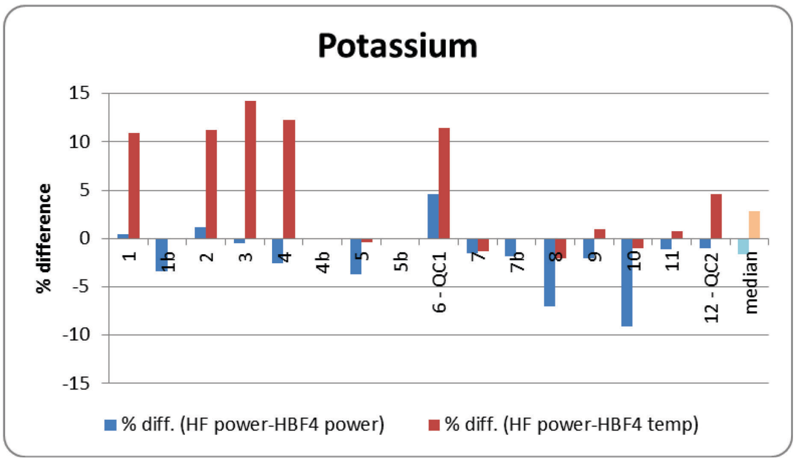

Figure 59 Difference between the reference method for K and the 2 alternative methods

3.7.5. ELEMENT CALCIUM

In Figure 60 the Ca results of the different soil samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the Ca results with the 3 digestion methods was calculated per sample and are presented in Figure 61. From all samples analysed the CV_R is situated below 10%. The pooled CV_R of the 14 samples (including duplicate and QC samples) amounted 4.0%.

When calculating the % difference between the reference method ($HF:HNO_3:HCl$, power controlled digestion) and the 2 alternative methods (HBF_4, power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively -0.8 and 4.8% difference is observed (see Figure 62).

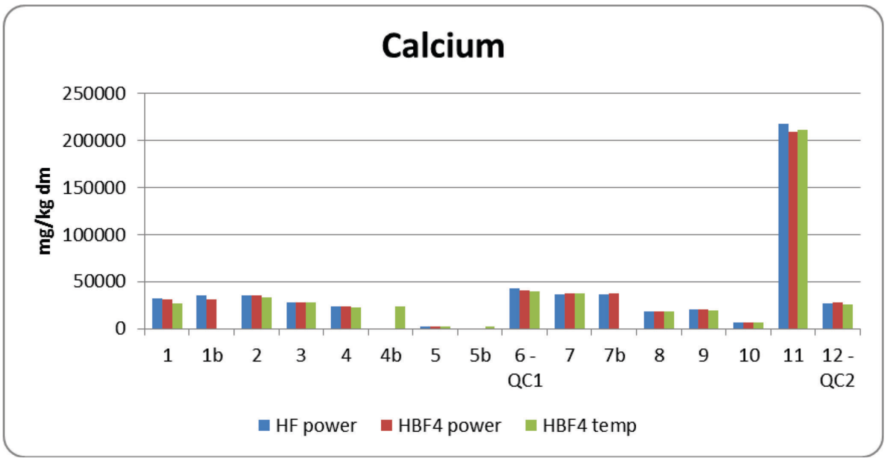

Figure 60 Ca results of the soil samples using the 3 digestion methods

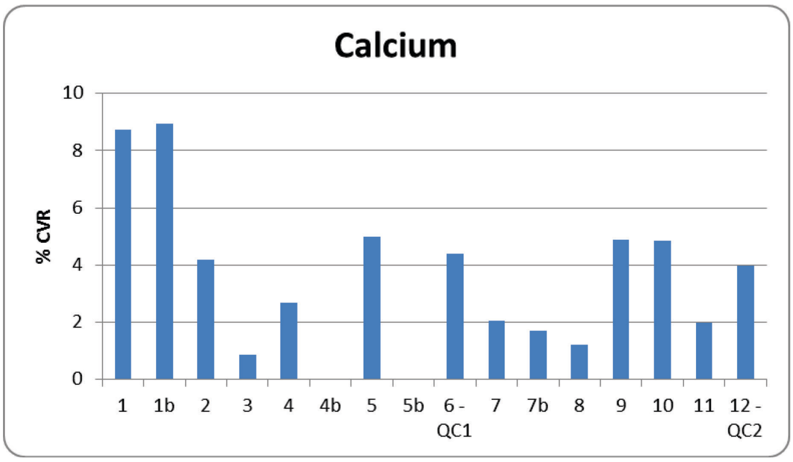

Figure 61 % CV_R of the 3 Ca results by sample

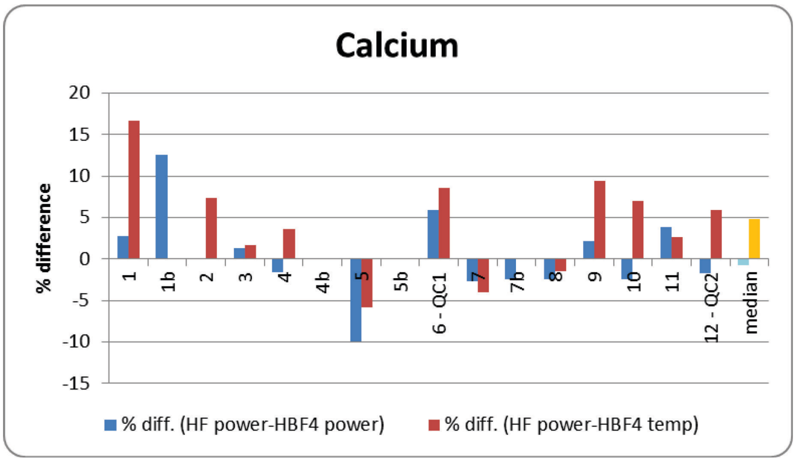

Figure 62 Difference between the reference method for Ca and the 2 alternative methods

3.7.6. ELEMENT TITANIUM

In Figure 63 the Ti results of the different soil samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the Ti results with the 3 digestion methods was calculated and are presented in Figure 64. From all samples analysed the CV_R is situated below 30%. The pooled CV_R of the 14 samples (including duplicate and QC samples) amounted 14%. For the Ti results differences are observed in comparison with the reference method, especially when applying the HBF_4 digestion with the power controlled microwave digestion. This digestion method results in a systematic underestimation of about 20%. When applying the HBF_4 digestion with the temperature controlled microwave digestion, this effect is not so pronounced present.

When calculating the % difference between the reference method ($HF:HNO_3:HCl$, power controlled digestion) and the 2 alternative methods (HBF_4, power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively 23 and 5.7% difference is observed (see Figure 65).

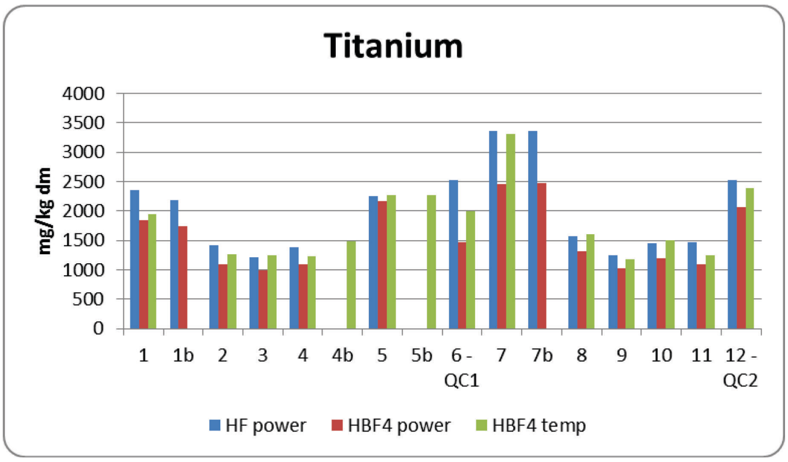

Figure 63 Ti results of the soil samples using the 3 digestion methods

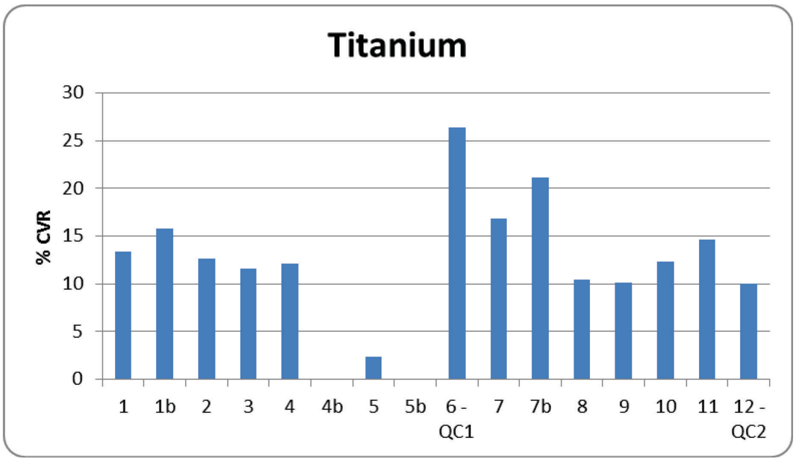

Figure 64 % CV$_R$ of the 3 Ti results by sample

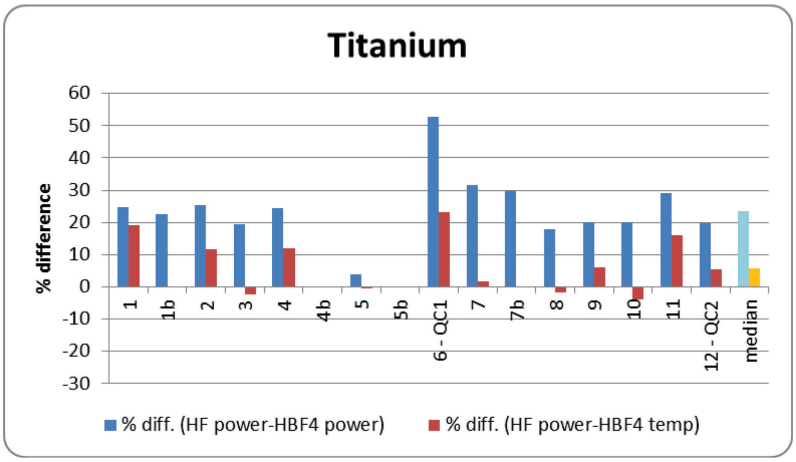

Figure 65 Difference between the reference method for Ti and the 2 alternative methods

3.7.7. ELEMENT MANGANESE

In Figure 66 the Mn results of the different soil samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the Mn results with the 3 digestion methods was calculated per sample and are presented in Figure 67. From all samples analysed the CV_R is situated below 8%. The pooled CV_R of the 14 samples (including duplicate and QC samples) amounted 3.7%.

When calculating the % difference between the reference method ($HF:HNO_3:HCl$, power controlled digestion) and the 2 alternative methods (HBF_4, power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively -4.5 and 0.7% difference is observed (see Figure 68).

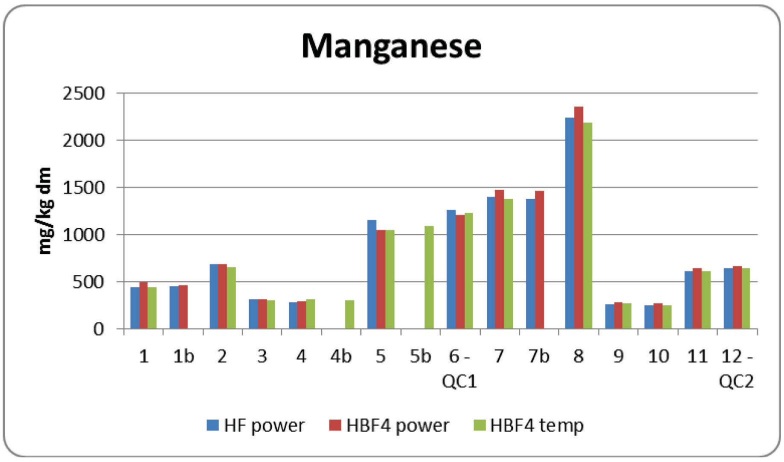

Figure 66 Mn results of the soil samples using the 3 digestion methods

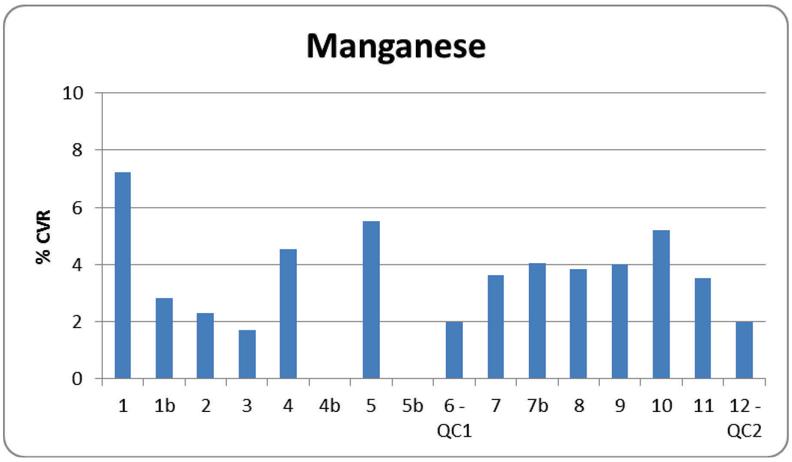

Figure 67 % CV_R of the 3 Mn results by sample

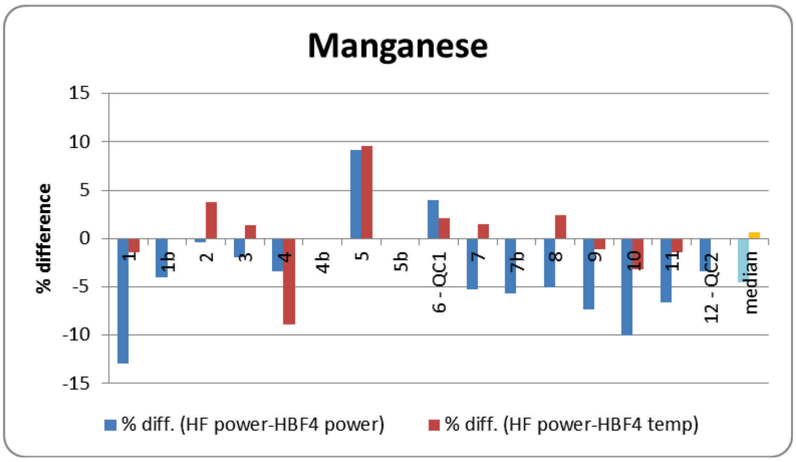

Figure 68 Difference between the reference method for Mn and the 2 alternative methods

3.7.8. ELEMENT IRON

In Figure 69 the Fe results of the different soil samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the Fe results with the 3 digestion methods was calculated per sample and are presented in Figure 70. From all samples analysed the CV_R is situated below 5%. The pooled CV_R of the 14 samples (including duplicate and QC samples) amounted 1.4%.

When calculating the % difference between the reference method ($HF:HNO_3:HCl$, power controlled digestion) and the 2 alternative methods (HBF_4, power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively -0.2 and -1.2% difference is observed (see Figure 71).

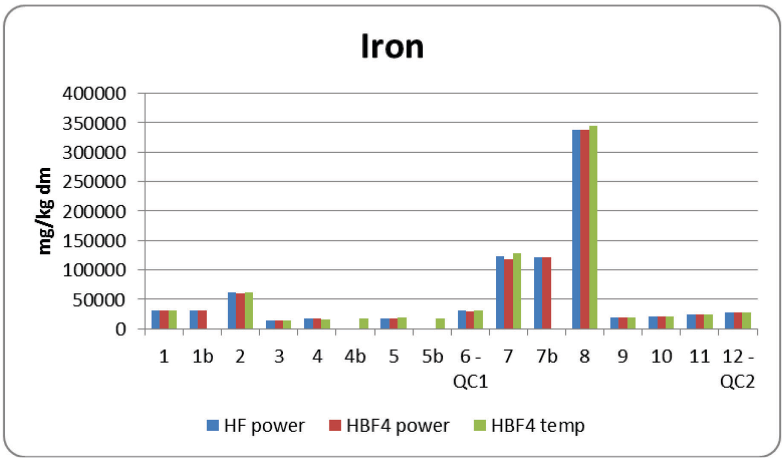

Figure 69 Fe results of the soil samples using the 3 digestion methods

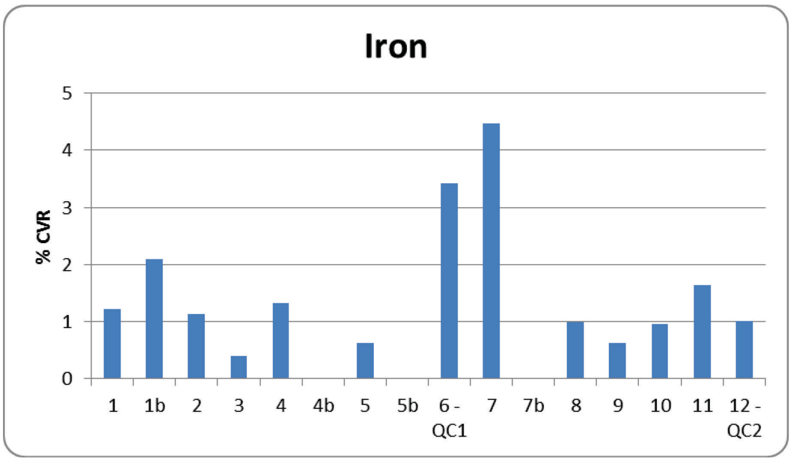

Figure 70 % CV_R of the 3 Fe results by sample

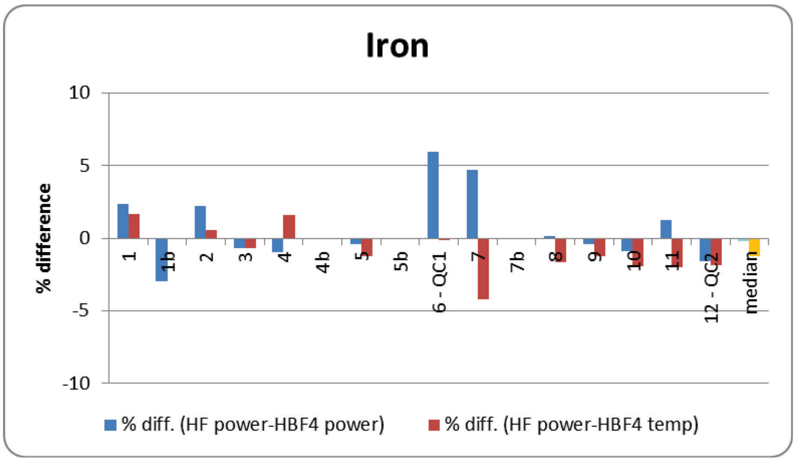

Figure 71 Difference between the reference method for Fe and the 2 alternative methods

3.8. EVALUATION OF THE TRUENESS OF THE QC SAMPLES IN THE DIGESTION RUN OF THE SOIL SAMPLES

During the digestion process two control samples were analysed together with the other soil samples. As control samples a round robin soil sample (SETOC 701) – QC1 - , distributed by Wageningen, and a certified soil samples (NIST 2711) – QC 2 – was included in the analytical process. For each digestion procedure, 2 digestion runs were carried out. The SETOC 701 control sample was always included in the first run of the digestion, the NIST 2711 was included in the second run. The obtained results and their recovery are presented in Table 2.

As reference value for the SETOC 701 QC sample, data of the available control chart were used. These control chart data were obtained after digestion with HF:HNO_3:HCl using a power controlled digestion programme. The reference value was derived on the basis of digestions with 4 ml HF (see remark) in stead of 2 ml HF. Maybe this might be the reason why the recovery for Cr is for the 3 applied digestion methods (with 2 ml of HF or HBF_4) limited to about 90%.

> Remark: To avoid gel formation in case Si is present in a high content (± 30%), 4 ml of HF is added for digestion.

Note that the performance check is based on the comparison of single measurement results.

Legend:

- HF power: digestion using HF:HNO_3:HCl with power controlled digestion procedure
- HBF_4 power: digestion using HBF_4 with power controlled digestion procedure
- HBF_4 temp: digestion using HBF_4 with temperature controlled digestion procedure

Table 2 Overview of the performance of the QC samples

	Digestion procedure	QC1 mg/kg dm	Ref.value mg/kg dm	Recovery %	Nist 2711 mg/kg dm	Ref. value mg/kg dm	Recovery %
As	**HF power**	35	33,6	105%	104	105	100%
	HBF4 power	35	33,6	103%	104	105	99%
	HBF4 temp	35	33,6	103%	100	105	95%
Cd	**HF power**	2,5	2,6	95%	39	41,7	95%
	HBF4 power	2,5	2,6	94%	41	41,7	98%
	HBF4 temp	2,5	2,6	96%	40	41,7	96%
Cr	**HF power**	121	131,8	92%	42	*47*	89%
	HBF4 power	117	131,8	89%	43	*47*	91%
	HBF4 temp	122	131,8	92%	42	*47*	89%
Cu	**HF power**	103	103,9	99%	119	114	105%
	HBF4 power	100	103,9	96%	115	114	101%
	HBF4 temp	101	103,9	97%	116	114	102%
Pb	**HF power**	167	171,5	97%	1102	1162	95%
	HBF4 power	167	171,5	98%	1124	1162	97%
	HBF4 temp	170	171,5	99%	1134	1162	98%
Ni	**HF power**	46	46,6	98%	21	20,6	101%
	HBF4 power	45	46,6	98%	22	20,6	106%
	HBF4 temp	45	46,6	97%	20	20,6	99%
Zn	**HF power**	487	515	95%	365	350,1	104%
	HBF4 power	492	515	95%	381	350,4	109%
	HBF4 temp	490	515	95%	356	350,4	102%
Sb	**HF power**				22	19,4	115%
	HBF4 power				22	19,4	112%
	HBF4 temp				21	19,4	111%
Ba	**HF power**				698	726	96%
	HBF4 power				681	726	94%
	HBF4 temp				657	726	90%
Co	**HF power**				9,3	*10*	93%
	HBF4 power				9,1	*10*	91%
	HBF4 temp				10	*10*	104%
Mo	**HF power**				1,7	*1,6*	105%
	HBF4 power				1,8	*1,6*	111%
	HBF4 temp				1,6	*1,6*	98%

	Digestion procedure	QC1 mg/kg dm	Ref.value mg/kg dm	Recovery %	Nist 2711 mg/kg dm	Ref. value mg/kg dm	Recovery %
V	**HF power**				91	81,6	112%
	HBF4 power				94	81,6	115%
	HBF4 temp				91	81,6	112%
Na	**HF power**				11093	11400	97%
	HBF4 power				11403	11400	100%
	HBF4 temp				10630	11400	93%
Mg	**HF power**				9487	10500	90%
	HBF4 power				10041	10500	96%
	HBF4 temp				8828	10500	84%
Al	**HF power**				63365	65300	97%
	HBF4 power				64150	65300	98%
	HBF4 temp				55086	65300	84%
K	**HF power**				23068	24500	94%
	HBF4 power				23299	24500	95%
	HBF4 temp				22023	24500	90%
Ca	**HF power**				27403	28800	95%
	HBF4 power				27876	28800	97%
	HBF4 temp				25820	28800	90%
Ti	**HF power**				2522	3060	82%
	HBF4 power				2067	3060	68%
	HBF4 temp				2388	3060	78%
Mn	**HF power**				638	638	100%
	HBF4 power				660	638	103%
	HBF4 temp				638	638	100%
Fe	**HF power**				27283	28900	94%
	HBF4 power				27721	28900	96%
	HBF4 temp				27800	28900	96%

Italic: indicative value

3.9. OVERVIEW OF ALL ELEMENTS

Per element and per sample the ratio was calculated between the alternative method (HBF_4 power or HBF_4 temp) and the reference method (HF power). The distribution for the different elements is presented by a Box and Whisker plot, as shown in Figure 72 till Figure 76. Note that the evaluation is based on the comparison of single measurement results.

Legend

R1	Ratio HBF_4 acid digestion, power controlled versus HF digestion, power controlled
R2	Ratio HBF_4 acid digestion, temperature controlled versus HF digestion, power controlled

For the elements As, Cd, Cr, Cu, Pb, Ni, Zn and Hg in soil samples the median values fluctuate around 1, indicating that comparable results are obtained with the reference method and the alternative methods. Globally, most of the data results in a ratio between 0.8 and 1.2.

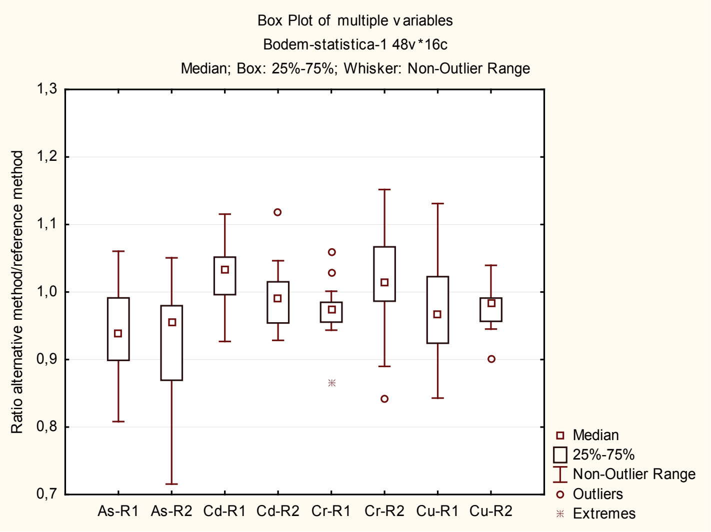

Figure 72 Overview ratio alternative methods vs the reference method for the elements As, Cd,Cr and Cu in soil samples

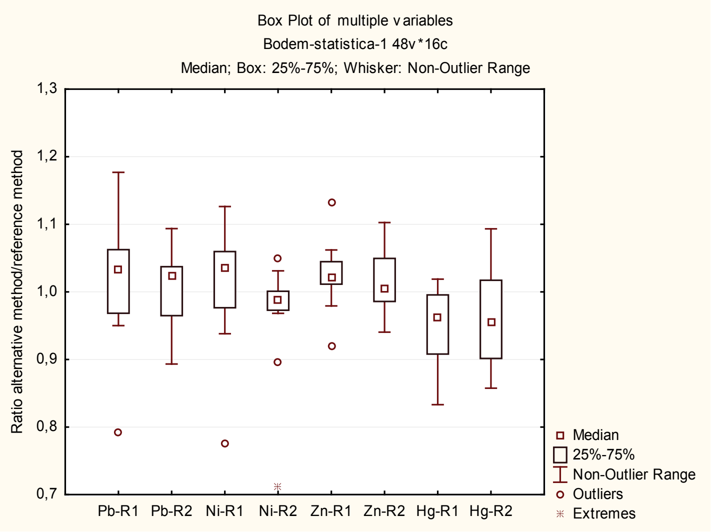

Figure 73 Overview ratio alternative methods vs the reference method for the elements Pb, Ni, Zn and Hg in soil samples

For the other trace elements Sb, Ba, Co , Mo and V in soil samples the median values also fluctuate around 1, indicating a good correspondence. Most of the data results in a ratio between 0.8 and 1.2.

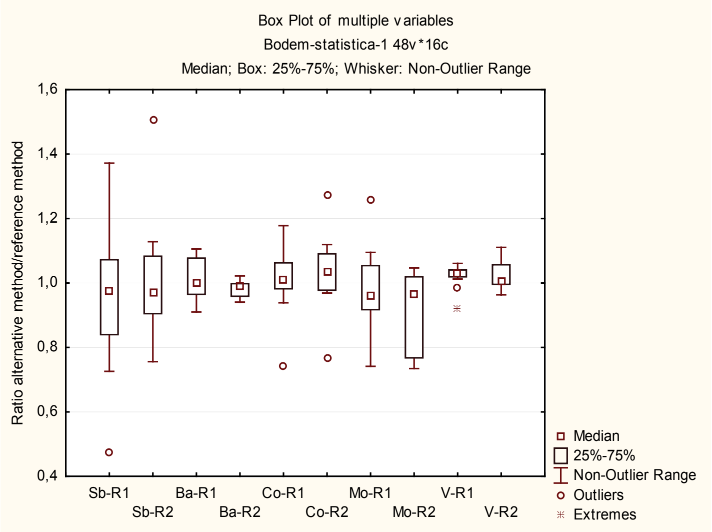

Figure 74 Overview ratio alternative methods vs the reference method for the elements Sb, Ba, Co , Mo and V in soil samples

For the major elements Na, Mg, Al, K, Ca, Ti, Mn and Fe in soil samples also a median ratio around 1 is obtained, except for the element Ti. Especially the results obtained with the ‘HBF_4 power’ method are significantly lower than with the reference method ‘HF power’. Globally, with exception for Ti, most of the data are situated between a ratio of 0.8 and 1.1.

