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Final report

Evaluation of different digestion procedures for soil and waste samples – part 2

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SAMENVATTING

Bij de beoordeling van milieugerelateerde wetgevende limietwaarden voor elementen (zware metalen), is het onmogelijk om alle onzekerheden in de meting, de veldvariabiliteit, de monsterheterogeniteit, ... te elimineren. Bovendien is het ook duur om deze onzekerheid te verlagen tot een (zeer) laag niveau. Het is daarom noodzakelijk om een modus vivendi te bekomen over hoe om te gaan met onzekerheden aan de ene kant en het leveren van een betrouwbare interpretatie van bv. de verontreiniging op een site of het hergebruik van afval aan de andere kant.

De bepaling van de concentratie van een element in een vaste matrix met een zuurontsluiting is operationeel gedefinieerd, dus bij het vergelijken van verschillende ontsluitingsmethoden geniet het gebruik van een 'tolerantiebereik' de voorkeur boven het aantonen van statistische gelijkwaardigheid. In een eerdere studie werd reeds de impact van de meetonzekerheid voor de interpretatie van de regelgeving grenzen beoordeeld[1]. In dit onderzoek kon een meetnauwkeurigheid van 20% beschouwd worden als fit-for-purpose voor het bepalen van elementen in bodem en afval. Daarom is in deze studie het tolerantiebereik vastgesteld op 20% voor de vergelijkbaarheid van de verschillende ontsluitingsmethoden.

De ontsluiting van vaste monsters (bodem en afval) is zonder twijfel een kritische stap bij de bepaling van elementen. 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 ontsluitingssystemen 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 2% HBF_4) ter vervanging van de tweestaps ontsluiting met 2% HF + H_3BO_3*
   Deze procedure houdt een éénstaps ontsluiting in, met behoud van hetzelfde vermogen van ontsluiting van de silicaat matrix, met 2% HBF_4 (vervanging HF met H_3BO_3). Bovendien geniet het gebruik van HBF_4 om veiligheidsredenen de voorkeur boven HF.
2. *Evaluatie van temperatuursgecontroleerde microgolf systemen als aanvulling op de vermogensgecontroleerde microgolf systemen*
   De 2% HBF_4 ontsluiting met vermogensgecontroleerde microgolfoven werd vergeleken met de temperatuursgecontroleerde ontsluiting.
3. *Evaluatie van de implementatie van de verwarmbare destructieblok als aanvulling op de microgolf systemen*
   De 2% en 4% HBF_4 ontsluiting werd vergeleken met de resultaten bekomen met de vorige ontsluitingsmethoden. De destructie werd uitgevoerd bij 105°C gedurende 2 uur.
4. *Evaluatie van de aqua regia ontsluiting met de verwarmbare destructieblok*
   De aqua regia ontsluiting werd vergeleken met de resultaten bekomen met de vorige ontsluitingsmethoden. De destructie werd uitgevoerd bij 105°C gedurende 2 uur.

In 2014 werden de taken 1 en 2 reeds onderzocht en werd de ontsluiting met 2% HBF_4 opgenomen in CMA/2/II/A.3, die de ontsluitingsmethoden beschrijft voor bodem- en afvalmonsters. Ook de temperatuursgecontroleerde microgolf ontsluiting werd succesvol gevalideerd en aanvaard als toepasbare methode.

In 2015 werden de taken 3 en 4 onderzocht en de volgende besluiten kunnen geformuleerd worden.

Evaluatie van de Vlarebo elementen (As, Cd, Cr, Cu, Pb, Ni, Zn en Hg)

Voor de 8 VLAREBO[1] elementen (As, Cd, Cr, Cu, Pb, Ni, Zn en Hg) komen de resultaten bekomen met de microgolf ontsluitingsmethoden en de verwarmbare destructieblok, gebruikmakend van 4% HBF_4 (38 gew%), overeen met deze van de referentiemethode (2% HF, vermogensgecontroleerde microgolfoven ontsluiting). In CHAPTER 6 op pagina 60 wordt weergegeven dat een totale meetspreiding van minder dan 20% wordt bekomen bij toepassing van deze verschillende ontsluitingsmethoden, wat men kan verwachten bij duplometingen. Bij de ontsluiting met 2% HBF_4 (38 gew%) bij 105°C gedurende 2 uur is de meetspreiding iets hoger (ongeveer 25%) in vergelijking met de microgolf ontsluitingen. Maar dit effect wordt gereduceerd wanneer 4% HBF_4 wordt gebruikt voor de ontsluiting bij 105°C gedurende 2 uur.
Bij de aqua regia ontsluiting is de meetspreiding beduidend hoger (ongeveer 30%) in combinatie met een aantal uitschieters en extreme waarden. Toepassen van de aqua regia ontsluiting zou een significante impact hebben op de terugvinding van de verschillende Vlarebo elementen in bodem- en afvalmonsters, terwijl de microgolf ontsluitingsmethodes en de ontsluiting met de verwarmbare destructieblok met 4% HBF_4 (38 wt%) bij 105°C gedurende 2 uur zal resulteren in vergelijkbare gegevens.

Evaluatie van VLAREMA elementen (As, Cd, Cr, Cu, Pb, Ni, Zn, Hg, Sb, Ba, Co, Mo, Se, Sn en V)

Voor de VLAREMA[2] elementen (As, Cd, Cr, Cu, Pb, Ni, Zn, Hg, Sb, Ba, Co, Mo, Se, Sn en V) komen de resultaten bekomen met de microgolf ontsluitingsmethoden en de verwarmbare destructieblok, gebruikmakend van 4% HBF_4 (38 gew%), overeen met deze van de referentiemethode (2% HF, vermogensgecontroleerde microgolfoven ontsluiting). Voor alle ontsluitingsmethoden worden sterk afwijkende waarden voor Sb, Co en V vastgesteld die kunnen toegeschreven worden aan hun laag gehalte, sterk afwijkende waarden voor Sn waarschijnlijk omwille van monsterheterogeniteit. In CHAPTER 6 op pagina 60 wordt weergegeven dat een totale meetspreiding van minder dan 20% wordt bekomen bij toepassing van deze verschillende ontsluitingsmethoden, wat men kan verwachten bij duplometingen. Bij de ontsluiting met 2% HBF_4 (38 gew%) bij 105°C gedurende 2 uur is de meetspreiding iets hoger (ongeveer 30%) in vergelijking met de microgolf ontsluitingen. Maar dit effect wordt gereduceerd wanneer 4% HBF_4 wordt gebruikt voor de ontsluiting bij 105°C gedurende 2 uur.
Bij de aqua regia ontsluiting is de meetspreiding beduidend hoger (ongeveer 40%) in combinatie met een aantal uitschieters in het laag meetgebied (onderschatting van de concentratie). Toepassen van de aqua regia ontsluiting zou een significante impact hebben op de terugvinding van de verschillende Vlarema elementen in bodem- en afvalmonsters, terwijl de microgolf ontsluitingsmethodes en de ontsluiting met de verwarmbare destructieblok met 4% HBF_4 (38 wt%) bij 105°C gedurende 2 uur zal resulteren in vergelijkbare gegevens.

Evaluatie van de hoofdelementen

Voor de hoofdelementen (Na, Mg, Al, K, Ca, Ti en Fe) wordt een goede overeenkomst waargenomen tussen de resultaten van de alternatieve methoden (behalve aqua regia ontsluiting) en de referentiemethode, behalve voor Ti.

Voor de Ti resultaten worden verschillen waargenomen tussen de verschillende ontsluitingsmethoden en de referentiemethode. De hoogste Ti waarden worden verkregen met de

[1] Vlaams Reglement betreffende de bodemsanering
[2] Vlaams reglement betreffende het duurzaam beheer van materiaalkringlopen en afvalstoffen – VLAREMA 4bis (dec 2013)

referentieontsluitingsmethode met 2% HF en vermogensgecontroleerde microgolfontsluiting. Slechts een lichte daling in Ti concentratiewaarden (gemiddeld ± 8%) wordt waargenomen bij toepassing van 2% HBF_4 en temperatuursgecontroleerde microgolfontsluiting. Het toepassen van de 2% HBF_4 ontsluiting met de vermogensgecontroleerde microgolfontsluiting resulteert in een systematische onderschatting van gemiddeld ± 25%. Ontsluiting met 2% of 4% HBF_4 bij 105°C gedurende 2 uur resulteert in een systematische onderschatting van gemiddeld ± 30%. Met de aqua regia ontsluitingsmethode werd zelfs een terugvinding van gemiddeld slechts 25% ten opzichte van de referentiemethode bekomen. Hoewel het element Ti niet is opgenomen in de wetgeving, geeft het een redelijk goed beeld over de impact van een bepaalde ontsluitingsmethode op het uiteindelijke resultaat.

SUMMARY

When assessing environmental regulatory limits for elements (heavy metals), it is impossible to eliminate all the uncertainty in measurements, field variability, sample heterogeneity, ... In addition, it is also costly to reduce this uncertainty to (very) low levels. It is therefore necessary to reach a modus vivendi on how to deal with uncertainties on the one hand and providing a reliable interpretation of, *e.g.*, contamination at a site or the reusability of waste on the other hand.

The determination of the concentration of an element in a solid matrix using acid adigestion is operationally defined, therefore when comparing different digestion methods a "range of tolerance" can preferably be used rather then proving statistically equivalence. In a previous study[1], the impact of the measurement uncertainty on the interpretation of regulatory limits was assessed. In this study a measurement precision of 20 % can be considered as fit-for-purpose for the determination of elements in soil and waste. Therefore, in this study the range of tolerance was set at 20 % for the comparability of the different digestion methods.

The digestion of solid samples (soils and waste) is without doubt a critical step in the determination of elements. In this study 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 digestion 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 (2% HBF_4) as replacement for the two-steps digestion with 2%HF + H_3BO_3*
   The procedure involves a one-step digestion, while maintaining the same power of digestion of the silicate matrix, by using 2% 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 2% HBF_4 digestion using power controlled microwave oven was compared with a temperature controlled digestion.
3. *Evaluation of the implementation of the heated block digestion as an addition to microwave systems*
   The 2% HBF_4 and 4% HBF_4 digestion was compared with the results obtained with the previous digestion methods using a microwave system. The heated block digestion was performed at 105°C during 2 hours.
4. *Evaluation of the aqua regia digestion using the heated block digestion*
   The aqua regia digestion was compared with the results obtained with the previous digestion methods. The heated block digestion was performed at 105°C during 2 hours.

In 2014 task 1 and task 2 were already investigated and the digestion using 2% of HBF_4 was included in CMA/2/II/A.3, describing the digestion procedures for soil and waste samples. Also the temperature controlled microwave digestion was successfully validated and accepted as applicable digestion method.

In 2015 task 3 and task 4 were investigated and the following conclusion can be formulated.