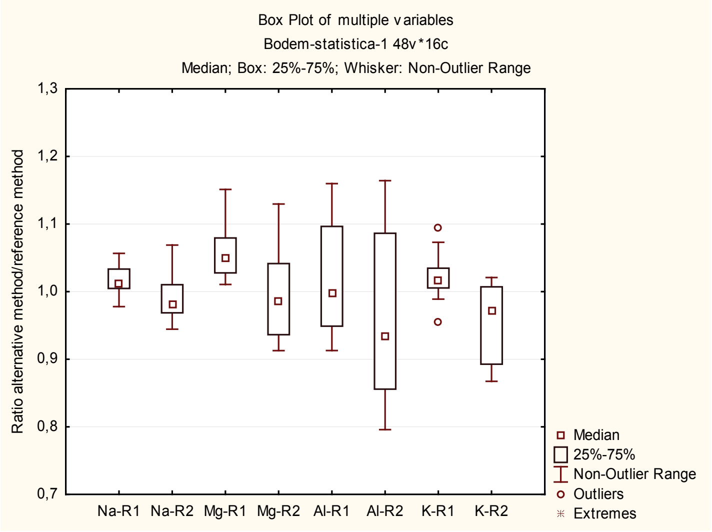

Figure 75 Overview ratio alternative methods vs the reference method for the elements Na, Mg, Al and K in soil samples

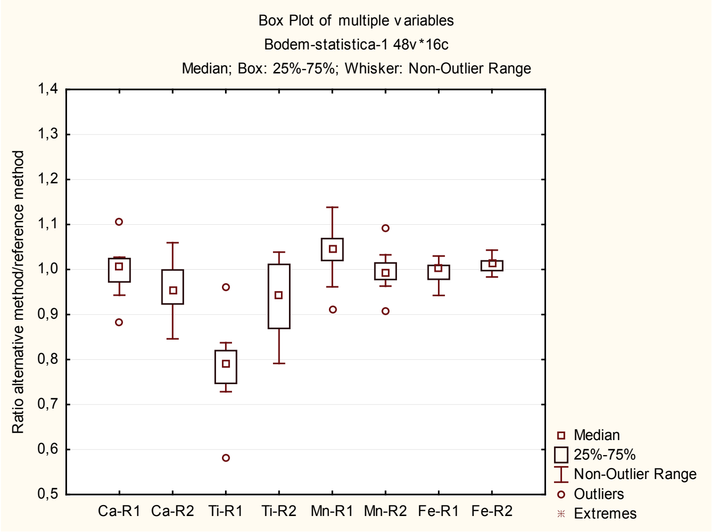

Figure 76 Overview ratio alternative methods vs the reference method for the elements Ca, Ti, Mn and Fe in soil samples

CHAPTER 4 DIGESTION OF WASTE SAMPLES

4.1. INTRODUCTION

In Flanders, soil and waste samples are digested using the same digestion method with HF:HNO_3:HCl. In case a soil sample is contaminated with several elements, it might be considered as a waste sample. Using the same digestion method, the obtained results can be verified towards the legislative values of soils as well as of waste.

Untill now waste samples were digested using an acid mixture of HF:HNO_3:HCl and a power controlled microwave digestion oven, according to the procedure describe in NBN EN 13656.
In this study the following two items were evaluated:

3. *Evaluation of an alternative acid (one-step digestion) as replacement for two-steps digestion with HF + H_3BO_3*
   This involves a one-step digestion, while maintaining the same power of digestion of the silicate matrix, by using HBF_4 (replacing HF with H_3BO_3). In addition, the use of HBF_4 is for safety reasons preferred over HF.
4. *Evaluation of temperature controlled microwave systems as an addition to power controlled microwave systems*
   Comparison of the CMA/2/II/A.3 procedure using power controlled microwave oven versus temperature controlled digestion. The evaluation was performed using the HBF_4 acid digestion.

4.2. SELECTED WASTE SAMPLES

A different range of waste samples were selected for evalution of the digestion procedure, among which also waste samples used in the validation study of EN 13656 and EN 13657, performed in 1999. The following waste samples were selected:

- 20143957: Shredder (< 1 mm)
- 20143958: Sewage sludge
- 20143959: Bottom ash
- 20143960: Sewage sludge
- 20143961: Sample CEN 6/99 Fly ash CW6
- 20143962: Sample CEN 7/99 Bottom ash CW4
- 20143963: Sample CEN 8/99 Ink waste CW12
- 20143964: Sample CEN 9/99 Sewage sludge of electronic waste SL 11
- 20143965: Sample CEN 10/99 Sewage sludge BCR 146R (certified reference sample)
- 20143966: Sample BCR 176R Incineration ash powder (replaces CEN 11/99 BCR 176: same matrix, other reference values)

The samples from 20143961 to 20143965 were the same samples used in the validation trial of EN 13656 and 13657, and they were already dried and fine ground. Sample 20143966 is a certified reference material which was also used in the validation trial of 1999, but now the successor was applied resulting in a sample with a similar matrix but with different concentrations. Before digestion, only a short drying period of about 4 hrs at 105°C was applied. The shredder sample was dried at 105°C and fine ground with a cutting mill to a particle size < 1 mm. The samples from 20143958 to 20143960 were dried at 105°C overnight and fine ground with the planetary ball mill (according to EN 13656 < 250 µm). As control samples a round robin soil sample (SETOC 701) – QC1 - , distributed by Wageningen, and a certified soil samples (NIST 2711) – QC 2 – were included in the analytical process.

4.3. DESCRIPTION DIGESTION PROCEDURE AND ICP-AES/CV-AFS MEASUREMENTS

All digestions were performed using an Anton Paar microwave system (Multiwave 3000). The system is equipped with an immersing temperature probe with integrated pressure sensor which is positioned in one reference vessel and infrared sensors are located underneath the rotor to simultaneously measure the temperature and pressure of each vessel. The system is capable of performing digestions using a power controlled or a temperature controlled microwave programme.

The digested solutions were analysed with ICP-AES[e] (Perkin Elmer, Optima 3000) for the determination of the elements. The calibration was set-up with matrix-matched standards fot both axial and radial view. After digestion a dilution of at least a factor of 5 was applied, except for the determination of element concentrations nearby the reporting limit. As internal standard Rh was used and the suppression of the internal standard was for all samples limited to maximum 10%. Data obtained in axial view were Rh corrected, while no Rh correction was applied on data measured in radial view.
Mercury was determined with CV-AFS[f] (Leeman, HYDRA AF Automated Hg-analyzer).

4.3.1. DIGESTION WITH HF:HNO_3:HCL AND POWER CONTROLLED MICROWAVE DIGESTION (HF POWER)

About 0.5 g of sample was weighed into the vessel. Then the following acids were separately added: 6 ml HCl, 2 ml HNO_3 and 2 ml HF. The digestion vessel was placed into the microwave unit (8 positions) and the following digestion process was applied:

	Time (min)	Power (W)
Stap 1	2	250
Stap 2	2	0
Stap 3	5	250
Stap 4	5	400
Stap 5	5	500

At the end of the programme the vessels were cooled down to room temperature. Subsequently, 22 ml of 4% m/m of boric acid was added and the vessels were placed in the microwave unit applying the following process:

Time (min)	Power (W)
3	300

After cooling the digested solution was transferred to a volumetric flask and filled up to 100 ml with ultrapure water.

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[e] Inductively coupled plasma atomic emission spectrometry
[f] Cold vapour atomic fluorescence spectrometry

Each batch contains 1 blank, 1 control sample (QC1 or QC2), 5 samples and 1 duplo sample.

4.3.2. DIGESTION WITH HBF_4 AND POWER CONTROLLED MICROWAVE DIGESTION (HBF_4 POWER)

About 0.5 g of sample was weighed into the vessel. Then the following acids were separately added: 6 ml HCl, 2 ml HNO_3 and 2 ml HBF_4 and the following digestion process was applied:

Time (min)	Power (W)
2	250
2	0
5	250
5	400
5	500

After cooling the digested solution was transferred to a volumetric flask and filled up to 100 ml with ultrapure water.

Each batch contains 1 blank, 1 control sample (QC1 or QC2), 5 samples and 1 duplo sample.

4.3.3. DIGESTION WITH HBF_4 AND TEMPERATURE CONTROLLED MICROWAVE DIGESTION (HBF_4 TEMP)

About 0.5 g of sample was weighed into the vessel. The acids 6 ml HCl, 2 ml HNO_3 and 2 ml HBF_4 were separately added. The digestion vessel was placed into the microwave unit (8 positions) and the temperature was raised with a heating rate of 15°C min^{-1} to 175°C and remained at 175°C for 10 minutes. After cooling the digested solution was transferred to a volumetric flask and filled up to 100 ml with ultrapure water.

Each batch contains 1 blank, 1 control sample (QC1 or QC2), 5 samples and 1 duplo sample.

4.4. EVALUATION OF THE DIGESTION PROCESS

As the system is equipped with an immersing temperature probe with integrated pressure sensor in the first reference vessel and infrared sensors to measure the temperature of each vessel, is was interesting to follow up the digestion profiles during the complete cycle.

In Figure 77 and Figure 78 the digestion profiles of the waste samples using HF:HNO_3:HCl (run 1 and run 2, respectively) with a power controlled program are shown. The temperature in vessel 1, monitored with the probe, raised up to 145-150°C when reaching the full power of 500 W. The temperature profiles, monitored with the IR sensor, looks quite similar (except the one of the blanc samples, which has a lower maximum temperature).

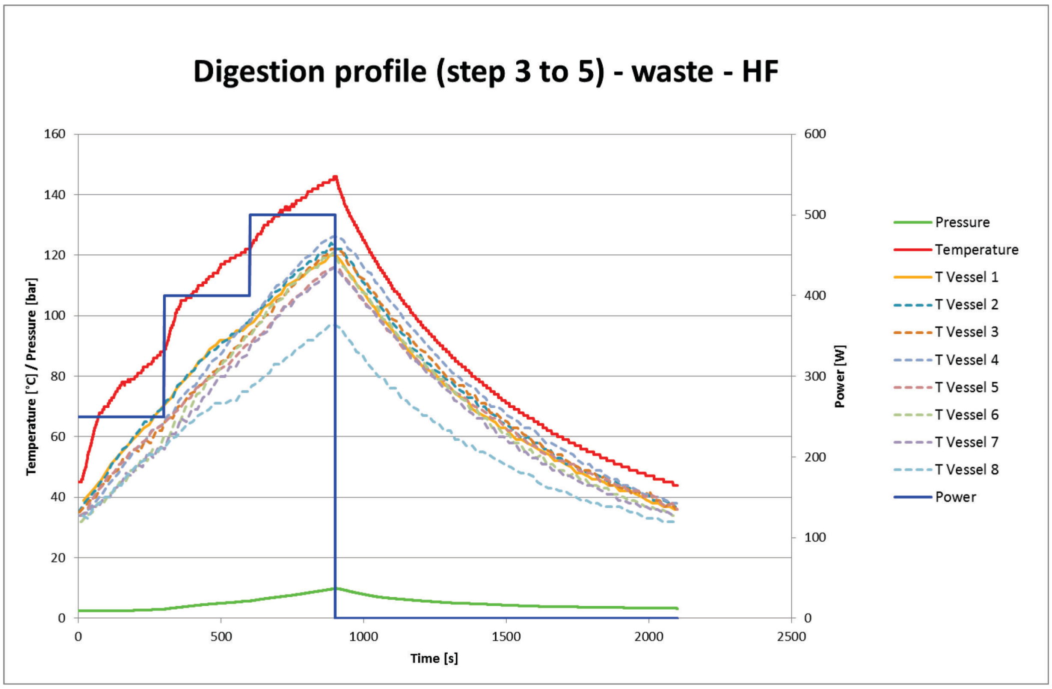

Figure 77 Digestion profile of the waste samples using HF:HNO_3:HCl (run 1) – power controlled program

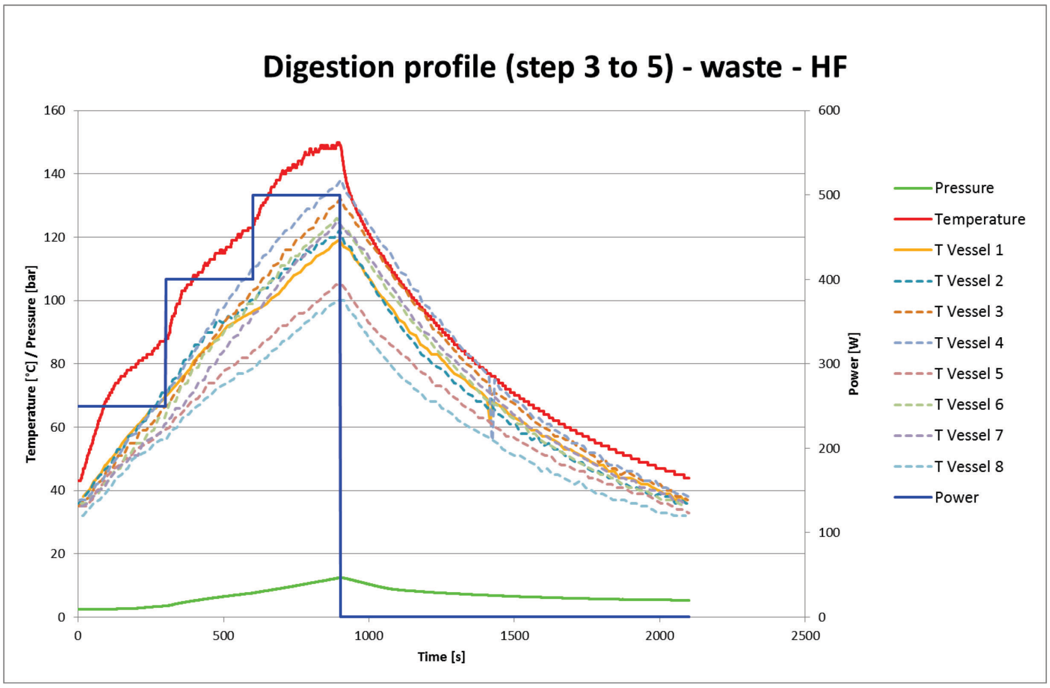

Figure 78 Digestion profile of the waste samples using HF:HNO_3:HCl (run 2) – power controlled program

In Figure 79 and Figure 80 the digestion profiles of the waste samples using HBF_4 (run 1 and run 2, respectively) with a power controlled program are shown. The temperature in vessel 1, monitored with the probe, raised up to 140-160°C when reaching the full power of 500 W. The temperature profiles, monitored with the IR sensor, looks quite similar (except the one of the blanc samples, which has a lower maximum temperature).

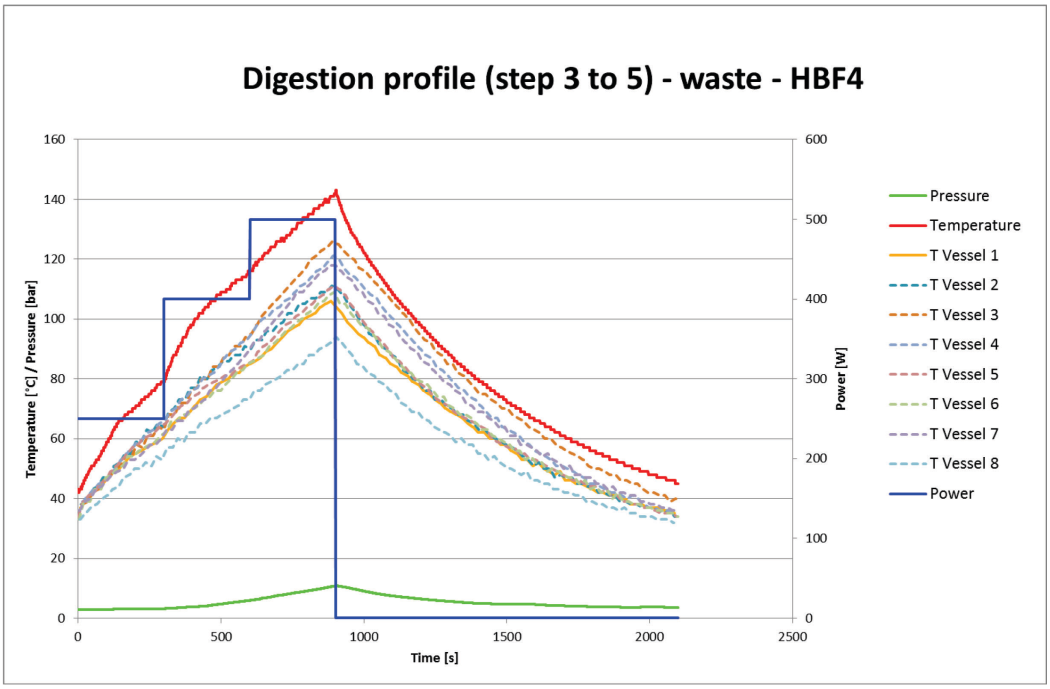

Figure 79 Digestion profile of the waste samples using HBF_4 (run 1) – power controlled program

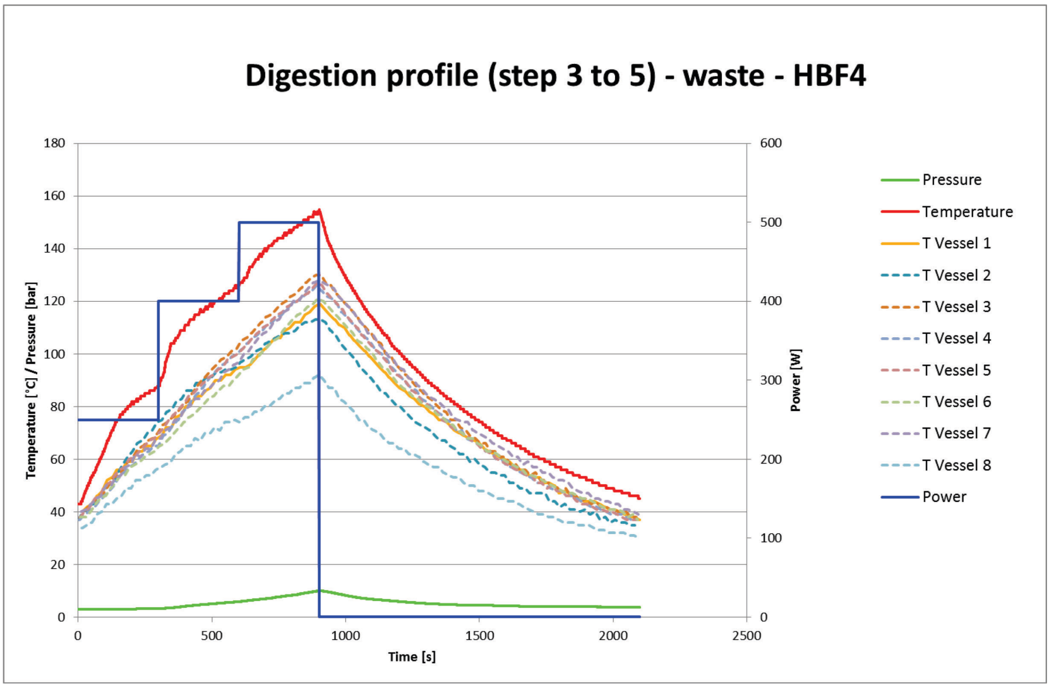

Figure 80 Digestion profile of the waste samples using HBF_4 (run 2) – power controlled program

In Figure 81 the digestion profile of the waste samples using HBF_4 (run 1) with a temperature controlled program are shown. In run 1 the temperature is raised up to 175°C. All the IR measurement shows comparable profiles with temperatures between 140 and 180°C. The power increased up to about 1100 W and then drops to about 400 W. In the meanwhile the pressure is increased up to 25 bar when reaching the max. power of 1100 W.

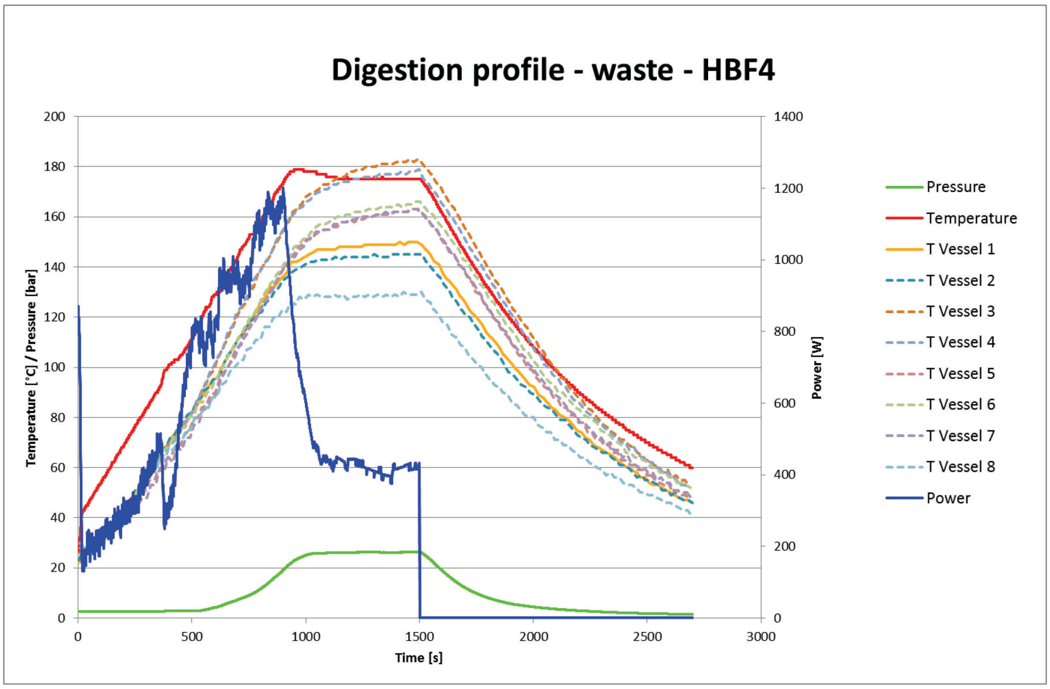

Figure 81 Digestion profile of the soil samples using HBF_4 (run 1) – temperature controlled program

4.5. RESULTS OF THE VLAREMA ELEMENTS

The EU Directive 99/31/EC on the landfill of waste and the EU Directive 2000/76/EC on the incineration of waste several elements is implemented in the Flemish regulation on sustainable management of material cycles and waste (VLAREMA). In VLAREMA 4bis (draft dec 2013) the following elements are of interest: As, Cd, Cr, Cu, Pb, Ni, Zn, Hg, Tl, Sb, Co, V, Sn, Ba and Mo. The element Mn is also treated in this chapter.

In the following paragraphs the results obtained with the different digestion procedures are presented per element. Duplicate samples (including digestion) are marked with ‘b’. The reference method is always indicated as ‘HF power’, while the alternative methods are indicated as ‘HBF_4 power’ and HBF_4 temp’. <u>Note that the evaluation is based on the comparison of single measurement results.</u>

The evaluation of the different samples, selected from the validation study of EN 13656:2002, is per sample described in paragraphs 4.8 till 4.13 starting on page 83. An overview of all elements is presented in paragraph 4.15 on page 95.

The individual results for all samples, parameters and digestions are compiled in Annex B.

4.5.1. ELEMENT ARSENIC

In Figure 82 the As results of the different waste samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the As results with the 3 digestion methods was calculated per sample and are presented in Figure 83. From all samples analysed the CV_R is situated below 18%. The pooled CV_R of the 14 samples (including duplicate and QC samples) amounted 8.7%.

When calculating the % difference between the reference method ($HF:HNO_3:HCl$, power controlled digestion) and the 2 alternative methods (HBF_4, power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively 2.5 and -4.5% difference is observed (see Figure 84).

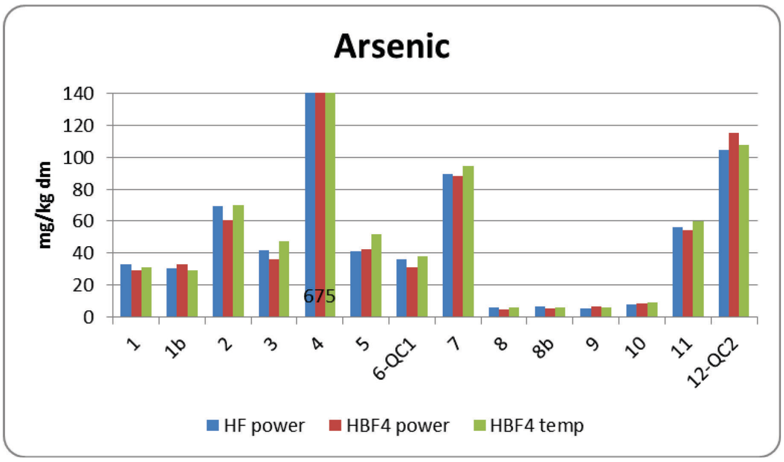

Figure 82 As results of the waste samples using the 3 digestion methods

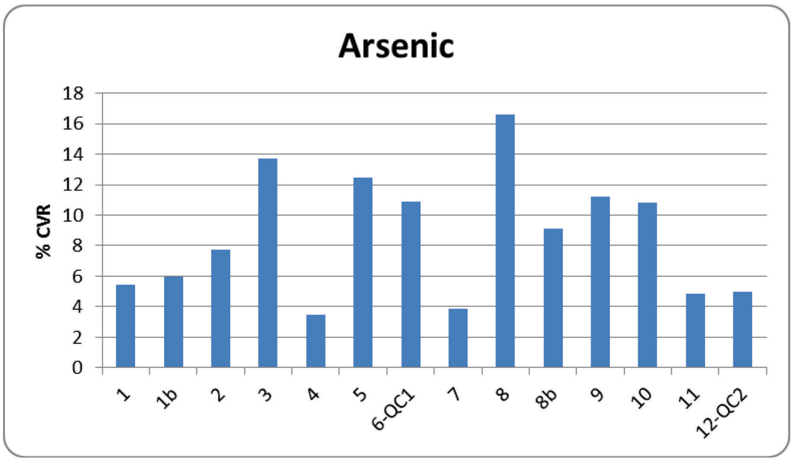

Figure 83 % CV_R of the 3 As results by sample

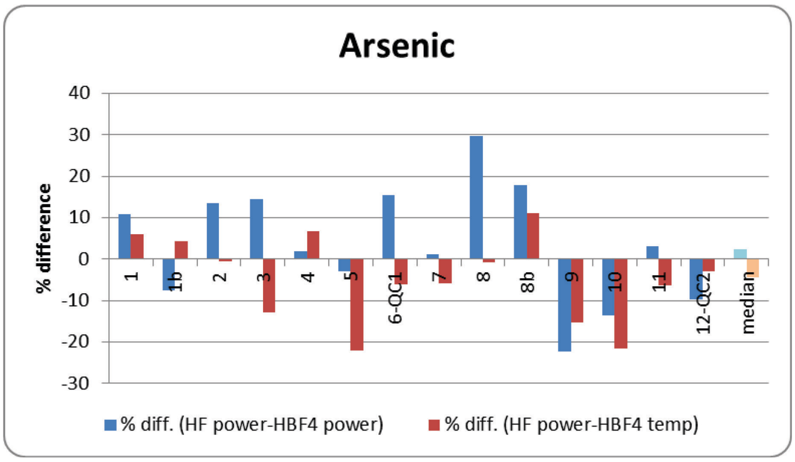

Figure 84 Difference between the reference method for As and the 2 alternative methods

4.5.2. ELEMENT CADMIUM

In Figure 85 the Cd results of the different waste samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the Cd results with the 3 digestion methods was calculated per sample and are presented in Figure 86. From all samples analysed the CV_R is situated below 8%. The pooled CV_R of the 11 samples (including duplicate and QC samples) amounted 3.8%.

When calculating the % difference between the reference method ($HF:HNO_3:HCl$, power controlled digestion) and the 2 alternative methods (HBF_4, power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively 2.2 and -1.1% difference is observed (see Figure 87).

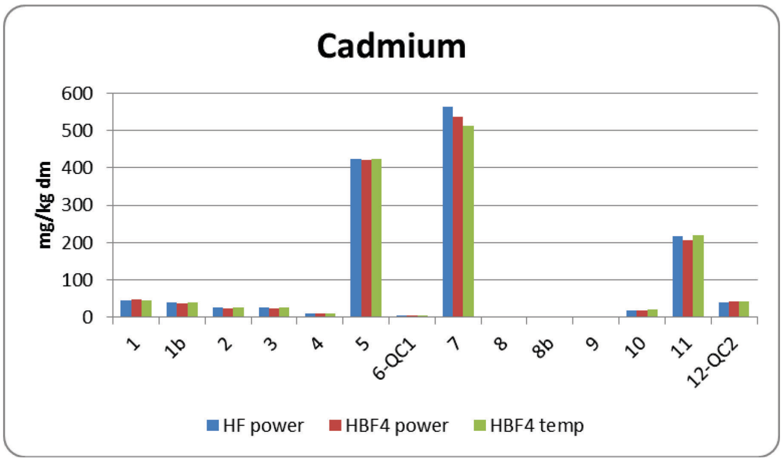

Figure 85 Cd results of the waste samples using the 3 digestion methods

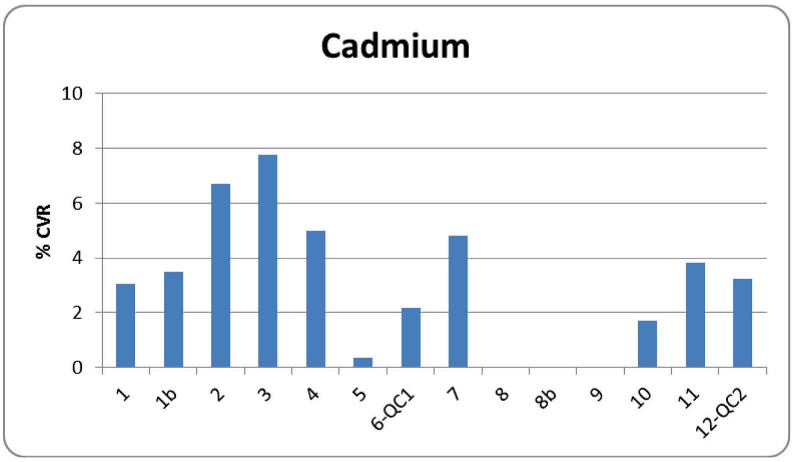

Figure 86 % CV_R of the 3 Cd results by sample

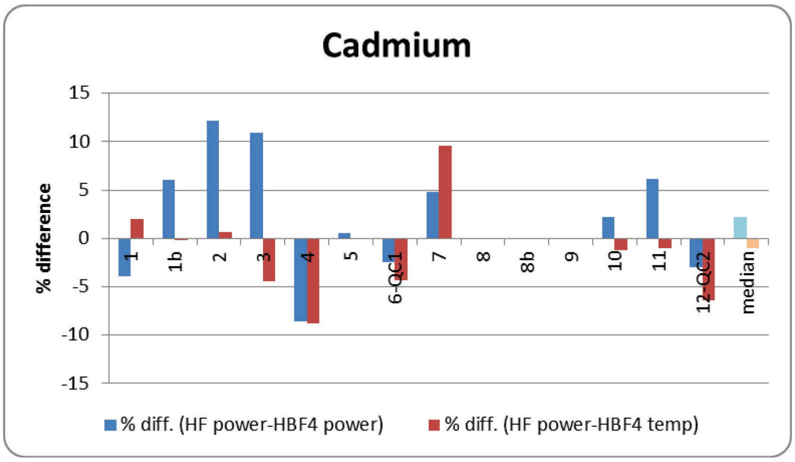

Figure 87 Difference between the reference method for Cd and the 2 alternative methods

4.5.3. ELEMENT CHROMIUM

In Figure 88 the Cr results of the different waste samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the Cr results with the 3 digestion methods was calculated per sample and are presented in Figure 89. From all samples analysed the CV_R is situated below 20%. The pooled CV_R of the 14 samples (including duplicate and QC samples) amounted 7.0%.