Evaluation of the Vlarebo elements (As, Cd, Cr, Cu, Pb, Ni, Zn and Hg)
For the 8 VLAREBO[3] elements (As, Cd, Cr, Cu, Pb, Ni, Zn and Hg) the results obtained with the microwave digestion methods and the heated block digestion using 4% HBF_4 (38 wt%) are comparable with the results of the reference method (2% HF, MW power controlled digestion). In CHAPTER 6 on page 60 it is shown that the measurement variation for these digestion methods is situated in a range of < 20%, which can also be expected from replicate/duplo analyses. For the digestion with 2% HBF_4 (38 wt%) at 105°C, 2 hrs the measurement variation is slightly higher (about 25%) compared to the microwave digestions. But this effect is reduced when 4% of HBF_4 is used when digesting at 105°C during 2 hours.
For the aqua regia digestion the measurement variation is more extended (about 30%) in combination with several outliers and extreme values. Introducing the aqua regia digestion would have an impact on the recovery of the different Vlarebo elements in soil and waste samples, while the microwave digestions methods and the digestion with the heated block digestor using 4% HBF_4 (38 wt%) at 105°C, 2 hrs would reveal comparable data.

Evaluation of the Vlarema elements (As, Cd, Cr, Cu, Pb, Ni, Zn, Hg, Sb, Ba, Co, Mo, Se, Sn and V)
For the VLAREMA[4] elements (As, Cd, Cr, Cu, Pb, Ni, Zn, Hg, Sb, Ba, Co, Mo, Se, Sn and V) the results obtained with the microwave digestion methods and the heated block digestion using 4% HBF_4 (38 wt%) corresponds with the results of the reference method (2% HF, MW power controlled digestion). For all digestion methods high deviated values for Sb, Se en V are observed which could be assigned to their low content, and for Sn probably due to the sample heterogeneities. In CHAPTER 6 on page 60 it is shown that the measurement variation is in general situated in a range of <20%, which can also be expected from replicate/duplo measurements. For the digestion with 2% HBF_4 at 105°C, 2 hrs the measurement variation is slightly higher (about 30%) compared to the microwave digestions. But this effect is reduced when 4% of HBF_4 is used when digesting at 105°C during 2 hours.
For the aqua regia digestion the measurement variation is more extended (about 40%) in combination with several outliers in the lower range (underestimation of the concentration). Introducing the aqua regia digestion would have an impact on the recovery of the different Vlarema elements in soil and waste samples, while the microwave digestions methods and the digestion with the heated block digestor using 4% HBF_4 (38 wt%) at 105°C, 2 hrs would reveal comparable data.

Evaluation of the major elements
For the major elements (Na, Mg, Al, K, Ca, Ti and Fe) a good correspondence is observed between the results of the alternative methods (except the aqua regia digestion) and the reference method, except for Ti.
For the Ti results differences are observed between the different digestion methods and the reference method. The highest Ti values are obtained with the reference digestion method using 2% HF and power controlled microwave digestion. Only a slight reduction in Ti concentration values (by average ± 8%) is observed when applying the 2% HBF_4 digestion with the temperature controlled microwave digestion. Applying the 2% HBF_4 digestion with the power controlled microwave digestion, resulted in a systematic underestimation of about 25% by average. Digestion with 2% or 4% HBF_4 digestion at 105°C, 2 hrs, resulted in a systematic underestimation of about 30% by average. Using aqua regia digestion even resulted in a recovery with respect to the reference method of only 25% by average. Although the element Ti is not included in the legislation it gives a fairly good overview about the impact a certain digestion method can have on the obtained results.

[3] Flemish regulation on soil remediation and protection regulations
[4] Flemish regulation on sustainable management of material cycles and waste – VLAREMA 4bis (dec 2013)

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CHAPTER 1 INTRODUCTION

When assessing environmental regulatory limits for elements (heavy metals), it is impossible to eliminate all the uncertainty in measurements, field variability, sample heterogeneity, ... In addition, it is also costly to reduce this uncertainty to (very) low levels. It is therefore necessary to reach a modus vivendi on how to deal with uncertainties on the one hand and providing a reliable interpretation of, *e.g.*, contamination at a site or the reusability of waste on the other hand.

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[2] (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[3]). 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[4] (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[5] (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^-.

Part 1 (performed in 2014): Evaluation of one-step digestion with HBF_4 and temperature controlled microwave digestion

In 2014 alternative digestion methods were evaluated to simplify the procedure and to extend the applicability of the procedure to different types of microwave instruments 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').

These digestion methods for the determination of elements were tested in various samples (soil and waste samples) and reference materials.

The following conslusions could be formulated:

Evaluation of 10 soil samples

For the 8 VLAREBO[5] 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. It was 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 4bis[6] 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. It was 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.

[5] Flemish regulation on soil remediation and protection regulations
[6] Flemish regulation on sustainable management of material cycles and waste – draft dec 2013

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.

Part 2 (performed in 2015): Evaluation of the digestion with HBF_4 using a heated block digestion system as an alternative for microwave digestion

It is well-known that the use of a microwave oven system remains a time-consuming procedure. Moreover, the operational costs of these systems are expensive (especially the replacement of components). The use of the heated block digestion system as compared to the microwave destruction does not result so much in time savings, but is mostly less labor intensive and has more opportunities for high-throughput and automation. Moreover, the evolution of new commercial techniques offers the ability to introduce more automated robots digestion in combination with a heated block digestor. These robots are able to automatically add acids, to digest simultaneously larger numbers of samples, to perform automatic dilutions, ... what is beneficial for the speed, safety and reproducibility of sample preparation.

In general the heated block digestion comprises a digestion of 0.25 g of sample using 2% HBF_4 at a temperature of 105°C during 2 hours. For these digestion disposable Polypropylene tubes are used and therefore no cleaning of the digestion bombs is required (which is necessary for microwave digestions). Due to the use of Polypropylene tubes, the applied temperature for digestion is limited. At increased temperatures and in combination with HBF_4 acid Teflon tubes are required, but then also cleaning of the tubes is necessary what makes the process more time consuming. For this reason, it was decided to keep the temperature limited at 105°C.

In the first part of this study the digestion method using the heated block digestor was optimised with respect to the digestion time (2 hrs versus 4 hrs) and the acid concentration (2% HBF_4 and 4% HBF_4). The tests were performed on a few selected samples (4 soil samples, 2 waste samples, 2 QC samples) and for a few selected elements (Cr, Ni, Ti, Zn).
Based on these results 3 digestion methods were defined to perform the overall evalution on 10 soil samples, 9 waste samples and 2 QA/QC samples, determining the following elements: Al, As, Ba, Ca, Cd, Co, Cr, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Tl, Ti, V, Zn and Hg. The same samples as used in 2014 (Part 1: Evaluation of one-step digestion with HBF_4 and temperature controlled microwave digestion) were selected.
The following digestion methods were evaluated:

- 2% HBF_4, heated block digestion 105°c, 2 hrs
- 4% HBF_4, heated block digestion 105°c, 2 hrs
- Aqua regia digestion, heated block digestion 105°c, 2 hrs

The aqua regia digestion was added to have a full overview of the influence of the different digestion acids (HF:HNO_3:HCl versus HBF_4:HNO_3:HCl versus HNO_3:HCl) on the recovery of the elements from the waste and the soil samples.

The obtained results were compared with the results obtained with the microwave digestion system (results from part 1 of this study).

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. This evalution was performed during part 1 (in 2014) of this study.

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.

In Table 1 the mean values of the duplicate analysis with the corresponding %RSD are shown. 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.

Additionally it shoud be noted that different concentrations of HBF_4 are available, varying between 38 and 50 wt%, and this might have an influence on the digestion efficiency. In this study all further experiments were performed using a 38 wt% HBF_4 solution. Therefore, the effect of using 2% and 4% HBF_4 during the digestion on the recovery of the different elements was investigated.

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 DESCRIPTION OF THE SAMPLES AND APPLIED METHODS

3.1. INTRODUCTION

In Flanders, soil and waste samples are digested using the same digestion method. 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.

In the compendium method for digestion (CMA/2/II/A.3, version February 2013) soil and waste samples have to be digested using an acid mixture of HF:HNO_3:HCl and a microwave digestion oven, according to the procedure describe in NBN EN 13656. In 2015 the digestion procedure using HBF_4 as acid in stead of HF was introduced (CMA/2/II/A.3, version November 2015). In this study the use of a heated block digestion system as alternative for the microwave system was evaluated.

3.2. SELECTED 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). Sample 8 was always digested and subsequently analysed in duplo.

Table 2 List of soil samples

Nr	VITOcode	Sample code	Description
1	150826-0205-1	20130194	Soil sample
2	150826-0206-1	20133326	Soil sample
3	150826-0207-1	20133334	Soil sample
4	150826-0208-1	20141237	Soil sample
5	150826-0209-1	20141454	Soil sample
6	150826-0210-1	20141455	Soil sample
7	150826-0211-1	20141456	Soil sample
8a	150826-0212-1	20141462	Soil sample
8b	150826-0212-2	20141462	Soil sample
9	150826-0213-1	20141463	Soil sample
10	150826-0214-1	LAGA S8	Soil sample

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

Table 3 List of waste samples

Nr	VITOcode	Sample code	Description
11	150826-0217-1	20143957	Shredder (< 1 mm)
12	150826-0218-1	20143958	Sewage sludge
13	150826-0219-1	20143959	Bottom ash

Nr	VITOcode	Sample code	Description
14	150826-0220-1	20143960	Sewage sludge
15	150826-0221-1	20143962	Sample CEN 7/99 Bottom ash CW4
16a	150826-0222-1	20143963	Sample CEN 8/99 Ink waste CW12
16b	150826-0222-2	20143963	Sample CEN 8/99 Ink waste CW12
17	150826-0223-1	20143964	Sample CEN 9/99 Sewage sludge of electronic waste SL 11
18	150826-0224-1	20143965	Sample CEN 10/99 Sewage sludge BCR 146R (certified reference sample)
19	150826-0225-1	20143966	Sample BCR 176R Incineration ash powder (replaces CEN 11/99 BCR 176: same matrix, other reference values)

The samples 15 to 18 were the same samples used in the validation trial of EN 13656 and 13657, and they were already dried and fine ground. Sample 19 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 12 to 14 were dried at 105°C overnight and fine ground with the planetary ball mill (according to EN 13656 < 250 µm).

Finally, 2 control samples i.e. a certified soil samples (NIST 2711) – QC1 – and a round robin soil sample (SETOC 701) – QC2 -, distributed by Wageningen, were included in the analytical process.

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

All digestions were performed using a heated block digestor (DigiPrep 24 positions).

The digested solutions were analysed with ICP-AES[g] (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 25%. 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[h] (Leeman, HYDRA AF Automated Hg-analyzer).

3.3.1. DIGESTION 1 USING 2% HBF4

About 0.25 g of sample was weighed into the tube. Then the following acids were separately added: 3 ml HCl, 1 ml HNO_3 and 1 ml HBF_4. The sample was digested at 105°C during 2 hours. After cooling the digested solution was filled up to 50 ml with ultrapure water (in the same tube).

In 1 digestion block it was possible to digest simultaneously 1 blank, 2 control samples (QC1 or QC2), 10 soil samples and 9 waste samples.

[g] Inductively coupled plasma atomic emission spectrometry
[h] Cold vapour atomic fluorescence spectrometry

Digestion 1b: The same procedure as described above was applied, with the exception of the digestion time which was increased to 4 hrs.

3.3.2. DIGESTION 2 USING 4% HBF_4

About 0.25 g of sample was weighed into the tube. Then the following acids were separately added: 3 ml HCl, 1 ml HNO_3 and 2 ml HBF_4. The sample was digested at 105°C during 2 hours. After cooling the digested solution was filled up to 50 ml with ultrapure water (in the same tube).

In 1 digestion block it was possible to digest simultaneously 1 blank, 2 control samples (QC1 or QC2), 10 soil samples and 9 waste samples.

Digestion 2b: The same procedure as described above was applied, with the exception of the digestion time which was increased to 4 hrs.

3.3.3. DIGESTION 3 USING AQUA REGIA

About 0.25 g of sample was weighed into the tube. Then the following acids were separately added: 3 ml HCl and 1 ml HNO_3. The sample was digested at 105°C during 2 hours. After cooling the digested solution was filled up to 50 ml with ultrapure water (in the same tube).

In 1 digestion block it was possible to digest simultaneously 1 blank, 2 control samples (QC1 or QC2), 10 soil samples and 9 waste samples.

CHAPTER 4 OPTIMISATION OF THE DIGESTION METHOD

4.1. INTRODUCTION

In a first step the digestion method using a heated block digestion system was optimised. For this purpose only a few samples were selected and the evaluation was performed based on the determination of only 4 elements.
The influence of the concentration of HBF_4 and the digestion time on the recovery of the different elements was investigated. The following procedures were evaluated:

- Digestion with 2% HBF_4, at 105°C during 2 hrs (digestion 1)
- Digestion with 2% HBF_4, at 105°C during 4 hrs (digestion 1b)
- Digestion with 4% HBF_4, at 105°C during 2 hrs (digestion 2)
- Digestion with 4% HBF_4, at 105°C during 4 hrs (digestion 2b)

The following selected samples were taken into account:

Nr	VITOcode	Sample code	Description
2	150826-0206-1	20133326	Soil sample
4	150826-0208-1	20141237	Soil sample
7	150826-0211-1	20141456	Soil sample
10	150826-0214-1	LAGA S8	Soil sample
15	150826-0221-1	20143962	Sample CEN 7/99 Bottom ash CW4
17	150826-0223-1	20143964	Sample CEN 9/99 Sewage sludge of electronic waste SL 11
QC1	150826-0215-1	-	N2711
QC2	150826-0216-1	-	SETOC701

The elements Cr, Ni, Ti and Zn were determined in the digested solutions.

4.2. ANALYTICAL RESULTS FOR CR, NI, TI AND ZN

The obtained results using the heated digestion block were compared with the data obtained in part 1 of this research project. Analytical results of Cr, Ni, Ti and Zn obtained according to the following digestion methods are available:

- 2% HF with power controlled microwave system (2% HF-MW power)
- 2% HBF_4 with power controlled microwave system (2% HBF_4-MW power)
- 2% HBF_4 with temperature controlled microwave system (2% HBF_4-MW temp)
- 2% HBF_4 with heated block digestion, 105°C, 2 uur (2% HBF_4 – 105-2u)
- 4% HBF_4 with heated block digestion, 105°C, 2 uur (4% HBF_4 – 105-2u)
- 2% HBF_4 with heated block digestion, 105°C, 4 uur (2% HBF_4 –105-4u)
- 4% HBF_4 with heated block digestion, 105°C, 4 uur (4% HBF_4 – 105-4u)

The individual results can be consulted in Annex A. The obtained results are visually represented for the element Cr, Ni, Ti and Zn in respectively Figure 1, Figure 2, Figure 3 and Figure 4.

For the element Cr a rather good correspondence is observed between the results obtained with the different digestion procedures. When calculating the coefficient of variation (CV_R) per sample and taken into account the different digestion procedures, the CV_R value is for all samples below 10%, except for sample 15 (15%) and for sample 7 (22%). For sample 15, the results obtained with HF (MW power controlled) and with 2% HBF_4 (MW temperature controlled) are slightly higher. Nevertheless the results with 2% HBF_4 (MW power controlled) are comparable with the results obtained with the heated digestion block. No significant difference is observed between the results obtained by 2% or 4% HBF_4 and digesting 2 or 4 hours. For sample 7 the higher CV_R value of 22% is especially attributed to a deviated result obtained with the heated digestion block using 2% HBF_4, 2 hours digestion.

For the element Ni a good correspondence is observed between the results obtained with the different digestion procedures. When calculating the coefficient of variation (CV_R) per sample and taken into account the different digestion procedures, the CV_R value is for all samples below 10%, except for sample 7 (26%). The results of sample 7 with a lower concentration around ± 50 mg/kg dm, indicate that a digestion with 4% HBF_4 gives a better recovery than a digestion with 2% HBF_4.

Although the element Ti is not included in the legislation, it is a good indicator to show the effect of the applied digestion procedure. The results obtained with HF (MW power controlled) and with 2% HBF_4 (MW temperature controlled) show in general the highest Ti values. Nevertheless the results with 2% HBF_4 (MW power controlled) are at the same concentration level as the results obtained with the heated digestion block using 4% of HBF_4. No significant difference is observed between the results obtained by digesting 2 or 4 hours. When calculating the coefficient of variation (CV_R) per sample and taken into account the different digestion procedures, the CV_R value varies for most samples between 15 and 20%, with an exception of 45% for QC2. Note that for sample 7 a CV_R value of 4% is obtained, which might indicate that the sample is easily digestable and that the larger deviation observed for Ni and Cr might be attributed to the heterogeneity of the soil sample.

For the element Zn a good correspondence is observed between the results obtained with the different digestion procedures. When calculating the coefficient of variation (CV_R) per sample and taken into account the different digestion procedures, the CV_R value is for all samples below 10%.

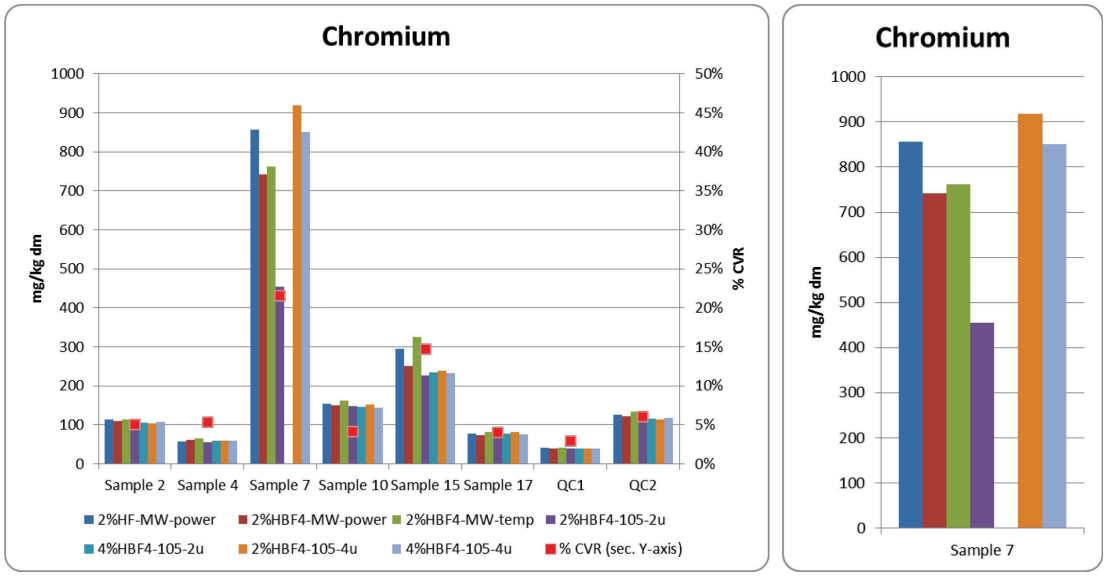

Figure 1 Comparison of the different digestion procedures for the element Cr in soil and waste samples

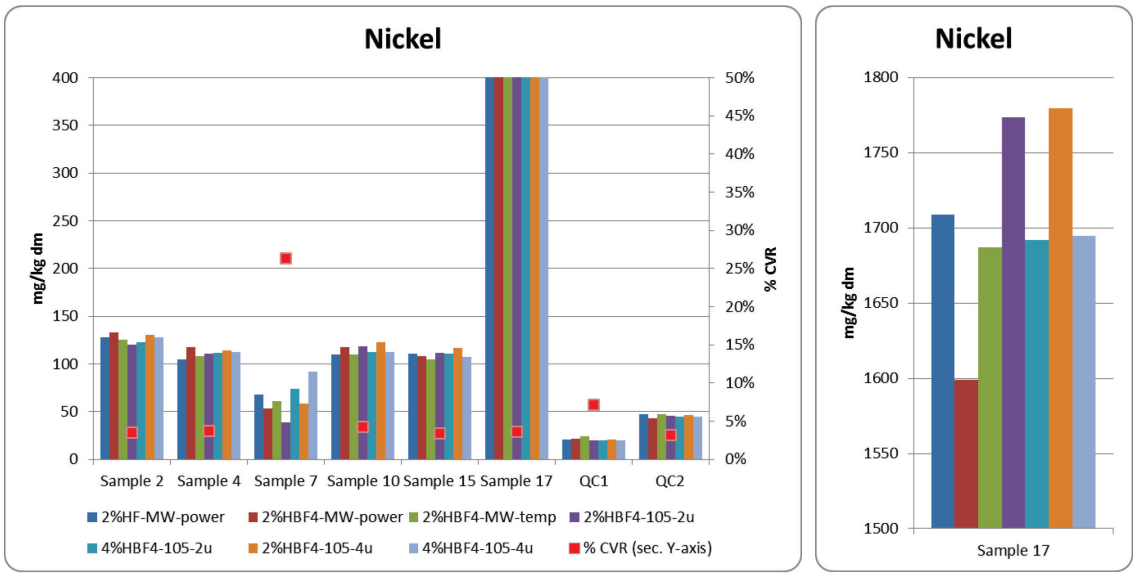

Figure 2 Comparison of the different digestion procedures for the element Ni in soil and waste samples

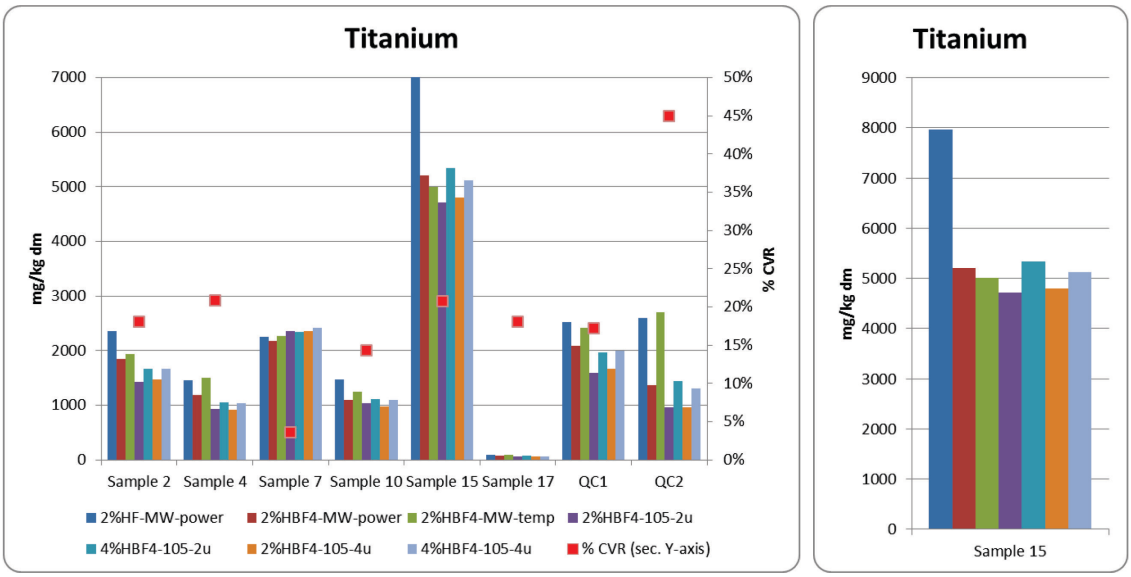

Figure 3 Comparison of the different digestion procedures for the element Ti in soil and waste samples