When calculating the % difference between the reference method (HF:HNO_3:HCl, power controlled digestion) and the 2 alternative methods (HBF_4, power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively 2.1 and -4.8% difference is observed (see Figure 90).

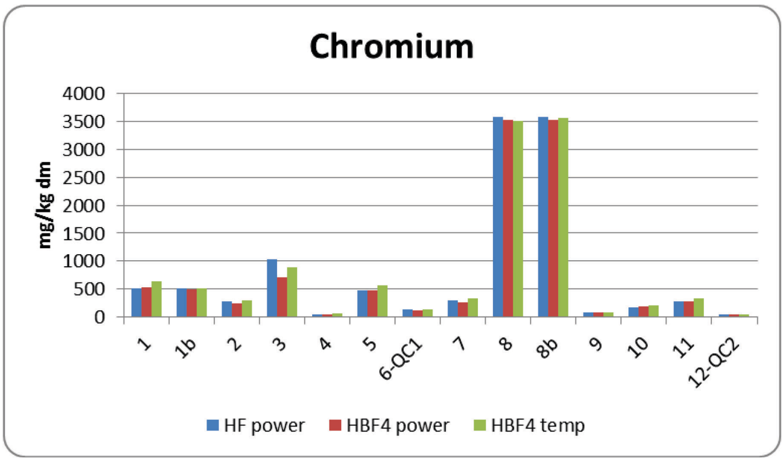

Figure 88 Cr results of the waste samples using the 3 digestion methods

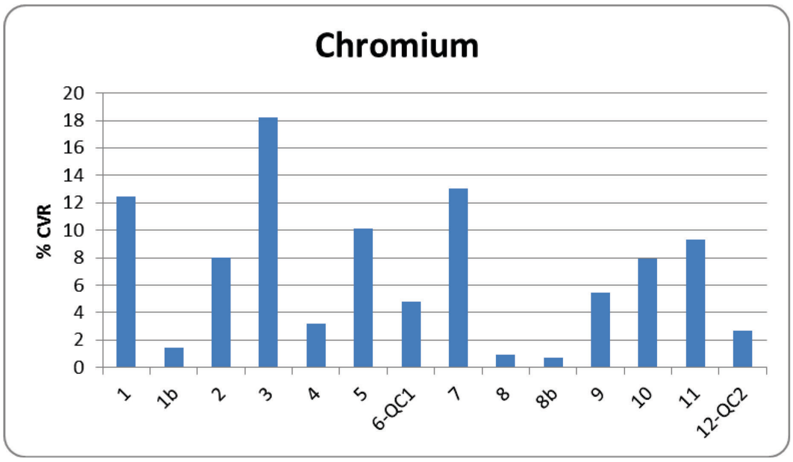

Figure 89 % CV$_R$ of the 3 Cr results by sample

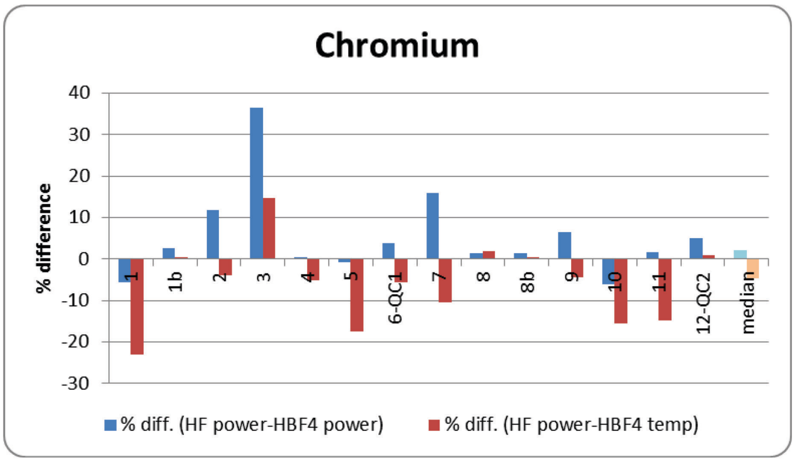

Figure 90 Difference between the reference method for Cr and the 2 alternative methods

4.5.4. ELEMENT CUPPER

In Figure 91 the Cu results of the different waste samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the Cu results with the 3 digestion methods was calculated per sample and are presented in Figure 92. From all samples analysed the CV_R is situated below 25%, for most of the samples even less than 10%. The pooled CV_R of the 14 samples (including duplicate and QC samples) amounted 6.3%. It should be noted that for sample 1 (shredder) the measurement deviation is larger compared to the other samples. This is also observed for other elements e.g. Mn, Mo, Na, Sn, Ti, and probably attributed to the heterogeneity of the sample rather than to the digestion procedure. Especially with a particle size of < 1 mm a larger measurement deviation can be expected.

When calculating the % difference between the reference method ($HF:HNO_3:HCl$, power controlled digestion) and the 2 alternative methods (HBF_4, power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively 0.4 and -1.2% difference is observed (see Figure 93).

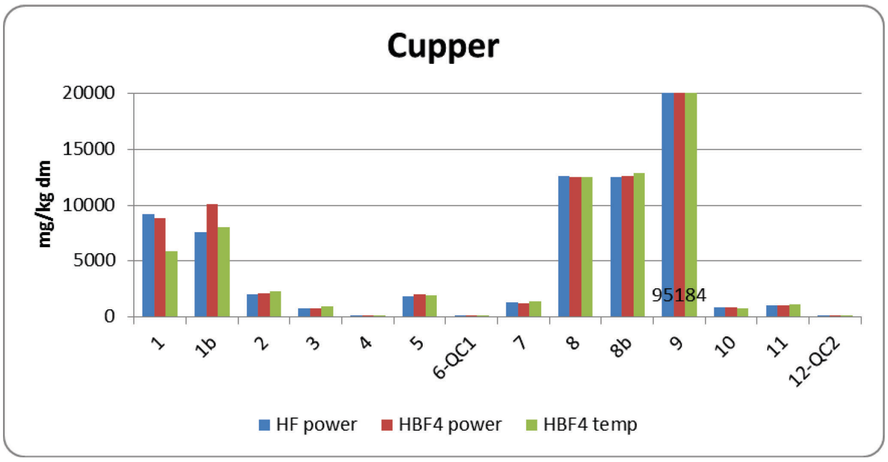

Figure 91 Cu results of the waste samples using the 3 digestion methods

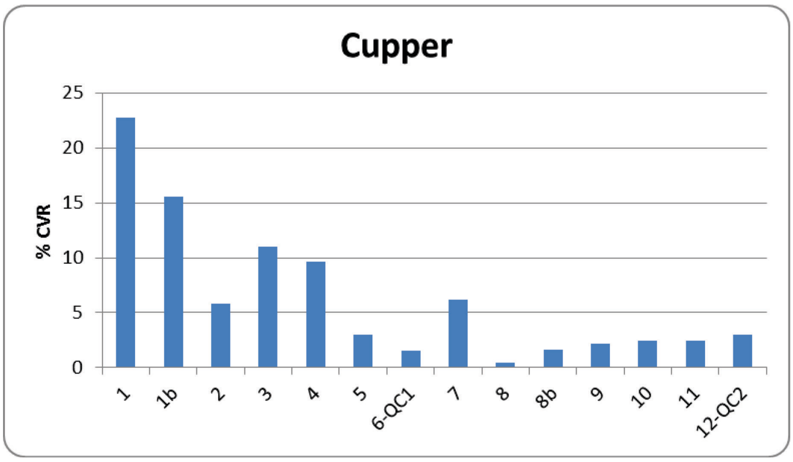

Figure 92 % CV_R of the 3 Cu results by sample

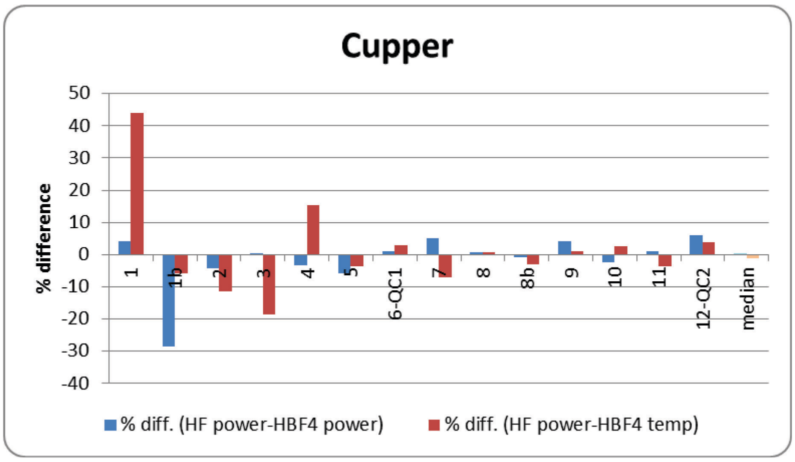

Figure 93 Difference between the reference method for Cu and the 2 alternative methods

4.5.5. ELEMENT LEAD

In Figure 94 the Pb results of the different waste samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the Pb results with the 3 digestion methods was calculated per sample and are presented in Figure 95. From all samples analysed the CV_R is situated below 10%. The pooled CV_R of the 14 samples (including duplicate and QC samples) amounted 3.1%.

When calculating the % difference between the reference method ($HF:HNO_3:HCl$, power controlled digestion) and the 2 alternative methods (HBF_4, power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively 0.3 and 0.1% difference is observed (see Figure 96).

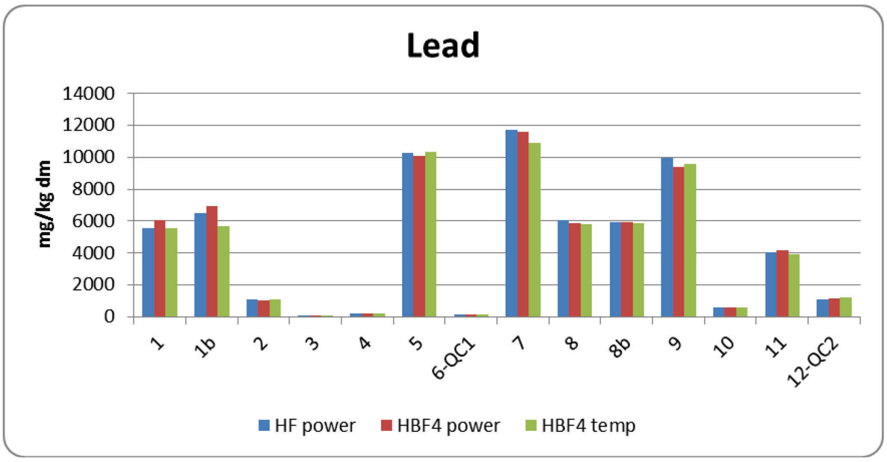

Figure 94 Pb results of the waste samples using the 3 digestion methods

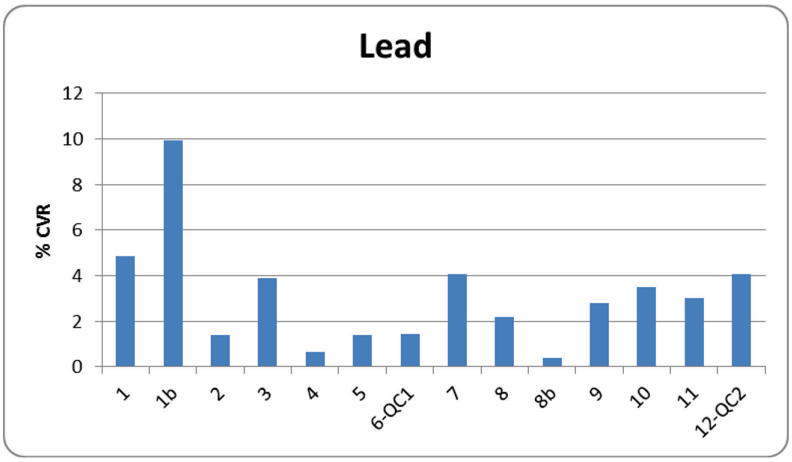

Figure 95 % CV_R of the 3 Pb results by sample

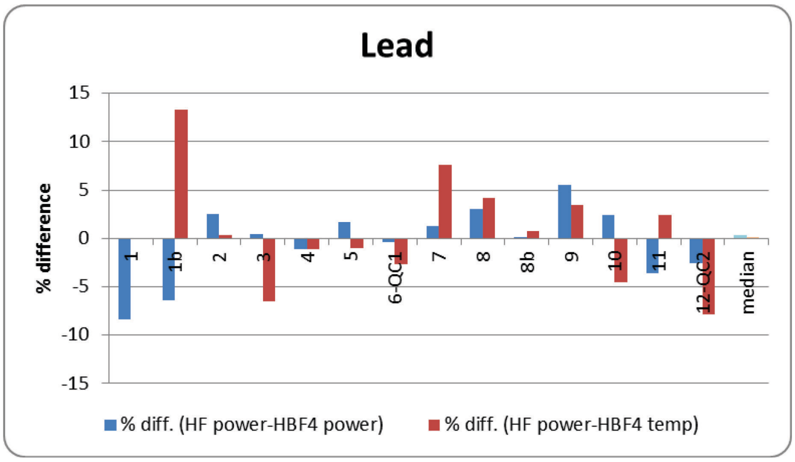

Figure 96 Difference between the reference method for Pb and the 2 alternative methods

4.5.6. ELEMENT NICKEL

In Figure 97 the Ni results of the different waste samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the Ni results with the 3 digestion methods was calculated per sample and are presented in Figure 98. From all samples analysed the CV_R is situated below 12%. The pooled CV_R of the 14 samples (including duplicate and QC samples) amounted 5.9%.

When calculating the % difference between the reference method ($HF:HNO_3:HCl$, power controlled digestion) and the 2 alternative methods (HBF_4, power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively 1.6 and -2.3% difference is observed (see Figure 99).

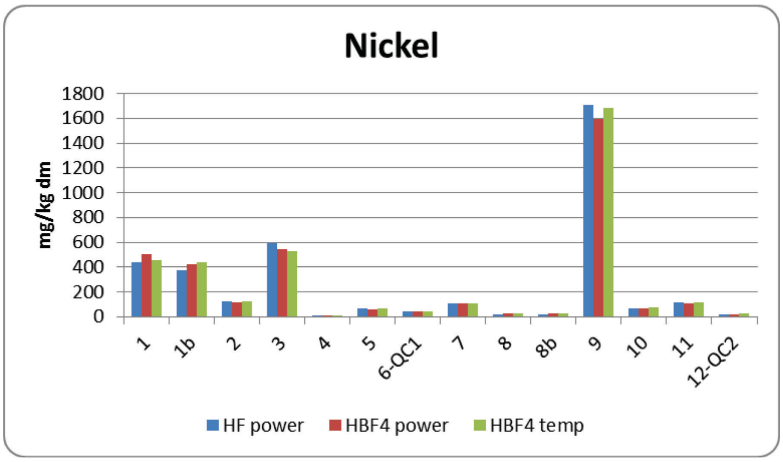

Figure 97 Ni results of the waste samples using the 3 digestion methods

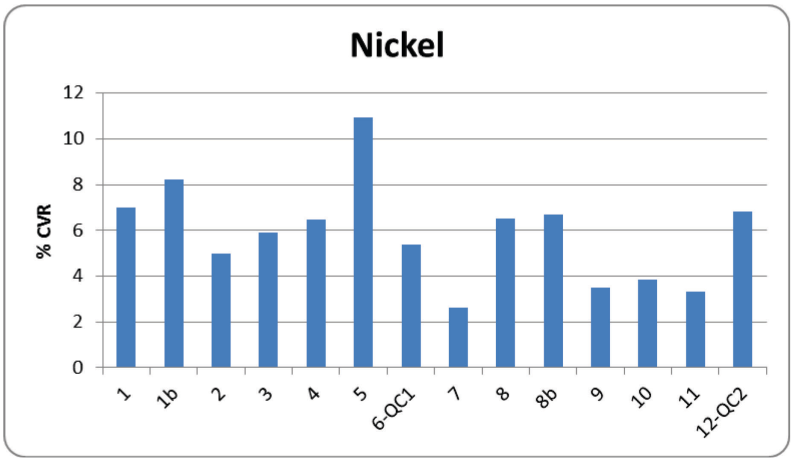

Figure 98 % CV_R of the 3 Ni results by sample

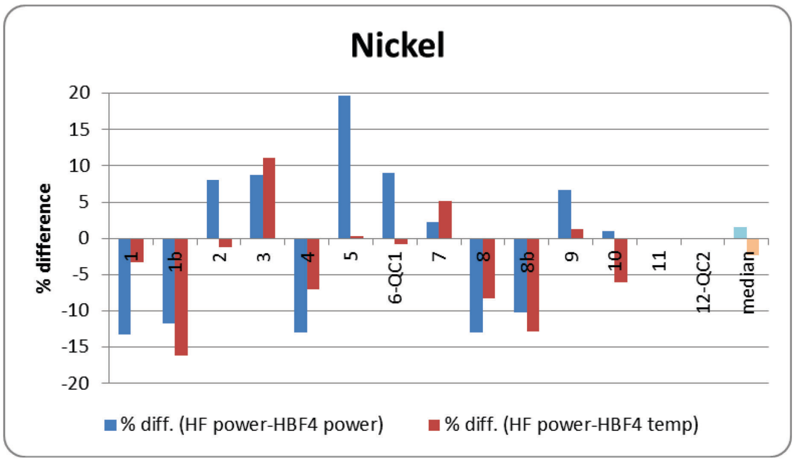

Figure 99 Difference between the reference method for Ni and the 2 alternative methods

4.5.7. ELEMENT ZINC

In Figure 100 the Zn results of the different waste samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the Zn results with the 3 digestion methods was calculated per sample and are presented in Figure 101. From all samples analysed the CV_R is situated below 12%. The pooled CV_R of the 14 samples (including duplicate and QC samples) amounted 4.5%.

When calculating the % difference between the reference method (HF:HNO_3:HCl, power controlled digestion) and the 2 alternative methods (HBF_4, power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively 1.1 and -1.6% difference is observed (see Figure 102).

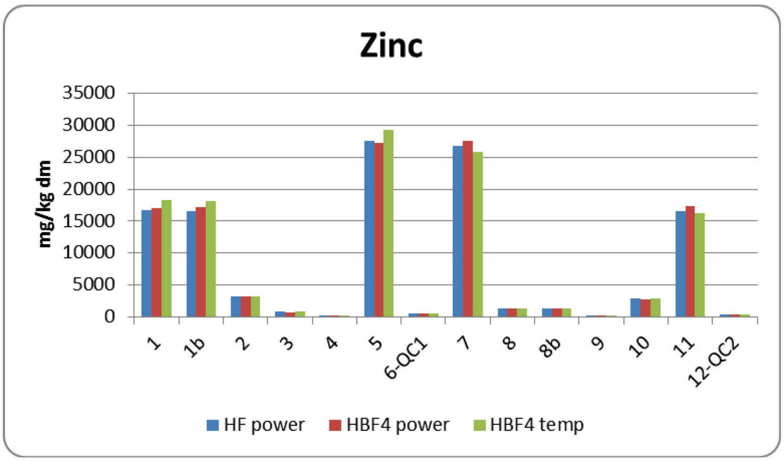

Figure 100 Zn results of the waste samples using the 3 digestion methods

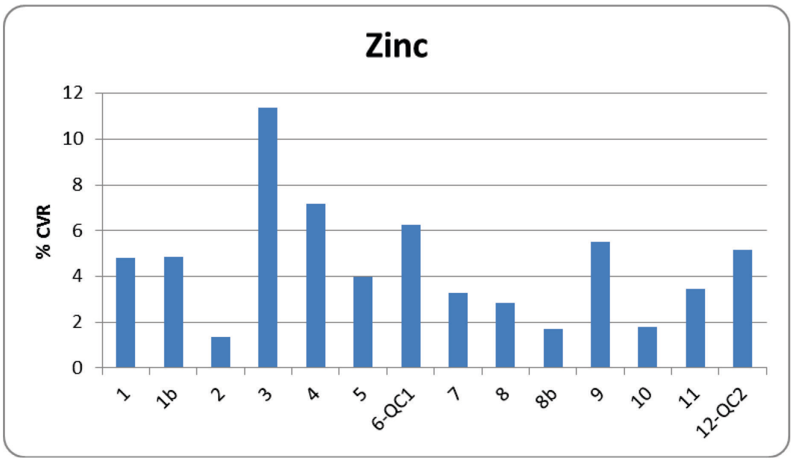

Figure 101 % CV_R of the 3 Zn results by sample

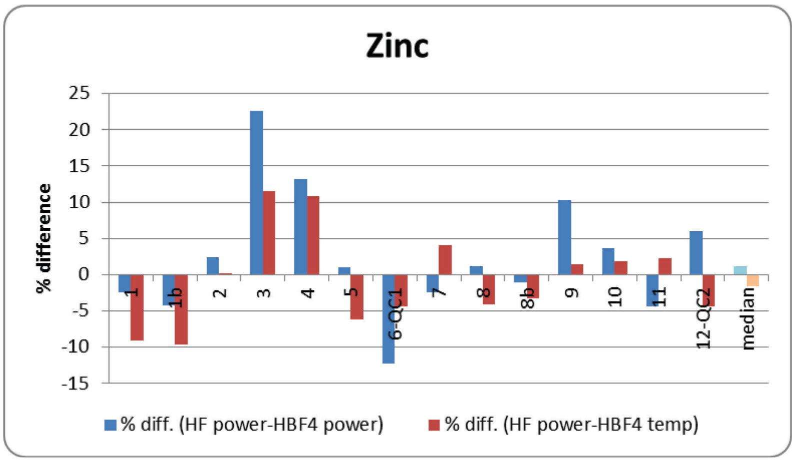

Figure 102 Difference between the reference method for Zn and the 2 alternative methods

4.5.8. ELEMENT MERCURY

In Figure 103 the Hg results of the different waste samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the Hg results with the 3 digestion methods was calculated per sample and are presented in Figure 104. From all samples analysed the CV_R is situated below 12%. The pooled CV_R of the 14 samples (including duplicate and QC samples) amounted 5.1%.

When calculating the % difference between the reference method ($HF:HNO_3:HCl$, power controlled digestion) and the 2 alternative methods (HBF_4, power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively 0.6 and -3.7% difference is observed (see Figure 105).

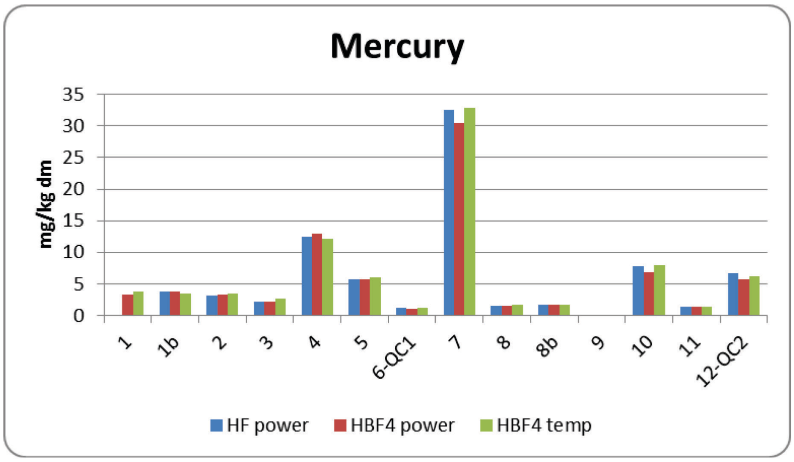

Figure 103 Hg results of the waste samples using the 3 digestion methods

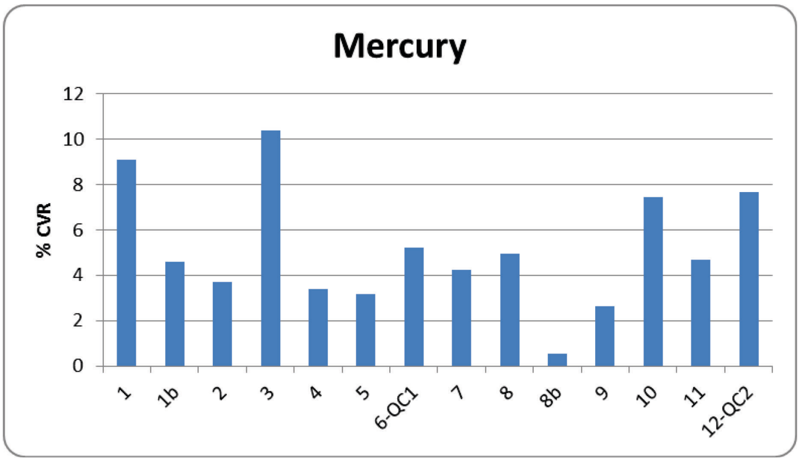

Figure 104 % CV_R of the 3 Hg results by sample

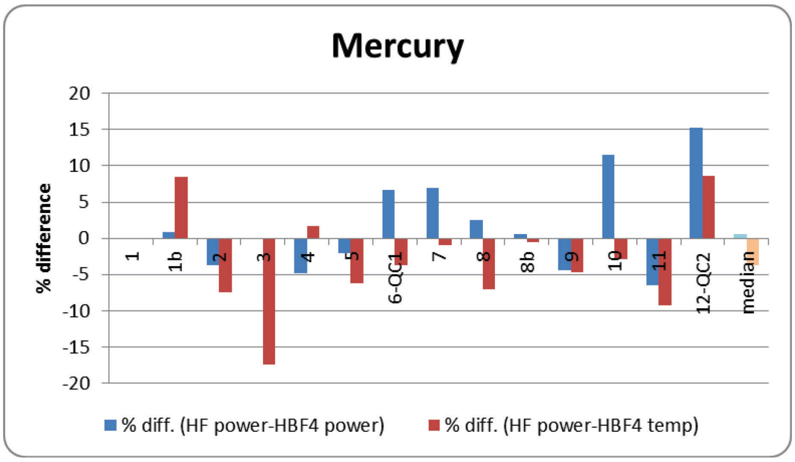

Figure 105 Difference between the reference method for Hg and the 2 alternative methods

4.5.9. ELEMENT ANTIMONY

In Figure 106 the Sb results of the different waste samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the Sb results with the 3 digestion methods was calculated per sample and are presented in Figure 107. From all samples analysed the CV_R is situated below 25%. The highest CV_R values (e.g. sample 3 and 4) were obtained on samples with a concentration level around or lower than 10 mg/kg dm. The pooled CV_R of the 13 samples (including duplicate and QC samples) amounted 11%.

When calculating the % difference between the reference method ($HF:HNO_3:HCl$, power controlled digestion) and the 2 alternative methods (HBF_4, power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively 6.1 and 0.0% difference is observed (see Figure 108).