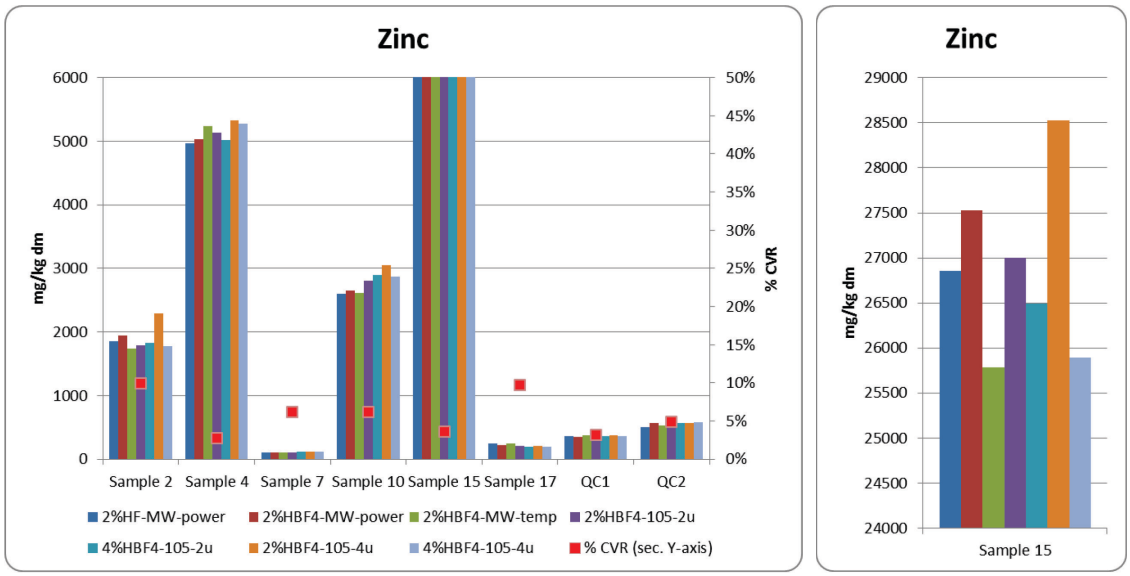

Figure 4 Comparison of the different digestion procedures for the element Zn in soil and waste samples

4.3. CONCLUSIONS

The digestion method using the heated block digestor was optimised with respect to the digestion time (2 hrs versus 4 hrs) and the acid concentration (2% HBF_4 and 4% HBF_4). These tests were performed on a few selected samples (4 soil samples, 2 waste samples, 2 QC samples) and for a few selected elements (Cr, Ni, Ti, Zn). The obtained results show that a digestion with 4% HBF_4 might results in a better recovery for some elements in comparison with a 2% HBF_4 digestion. Extending the digestion time from 2 to 4 hours doesn't reflect any improvement in the recovery of the determined elements.

Based on these results an overall evalution was performed on 10 soil samples, 9 waste samples and 2 QA/QC samples using the digestion methods with 2% HBF_4 and 4% HBF_4 and a digestion time of 2 hours. The following elements were determined and evaluated: Al, As, Ba, Ca, Cd, Co, Cr, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Tl, Ti, V, Zn and Hg. The same samples as used in 2014 (Part 1: Evaluation of one-step digestion with HBF_4 and temperature controlled microwave digestion) were selected.

CHAPTER 5 RESULTS OF ALL SOIL AND WASTE SAMPLES

To perform the overall evalution 3 digestion procedures were additionally evaluated on 10 soil samples, 9 waste samples and 2 QA/QC samples,. The following elements were determined: Al, As, Ba, Ca, Cd, Co, Cr, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Tl, Ti, V, Zn and Hg. The same samples as used in 2014 (Part 1: Evaluation of one-step digestion with HBF_4 and temperature controlled microwave digestion) were selected (see chapter 3.2 on page 7).
The following digestion methods were additionally evaluated:

- 2% HBF_4, heated block digestion 105°c, 2 hrs
- 4% HBF_4, heated block digestion 105°c, 2 hrs
- Aqua regia digestion, heated block digestion 105°c, 2 hrs

The aqua regia digestion was added to have a full overview of the influence of the different digestion acids (HF:HNO_3:HCl versus HBF_4:HNO_3:HCl versus HNO_3:HCl) on the recovery of the elements from soil and waste samples.
A full description of the applied digestion methods is decibed in chapter 3.3 on page 8.

5.1. RESULTS OF THE TRACE 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.

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, Sb, Se, Co, V, Sn, Ba and Mo. The element Mn is also treated in this chapter.

Note: no data of Se are presented because the measured concentrations are situated below the limit of quantification (< 5 mg/kg dm) for most of the samples.

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 following digestion procedures were evaluated:

- Digestion 1: Digestion with 2% HF, microwave digestion – power controlled (2% HF MW power)
- Digestion 2: Digestion with 2% HBF_4, microwave digestion – power controlled (2% HBF_4 MW power)
- Digestion 3: Digestion with 2% HBF_4, microwave digestion – temperature controlled (2% HBF_4 MW temp)
- Digestion 4: Digestion with 2% HBF_4, heated block digestion at 105°C during 2 hrs (2% HBF_4, HBD 2u,105°C)
- Digestion 5: Digestion with 4% HBF_4, heated block digestion at 105°C during 2 hrs (4% HBF_4,HBD 2u,105°C)

- Digestion 6: Digestion with aqua regia, heated block digestion at 105°C during 4 hrs (AR,HBD 2u,105°C)

The results obtained by digestion 1, 2 and 3 were collected in part 1 of this study (2014). The results obtained by digestion 4, 5 and 6 were collected in 2015.

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

An overview of all elements is presented in paragraph 5.4 on page 53.

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

In the paragraphs below the following data per element are presented in figures:
- Individual measured concentration as a function of the digestion procedures.
- % coefficient of variation (CV_R), calculated per sample from the results with the different applied digestion methods. The data of the aqua regia digestion were excluded as this digestion method is not allowed for soil and waste analysis conform CMA.
- For each sample the ratio was calculated between the alternative methods and the reference method (2% HF – MW power)

5.1.1. ELEMENT ARSENIC

In Figure 5 the As results of the different samples and the 2 quality control (QC) samples are presented. From the dataset 1 outlier was removed (sample 8b: AR digestion 2 hrs 105°C).

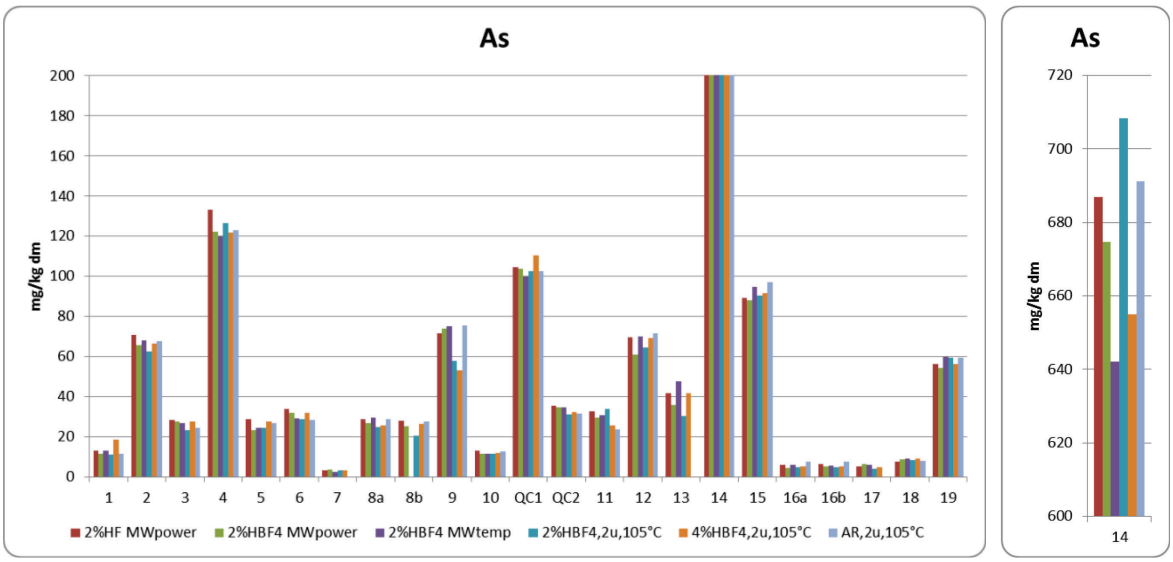

Figure 5 As results of the samples using the 6 digestion methods

The % coefficient of variation (CV_R) of the As results with the applied digestion methods (with the exception of the aqua regia digestion) was calculated per sample and is presented in Figure 6. This figure also include the CV_R – red bar at the right side of the figure - obtained from the control chart of QC1 (HF digestion with power controlled microwave digestion). From all samples analysed the CV_R is situated below 23% and in most cases below 15%. The pooled CV_R of the 23 samples (including duplicates and QC samples) amounted 9.3%.

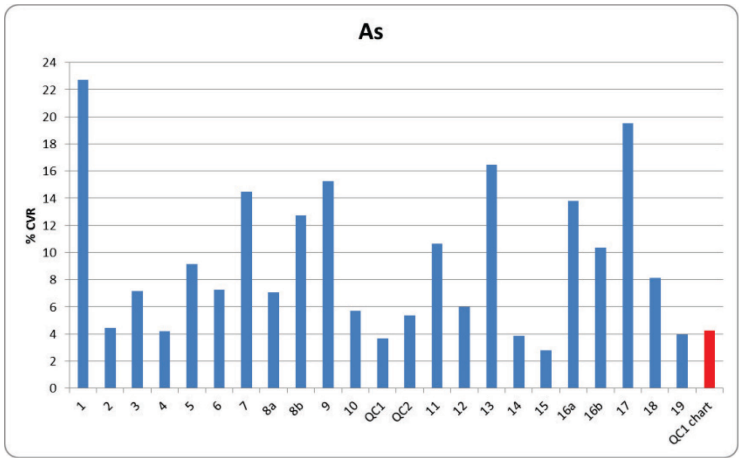

Figure 6 % CV_R of the 5 As results by sample (excl. aqua regia digestion)

In Figure 7 for each sample the ratio was calculated between the alternative methods and the reference method (2% HF – MW power). Although the value obtained with the reference method is also subjected to an measurement error, this value was considered as the 'true' value. In the evaluation process this has to be taken into account when drawing any conclusions. In case there would be a perfect match between both digestion results the calculated ratio would be 1.

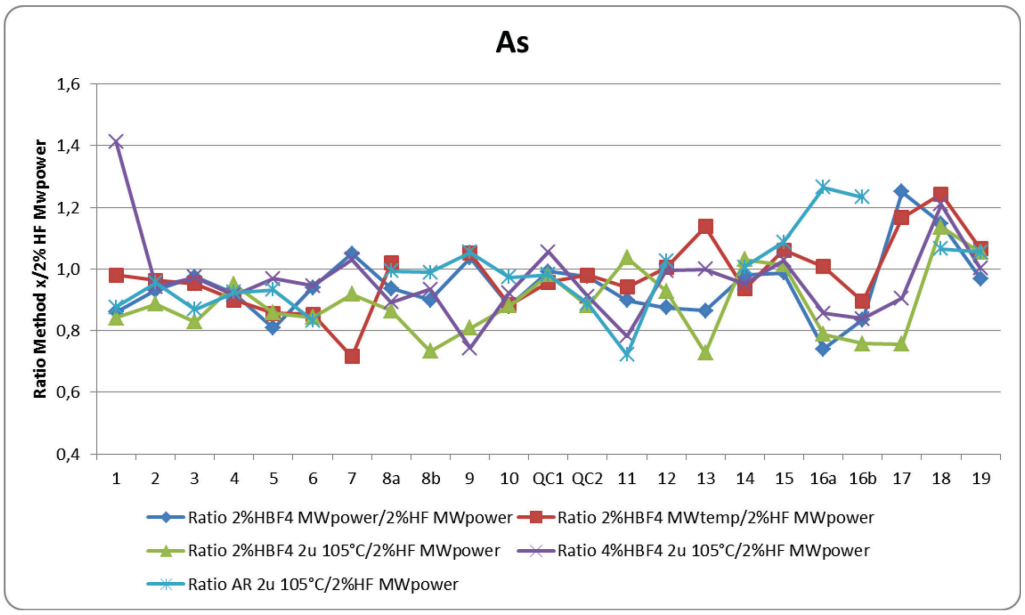

Figure 7 Ratio calculations of the alternative methods vs the reference method (2% HF – MW power) for As

5.1.2. ELEMENT CADMIUM

In Figure 8 the Cd results of the different samples and the 2 quality control (QC) samples are presented.

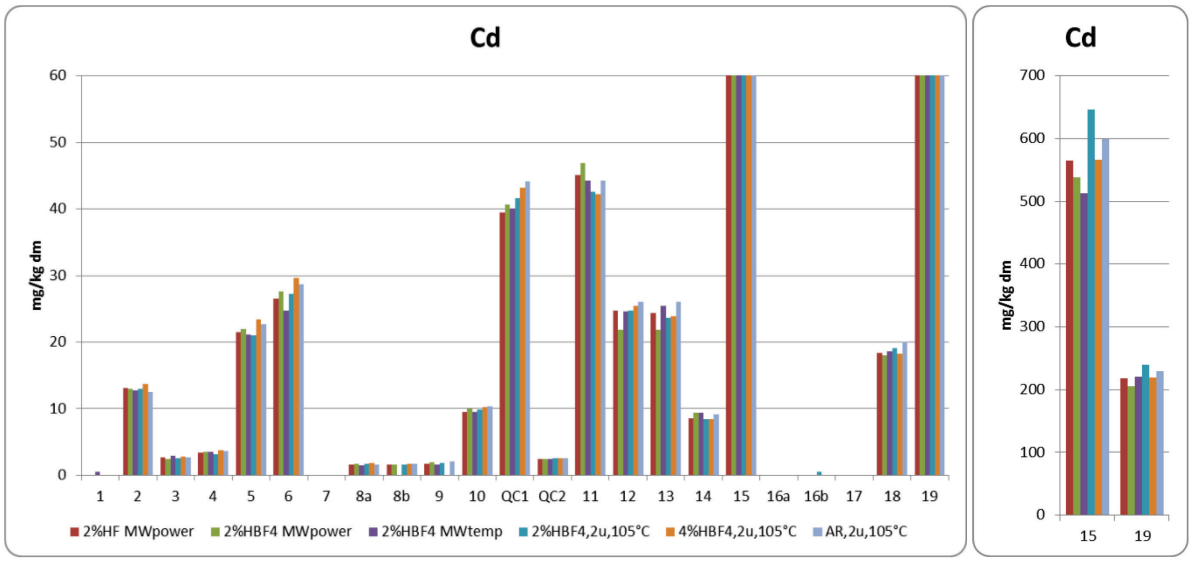

Figure 8 Cd results of the samples using the 6 digestion methods

The % coefficient of variation (CV_R) of the Cd results with the applied digestion methods (with the exception of the aqua regia digestion) was calculated per sample and is presented in Figure 9. This figure also include the CV_R – red bar at the right side of the figure - obtained from the control chart of QC1 (HF digestion with power controlled microwave digestion). From all samples analysed the CV_R is situated below 10%. The pooled CV_R of the 23 samples (including duplicates and QC samples) amounted 5.2%.

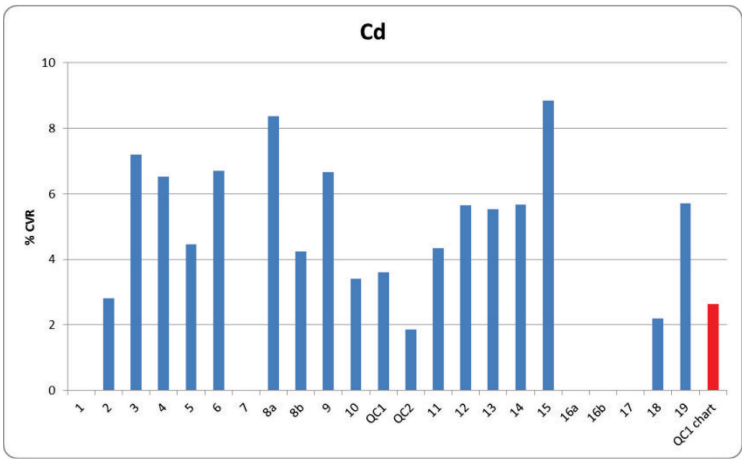

Figure 9 % CV_R of the 5 Cd results by sample (excl. aqua regia digestion)

In Figure 10 for each sample the ratio was calculated between the alternative methods and the reference method (2% HF – MW power). Although the value obtained with the reference method is also subjected to an measurement error, this value was considered as the 'true' value. In the evaluation process this has to be taken into account when drawing any conclusions. In case there would be a perfect match between both digestion results the calculated ratio would be 1.

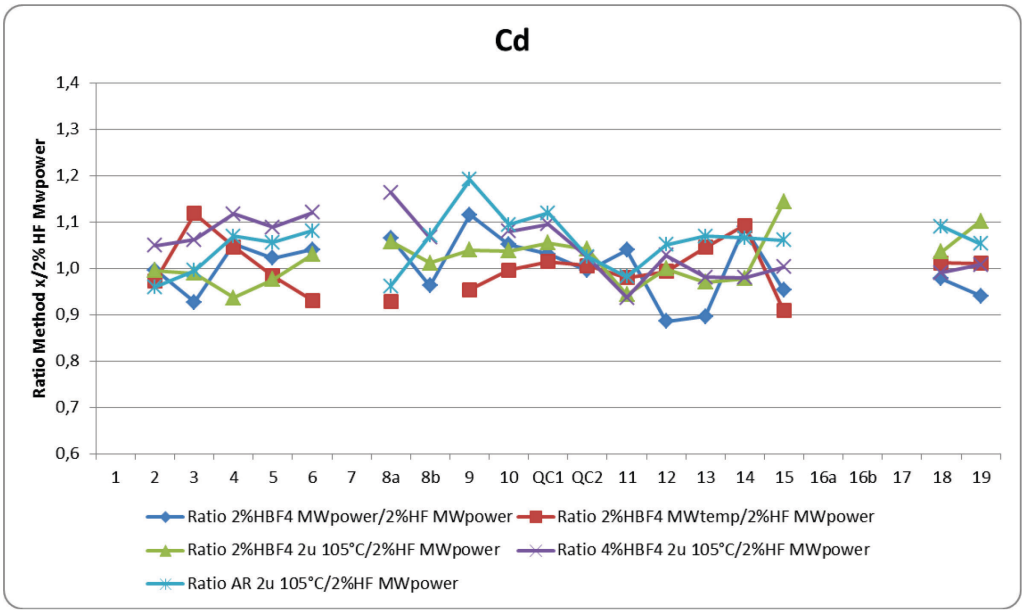

Figure 10 Ratio calculations of the alternative methods vs the reference method (2% HF – MW power) for Cd

5.1.3. ELEMENT CHROMIUM

In Figure 11 the Cr results of the different samples and the 2 quality control (QC) samples are presented. From the dataset 3 outliers were removed (sample 7: 4% HBF_4, 2 hrs 105°C, sample 8: 4% HBF_4, 2 hrs 105°C and AR, 2 hrs 105°C).

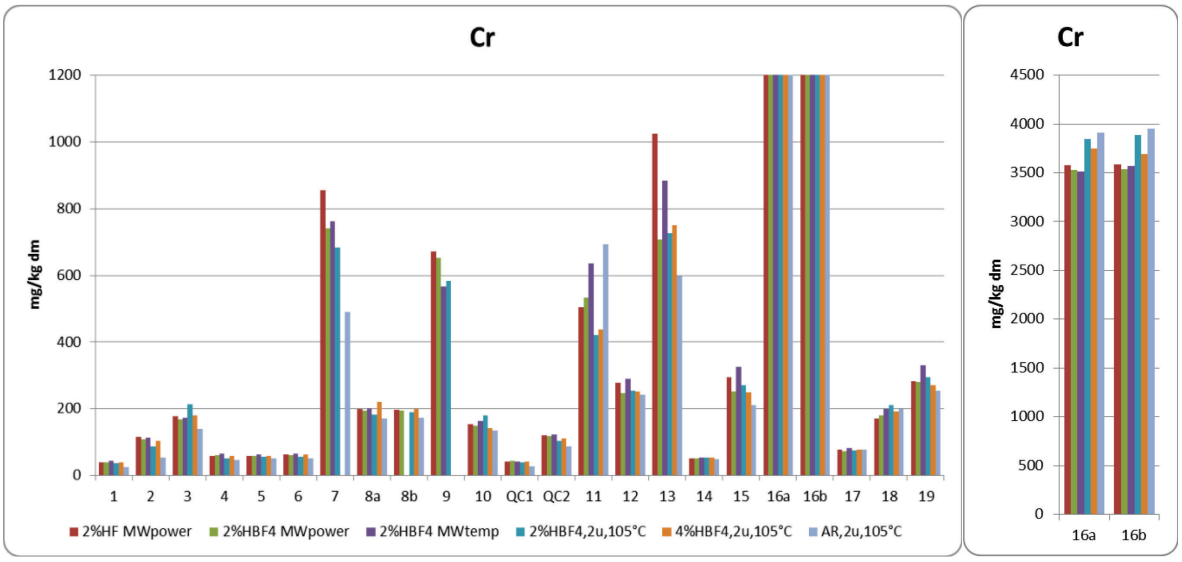

Figure 11 Cr results of the samples using the 6 digestion methods

The % coefficient of variation (CV_R) of the Cr results with the applied digestion methods (with the exception of the aqua regia digestion) was calculated per sample and is presented in Figure 12. This figure also include the CV_R – red bar at the right side of the figure - obtained from the control chart of QC1 (HF digestion with power controlled microwave digestion). From all samples analysed the

CV_R is situated below 17% and in most cases below 10%. The pooled CV_R of the 23 samples (including duplicates and QC samples) amounted 7.7%.