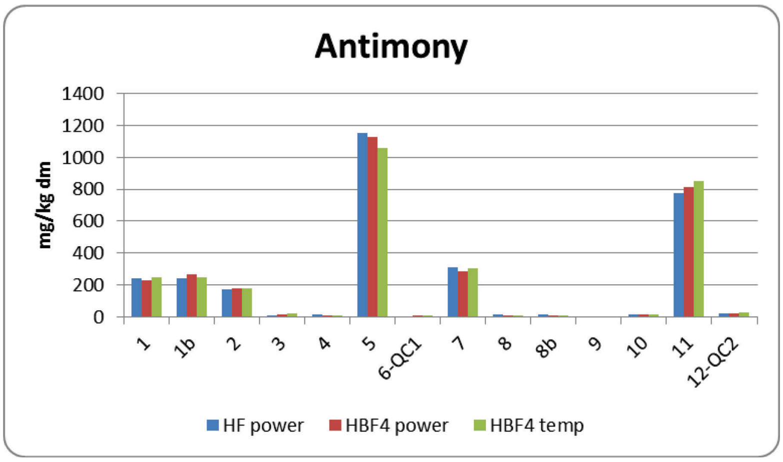

Figure 106 Sb results of the waste samples using the 3 digestion methods

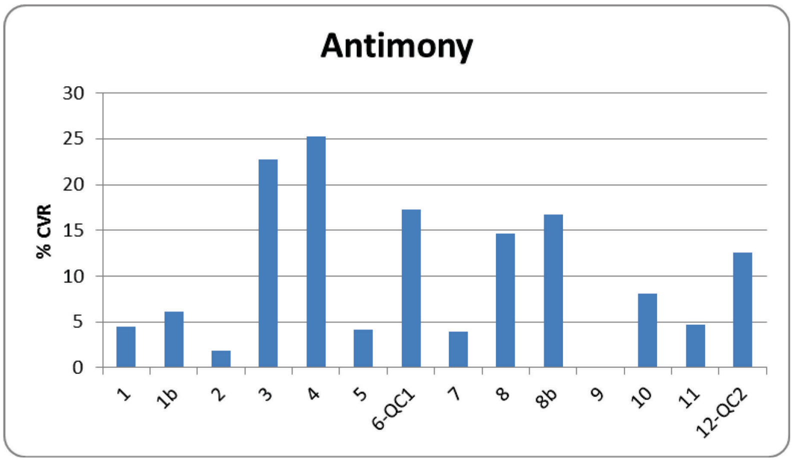

Figure 107 % CV$_R$ of the 3 Sb results by sample

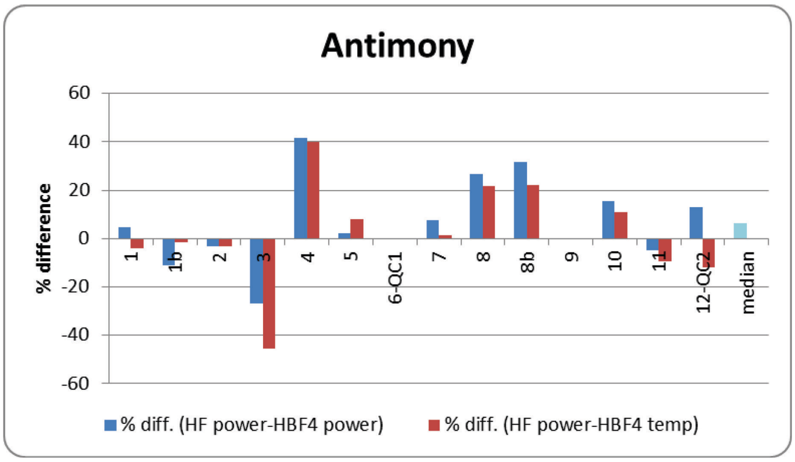

Figure 108 Difference between the reference method for Sb and the 2 alternative methods

4.5.10. ELEMENT BARIUM

In Figure 109 the Ba results of the different waste samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the Ba results with the 3 digestion methods was calculated per sample and are presented in Figure 110. From all samples analysed, except sample 7, the CV_R is situated below 25%. For sample 4 a high deviation between the 3 methods is observed, especially the HF power method results in a higher measured concentration compared to the 2 alternative methods. The pooled CV_R of the 14 samples (including duplicate and QC samples) amounted 14%.

When calculating the % difference between the reference method (HF:HNO_3:HCl, power controlled digestion) and the 2 alternative methods (HBF_4, power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively 2.6 and -6.5% difference is observed (see Figure 111).

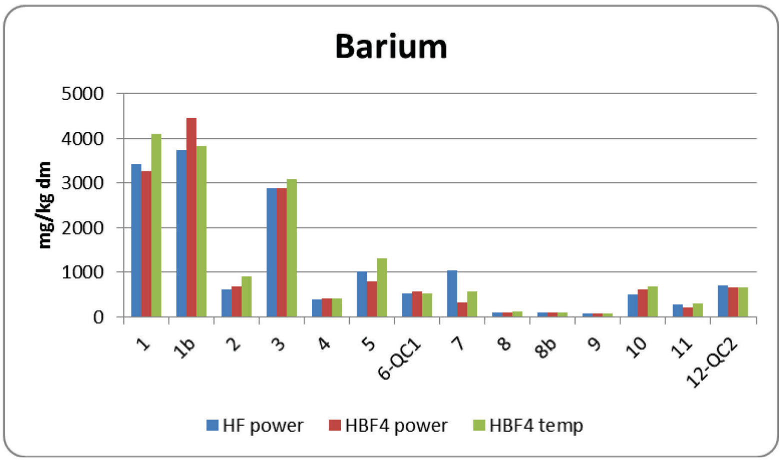

Figure 109 Ba results of the waste samples using the 3 digestion methods

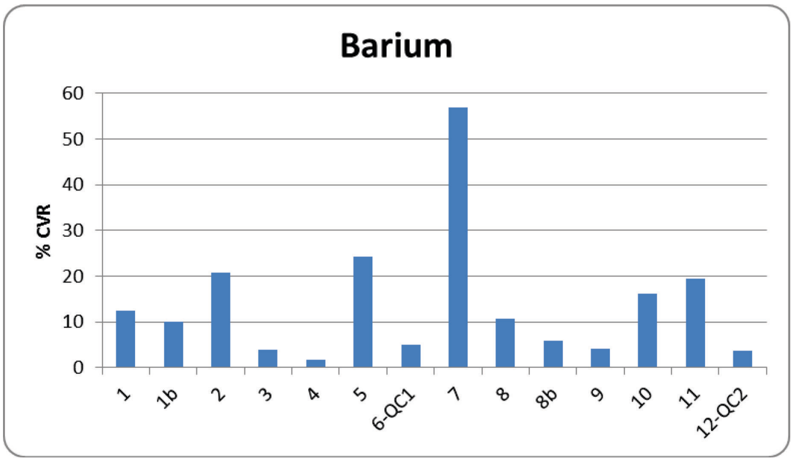

Figure 110 % CV_R of the 3 Ba results by sample

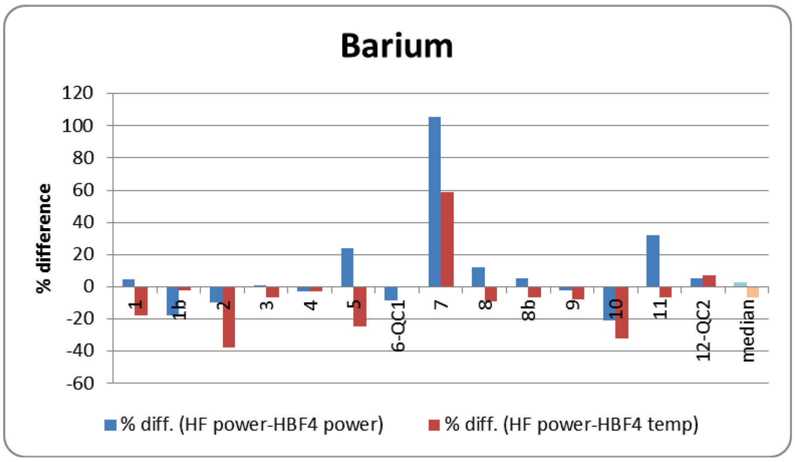

Figure 111 Difference between the reference method for Ba and the 2 alternative methods

4.5.11. ELEMENT COBALT

In Figure 112 the Co results of the different waste samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the Co results with the 3 digestion methods was calculated per sample and are presented in Figure 113. From all samples analysed, except for sample 9, the CV_R is situated below 13%. For sample 9 with a low concentration level of less than 5 mg/kg dm a CV_R of 22% was obtained. The pooled CV_R of the 13 samples (including duplicate and QC samples) amounted 8.1%.

When calculating the % difference between the reference method ($HF:HNO_3:HCl$, power controlled digestion) and the 2 alternative methods (HBF_4, power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively 1.8 and -3.6% difference is observed (see Figure 114).

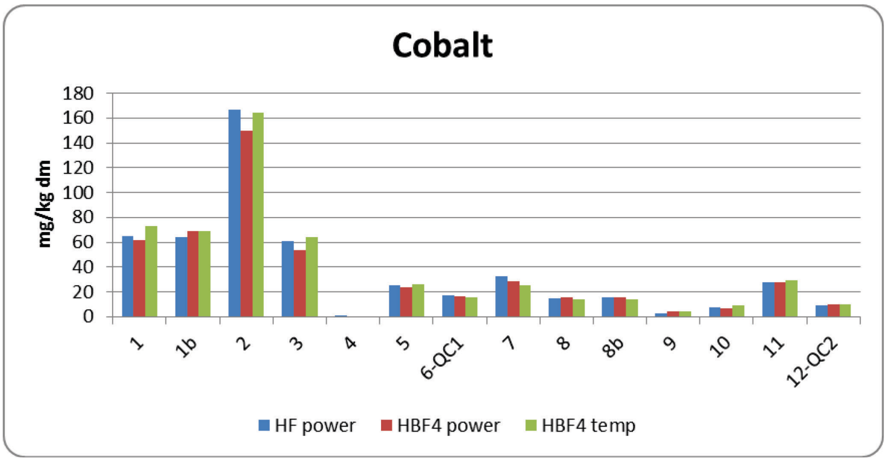

Figure 112 Co results of the waste samples using the 3 digestion methods

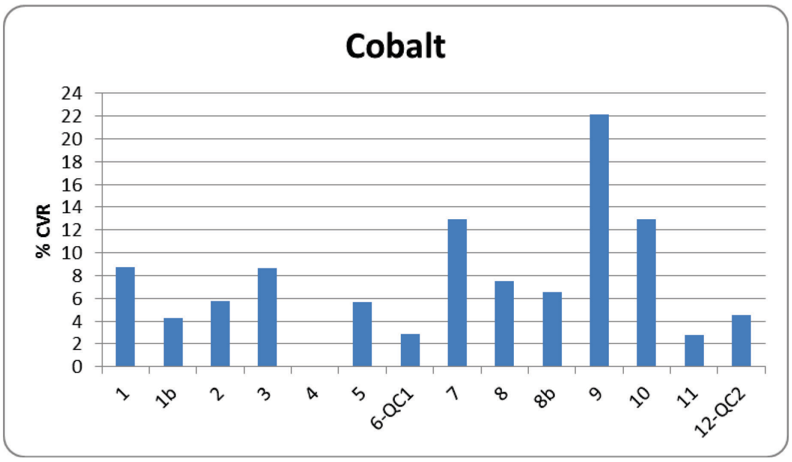

Figure 113 % CV_R of the 3 Co results by sample

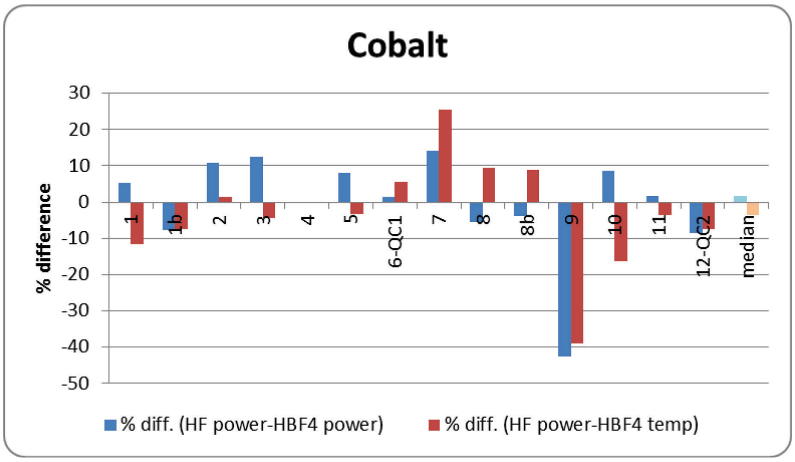

Figure 114 Difference between the reference method for Co and the 2 alternative methods

4.5.1. ELEMENT MANGANESE

In Figure 115 the Mn results of the different waste samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the Mn results with the 3 digestion methods was calculated per sample and are presented in Figure 116. From all samples analysed the CV_R is situated below 12%. The pooled CV_R of the 14 samples (including duplicate and QC samples) amounted 5.2%.

When calculating the % difference between the reference method ($HF:HNO_3:HCl$, power controlled digestion) and the 2 alternative methods (HBF_4, power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively 1.2 and -3.8% difference is observed (see Figure 117).

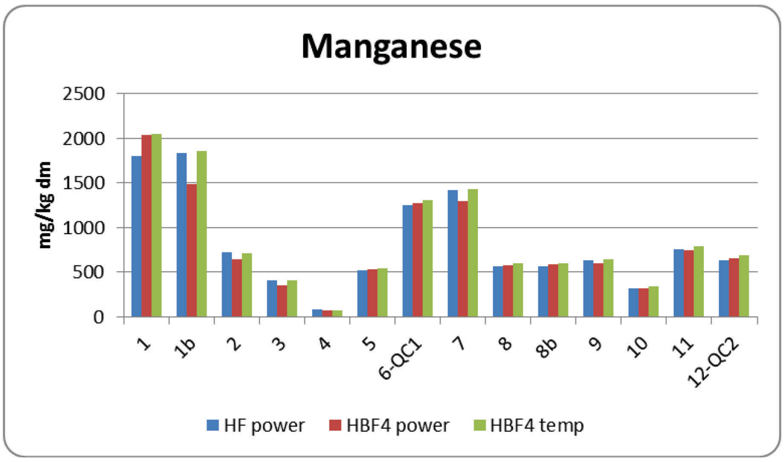

Figure 115 Mn results of the waste samples using the 3 digestion methods

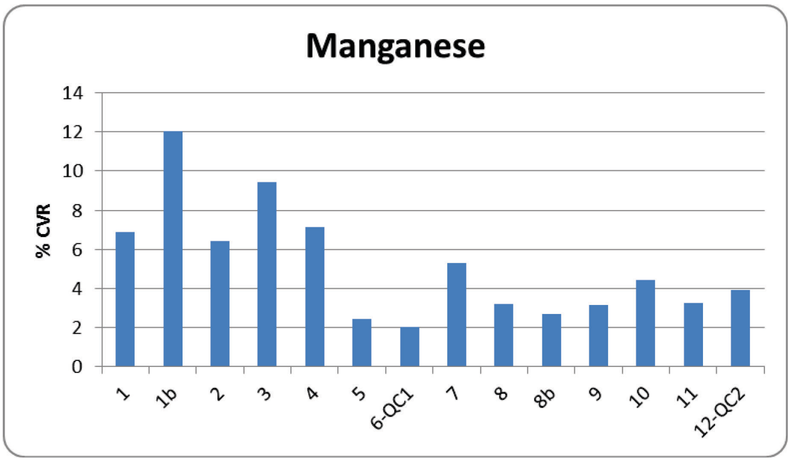

Figure 116 % CV$_R$ of the 3 Mn results by sample

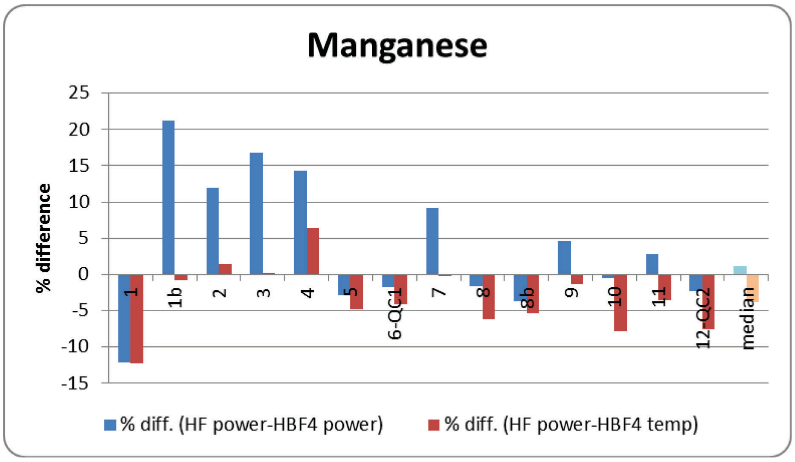

Figure 117 Difference between the reference method for Mn and the 2 alternative methods

4.5.2. ELEMENT MOLYBDENUM

In Figure 118 the Mo results of the different waste samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the Mo results with the 3 digestion methods was calculated per sample and are presented in Figure 119. From all samples analysed the CV_R is situated below 14%. The pooled CV_R of the 12 samples (including duplicate and QC samples) amounted 7.4%.

When calculating the % difference between the reference method ($HF:HNO_3:HCl$, power controlled digestion) and the 2 alternative methods (HBF_4, power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively 4.8 and -5.8% difference is observed (see Figure 120).

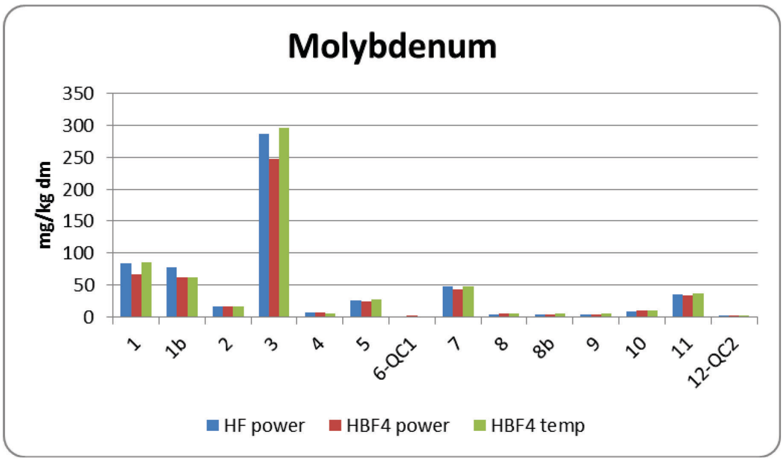

Figure 118 Mo results of the waste samples using the 3 digestion methods

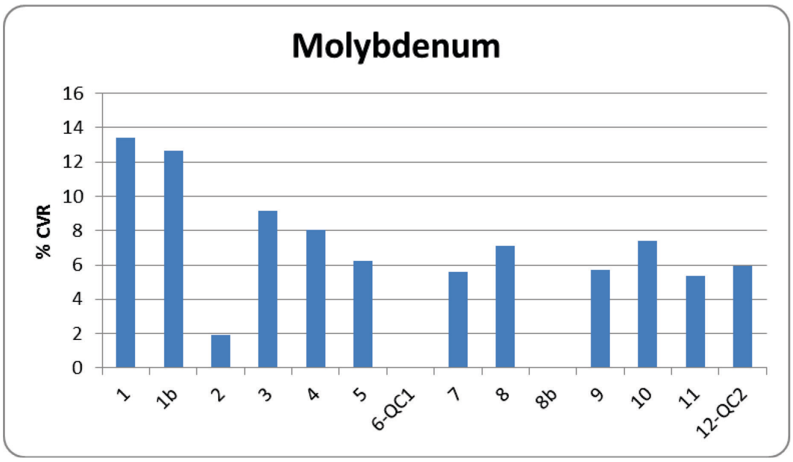

Figure 119 % CV_R of the 3 Mo results by sample

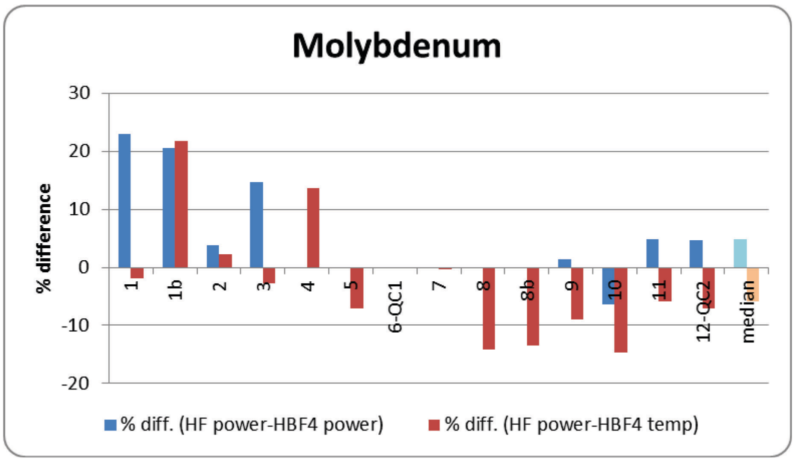

Figure 120 Difference between the reference method for Mo and the 2 alternative methods

4.5.3. ELEMENT SELENIUM

In Figure 121 the Se results of the different waste samples are presented. Only 4 samples contained measurable value of Se.

The % coefficient of variation (CV_R) of the Se results with the 3 digestion methods was calculated per sample and are presented in Figure 122. From the 4 samples the CV_R is situated below 13%. The pooled CV_R of the 4 samples (including duplicate and QC samples) amounted 7.6%.

When calculating the % difference between the reference method ($HF:HNO_3:HCl$, power controlled digestion) and the 2 alternative methods (HBF_4, power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively -8.2 and -2.6% difference is observed (see Figure 123).

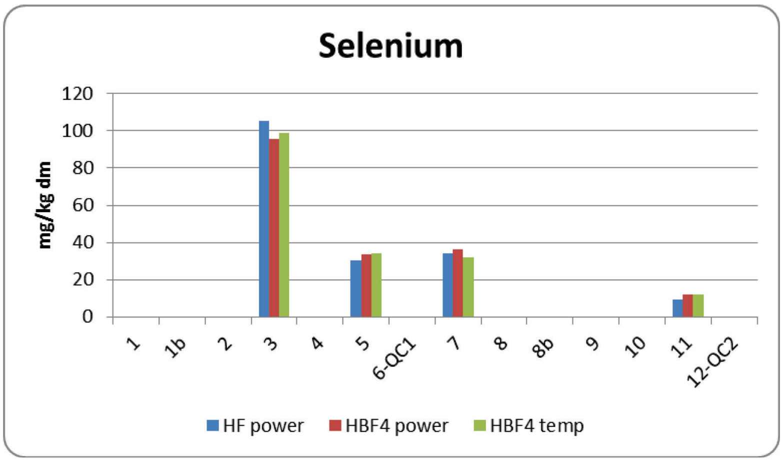

Figure 121 Se results of the waste samples using the 3 digestion methods

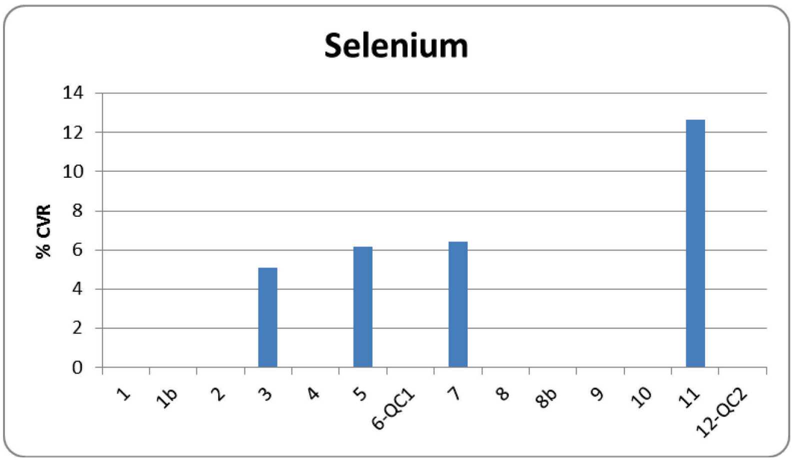

Figure 122 % CV_R of the 3 Se results by sample

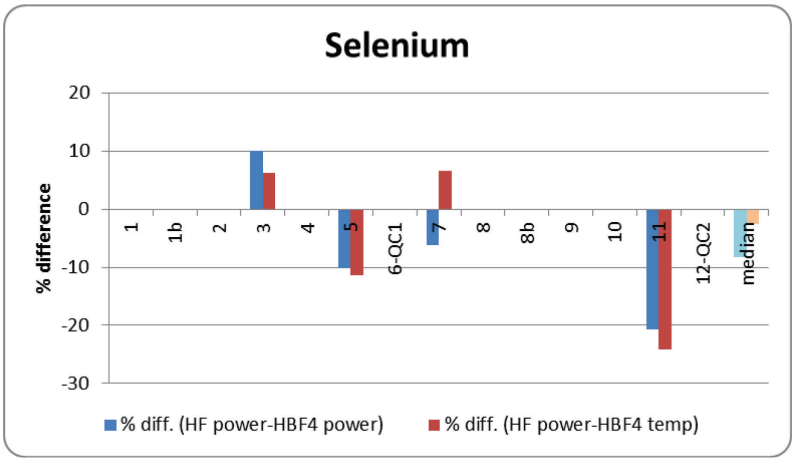

Figure 123 Difference between the reference method for Se and the 2 alternative methods

4.5.4. ELEMENT TIN

In Figure 124 the Sn results of the different waste samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the Sn results with the 3 digestion methods was calculated per sample and are presented in Figure 125. From all samples analysed, except sample 1b, the CV_R is situated below 16%. A higher value of 35% was obtained of the duplicate sample 1b – a shredder < 1 mm - (note that sample 1 had a CV_R of 10%). The pooled CV_R of the 10 samples (including duplicate and QC sample) amounted 9.9%.

When calculating the % difference between the reference method ($HF:HNO_3:HCl$, power controlled digestion) and the 2 alternative methods (HBF_4, power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively 3.8 and 2.0% difference is observed (see Figure 126).

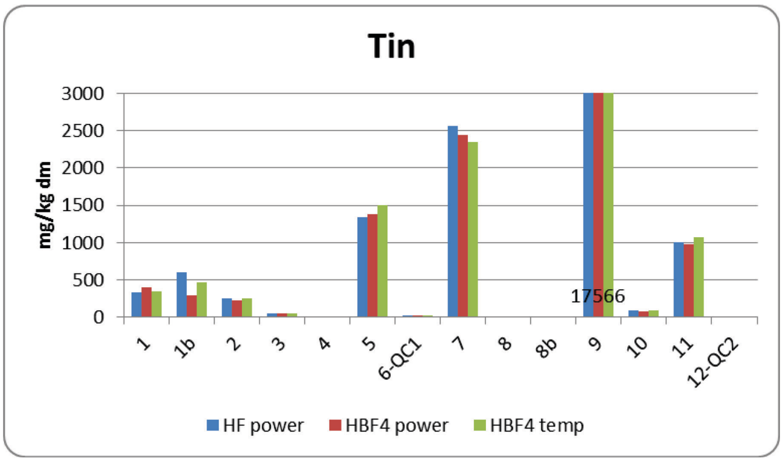

Figure 124 Sn results of the waste samples using the 3 digestion methods

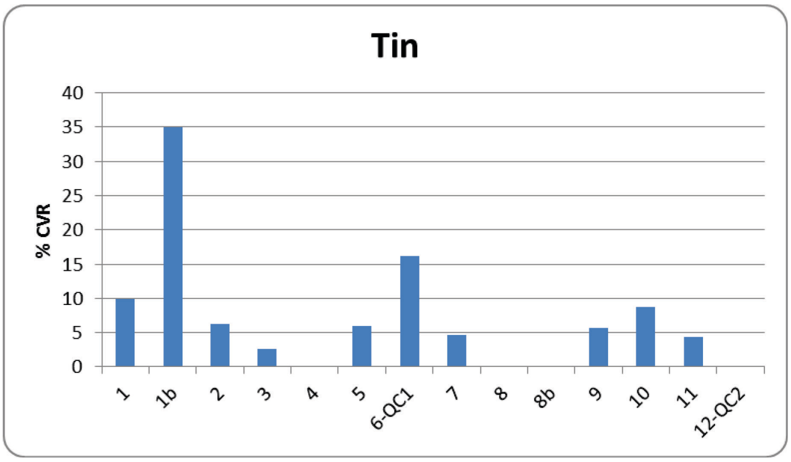

Figure 125 % CV$_R$ of the 3 Sn results by sample

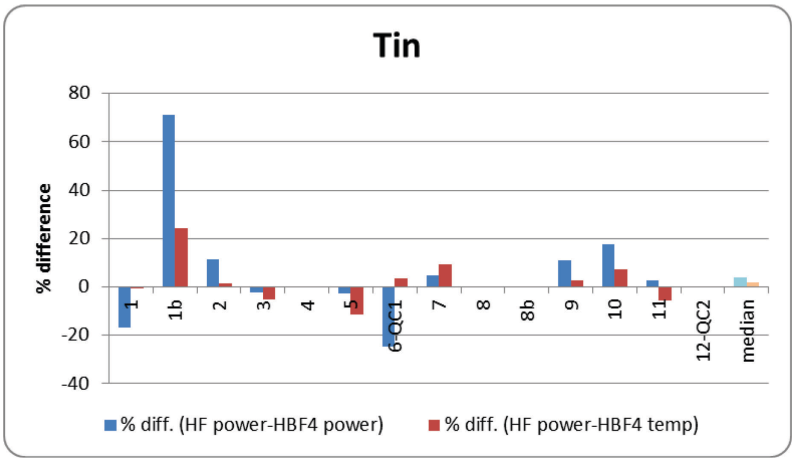

Figure 126 Difference between the reference method for Sn and the 2 alternative methods

4.5.5. ELEMENT VANADIUM

In Figure 127 the V results of the different waste samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the V results with the 3 digestion methods was calculated per sample and are presented in Figure 128. From all samples analysed the CV_R is situated below 14%. The pooled CV_R of the 14 samples (including duplicate and QC samples) amounted 6.5%.

When calculating the % difference between the reference method (HF:HNO_3:HCl, power controlled digestion) and the 2 alternative methods ($HBF_{4,}$ power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively 1.4 and -5.3% difference is observed (see Figure 129).