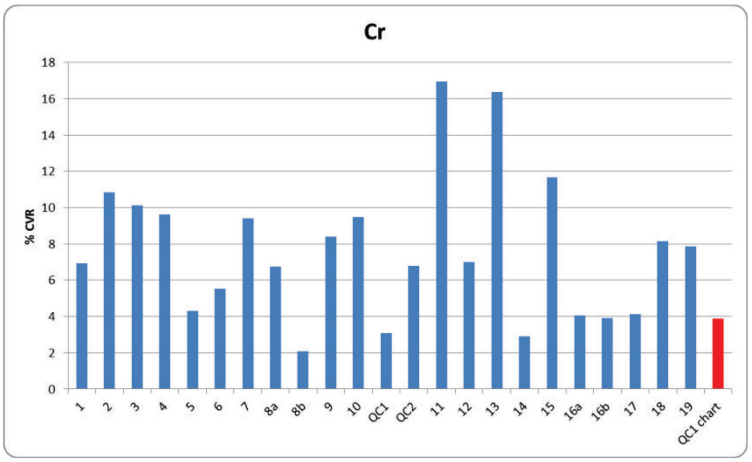

Figure 12 % CV_R of the 5 Cr results by sample (excl. aqua regia digestion)

In Figure 13 for each sample the ratio was calculated between the alternative methods and the reference method (2% HF – MW power). Although the value obtained with the reference method is also subjected to an measurement error, this value was considered as the 'true' value. In the evaluation process this has to be taken into account when drawing any conclusions. In case there would be a perfect match between both digestion results the calculated ratio would be 1.
The presented data show that for some samples the digestion with 2% HBF_4, 2 hrs 105°C resulted in a slight underestimation of the Cr value as compared with the reference method (ratio < 1). The use of 4% HBF_4 with digestion at 105°C, 2 hrs, on the other hand, shows comparable results with those of the reference method (ratio around 1). When evaluating the data obtained with the aqua regia digestion method, these data show for several samples a significant underestimation of the Cr results, with ratio factors down to 0.5.

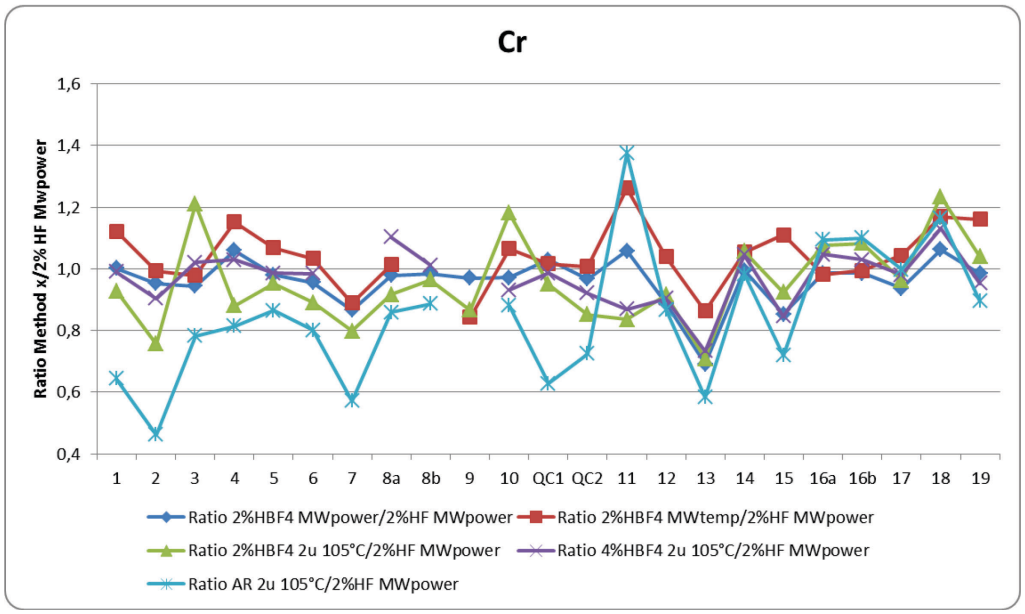

Figure 13 Ratio calculations of the alternative methods vs the reference method (2% HF – MW power) for Cr

5.1.4. ELEMENT CUPPER

In Figure 14 the Cu results of the different samples and the 2 quality control (QC) samples are presented. From the dataset 4 outliers were removed (sample 2: 2% HBF_4, 2 hrs 105°C and AR, 2 hrs 105°C, sample 11: 2% HBF_4, MW temperature controlled and AR, 2 hrs 105°C).

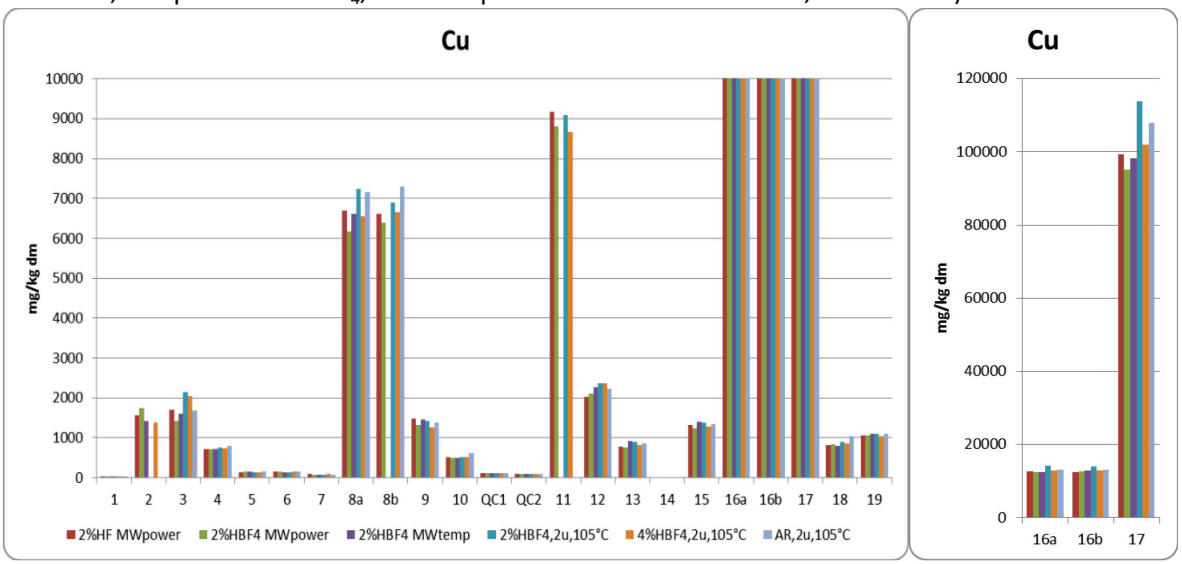

Figure 14 Cu results of the samples using the 6 digestion methods

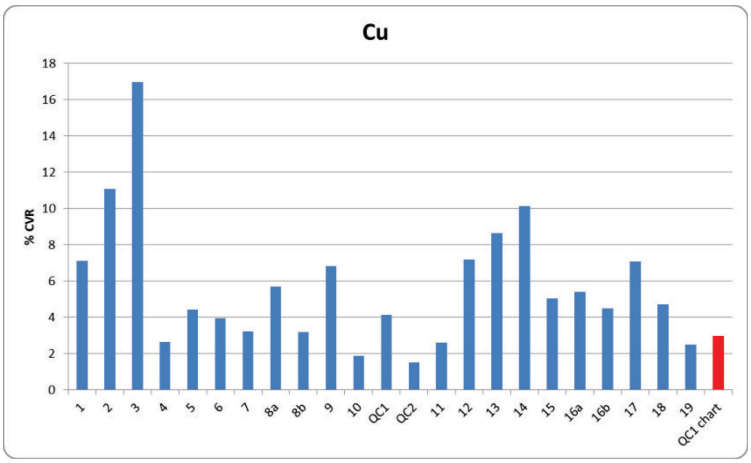

Figure 15 % CV_R of the 5 Cu results by sample (excl. aqua regia digestion)

In Figure 16 for each sample the ratio was calculated between the alternative methods and the reference method (2% HF – MW power). Although the value obtained with the reference method is also subjected to an measurement error, this value was considered as the 'true' value. In the evaluation process this has to be taken into account when drawing any conclusions. In case there would be a perfect match between both digestion results the calculated ratio would be 1.

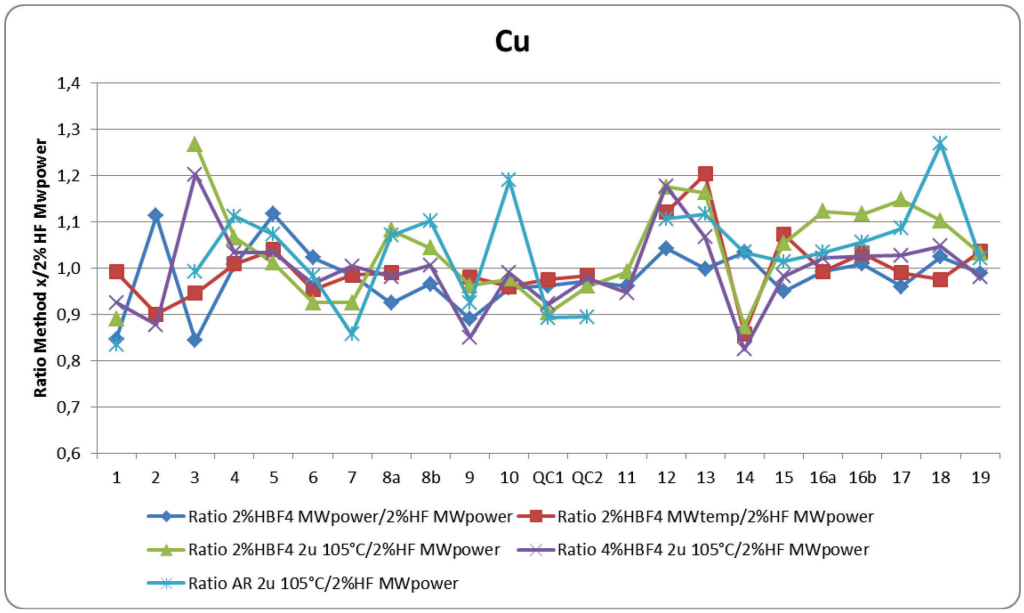

Figure 16 Ratio calculations of the alternative methods vs the reference method (2% HF – MW power) for Cu

5.1.5. ELEMENT LEAD

In Figure 17 the Pb results of the different samples and the 2 quality control (QC) samples are presented. From the dataset 2 outliers were removed (sample 11: 2% and 4% HBF_4, 2 hrs 105°C).

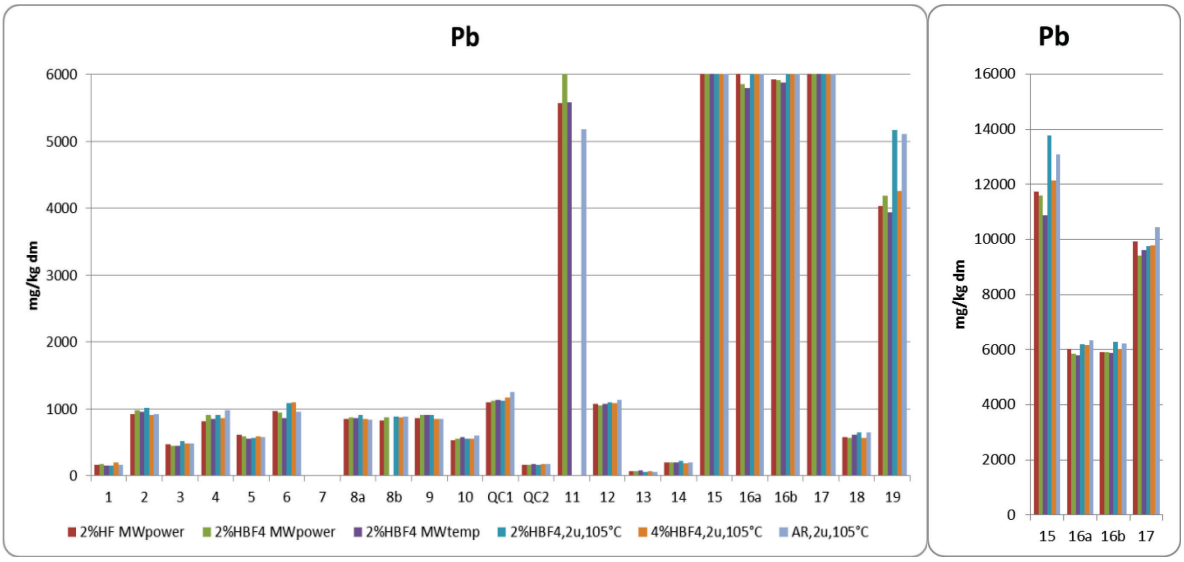

Figure 17 Pb results of the samples using the 6 digestion methods

The % coefficient of variation (CV_R) of the Pb results with the applied digestion methods (with the exception of the aqua regia digestion) was calculated per sample and is presented in Figure 18. This figure also include the CV_R – red bar at the right side of the figure - obtained from the control chart of QC1 (HF digestion with power controlled microwave digestion). From all samples analysed the CV_R is situated below 13%. The pooled CV_R of the 23 samples (including duplicates and QC samples) amounted 5.4%.

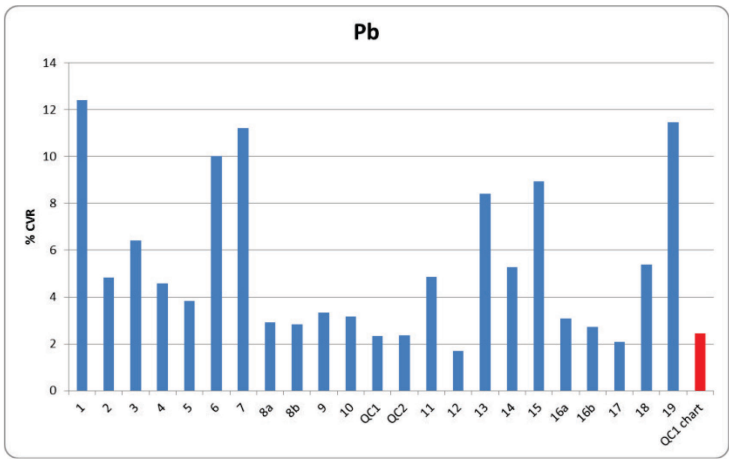

Figure 18 % CV_R of the 5 Pb results by sample (excl. aqua regia digestion)

In Figure 19 for each sample the ratio was calculated between the alternative methods and the reference method (2% HF – MW power). Although the value obtained with the reference method is also subjected to an measurement error, this value was considered as the 'true' value. In the evaluation process this has to be taken into account when drawing any conclusions. In case there would be a perfect match between both digestion results the calculated ratio would be 1.

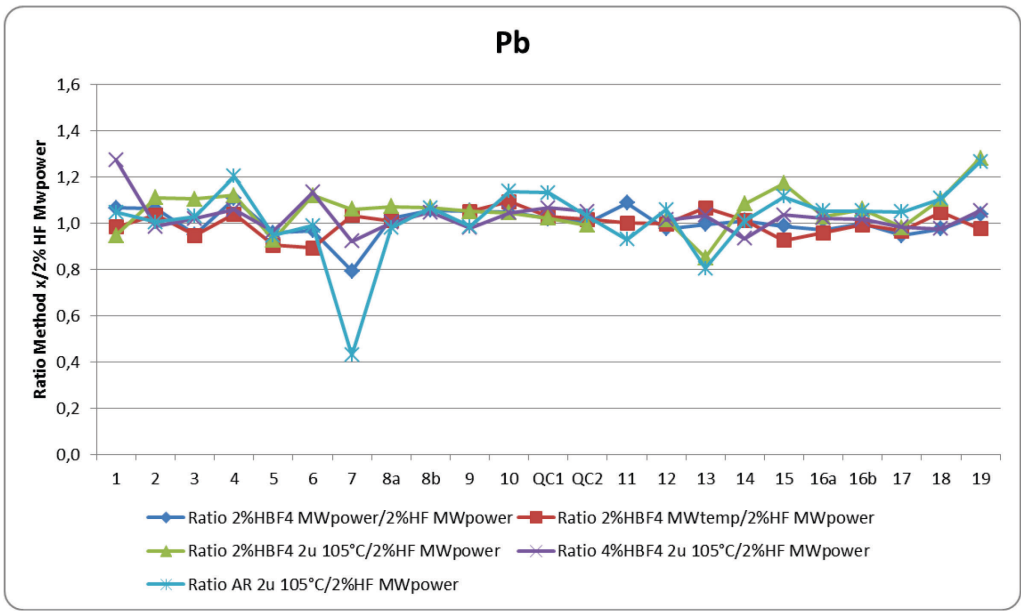

Figure 19 Ratio calculations of the alternative methods vs the reference method (2% HF – MW power) for Pb

5.1.6. ELEMENT NICKEL

In Figure 20 the Ni results of the different samples and the 2 quality control (QC) samples are presented. From the dataset 3 outliers were removed (sample 9: 4% HBF_4, 2 hrs 105°C and AR, 2 hrs 105°C, sample 10: 2% HBF_4, 2 hrs 105°C).

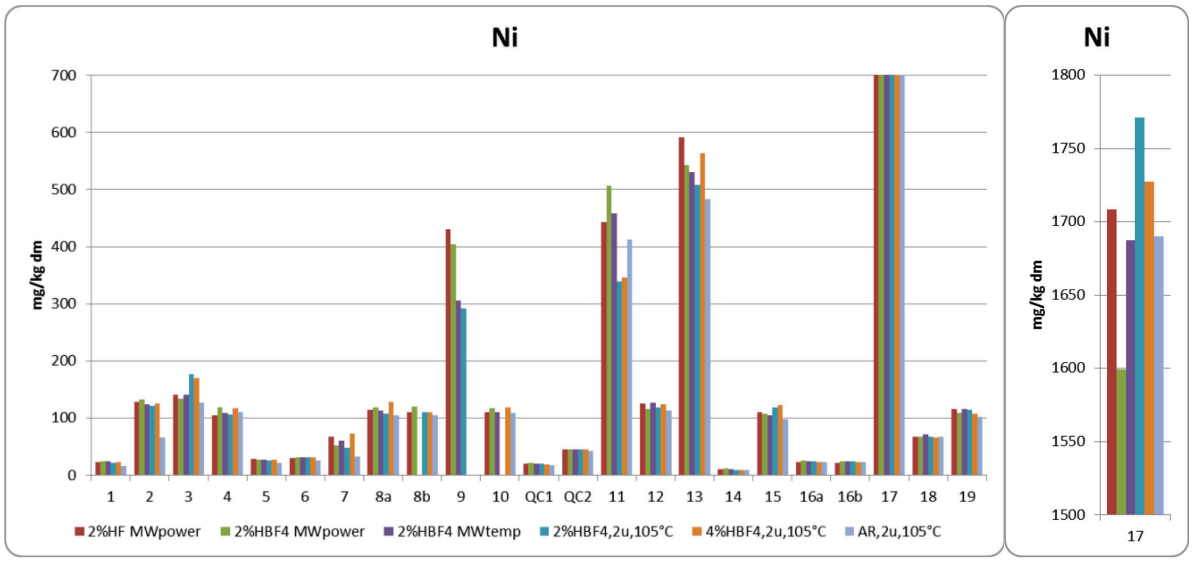

Figure 20 Ni results of the samples using the 6 digestion methods

The % coefficient of variation (CV_R) of the Ni results with the applied digestion methods (with the exception of the aqua regia digestion) was calculated per sample and is presented in Figure 21. This figure also include the CV_R – red bar at the right side of the figure - obtained from the control chart of QC1 (HF digestion with power controlled microwave digestion). From all samples analysed the CV_R is situated below 10%, except samples 3, 7, 9 and 11 with a CV_R up to 20%. The pooled CV_R of the 23 samples (including duplicates and QC samples) amounted 6.5%.

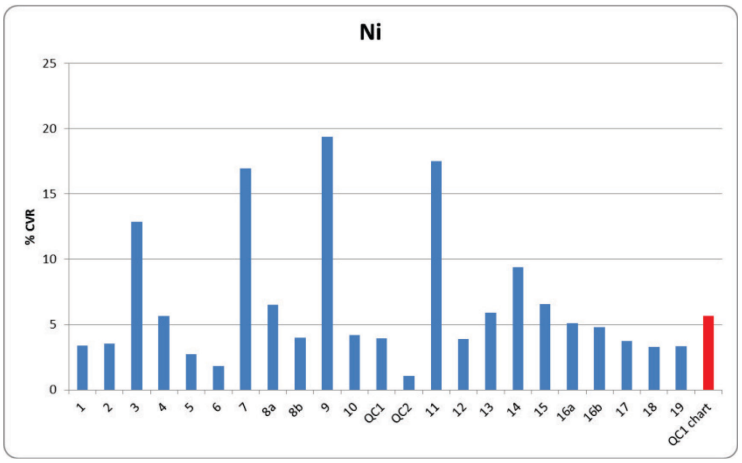

Figure 21 % CV_R of the 5 Ni results by sample (excl. aqua regia digestion)

In Figure 22 for each sample the ratio was calculated between the alternative methods and the reference method (2% HF – MW power). Although the value obtained with the reference method is also subjected to an measurement error, this value was considered as the 'true' value. In the evaluation process this has to be taken into account when drawing any conclusions. In case there would be a perfect match between both digestion results the calculated ratio would be 1.
The presented data show that for some samples the digestion with 2% HBF_4, 2 hrs 105°C resulted in a slight underestimation of the Ni value as compared with the reference method (ratio < 1). The use of 4% HBF_4 with digestion at 105°C 2 hrs, on the other hand, shows comparable results with those of the reference method (ratio around 1). When evaluating the data obtained with the aqua regia digestion method, these data show for several samples a significant underestimation of the Ni

results, with ratio factors down to 0.5. A similar trend, but more pronounced was observed for the element Cr.