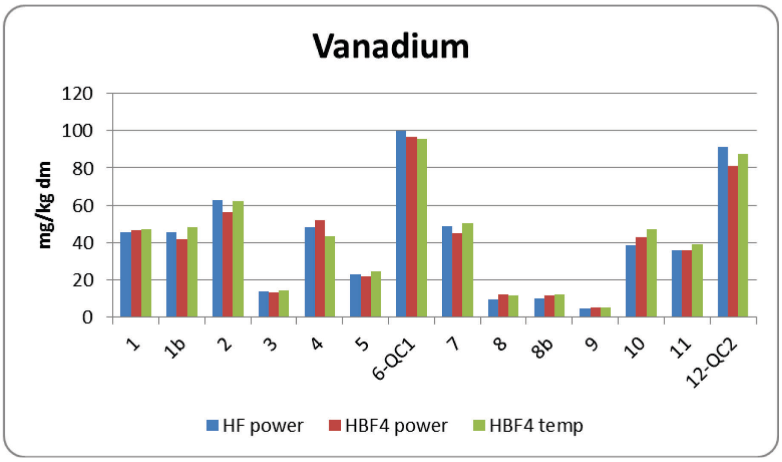

Figure 127 V results of the waste samples using the 3 digestion methods

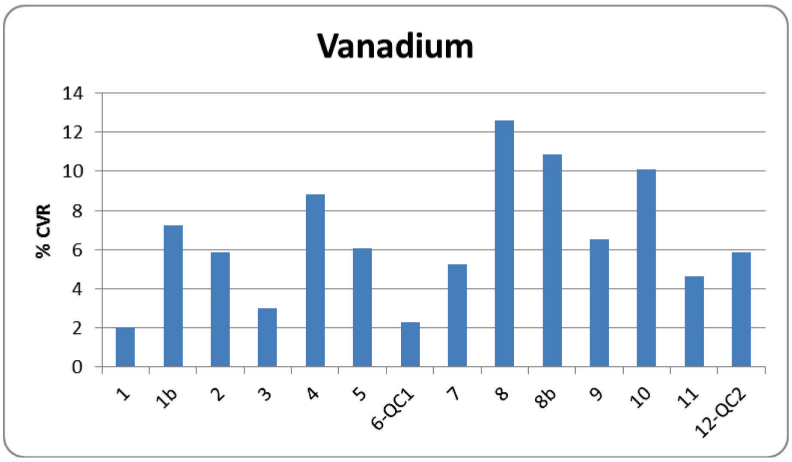

Figure 128 % CV_R of the 3 V results by sample

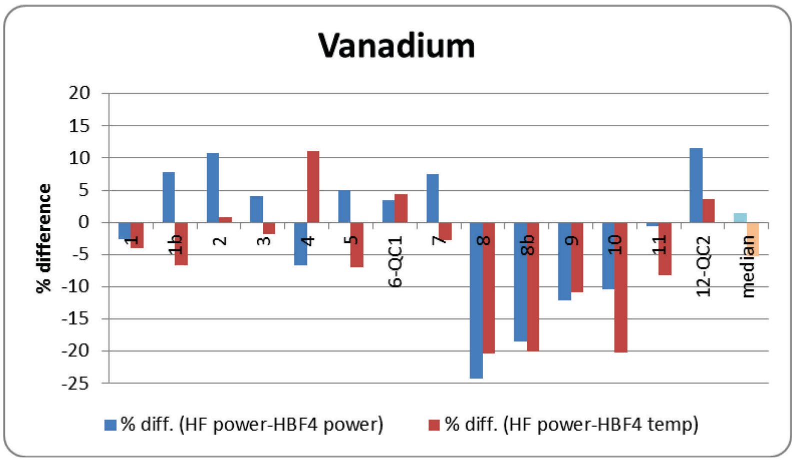

Figure 129 Difference between the reference method for V and the 2 alternative methods

4.6. RESULTS OF MAJOR ELEMENTS

4.6.1. ELEMENT SODIUM

In Figure 130 the Na results of the different waste samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the Na results with the 3 digestion methods was calculated per sample and are presented in Figure 131. From all samples analysed the CV_R is situated below 15%. The pooled CV_R of the 14 samples (including duplicate and QC samples) amounted 5.8%.

When calculating the % difference between the reference method ($HF:HNO_3:HCl$, power controlled digestion) and the 2 alternative methods (HBF_4, power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively -3.9 and -5.1% difference is observed (see Figure 132).

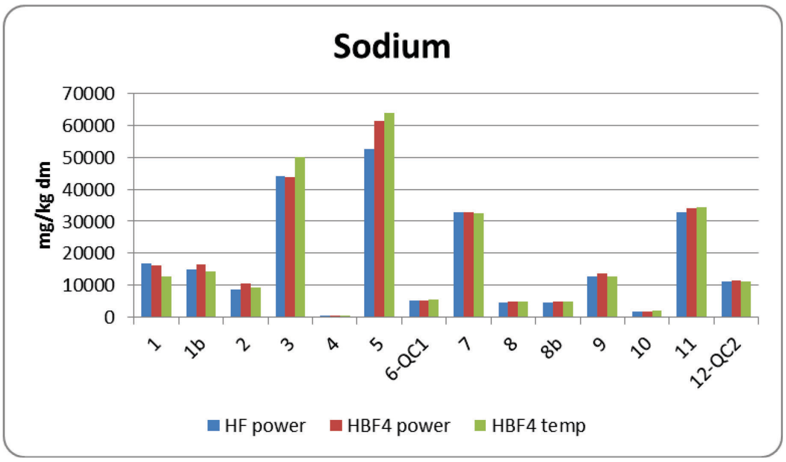

Figure 130 Na results of the waste samples using the 3 digestion methods

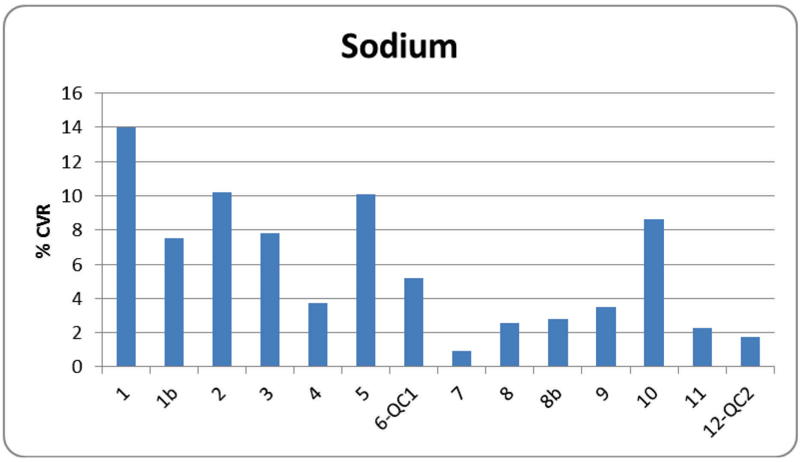

Figure 131 % CV_R of the 3 Na results by sample

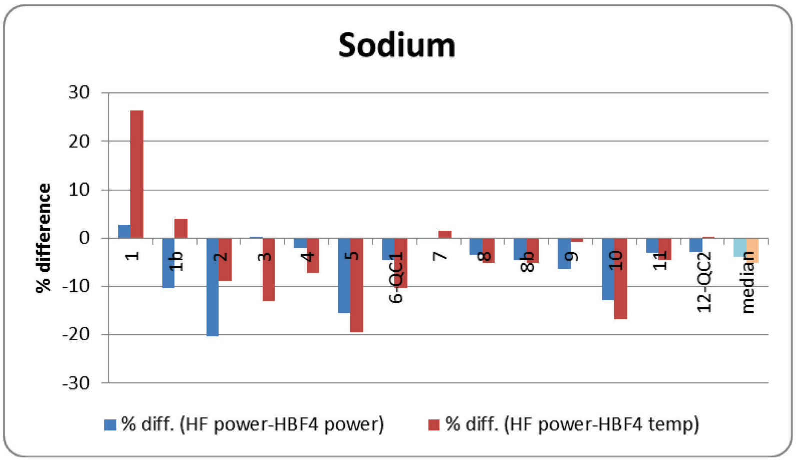

Figure 132 Difference between the reference method for Na and the 2 alternative methods

4.6.2. ELEMENT MAGNESIUM

In Figure 133 the Mg results of the different waste samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the Mg results with the 3 digestion methods was calculated per sample and are presented in Figure 134. From all samples analysed the CV_R is situated below 14%. The pooled CV_R of the 14 samples (including duplicate and QC samples) amounted 4.3%.

When calculating the % difference between the reference method ($HF:HNO_3:HCl$, power controlled digestion) and the 2 alternative methods ($HBF_{4,}$ power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively -1.2 and 0.8% difference is observed (see Figure 135).

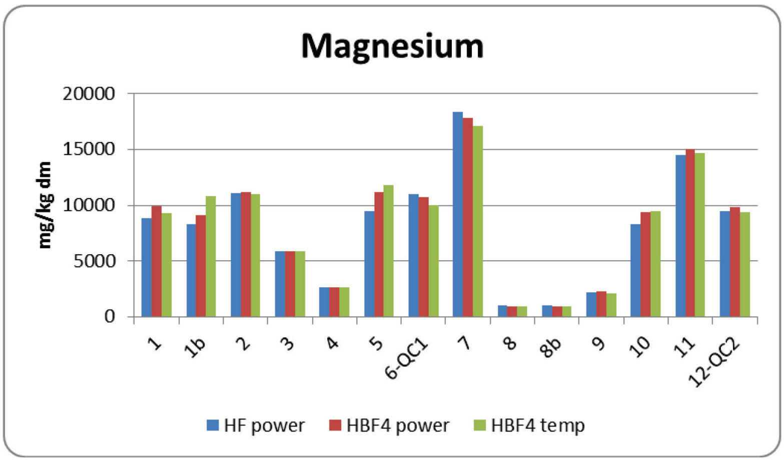

Figure 133 Mg results of the waste samples using the 3 digestion methods

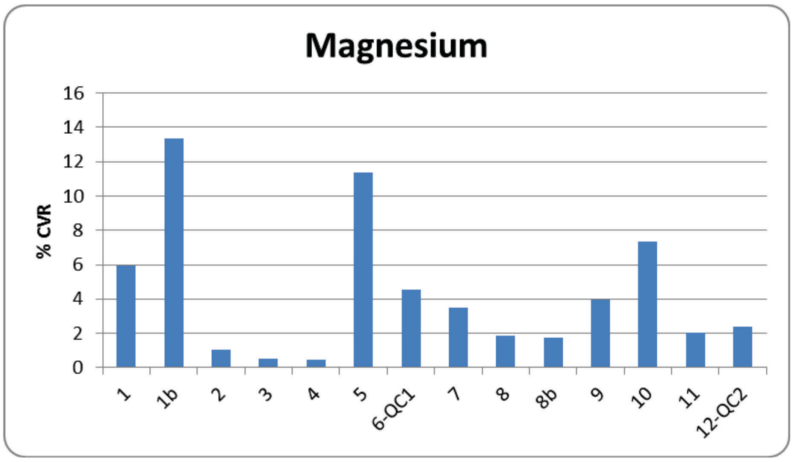

Figure 134 % CV$_R$ of the 3 Mg results by sample

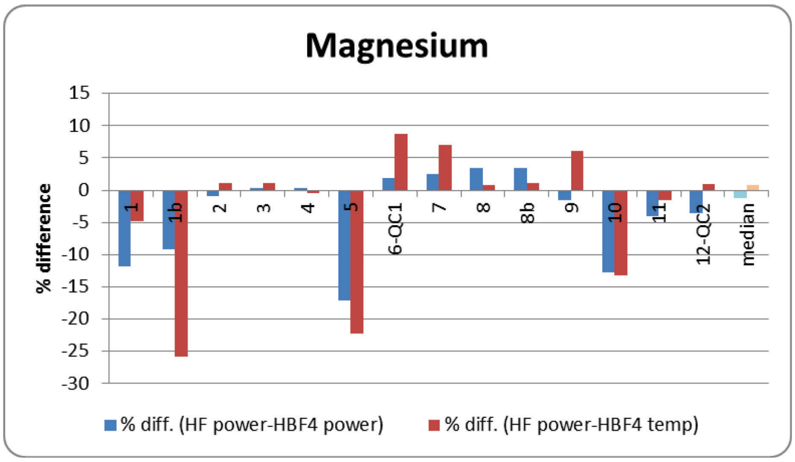

Figure 135 Difference between the reference method for Mg and the 2 alternative methods

4.6.3. ELEMENT ALUMINIUM

In Figure 136 the Al results of the different waste samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the Al results with the 3 digestion methods was calculated per sample and are presented in Figure 137. From all samples analysed the CV_R is situated below 14%. The pooled CV_R of the 14 samples (including duplicate and QC samples) amounted 4.7%.

When calculating the % difference between the reference method ($HF:HNO_3:HCl$, power controlled digestion) and the 2 alternative methods ($HBF_{4,}$ power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively -0.3 and 0.2% difference is observed (see Figure 138).

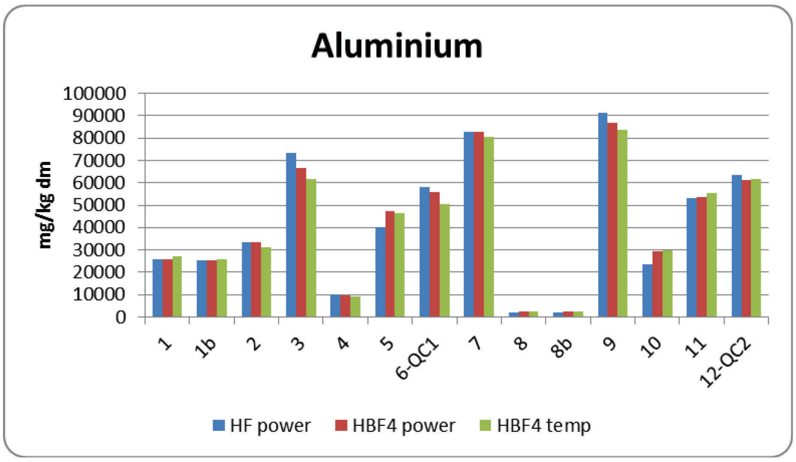

Figure 136 Al results of the waste samples using the 3 digestion methods

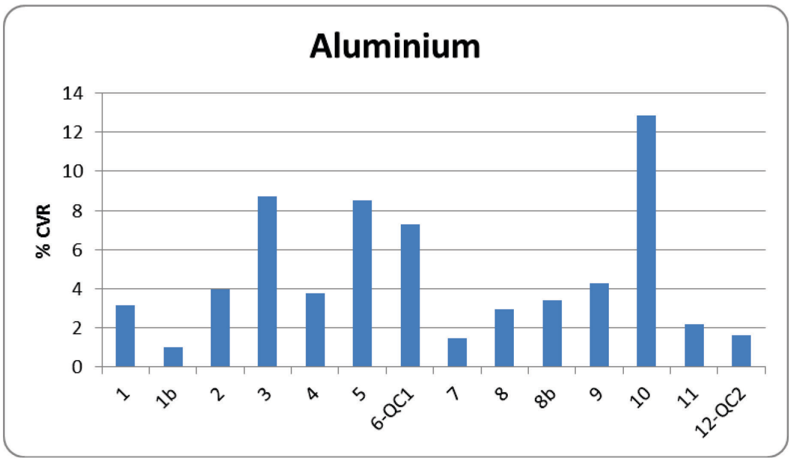

Figure 137 % CV_R of the 3 Al results by sample

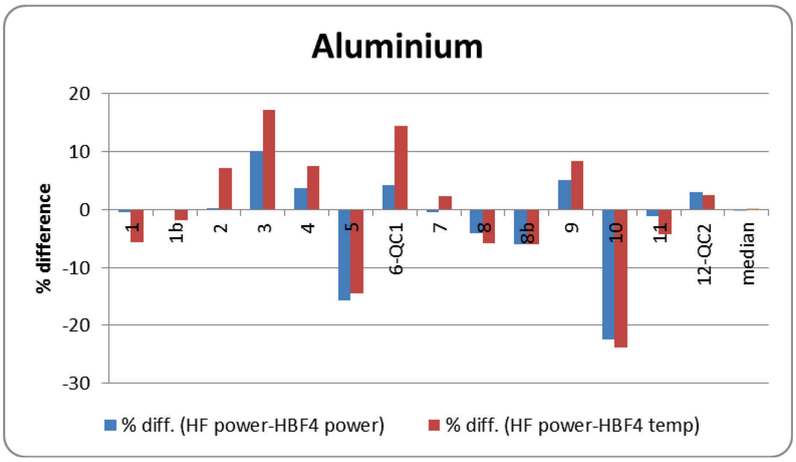

Figure 138 Difference between the reference method for Al and the 2 alternative methods

4.6.4. ELEMENT POTASSIUM

In Figure 139 the K results of the different waste samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the K results with the 3 digestion methods was calculated per sample and are presented in Figure 140. From all samples analysed the CV_R is situated below 14%. The pooled CV_R of the 14 samples (including duplicate and QC samples) amounted 6.4%.

When calculating the % difference between the reference method (HF:HNO_3:HCl, power controlled digestion) and the 2 alternative methods (HBF_4, power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively -4.7 and -7.2% difference is observed (see Figure 141).

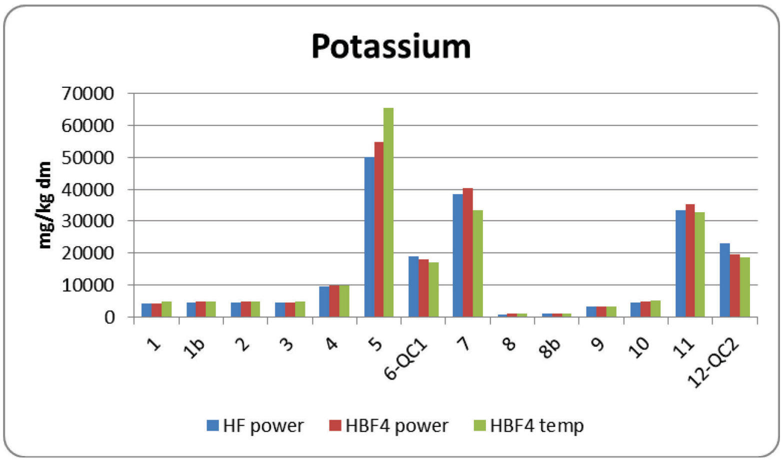

Figure 139 K results of the waste samples using the 3 digestion methods

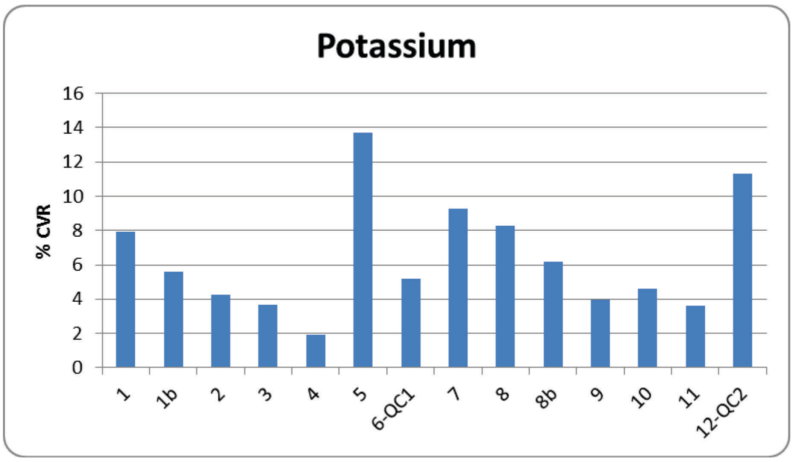

Figure 140 % CV_R of the 3 K results by sample

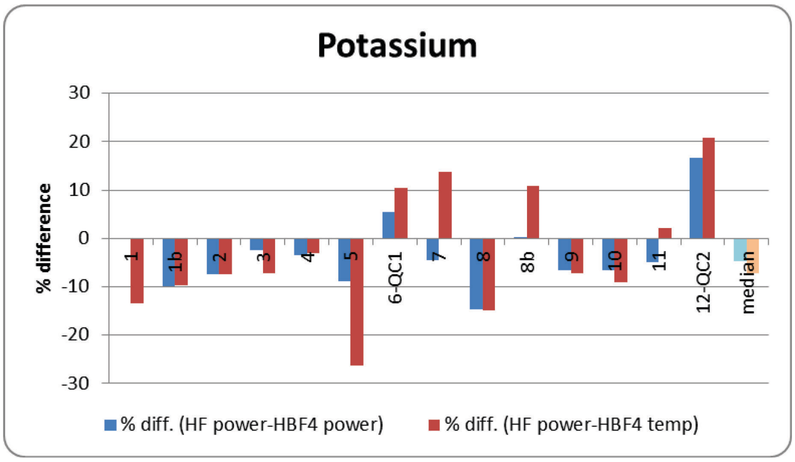

Figure 141 Difference between the reference method for K and the 2 alternative methods

4.6.5. ELEMENT CALCIUM

In Figure 142 the Ca results of the different waste samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the Ca results with the 3 digestion methods was calculated per sample and are presented in Figure 143. From all samples analysed, except sample 10, the CV_R is situated below 8%. Only sample 10 had a CV_R of 22% which is caused by a lower concentration obtained with the reference method in comparison with the 2 alternative methods. The pooled CV_R of the 14 samples (including duplicate and QC samples) amounted 4.4%.

When calculating the % difference between the reference method ($HF:HNO_3:HCl$, power controlled digestion) and the 2 alternative methods (HBF_4, power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively -0.8 and -0.1% difference is observed (see Figure 144).

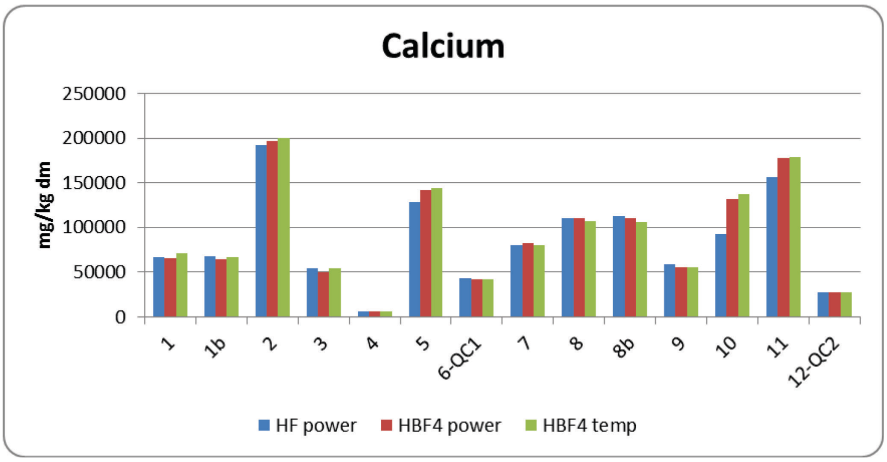

Figure 142 Ca results of the waste samples using the 3 digestion methods

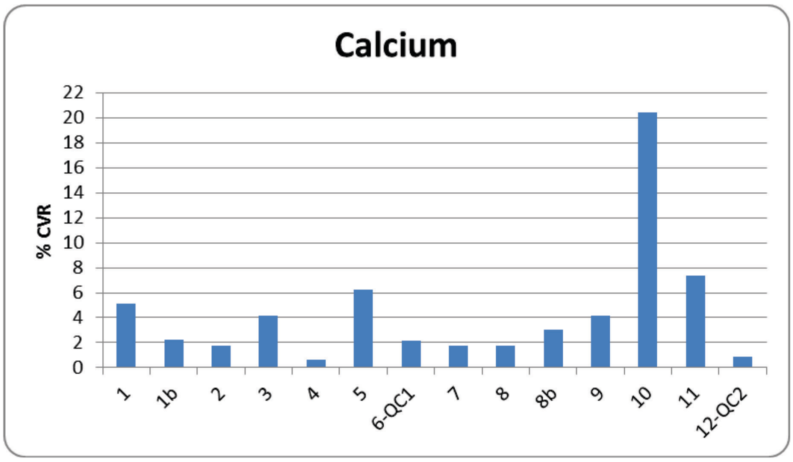

Figure 143 % CV$_R$ of the 3 Ca results by sample

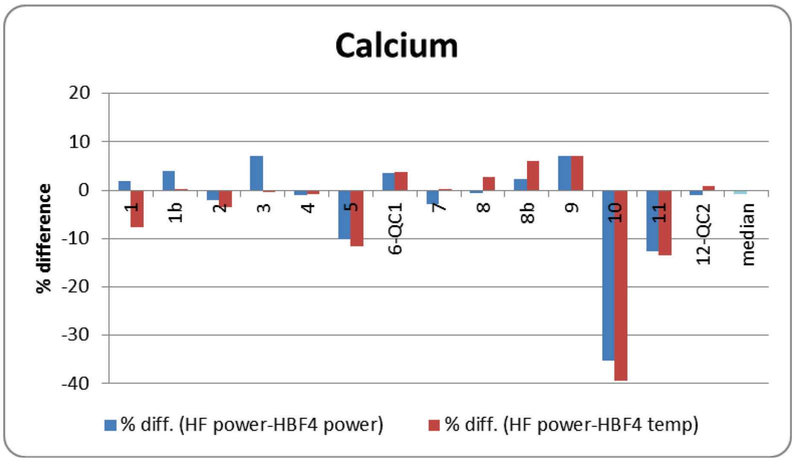

Figure 144 Difference between the reference method for Ca and the 2 alternative methods

4.6.6. ELEMENT TITANIUM

In Figure 145 the Ti results of the different waste samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the Ti results with the 3 digestion methods was calculated per sample and are presented in Figure 146. The CV_R of all samples fluctuates between 8 and 50%. The pooled CV_R of the 14 samples (including duplicate and QC samples) amounted 22%. For the Ti results differences are observed for the alternative methods in comparison with the reference method, especially when applying the HBF_4 digestion with the power controlled microwave digestion. This digestion method results in a systematic underestimation of about 20%. When applying the HBF_4 digestion with the temperature controlled microwave digestion, this effect is less pronounced. A silimar profile was observed for the soil samples.

When calculating the % difference between the reference method ($HF:HNO_3:HCl$, power controlled digestion) and the 2 alternative methods ($HBF_{4,}$ power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively 33 and 9.3% difference is observed (see Figure 147).

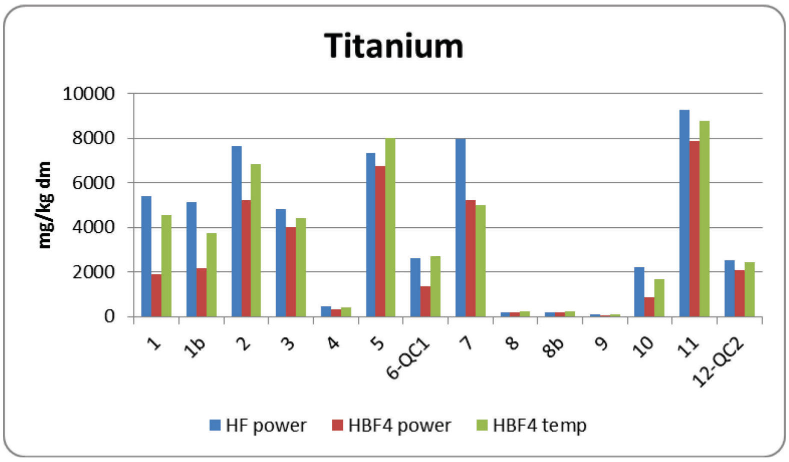

Figure 145 Ti results of the waste samples using the 3 digestion methods

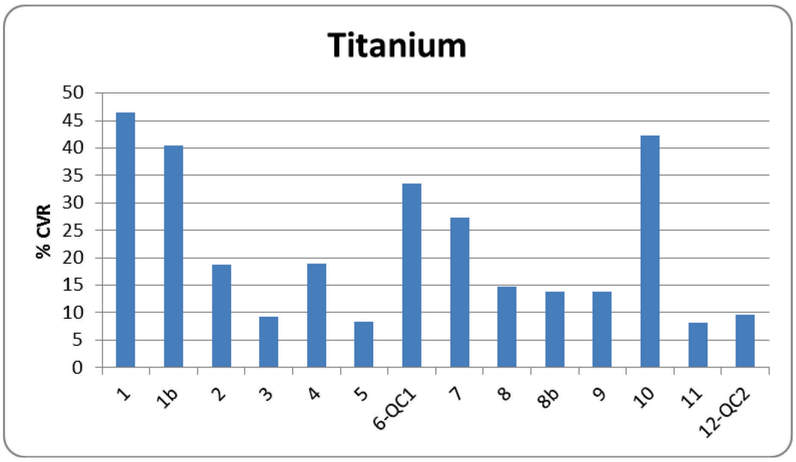

Figure 146 % CV_R of the 3 Ti results by sample

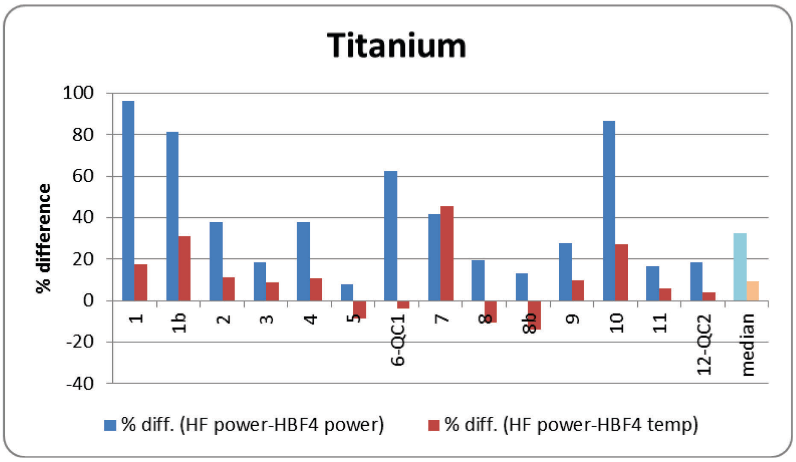

Figure 147 Difference between the reference method for Ti and the 2 alternative methods

4.6.7. ELEMENT IRON

In Figure 148 the Fe results of the different waste samples and the quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the Fe results with the 3 digestion methods was calculated per sample and are presented in Figure 149. From all samples analysed the CV_R is situated below 16%. The pooled CV_R of the 14 samples (including duplicate and QC samples) amounted 4.3%.

When calculating the % difference between the reference method ($HF:HNO_3:HCl$, power controlled digestion) and the 2 alternative methods (HBF_4, power controlled digestion and HBF_4, temperature controlled digestion), a median value of respectively 2.0 and -1.0% difference is observed (see Figure 150).

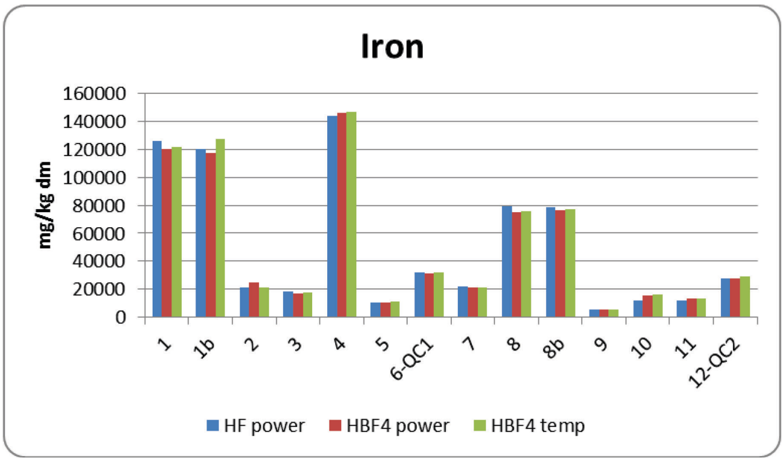

Figure 148 Fe results of the waste samples using the 3 digestion methods

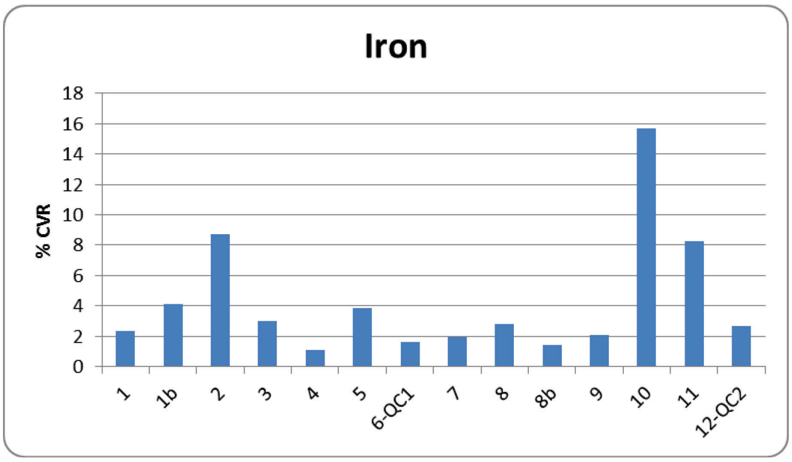

Figure 149 % CV$_R$ of the 3 Fe results by sample

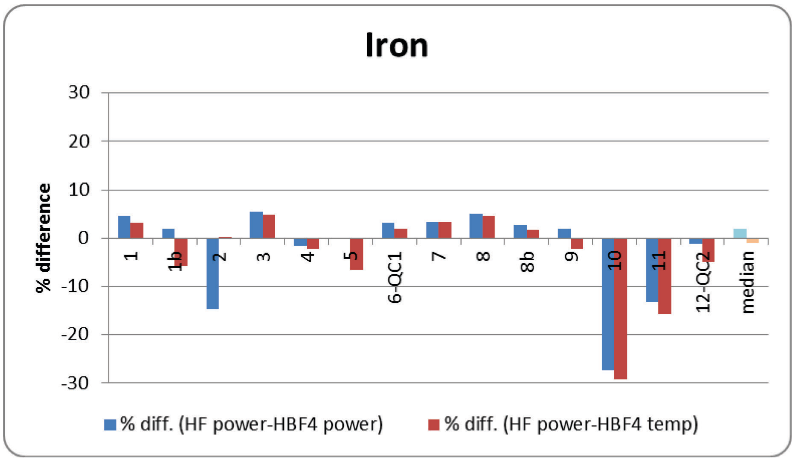

Figure 150 Difference between the reference method for Fe and the 2 alternative methods

4.7. EVALUATION OF THE TRUENESS OF THE QC SAMPLES IN THE DIGESTION RUN OF THE WASTE SAMPLES

During the digestion process two control samples were analysed together with the other waste samples. As control samples a round robin soil sample (SETOC 701) – QC1 - , distributed by Wageningen, and a certified soil samples (NIST 2711) – QC 2 – was included in the analytical process. For each digestion procedure, 2 digestion runs were carried out. The SETOC 701 control sample was always included in the first run of the digestion, the NIST 2711 was included in the second run. The obtained results and their recovery are presented in Table 2.

As reference value for the SETOC 701 QC sample, data of the available control chart were used. These control chart data were obtained after digestion with HF:HNO$_3$:HCl using a power controlled digestion programme. The reference value was derived on the basis of digestions with 4 ml HF (see remark) in stead of 2 ml HF. Maybe this might be the reason why the recovery for Cr is for the 3 applied digestion methods (with 2 ml of HF or HBF$_4$) limited to about 90%.

> Remark: To avoid gel formation in case Si is present in a high content (± 30%), 4 ml of HF is added for digestion.

Note that the performance check is based on the comparison of single measurement results.

Legend:

- HF power: digestion using HF:HNO_3:HCl with power controlled digestion procedure
- HBF_4 power: digestion using HBF_4 with power controlled digestion procedure
- HBF_4 temp: digestion using HBF_4 with temperature controlled digestion procedure

Table 3 Overview of the performance of the QC samples

	Digestion procedure	QC1 mg/kg dm	Ref.value mg/kg dm	Recovery %	Nist 2711 mg/kg dm	Ref. value mg/kg dm	Recovery %
As	**HF power**	36	33,6	107%	105	105	100%
	HBF4 power	31	33,6	92%	115	105	110%
	HBF4 temp	38	33,6	114%	108	105	103%
Cd	**HF power**	2,4	2,6	93%	40	41,7	95%
	HBF4 power	2,5	2,6	96%	41	41,7	98%
	HBF4 temp	2,5	2,6	96%	42	41,7	101%
Cr	**HF power**	125	131,8	95%	42	47	89%
	HBF4 power	121	131,8	91%	40	47	85%
	HBF4 temp	133	131,8	101%	42	47	89%
Cu	**HF power**	104	103,9	100%	119	114	104%
	HBF4 power	103	103,9	99%	112	114	98%
	HBF4 temp	101	103,9	97%	115	114	101%
Pb	**HF power**	175	171,5	102%	1102	1162	95%
	HBF4 power	176	171,5	102%	1131	1162	97%
	HBF4 temp	180	171,5	105%	1193	1162	103%
Ni	**HF power**	47	46,6	101%	21	20,6	102%
	HBF4 power	43	46,6	92%	22	20,6	106%
	HBF4 temp	47	46,6	102%	24	20,6	116%
Zn	**HF power**	505	515	98%	365	350,1	104%
	HBF4 power	570	515	111%	344	350,4	98%
	HBF4 temp	527	515	102%	381	350,4	109%
Sb	**HF power**				22	19,4	114%
	HBF4 power				19	19,4	100%
	HBF4 temp				25	19,4	129%
Ba	**HF power**				698	726	96%
	HBF4 power				661	726	91%
	HBF4 temp				650	726	89%
Co	**HF power**				9,3	10	93%
	HBF4 power				10,1	10	101%
	HBF4 temp				10	10	100%
Mo	**HF power**				1,7	1,6	106%
	HBF4 power				1,6	1,6	101%
	HBF4 temp				1,8	1,6	114%
V	**HF power**				91	81,6	112%

	Digestion procedure	QC1 mg/kg dm	Ref.value mg/kg dm	Recovery %	Nist 2711 mg/kg dm	Ref. value mg/kg dm	Recovery %
	HBF4 power				81	81,6	99%
	HBF4 temp				88	81,6	108%
Na	**HF power**				11093	11400	97%
	HBF4 power				11414	11400	100%
	HBF4 temp				11059	11400	97%
Mg	**HF power**				9487	10500	90%
	HBF4 power				9830	10500	94%
	HBF4 temp				9395	10500	89%
Al	**HF power**				63365	65300	97%
	HBF4 power				61460	65300	94%
	HBF4 temp				61783	65300	95%
K	**HF power**				23068	24500	94%
	HBF4 power				19506	24500	80%
	HBF4 temp				18720	24500	76%
Ca	**HF power**				27403	28800	95%
	HBF4 power				27673	28800	96%
	HBF4 temp				27179	28800	94%
Ti	**HF power**				2522	3060	82%
	HBF4 power				2092	3060	68%
	HBF4 temp				2424	3060	79%
Mn	**HF power**				638	638	100%
	HBF4 power				653	638	102%
	HBF4 temp				688	638	108%
Fe	**HF power**				27283	28900	94%
	HBF4 power				27586	28900	95%
	HBF4 temp				28693	28900	99%

Italic: indicative value

4.8. OVERVIEW OF SAMPLE CEN 6/99 FLY ASH (20143961)

The results of sample CEN 6/99 (20143961) obtained with the 3 digestion methods were compared with the mean values of this sample obtained during the validation trial of EN 13656 in 1999. For each element and digestion method the recovery was calculated relative to the mean value included in EN 13656. The obtained results are presented in Table 4 and Figure 151. The figure also includes the reproducibility coefficient of variation (2 x CV_R, 95% confidence interval) of the validation trial.

The results obtained with the 'HF power' method are results obtained according to EN 13656. The other methods 'HBF_4 power' and HBF_4 temp' are modified methods. In general, the obtained results fit within the measurement uncertainty of the validation trial. Only for Ti deviated results are observed, applicable for all 3 digestion methods. There is no indication that different results are obtained with the reference method and the 2 alternative methods.

Table 4 Results of CEN 6/99 Fly ash for the 3 digestion methods

	EN 13656 Mean* mg/kg dm	EN 13656 Reprod. %	Sample HF power	Rec. %	Sample HBF4 power	Rec %	Sample HBF4 temp	Rec. %
Al	39207	42	40258	103%	47124	120%	46563	119%
Sb	1250	8,3	1151	92%	1126	90%	1061	85%
As	41	31	41	102%	42	105%	52	127%
Ba	1131	31	1020	90%	804	71%	1308	116%
Cd	435	7,7	424	98%	422	97%	425	98%
Ca	149675	6	127951	85%	141678	95%	143719	96%
Cr	528	11	469	89%	472	89%	558	106%
Co	31	32	25	81%	23	75%	26	83%
Fe	10060	10	10278	102%	10297	102%	10990	109%
K	65117	12	50225	77%	54941	84%	65463	101%
Cu	2076	5,7	1874	90%	1989	96%	1944	94%
Pb	10085	10	10259	102%	10084	100%	10363	103%
Mg	11461	7,6	9424	82%	11197	98%	11784	103%
Mn	541	3,4	519	96%	534	99%	545	101%
Mo	38	70	25	67%	24	64%	27	72%
Na	63630	4,8	52575	83%	61488	97%	63956	101%
Ni	78	16	70	90%	57	74%	69	89%
Se	31	44	31	100%	34	110%	34	112%
Sn	1458	15	1338	92%	1378	94%	1499	103%
Ti	9074	4,1	7320	81%	6760	74%	7992	88%
V	26	32	23	89%	22	85%	25	96%
Zn	30002	8,9	27529	92%	27254	91%	29303	98%
Hg	6,0	7,3	5,7	94%	5,8	96%	6,1	100%

*Result from the validation study of EN 13626:2002; considered as reference value

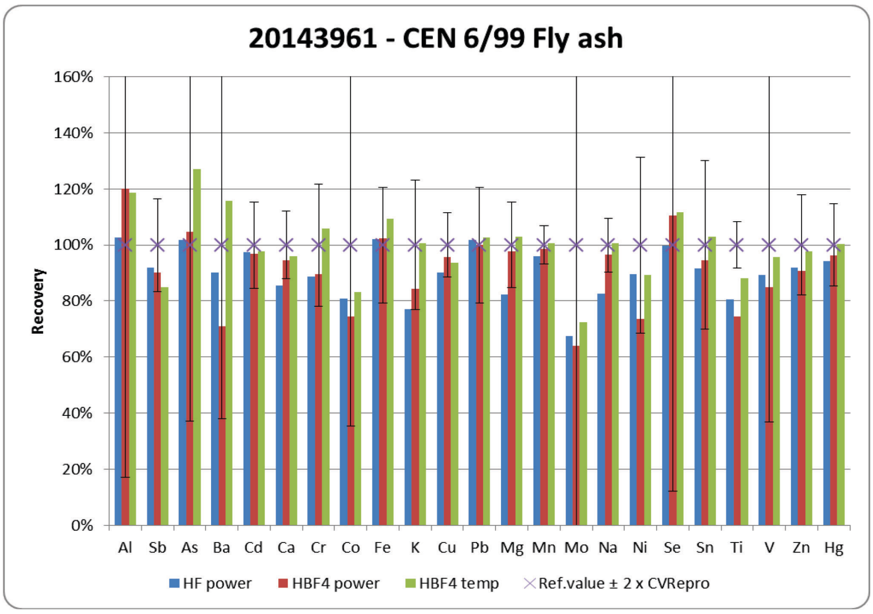

Figure 151 Results of CEN 6/99 Fly ash for the 3 digestion methods

4.9. OVERVIEW OF SAMPLE CEN 7/99 BOTTOM ASH (20143962)

The results of sample CEN 7/99 (20143962) obtained with the 3 digestion methods were compared with the mean values of this sample obtained during the validation trial of EN 13656 in 1999. For each element and digestion method the recovery was calculated towards the mean value included in EN 13656. The obtained results are presented in Table 5 and Figure 152. The figure also includes the reproducibility coefficient of variation (2 x CV_R, 95% confidence interval) of the validation trial.

The results obtained with the 'HF power' method are results obtained according to EN 13656. The other methods 'HBF_4 power' and HBF_4 temp' are modified methods. In general the obtained results fit within the measurement uncertainty of the validation trial. For the element Ti differences are observed between the reference method and the two alternative methods, similar as the previous sample. For Ba low recoveries are obtained, but also in the validation trial a high measurement deviation was obtained. Potassium doesn't fit within the (low) measurement uncertainty – note that in the CEN validation trial 14 of the 23 results were considered as outliers - , but it is probably due to the measurement rather than to the digestion method. There is no indication to declare that different results are obtained with the reference method and the 2 alternative methods.

Table 5 Results of CEN 7/99 Bottom ash for the 3 digestion methods

	EN 13656 Mean* mg/kg dm	EN 13656 Reprod. %	Sample HF power	Rec. %	Sample HBF4 power	Rec %	Sample HBF4 temp	Rec. %
Al	71894	37	82588	115%	82993	115%	80759	112%
Sb	318	12	308	97%	286	90%	304	95%
As	82	14	89	108%	88	107%	95	115%
Ba	2580	55	1033	40%	319	12%	563	22%
Cd	531	6,5	565	106%	538	101%	513	97%
Ca	66125	47	80344	122%	82776	125%	80227	121%
Cr	305	14	294	97%	251	82%	326	107%
Co	36	30	33	91%	29	79%	25	70%
Fe	20258	8,9	22052	109%	21310	105%	21307	105%
K	40426	1,6	38505	95%	40275	100%	33558	83%
Cu	1294	8,8	1315	102%	1248	96%	1411	109%
Pb	11526	9,3	11746	102%	11598	101%	10883	94%
Mg	17561	15	18309	104%	17854	102%	17079	97%
Mn	1301	7,1	1424	109%	1298	100%	1427	110%
Mo	52	45	48	91%	43	83%	48	92%
Na	28931	21	32912	114%	32913	114%	32398	112%
Ni	115	23	129	112%	108	94%	105	91%
Se	41	13	34	84%	36	89%	32	78%
Sn	2552	13	2659	104%	2447	96%	2344	92%
Ti	9090	11	7963	88%	5209	57%	5006	55%
V	42	24	49	116%	45	108%	50	119%
Zn	27791	8,7	26852	97%	27524	99%	25782	93%
Hg	31	8,2	33	105%	30	98%	33	106%

*Result from the validation study of EN 13626:2002; considered as reference value

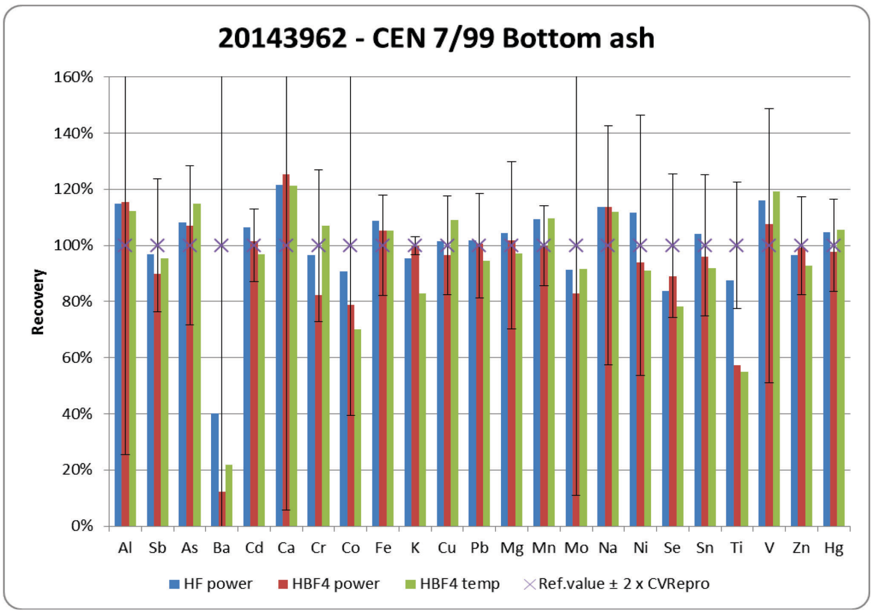

Figure 152 Results of CEN 7/99 Bottom ash for the 3 digestion methods

4.10. OVERVIEW OF SAMPLE CEN 8/99 INK WASTE (20143963)

The results of sample CEN 8/99 (20143963) obtained with the 3 digestion methods were compared with the mean values of this sample obtained during the validation trial of EN 13656 in 1999. For each element and digestion method the recovery was calculated towards the mean value included in EN 13656. The obtained results are presented in Table 6 and Figure 153. The figure also includes the reproducibility coefficient of variation (2 x CV_R, 95% confidence interval) of the validation trial.

The results obtained with the 'HF power' method are results obtained according to EN 13656. The other methods 'HBF_4 power' and HBF_4 temp' are modified methods. In general the obtained results fit within the measurement uncertainty of the validation trial. Only for Ti deviated results are observed, applicable for all 3 digestion methods. There is no indication to declare that different results are obtained with the reference method and the 2 alternative methods.

Table 6 Results of CEN 8/99 Ink waste for the 3 digestion methods

	EN 13656 Mean* mg/kg dm	EN 13656 Reprod. %	Sample HF power	Rec. %	Sample HBF4 power	Rec %	Sample HBF4 temp	Rec. %
Al	2056	31	2163	105%	2252	110%	2292	111%
Sb	70	100	12	18%	9,4	14%	10	14%
As	7,5	25	6,1	82%	4,5	61%	6,2	82%
Ba	101	8,2	102	100%	90	89%	112	110%
Ca	111589	5,4	109974	99%	110620	99%	106958	96%
Cr	3638	7,6	3577	98%	3527	97%	3512	97%
Co	15	19	15	104%	16	110%	14	94%
Fe	76239	4,7	79179	104%	75286	99%	75544	99%
K	972	33	865	89%	1001	103%	1003	103%
Cu	12487	8,5	12640	101%	12548	100%	12540	100%

	EN 13656 Mean* mg/kg dm	EN 13656 Reprod. %	Sample HF power	Rec. %	Sample HBF4 power	Rec %	Sample HBF4 temp	Rec. %
Pb	5945	7,2	6038	102%	5856	98%	5789	97%
Mg	977	7,8	982	101%	948	97%	975	100%
Mn	543	5,8	563	104%	572	105%	599	110%
Mo	5,6	85	4,5	81%	4,9	87%	5,2	94%
Na	7013	38	4676	67%	4837	69%	4918	70%
Ni	24	23	23	97%	26	111%	25	106%
Ti	244	13	215	88%	177	73%	239	98%
V	15	12	10	66%	12	84%	12	80%
Zn	1210	9,3	1259	104%	1244	103%	1312	108%
Hg	1,9	17	1,6	85%	1,6	83%	1,8	91%

*Result from the validation study of EN 13626:2002; considered as reference value

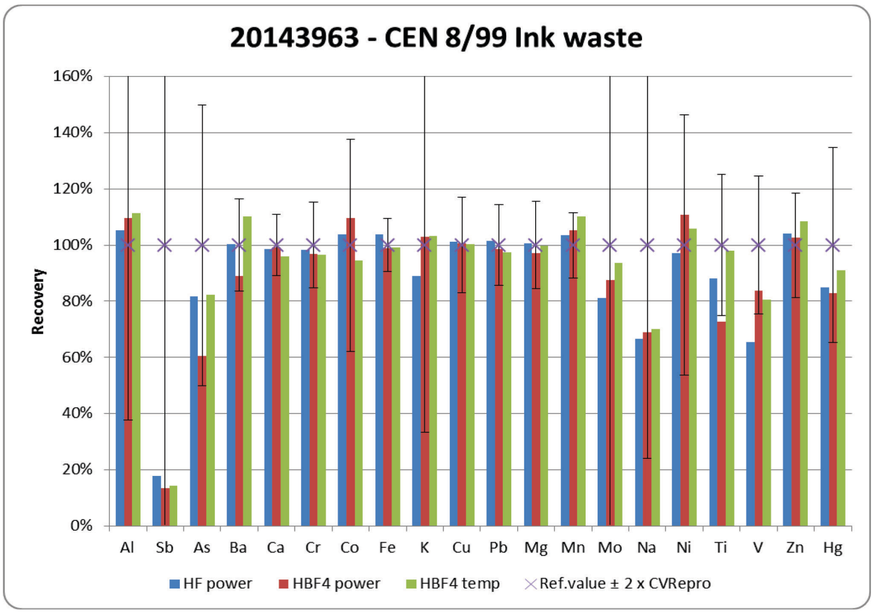

Figure 153 Results of CEN 8/99 Ink waste for the 3 digestion methods

4.11. OVERVIEW OF SAMPLE CEN 9/99 SEWAGE SLUDGE – ELECTRONIC (20143964)

The results of sample CEN 9/99 (20143964) obtained with the 3 digestion methods were compared with the mean values of this sample obtained during the validation trial of EN 13656 in 1999. For each element and digestion method the recovery was calculated towards the mean value included in EN 13656. The obtained results are presented in Table 7 and Figure 154. The figure also includes the reproducibility coefficient of variation (2 x CV_R, 95% confidence interval) of the validation trial.

The results obtained with the ‘HF power’ method are results obtained according to EN 13656. The other methods ‘HBF_4 power’ and HBF_4 temp’ are modified methods. The obtained results fit within the measurement uncertainty of the validation trial. There is no indication to declare that different results are obtained with the reference method and the 2 alternative methods.

Table 7 Results of CEN 9/99 Sewage Sludge for the 3 digestion methods

	EN 13656 Mean* mg/kg dm	**EN 13656 Reprod. %**	**Sample HF power**	**Rec. %**	**Sample HBF4 power**	**Rec %**	**Sample HBF4 temp**	**Rec. %**
Al	73799	34	91099	123%	86638	117%	83729	113%
As	4,7	78	5,2	111%	6,5	139%	6,0	130%
Ba	71	33	74	105%	76	108%	80	114%
Ca	53986	12	59368	110%	55306	102%	55270	102%
Cr	86	14	78	90%	73	85%	81	94%
Co	3,7	18	2,9	80%	4,5	123%	4,3	118%
Fe	5065	16	5538	109%	5430	107%	5663	112%
K	3138	14	3116	99%	3329	106%	3351	107%
Cu	94981	7,4	99213	104%	95184	100%	98234	103%
Pb	9455	6,7	9943	105%	9405	99%	9609	102%
Mg	2144	37	2213	103%	2247	105%	2083	97%
Mn	622	7,4	631	101%	602	97%	640	103%
Mo	4,5	20	4,4	98%	4,3	97%	4,8	107%
Na	13232	7,5	12731	96%	13567	103%	12833	97%
Ni	1751	7,5	1709	98%	1599	91%	1687	96%
Sn	18756	8,7	19626	105%	17566	94%	19098	102%
Ti	118	22	98	83%	74	63%	89	75%
V	4,9	41	4,6	93%	5,2	105%	5,1	104%
Zn	231	35	244	106%	220	95%	241	104%
Hg	0,18	20	0,13	73%	0,14	77%	0,14	77%

*Result from the validation study of EN 13626:2002; considered as reference value

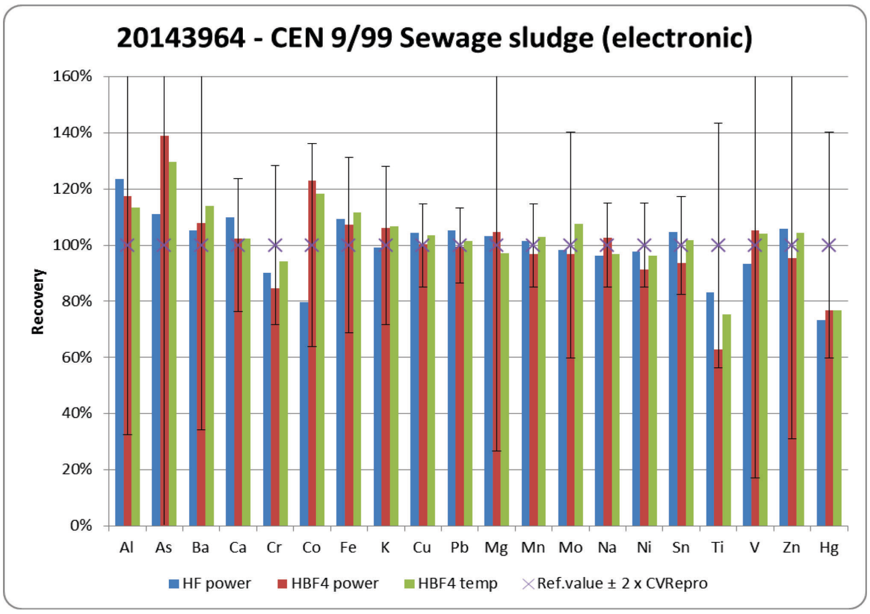

Figure 154 Results of CEN 9/99 sewage sludge for the 3 digestion methods

4.12. OVERVIEW OF SAMPLE CEN 10/99 SEWAGE SLUDGE – BCR 146R (20143965)

The results of sample CEN 10/99 (20143965) obtained with the 3 digestion methods were compared with the mean values of this sample obtained during the validation trial of EN 13656 in 1999. For each element and digestion method the recovery was calculated towards the mean value included in EN 13656. The obtained results are presented in Table 8 and Figure 155. The figure also includes the reproducibility coefficient of variation (2 x CV_R, 95% confidence interval) of the validation trial.

The results obtained with the 'HF power' method are results obtained according to EN 13656. The other methods 'HBF_4 power' and HBF_4 temp' are modified methods. In general the obtained results fit within the measurement uncertainty of the validation trial. For the element Ti differences are observed, applicable for all 3 digestion methods. Nevertheless, in general there is no indication to declare that different results are obtained with the reference method and the 2 alternative methods.

Table 8 Results of CEN 10/99 Sewage sludge for the 3 digestion methods

	EN 13656 Mean* mg/kg dm	**EN 13656 Reprod. %**	**Sample HF power**	**Rec. %**	**Sample HBF4 power**	**Rec %**	**Sample HBF4 temp**	**Rec. %**
Al	28658	23	23618	82%	29570	103%	30020	105%
Sb	13	21	14	115%	12	98%	13	103%
As	6,9	43	7,5	109%	8,6	125%	9,4	136%
Ba	660	16	495	75%	610	92%	687	104%
Cd	16 (18.8)	14	18	115%	18	112%	19	116%
Ca	134370	7,4	92356	69%	131819	98%	137852	103%
Cr	178 (196)	7,4	170	96%	181	101%	199	112%
Co	7,9 (7.39)	27	7,7	97%	7,0	89%	9,0	114%
Fe	14215	12	11153	78%	15539	109%	15837	111%
K	5466	16	4646	85%	4960	91%	5086	93%
Cu	810 (838)	8,7	813	100%	833	103%	793	98%
Pb	556 (609)	10	583	105%	569	102%	609	110%
Mg	9385	17	8254	88%	9378	100%	9429	100%
Mn	305 (323)	6,7	317	104%	318	104%	343	112%
Mo	7,8	22	8,9	113%	9,5	121%	10	132%
Na	2710	54	1598	59%	1818	67%	1892	70%
Ni	65 (70)	19	68	104%	67	103%	72	111%
Sn	76	79	92	121%	77	102%	85	113%
Ti	2314	7,6	2203	95%	872	38%	1677	72%
V	38	24	37	98%	43	112%	47	124%
Zn	2848 (3060)	7,3	2913	102%	2810	99%	2861	100%
Hg	7,2 (8.6)	22	7,7	107%	6,9	96%	8,0	110%

*Result from the validation study of EN 13626:2002; considered as reference value
( ) certified values of BCR 146R

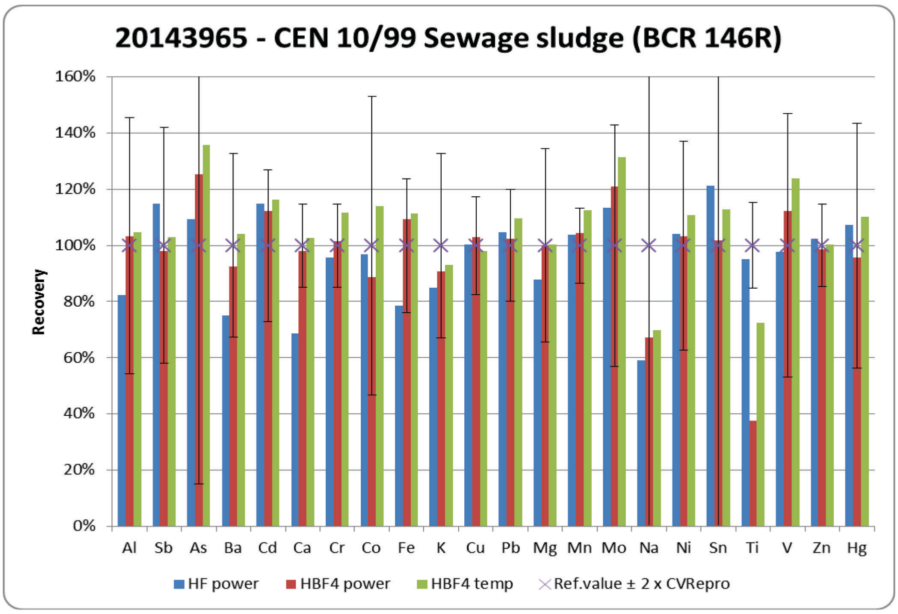

Figure 155 Results of CEN 10/99 Sewage sludge for the 3 digestion methods

4.13. OVERVIEW OF SAMPLE BCR 176R (20143966)

The results of the certified sample BCR 176R obtained with the 3 digestion methods were compared with the certified values and for each element and digestion method the recovery was calculated. The obtained results are presented in Table 9 and Figure 156. This certified material was the successor of the sample CEN 11/99 (BCR176) used in the validation trial of EN 13656 in 1999. The matrix is the same but the concentration of the different elements might change between both samples. Therefore the current data cannot be compared with the mean values of EN 13656 data. Nevertheless, Figure 156 includes the reproducibility coefficient of variation (2 x CV_R, 95% confidence interval) of the validation trial to have an idea of the expected measurement deviation. In Table 9 also the element recovery is shown as obtained on the sample BCR176 of the EN 13656 standard.

The results obtained with the 'HF power' method are results obtained according to EN 13656. The other methods 'HBF$_4$ power' and HBF$_4$ temp' are modified methods. In general the obtained results fit within the measurement uncertainty of the validation trial. If deviated results are observed, it is in most cases applicable for all 3 digestion methods. For the elements Ba, Cr (and Se) there is a significant underestimation with respect tot the reference value, but it should be noted that the indicative value of Ba is obtained by k_0-NAA (Neutron activation analysis using k_0-method) and the certified value of Cr is mostly based on neutron activation analyses. Also for the sample BCR 176 of the validation trial in 1999 the recovery of Cr was limited to 37%, which is in line with the current results.

Table 9 Results of BCR 176R for the 3 digestion methods

	Certified value mg/kg dm	Sample HF power	Rec. %	Sample HBF4 power	Rec %	Sample HBF4 temp	Rec. %	Element Rec. (%) in EN 13656
Sb	850	776	91%	816	96%	853	100%	80%
As	54	56	104%	54	101%	60	111%	89%

	Certified value mg/kg dm	Sample HF power	Rec. %	Sample HBF4 power	Rec %	Sample HBF4 temp	Rec. %	Element Rec. (%) in EN 13656
Ba	4650	287	6%	208	4%	306	7%	61%
Cd	226	218	96%	205	91%	220	97%	96%
Cr	810	284	35%	329	41%	346	43%	37%
Co	27	28	105%	28	103%	29	109%	232%
Fe	13100	11448	87%	13059	100%	13394	102%	98%
Cu	1050	1068	102%	1056	101%	1106	105%	100%
Pb	5000	4033	81%	4181	84%	3938	79%	98%
Mn	730	762	104%	740	101%	790	108%	91%
Na	34800	32962	95%	33985	98%	34464	99%	63%
Ni	117	116	99%	109	93%	116	99%	100%
Se	18	10	52%	12	65%	12	67%	92%
V	35	36	102%	36	103%	39	111%	115%
Zn	16800	16572	99%	17326	103%	16192	96%	102%
Hg	1,6	1,3	84%	1,4	89%	1,5	92%	98%

*light grey: indicative values

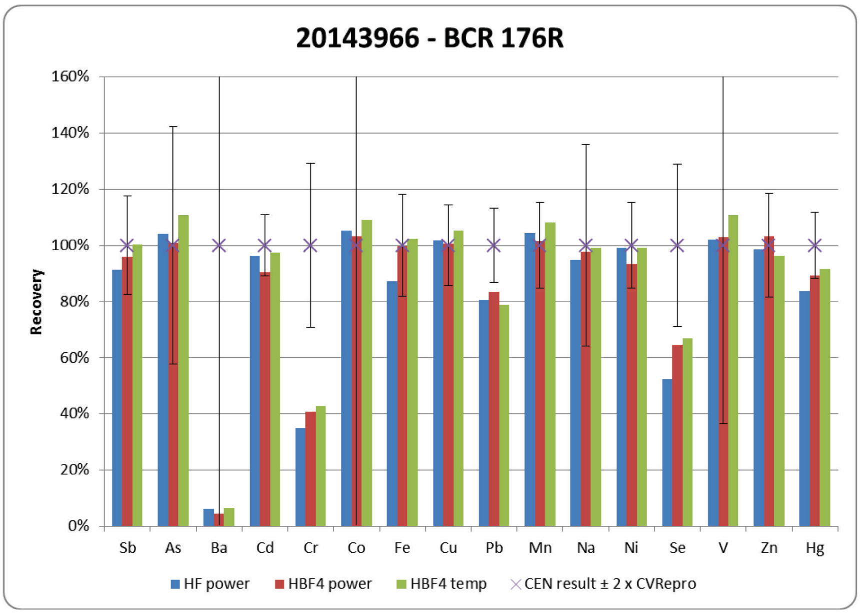

Figure 156 Results of BCR 176R for the 3 digestion methods

4.14. OVERVIEW OF CEN SAMPLES

Based on the above results it can be stated that the results obtained with the alternative methods are for all elements situated within the measurement uncertainty (2 x CV_R) with the exception of:

- Ti: systematic bias of -20% with the 'HF power' method for all samples
- K: for sample CEN 7/99 with the 'HBF4 temp' method (no systematic error)
- Cr: for sample BCR 176R with all digestion methods (sample BCR 176 analysed during the validation trial in 1999, resulted also in a low recovery of Cr of 37%, which is in line with the

results obtained with the alternative methods). No indication for systematic error with respect to other samples.

- Pb: for sample BCR 176R with all digestion methods. No indication for systematic error with respect to other samples.
- Se: for sample BCR 176R with all digestion methods. Low concentration level. No indication for systematic error with respect to other samples.

For the waste samples selected from the validation study of EN 13656, per element the ratio was calculated between the alternative method (HBF_4 power or HBF_4 temp) and the reference method (HF power). The distribution for the different elements is presented by a Box and Whisker plot, as shown in Figure 157 until Figure 162. A ratio of 1 is achieved when the alternative method give the same results as the reference method. A ratio below 1 indicates that higher values are obtained with the reference method, while a ratio above 1 indicates higher values with the alternative method.

<u>Note that the evaluation is based on the comparison of single measurement results.</u>

Legend

R1	Ratio HBF_4 acid digestion, power controlled versus HF digestion, power controlled
R2	Ratio HBF_4 acid digestion, temperature controlled versus HF digestion, power controlled

For the elements As, Cd, Cr, Cu, Pb, Ni , Zn and Hg the median value of the ratio fluctuates around 1, indicating a good correspondence between the 3 digestion methods. For the element As a broader distribution is observed in comparison with the other elements, but this is attributed to the fact that several samples have a low concentration of less than 10 mg/kg dm.

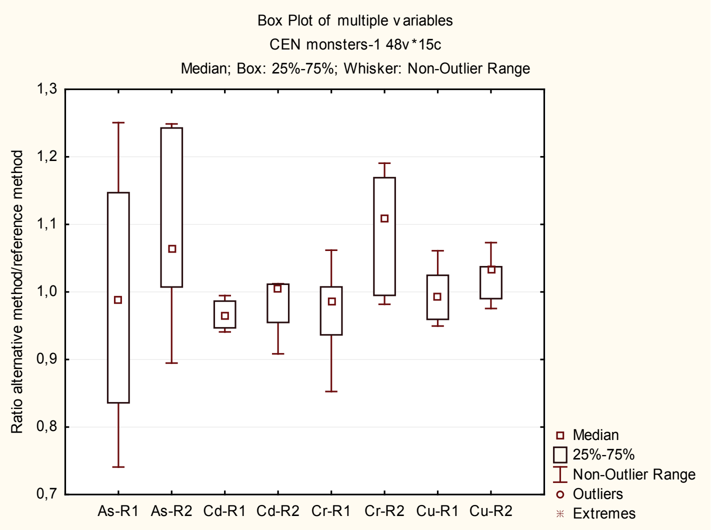

Figure 157 Overview ratio alternative methods vs the reference method for the elements As, Cd,Cr and Cu in the CEN waste samples

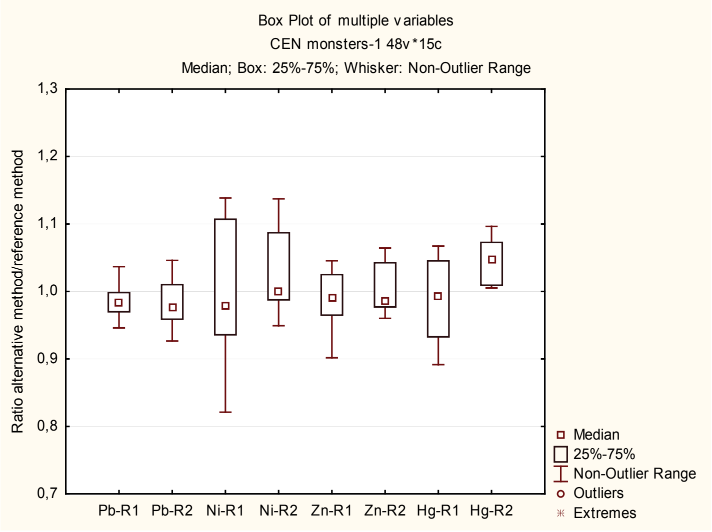

Figure 158 Overview ratio alternative methods vs the reference method for the elements Pb, Ni, Zn and Hg in the CEN waste samples

For the other trace elements Sb, Ba, Co, Mn, Mo, Se, Sn and V the median value also fluctuates around 1. It should be noted that for some samples the concentration level of Mo, V and Co is low (around 10 mg/kg dm or lower), introducing a broader distribution profile. For the element Ba also a larger spread is observed, due to the difficulty to get the element in solution. This was also observed in the validation trial of 1999. The obtained result is strongly dependent on the type of sample.

Note: In the VITO laboratory it was already observed that for the digestion of fly ash it is necessary to reduce the sample intake to about 0.25 g in order to obtain a maximum yield. During this study the sample intake was remained constant at about 0.5 g.

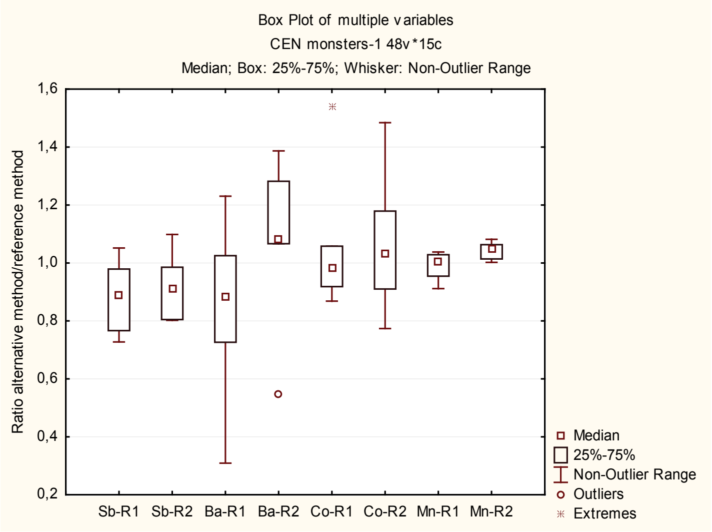

Figure 159 Overview ratio alternative methods vs the reference method for the elements Sb, Ba, Co, Mn in the CEN waste samples

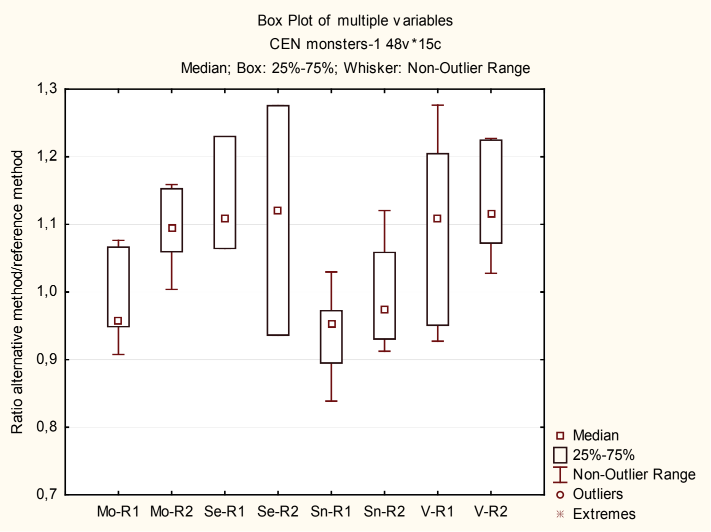

Figure 160 Overview ratio alternative methods vs the reference method for the elements Mo, Se, Sn and V in the CEN waste samples

For the major elements, except Ti, the median value of the ratio fluctuates around 1 or above, meaning that when applying the alternative methods at least the concentration obtained with the reference method was obtained. For Ti differences are observed for the alternative methods in comparison with the reference method, especially when applying the HBF_4 digestion with the power controlled microwave digestion. This digestion method results in a systematic underestimation of about 20%. When applying the HBF_4 digestion with the temperature controlled microwave digestion, this effect is less pronounced.

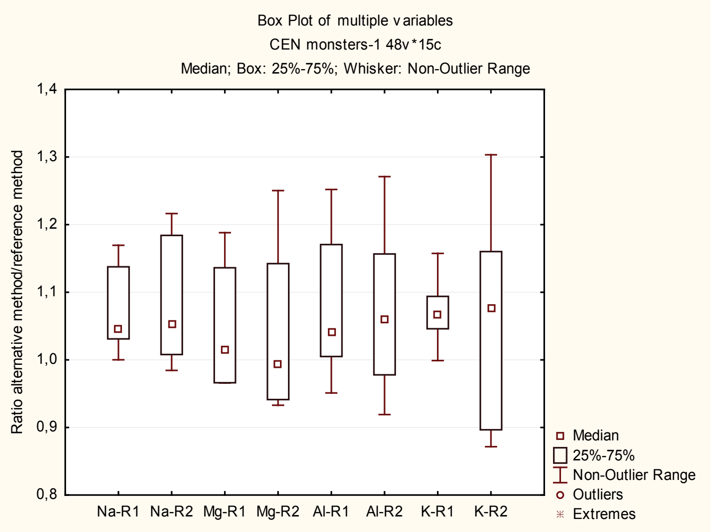

Figure 161 Overview ratio alternative methods vs the reference method for the elements Na, Mg, Al and K in the CEN waste samples

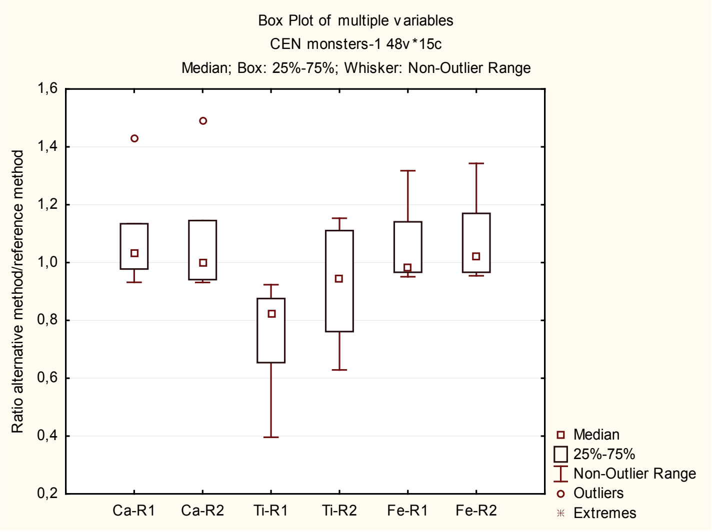

Figure 162 Overview ratio alternative methods vs the reference method for the elements Ca, Ti and Fe in the CEN waste samples

4.15. OVERVIEW OF ALL ELEMENTS

Per element the ratio was calculated between the alternative method (HBF_4 power or HBF_4 temp) and the reference method (HF power). The distribution for the different elements is presented by a Box and Whisker plot, as shown in Figure 163 til Figure 168. Note that the evaluation is based on the comparison of single measurement results.

Legend

R1	Ratio HBF_4 acid digestion, power controlled versus HF digestion, power controlled
R2	Ratio HBF_4 acid digestion, temperature controlled versus HF digestion, power controlled

For the elements As, Cd, Cr, Cu, Pb, Ni, Zn and Hg in waste samples the median values fluctuate around 1, indicating that comparable results are obtained with the reference method and the alternative methods. In most cases, the ratio with ‘HBF_4 power’ (R1) is situated slightly below 1 (i.e. higher values with reference method) while the ratio with ‘HBF_4 temp’ (R2) is situated above 1 (i.e. higher values with alternative method). Globally, most of the data are situated between a ratio of 0.8 and 1.2.

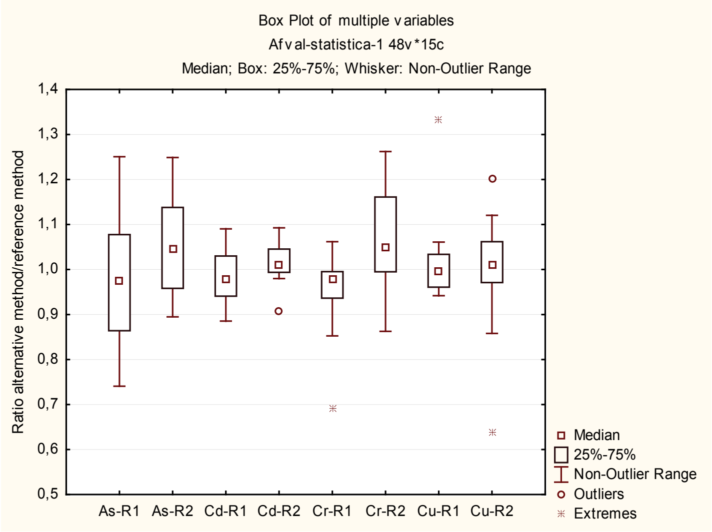

Figure 163 Overview ratio alternative methods vs the reference method for the elements As, Cd,Cr and Cu in waste samples

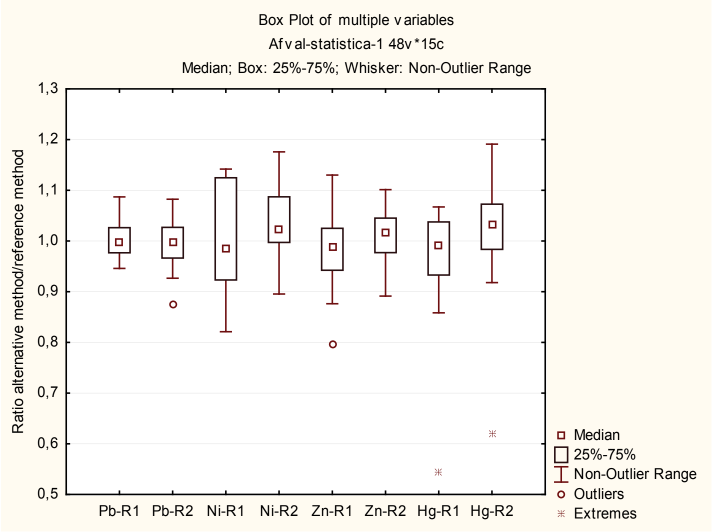

Figure 164 Overview ratio alternative methods vs the reference method for the elements Pb, Ni, Zn and Hg in waste samples

For the other trace elements Sb, Ba, Co , Mo and V in waste samples the median values also fluctuate around 1, indicating a good correspondence. Most of the data results in a ratio between 0.8 and 1.2.

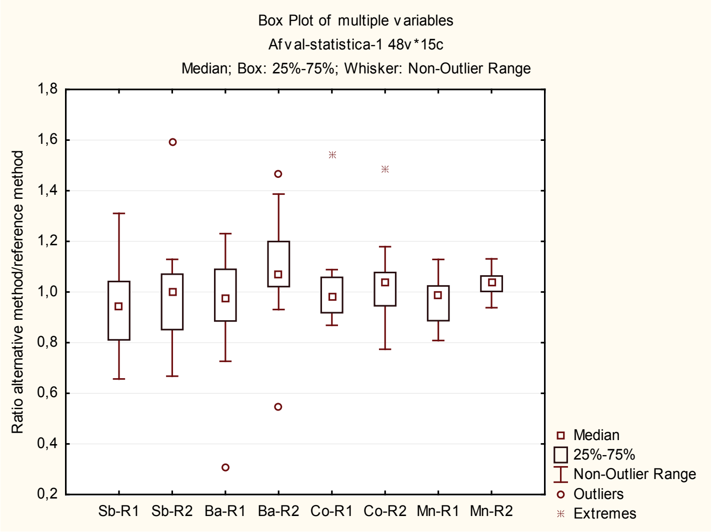

Figure 165 Overview ratio alternative methods vs the reference method for the elements Sb, Ba, Co and Mn in waste samples

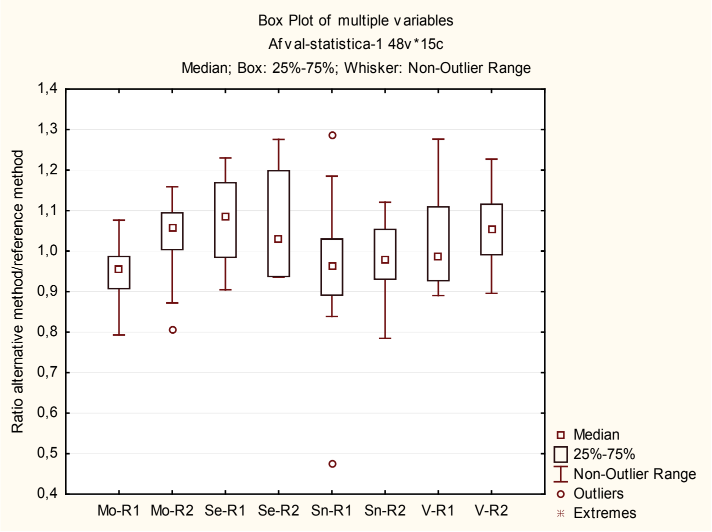

Figure 166 Overview ratio alternative methods vs the reference method for the elements Mo, Se, Sn and V in waste samples

For the major elements Na, Mg, Al, K, Ca, Ti, Mn and Fe in waste samples also a median ratio of 1 is obtained, except for the element Ti. Especially the results obtained with the 'HBF$_4$ power' method are significantly lower than with the reference method 'HF power'. Globally, with exception for Ti, most of the data are situated between a ratio of 0.8 and 1.2.

The results of the waste samples corresponds with the results obtained on the soil samples.

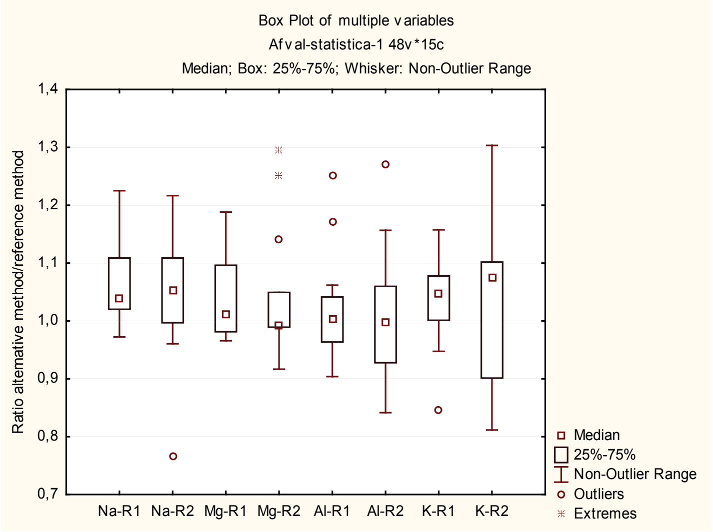

Figure 167 Overview ratio alternative methods vs the reference method for the elements Na, Mg, Al, K in waste samples

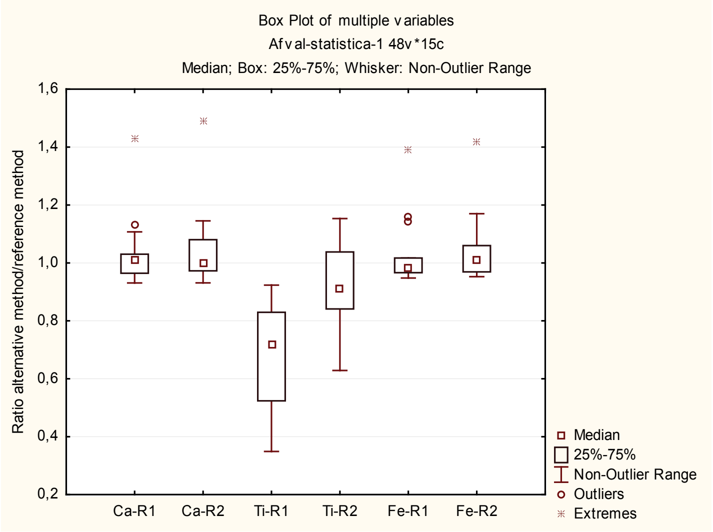

Figure 168 Overview ratio alternative methods vs the reference method for the elements Ca, Ti and Fe in waste samples

CHAPTER 5 OVERALL EVALUATION OF THE DIGESTION METHODS

5.1. EVALUATION OF THE MEASUREMENT VARIATION

The overall measurement variation which can be expected when different digestion procedures are applied, are summarized in Figure 169 for soil samples and in Figure 170 for waste samples.

For the soil samples the ratio calculations (R1 and R2, see legend) for the Vlarebo elements (As, Cd, Cr, Cu, Pb, Ni, Zn and Hg) were pooled. It should be noted that low concentration values for As (< 15 mg/kg dm) and for Pb (< 10 mg/kg dm) were excluded. Figure 169 includes the pooled results for R1 (HBF_4 power/HF power), R2 (HBF_4 temp/HF power) and R1+R2 combined (HBF_4 (power+temp)/HF power). The latter gives an overview of the overall measurement variation which was obtained when applying all 3 digestion methods. The mean value of the ratios is always closely related to 1, indicating a good correspondence between the trueness of the alternative methods and the reference method. The non-outlier range is situated between a ratio of 0.8 and 1.2, which can also be expected from replicate/duplo measurements determined with the reference method only (see Table 10). One extreme value is observed, attributed to the determination of Ni in 1 soil sample. There is no indication of a systematic error.

Legend

R1 Ratio HBF_4 acid digestion, power controlled versus HF digestion, power controlled

R2 Ratio HBF_4 acid digestion, temperature controlled versus HF digestion, power controlled

R1+R2 Ratio HBF_4 acid digestion, temperature + power controlled versus HF digestion, power controlled

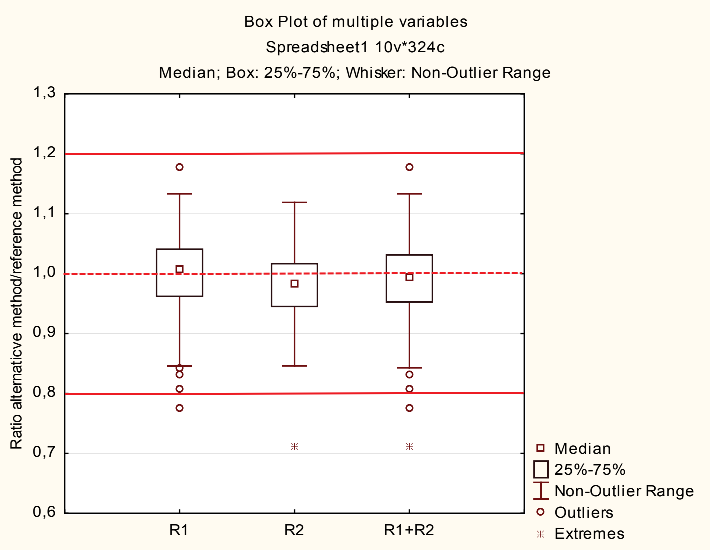

Figure 169 Overview ratio alternative methods vs the reference method in soil samples (elements included are Vlarebo elements)

Table 10 Limit values and intralaboratory measurement uncertainty for soil samples obtained with the reference method[5]

Parameter	BSN (1) mg/kg dm	SW(2) mg/kg dm	LOQ (3) mg/kg dm	Intralab. Meas. Uncertainty (at the level of BSN)(6)		
				Bias (%)	CV_R (%)	U (%)
As	45	19	3.8	-6	8.7	23
Cd	2	0.8	0.6	-4	4.6	13
Cr	130	37	1.2	-16	11	39(4)
				-0.9	11	24(5)
Cu	200	17	0.6	-3	12	27
Ni	100	9	1.2	-6	7.1	20
Pb	200	40	5.2	-5	11	26
Zn	600	62	2.0	-7	7.5	22
Hg	10	0.55	0.04	-0.6	8.3	17

(1) BSN: soil remediation value (10% clay, 2% organic matter)
(2) SW: target value (10% klei, 2% organisch materiaal)
(3) LOQ: limit of quantification
(4) U measurement uncertainty calculated with respect to reference value
(5) U measurement uncertainty calculated with respect to consensus value (mean of the method)
(6) U = 2 * CV_R + bias

For the waste samples the ratio calculations (R1 and R2, see legend) for the Vlarema 4bis-elements (As, Cd, Cr, Cu, Pb, Ni, Zn, Hg, Sb, Ba, Co, Mo, Se, Sn and V) and Mn were pooled. It should be noted that low concentration values (in the range of less then 10 mg/kg dm) were excluded. Figure 170 includes the pooled results for R1 (HBF_4 power/HF power), R2 (HBF_4 temp/HF power) and R1+R2 combined (HBF_4 (power+temp)/HF power). The latter gives an overview of the overall measurement variation which was obtained when applying all 3 digestion methods. The mean value of the ratios is always closely related to 1, indicating a good correspondence between the alternative methods and the reference method. The non-outlier range is situated between a ratio of 0.8 and 1.2, which can be expected from replicate measurements (see Table 11). The extreme values observed (2) are all attributed to the determination of Ba. Also 50% of the outliers are related to Ba, the other outliers can be assigned to the elements Cr, Co and V.

For all Vlarema 4bis-elements, except Ba, there is no indication of a systematic error. For the determination of Ba, on the other hand, the digestion procedure can be critical and can have an influence on the obtained results (operational defined). In waste samples it is observed that the total release of Ba from the matrix is not always evident (e.g. ashes). This was also observed in the validation trial of EN 13656 in 1999. The obtained result is strongly dependent on the type of sample.

> Note: In the VITO laboratory it was already observed that for the digestion of fly ash it is necessary to reduce the sample intake to about 0.25 g in order to obtain a maximum yield. During this study the sample intake was remained constant at about 0.5 g.

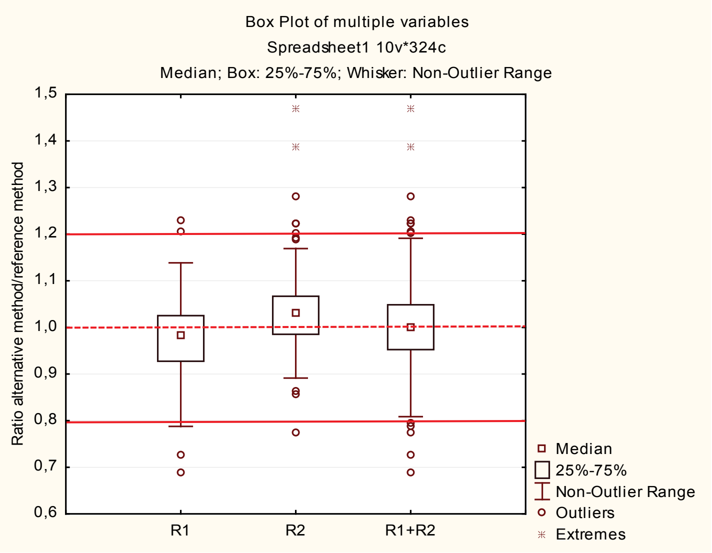

Figure 170 Overview ratio alternative method vs the reference methods in waste samples (elements included are Vlarema elements)

Table 11 Intralaboratory measurement uncertainty for waste sample obtained with the reference method[6]

Parameter	**LOQ** (1) **mg/kg dm**	**Intralab. Meas. Uncertainty** (4)		
		Bias (%)	CV_R (%)	U (%)
Sb	1.0	7.0	6.2	16
As	0.94	-4.5	6.9	18
Ba	0.14	-3.0	12	27
Be	1.1	-0.7	4.1	8.8
Cd	0.02	-4.0	9.1	22
Cr	0.22	-2.0	7.7	17
Cu	1.2	-3.0	12	28
Pb	0.88	-4.8	2.7	10
Mo	0.28	-7.1	5.4	18
Ni	0.48	-6.7	7.3	21
Se	5.6	8.1	-	-(2)
Tl	3.2	-	-	-(2)
Zn	0.80	-3.6	9.7	23
Hg	0.04	3.5	(2.5)	(8.5)(3)

(1) LOQ: limit of quantification
(2) No samples available above LOQ
(3) Determined on the basis of 1 sample
(4) U = 2 * CV_R + bias

5.2. EVALUATION OF DATA OF RECOGNIZED LABORATORIES

At the moment a few laboratories already apply the HBF_4 digestion using temperature controlled microwave digestion. Based on their validation data and good evaluations in round robin tests (organized by VITO) for the determination of elements in soil and waste samples, the validity of the alternative methods is confirmed.

With respect to the round robin tests (organized by VITO), the obtained measurement variation for the analysis of elements in soil and waste samples was derived from the final evaluation reports. For soil samples, the results of the Vlarebo elements of 2012, 2013 and 2014 were considered and resulted in an overall measurement variation (2^*CV_R, 95% C.I.) of 25%. For waste samples, the round robin test of 2012 and 2013 were taken into account, resulting in an overall measurement variation (2^*CV_R, 95% C.I.) of 23%.

From 1 laboratory comparable data were received from the analysis of a round robin sample (N ≈ 70). These data were obtained on the round robin sample ISE 989 (a river clay containing 24.7 % of Si, 28.4% of clay and 12.7 % > 63 µm) that was digested with both $HF:HNO_3:HCl$ and $HBF_4:HNO_3:HCl$. For evaluation, the obtained measurement values of the 8 Vlarebo elements were divided by their consensus value (=reference value) from the round robin test. The obtained results are shown in Figure 171 and Figure 172.

The mean value of the ratios is always closely related to 1, indicating a good correspondence between the measurement value and the reference value, and this for both digestion methods. The non-outlier range is situated between a ratio of 0.8 and 1.2, which can be expected from replicate measurements. Comparable results are obtained with both digestion methods. These data confirm the results previously described in the report.

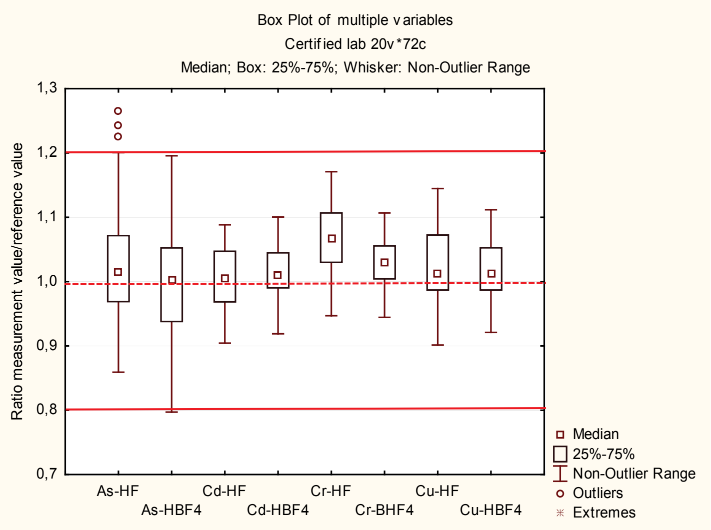

Figure 171 Ratio measurement value vs reference value in a soil sample (N ≈ 70) for As, Cd, Cr and Cu for both HF and HBF_4 digestions

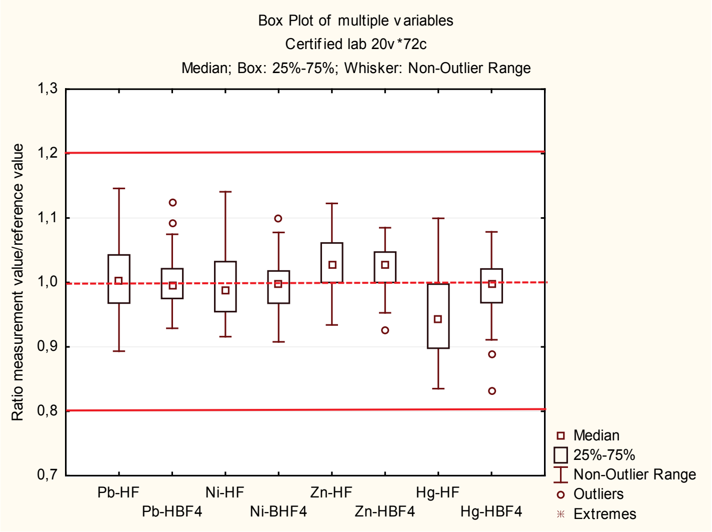

Figure 172 Ratio measurement value vs reference value in a soil sample (N ≈ 70) for Pb, Ni, Zn and Hg for both HF and HBF_4 digestions

CHAPTER 6 CONCLUSION

In this study some alternative digestion methods were evaluated to simplify the current procedure on one hand and to extend the applicability of the procedure to different types of micro wave instruments on the other for the determination of elements in soil and waste samples. In this framework the following aspects were considered:

1. *Evaluation of an one-step digestion (*HBF_4*) as replacement for the two-steps digestion with HF +* H_3BO_3 *('HF power')*
   The procedure involves a one-step digestion, while maintaining the same power of digestion of the silicate matrix, by using HBF_4 (replacing HF with H_3BO_3). In addition, the use of HBF_4 is for safety reasons preferred over HF.
2. *Evaluation of temperature controlled microwave systems as an addition to power controlled microwave systems*
   The HBF_4 digestion using power controlled microwave oven ('HBF_4 power') was compared versus temperature controlled digestion ('HBF_4 temp').

Evaluation of 10 soil samples
For the 8 VLAREBO[g] elements (As, Cd, Cr, Cu, Pb, Ni, Zn and Hg) the results obtained with the alternative methods ('HBF_4 power' and 'HBF_4 temp'), corresponds with the results of the reference method ('HF power'). Higher measurements deviations are sometimes observed on samples with lower concentration levels. But there is no indication of a systematic error when applying the alternative methods with respect to the reference method. In paragraph 5.1 on page 99 it is shown that the overall measurement variation is situated in a range of < 20% if different digestion procedures are applied, which can also be expected from replicate/duplo analyses determined with the reference method only. Tests and analyses carried out by a few recognized laboratories confirm the applicability of the evaluated alternative methods to replace the time-consuming reference method.

For the other trace elements (Sb, Ba, Co, Mn, Mo, Se, Sn and V) the same conclusion can be formulated. Often low concentrations of these elements are measured resulting in a higher measurement deviation, but nevertheless it can be stated that comparable results are obtained with the 3 digestion methods.

For the major elements (Na, Mg, Al, K, Ca, Ti, Mn and Fe) a good correspondence is observed between the results of the alternative methods and the reference method, except for Ti. Especially the results obtained with the 'HBF_4 power' method are significantly lower than with the reference method 'HF power'.

Evaluation of 10 waste samples (of which 6 from the validation study of EN 13656)
For the VLAREMA[h] elements (As, Cd, Cr, Cu, Pb, Ni, Zn, Hg, Sb, Ba, Co, Mo, Se, Sn and V) and element Mn comparable results are obtained with the alternative methods and the reference method. In paragraph 5.1 on page 99 it is shown that the overall measurement variation is situated in a range of < 20% if different digestion procedures are applied, which can also be expected from replicate/duplo analyses determined with the reference method only. Moreover, for the

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[g] Flemish regulation on soil remediation and protection regulations

[h] Flemish regulation on sustainable management of material cycles and waste – VLAREMA 4bis (dec 2013)

determination of Ba it is observed that the digestion procedure can be critical and can have an influence on the obtained results (operational defined). Special attention needs to be given to the digestion procedure for the determination of this element. This effect is no surprise as it was also established during the validation trial of EN 13656 in 1999. Tests and analyses carried out by a few recognized laboratories confirm the applicability of the evaluated alternative methods to replace the time-consuming reference method.

For the major elements (Na, Mg, Al, K, Ca, Ti and Fe) the same conclusion can be formumated as for the soil samples. A good correspondence is observed between the results of the alternative methods and the reference method, except for Ti. Especially the results obtained with the 'HBF_4 power' method are significantly lower than with the reference method 'HF power'.

ANNEX A ANALYTICAL RESULTS OF THE SOIL SAMPLES USING DIFFERENT DIGESTION PROCEDURES

	mg/kg ds	1	1b	2	3	4	4b	5	5b	6 - QC1	7	7b	8	9	10	11	12 - QC2
As	HF power	71	63	28	29	34		3,4		35	29	28	71	13	133	13	104
	HBF4 power	66	66	28	23	32		3,5		35	27	25	74	11	122	11	104
	HBF4 temp	68		27	24	29	30,3	2,4	3,9	35	29		75	13	120	12	100
Cd	HF power	13	13	2,6	21	27		<0.5		2,5	1,6	1,6	1,7	<0.5	3,4	9,5	39
	HBF4 power	13	13	2,4	22	28		<0.5		2,5	1,7	1,6	1,9	<0.5	3,6	10,0	41
	HBF4 temp	13		2,9	21	25	26,5	<0.5	<0.5	2,5	1,5		1,7	0,5	3,5	9,5	40
Cr	HF power	115	109	177	59	63		856		121	199	196	673	40	58	153	42
	HBF4 power	109	106	167	58	60		742		117	195	193	653	40	61	149	43
	HBF4 temp	114		173	63	65	74	762	772	122	202		567	45	66	163	42
Cu	HF power	1573	1933	1696	139	150		85		103	6685	6613	1490	41	710	526	119
	HBF4 power	1751	2186	1430	155	153		84		100	6178	6384	1325	34	715	504	115
	HBF4 temp	1416	1347	1603	145	143	157	84	98	101	6618		1461	40	716	505	116
Pb	HF power	918	893	468	610	971		8,2		167	852	828	863	159	817	531	1102
	HBF4 power	976	1051	444	584	940		6,5		167	869	875	909	170	904	555	1124
	HBF4 temp	951		443	551	867	901	8,5	8,3	170	860		907	157	849	580	1134
Ni	HF power	128	123	141	28	31		68		46	114	110	431	23	105	110	21
	HBF4 power	133	128	133	28	31		53		45	118	120	404	24	118	118	22
	HBF4 temp	125		141	27	31	33	61	86	45	113		306	24	108	110	20
Zn	HF power	1854	1712	1553	1591	1924		101		487	4047	4030	1660	159	4973	2595	365
	HBF4 power	1939	1940	1428	1558	2011		102		492	4118	4108	1704	169	5029	2653	381
	HBF4 temp	1743		1523	1577	1928	1979	111	105	490	4163		1736	169	5238	2610	356
Hg	HF power	0,58	0,59	0,99	2,5	2,6		<0.1		1,1	1,1	1,2	65	77	0,39	0,58	6,7
	HBF4 power	0,59	0,57	0,95	2,5	2,6		<0.1		1,1	1,0	1,0	65	72	0,35	0,48	6,1
	HBF4 temp	0,60		1,01	2,8	2,6	2,61	<0.1	<0.1	1,1	1,0		63	70	0,34	0,50	6,0
Sb	HF power	14,7	15,5	13,1	9,1	5,4		10,4		<2	33,3	32,5	34,2	4,3	15,9	63,3	22,2
	HBF4 power	11,0	18,0	12,9	6,6	7,4		4,9		4,3	31,2	31,8	32,0	<2	18,4	61,9	21,7
	HBF4 temp	16,6		13,9	8,2	8,2	8,7	<2	3,0	5,4	31,1		33,3	3,3	17,2	54,3	21,5
Ba	HF power	523	531	864	405	453		103		570	1339	1360	517	319	940	415	698
	HBF4 power	575	587	931	434	500		104		550	1256	1238	516	316	941	394	681
	HBF4 temp	519		877	401	463	456	99	102	541	1340		514	307	936	399	657
Co	HF power	64,5	63,0	19,3	11,2	9,8		6,4		15,2	34,8	33,8	37,6	12,1	20,1	10,9	9,3
	HBF4 power	64,6	63,7	18,1	11,2	9,9		4,7		14,9	35,3	35,7	44,3	13,1	21,7	11,6	9,1
	HBF4 temp	62,9		18,9	11,5	10,2	11,1	4,9	4,8	14,7	35,2		41,3	13,0	21,5	13,8	10,4
Mo	HF power	9,3	9,1	8,4	1,5	1,6		8,6		1,3	16,0	15,5	66,2	1,7	2,8	32,1	1,7
	HBF4 power	8,6	8,7	6,3	1,1	<1		9,4		<1	16,0	14,8	83,3	1,5	2,7	33,7	1,8
	HBF4 temp	8,6		6,4	1,1	1,1	1,2	8,3	7,4	<1	15,8		68,3	1,7	2,7	33,5	1,6
Sn	HF power	88	78	49	27	21		3,2		11	439	444	36	6,4	154	77	<2
	HBF4 power	160	181	43	30	23		<2		9,3	443	453	37	4,3	170	82	<2
	HBF4 temp	145		41	26	23	23	<2	3	10	437		33	6,9	158	77	<2
V	HF power	146	142	74	48	46		41		98	113	112	47	49	37	48	91
	HBF4 power	147	147	76	49	48		37		96	115	116	48	52	39	50	94
	HBF4 temp	146		74	49	46	52	40	38	94	119		47	53	41	51	91
Na	HF power	3830	3856	4670	1965	2416		2129		5240	3274	3274	1345	2604	2238	3191	11093
	HBF4 power	3759	3771	4695	1976	2437		2158		5143	3384	3369	1414	2751	2358	3207	11403
	HBF4 temp	3729		4592	1920	2340	2398	2154	2114	4949	3261		1437	2627	2278	3091	10630
Mg	HF power	3445	3581	2518	3071	3159		2125		10711	5166	5245	1511	2436	1342	5519	9487
	HBF4 power	3758	3751	2545	3185	3246		2303		11005	5423	5662	1589	2627	1545	5619	10041
	HBF4 temp	3144		2327	3035	2996	3182	2121	2062	10574	5615		1707	2397	1264	5986	8828
Al	HF power	45361	45231	22695	20212	22780		43413		56148	40381	40560	14427	22058	19646	21218	63365
	HBF4 power	43686	44388	21536	18451	21525		48178		54291	42296	43646	15873	24186	22787	19961	64150
	HBF4 temp	36101		19111	19539	21215	22872	50543	49177	46866	43257		15890	20636	22461	19249	55086
K	HF power	11843	11599	8235	7666	8769		1433		19041	11120	11173	5037	11510	7338	21415	23068
	HBF4 power	11795	12001	8143	7708	9002		1488		18182	11291	11379	5405	11754	8036	21646	23299
	HBF4 temp	10620		7358	6649	7759	8513	1439	1261	16980	11268		5142	11397	7414	21263	22023
Ca	HF power	31761	35370	35648	28167	23312		2478		43121	36128	36447	17911	20916	6882	217327	27403
	HBF4 power	30885	31168	35618	27808	23698		2737		40661	37114	37328	18347	20479	7053	209124	27876
	HBF4 temp	26869		33111	27704	22488	23841	2625	2533	39587	37620		18168	19036	6418	211662	25820
Ti	HF power	2358	2189	1412	1211	1390		2257		2534	3367	3356	1572	1251	1454	1471	2522
	HBF4 power	1841	1749	1095	997	1089		2173		1477	2453	2484	1316	1023	1191	1099	2067
	HBF4 temp	1944		1257	1241	1233	1483	2269	2263	2005	3307		1600	1178	1510	1252	2388
Mn	HF power	437	447	682	307	284		1150		1257	1396	1380	2238	263	244	605	638
	HBF4 power	497	465	685	314	293		1048		1209	1472	1461	2354	283	270	647	660
	HBF4 temp	443		657	303	310	304	1045	1090	1231	1375		2185	266	252	614	638
Fe	HF power	31287	30554	61756	14631	16714		18184		31217	123050	121243	338601	18371	20300	23848	27283
	HBF4 power	30563	31470	60413	14727	16879		18255		29419	117356	121272	338101	18445	20485	23555	27721
	HBF4 temp	30768		61386	14733	16443	17288	18409	17087	31254	128351		344186	18596	20691	24334	27800

ANNEX B ANALYTICAL RESULTS OF THE WASTE SAMPLES USING DIFFERENT DIGESTION PROCEDURES

	mg/kg ds	1	1b	2	3	4	5	6-QC1	7	8	8b	9	10	11	12-QC2
As	HF power	33	31	70	42	687	41	36	89	6,1	6,3	5,2	7,5	56	105
	HBF4 power	29	33	61	36	675	42	31	88	4,5	5,2	6,5	8,6	54	115
	HBF4 temp	31	29	70	47	642	52	38	95	6,2	5,6	6,0	9,4	60	108
Cd	HF power	45	39	25	24	8,6	424	2,4	565	<0.5	<0.5	<0.5	18	218	40
	HBF4 power	47	36	22	22	9,4	422	2,5	538	<0.5	<0.5	<0.5	18	205	41
	HBF4 temp	44	39	25	25	9,4	425	2,5	513	<0.5	<0.5	<0.5	19	220	42
Cr	HF power	504	511	278	1024	50	469	125	294	3577	3588	78	170	284	42
	HBF4 power	533	498	247	708	50	472	121	251	3527	3536	73	181	279	40
	HBF4 temp	635	510	289	883	53	558	133	326	3512	3570	81	199	329	42
Cu	HF power	9163	7588	2019	769	21	1874	104	1315	12640	12491	99213	813	1068	119
	HBF4 power	8804	10102	2105	768	22	1989	103	1248	12548	12597	95184	833	1056	112
	HBF4 temp	5861	8057	2262	926	18	1944	101	1411	12540	12892	98234	793	1106	115
Pb	HF power	5570	6508	1076	71	200	10259	175	11746	6038	5922	9943	583	4033	1102
	HBF4 power	6055	6939	1049	71	202	10084	176	11598	5856	5912	9405	569	4181	1131
	HBF4 temp	5576	5694	1072	76	202	10363	180	10883	5789	5880	9609	609	3938	1193
Ni	HF power	443	377	126	592	10	70	47	111	23	22	1709	68	116	21
	HBF4 power	506	424	116	542	12	57	43	108	26	25	1599	67	109	22
	HBF4 temp	458	443	127	530	11	69	47	105	25	25	1687	72	116	24
Zn	HF power	16690	16537	3245	908	227	27529	505	26852	1259	1269	244	2913	16572	365
	HBF4 power	17100	17251	3170	723	199	27254	570	27524	1244	1282	220	2810	17326	344
	HBF4 temp	18290	18212	3244	809	204	29303	527	25782	1312	1311	241	2861	16192	381
Hg	HF power	6,2	3,8	3,2	2,2	12	5,7	1,2	33	1,6	1,7	0,13	7,7	1,3	6,7
	HBF4 power	3,4	3,7	3,3	2,2	13	5,8	1,1	30	1,6	1,7	0,14	6,9	1,4	5,8
	HBF4 temp	3,9	3,5	3,4	2,7	12	6,1	1,3	33	1,8	1,7	0,14	8,0	1,5	6,2
Sb	HF power	240	241	172	12	17	1151	<2	308	12	13	<2	14	776	22
	HBF4 power	229	269	178	15	11	1126	5,0	286	9,4	9,7	<2	12	816	19
	HBF4 temp	250	245	178	18	11	1061	3,9	304	9,9	11	<2	13	853	25
Ba	HF power	3415	3735	618	2894	393	1020	530	1033	102	103	74	495	287	698
	HBF4 power	3256	4462	681	2881	405	804	578	319	90	98	76	610	208	661
	HBF4 temp	4095	3815	908	3084	404	1308	533	563	112	110	80	687	306	650
Co	HF power	65	64	167	61	1,2	25	17	33	15	15	2,9	7,7	28	9,3
	HBF4 power	62	69	150	54	<1	23	17	29	16	16	4,5	7,0	28	10
	HBF4 temp	73	69	165	64	<1	26	16	25	14	14	4,3	9,0	29	10
Mn	HF power	1806	1838	724	411	80	519	1254	1424	563	568	631	317	762	638
	HBF4 power	2038	1487	642	347	69	534	1276	1298	572	590	602	318	740	653
	HBF4 temp	2042	1853	713	411	75	545	1306	1427	599	599	640	343	790	688
Mo	HF power	84	77	17	287	6,3	25	<1	48	4,5	4,5	4,4	8,9	35	1,7
	HBF4 power	67	63	16	248	6,3	24	1,3	43	4,9	4,3	4,3	9,5	33	1,6
	HBF4 temp	86	62	16	296	5,5	27	<1	48	5,2	5,2	4,8	10	37	1,8
Se	HF power	<5	8	<5	106	<5	31	<5	34	<5	<5	<5	<5	10	
	HBF4 power	<5	<5	<5	95	<5	34	<5	36	<5	<5	<5	<5	12	
	HBF4 temp	<5	<5	<5	99	<5	34	<5	32	<5	<5	<5	<5	12	
Tl	HF power	<5	<5	69	12	<5	<5	<5	<5	<5	<5	<5	<5	<5	
	HBF4 power	<5	<5	65	8	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
	HBF4 temp	<5	<5	72	59	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Sn	HF power	333	599	253	46	<2	1338	9	2569	<2	<2	19626	92	1005	
	HBF4 power	395	285	225	47	<2	1378	12	2447	<2	<2	17566	77	978	<3
	HBF4 temp	336	470	249	49	<2	1499	9	2344	<2	<2	19098	85	1064	<2
V	HF power	45	45	63	14	48	23	100	49	10	10	5	39	36	91
	HBF4 power	46	42	57	13	52	22	97	45	12	12	5	43	36	81
	HBF4 temp	47	48	62	14	43	25	96	50	12	12	5	47	39	88
Na	HF power	16692	14956	8484	44082	383	52575	5003	32912	4676	4645	12731	1598	32962	11093
	HBF4 power	16230	16582	10393	43938	391	61488	5240	32913	4837	4859	13567	1818	33985	11414
	HBF4 temp	12794	14367	9272	50222	412	63956	5547	32398	4918	4891	12833	1892	34464	11059
Mg	HF power	8808	8309	11099	5889	2612	9424	10956	18309	982	979	2213	8254	14468	9487
	HBF4 power	9911	9109	11204	5870	2603	11197	10751	17854	948	946	2247	9378	15069	9830
	HBF4 temp	9242	10773	10978	5830	2626	11784	10043	17079	975	969	2083	9429	14689	9395
Al	HF power	25605	25483	33464	73485	9892	40258	58245	82588	2163	2150	91099	23618	52955	63365
	HBF4 power	25731	25530	33367	66418	9532	47124	55847	82993	2252	2283	86638	29570	53612	61460
	HBF4 temp	27087	25965	31168	61841	9177	46563	50457	80759	2292	2282	83729	30020	55227	61783
K	HF power	4277	4379	4605	4407	9546	50225	18985	38505	865	1029	3116	4646	33509	23068
	HBF4 power	4281	4839	4964	4519	9884	54941	17988	40275	1001	1028	3329	4960	35200	19506
	HBF4 temp	4894	4824	4956	4737	9851	65463	17109	33558	1003	922	3351	5086	32806	18720
Ca	HF power	66325	67364	192900	53831	5686	127951	43119	80344	109974	112738	59368	92356	156348	27403
	HBF4 power	65066	64694	197116	50115	5751	141678	41589	82776	110620	110221	55306	131819	177344	27673
	HBF4 temp	71646	67212	199863	54018	5738	143719	41539	80227	106958	106100	55270	137852	179043	27179
Ti	HF power	5402	5118	7652	4841	486	7320	2601	7963	215	217	98	2203	9279	2522
	HBF4 power	1886	2155	5224	4014	332	6760	1363	5209	177	190	74	872	7875	2092
	HBF4 temp	4543	3736	6836	4436	437	7992	2700	5006	239	251	89	1677	8766	2424
Fe	HF power	125696	120059	21414	18092	143802	10278	32248	22052	79179	78833	5538	11795	11448	27283
	HBF4 power	119987	117674	24790	17148	146223	10297	31221	21310	75286	76673	5430	15539	13059	27586
	HBF4 temp	121806	127251	21372	17236	146947	10990	31671	21307	75544	77457	5663	15837	13394	28693

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