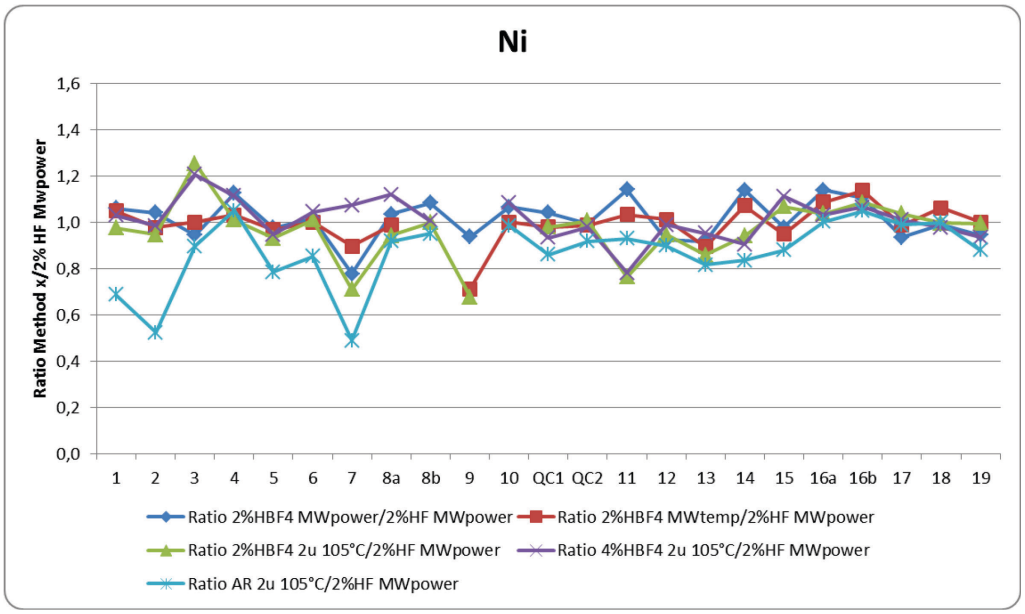

Figure 22 Ratio calculations of the alternative methods vs the reference method (2% HF – MW power) for Ni

5.1.7. ELEMENT ZINC

In Figure 23 the Zn results of the different samples and the 2 quality control (QC) samples are presented.

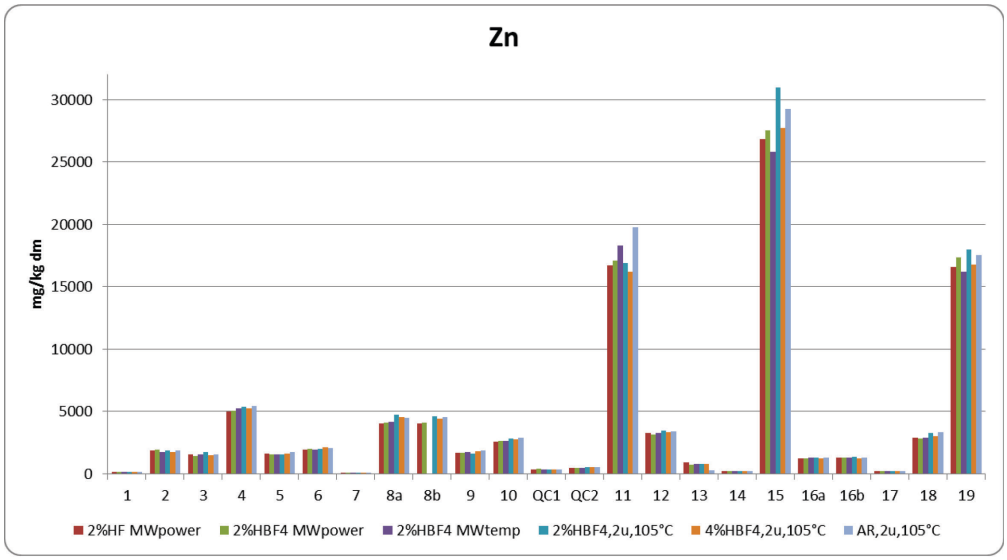

Figure 23 Zn results of the samples using the 6 digestion methods

The % coefficient of variation (CV_R) of the Zn results with the applied digestion methods (with the exception of the aqua regia digestion) was calculated per sample and is presented in Figure 24. This figure also include the CV_R – red bar at the right side of the figure - obtained from the control chart

of QC1 (HF digestion with power controlled microwave digestion). From all samples analysed the CV_R is situated below 10%. The pooled CV_R of the 23 samples (including duplicates and QC samples) amounted 5.1%.

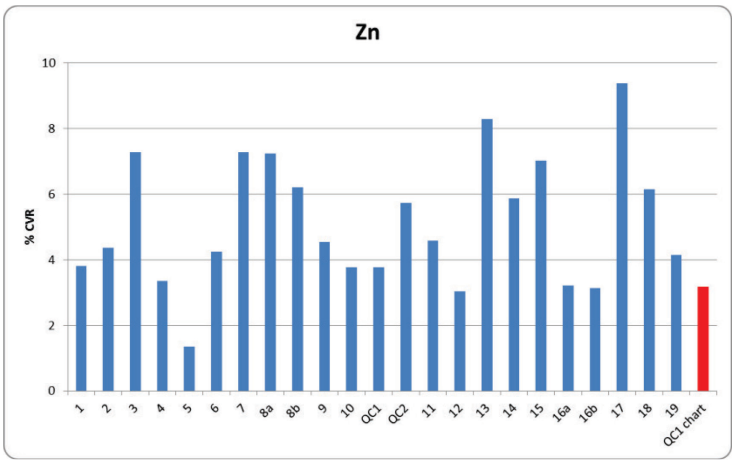

Figure 24 % CV_R of the 5 Zn results by sample (excl. aqua regia digestion)

In Figure 25 for each sample the ratio was calculated between the alternative methods and the reference method (2% HF – MW power). Although the value obtained with the reference method is also subjected to an measurement error, this value was considered as the 'true' value. In the evaluation process this has to be taken into account when drawing any conclusions. In case there would be a perfect match between both digestion results the calculated ratio would be 1.
For sample 7 and sample 13 a low ratio factor (0.3-0.4) was obtained when comparing the aqua regia data with de reference digestion method. This effect is also observed for the element Sb, as will be shown later on.

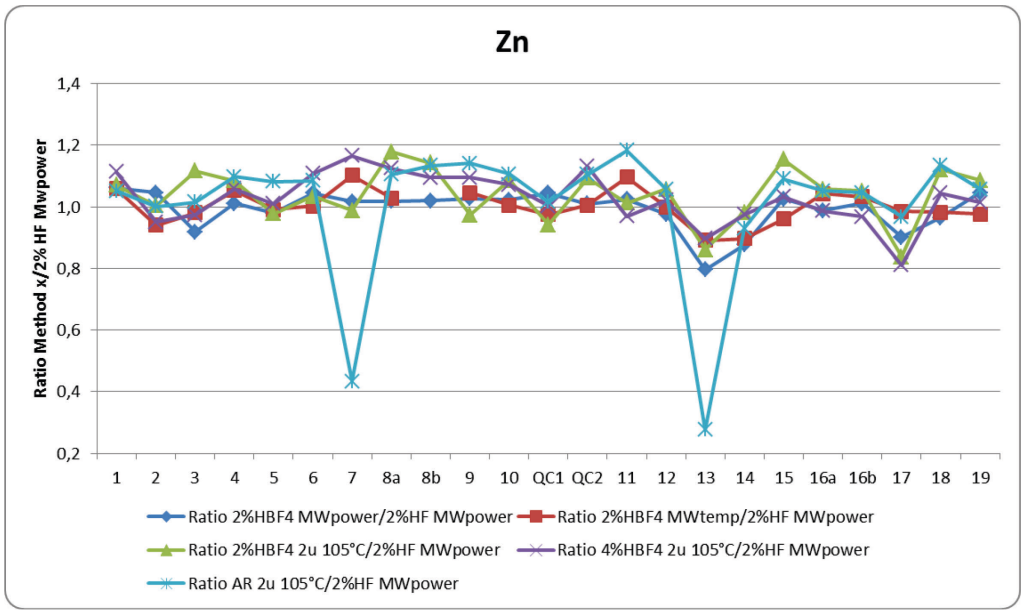

Figure 25 Ratio calculations of the alternative methods vs the reference method (2% HF – MW power) for Zn

5.1.8. ELEMENT MERCURY

In Figure 26 the Hg results of the different samples and the 2 quality control (QC) samples are presented. From the dataset 1 outlier was removed (sample 11: 2% HF, MW power controlled).

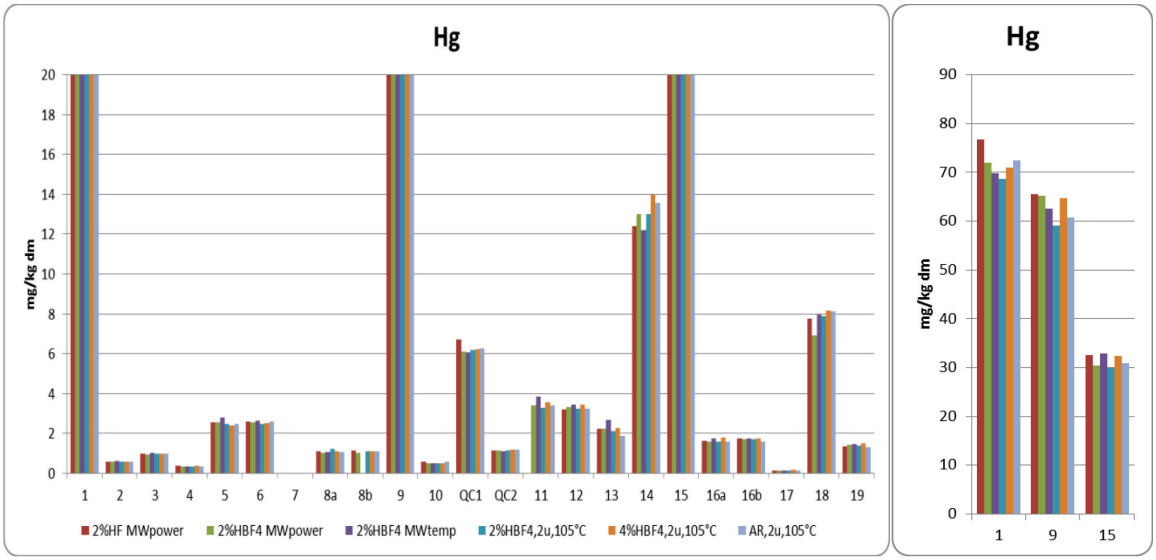

Figure 26 Hg results of the samples using the 6 digestion methods

The % coefficient of variation (CV_R) of the Hg results with the applied digestion methods (with the exception of the aqua regia digestion) was calculated per sample and is presented in Figure 27. This figure also include the CV_R – red bar at the right side of the figure - obtained from the control chart of QC1 (HF digestion with power controlled microwave digestion). From all samples analysed the CV_R is situated below 10%. The pooled CV_R of the 23 samples (including duplicates and QC samples) amounted 5.0%.

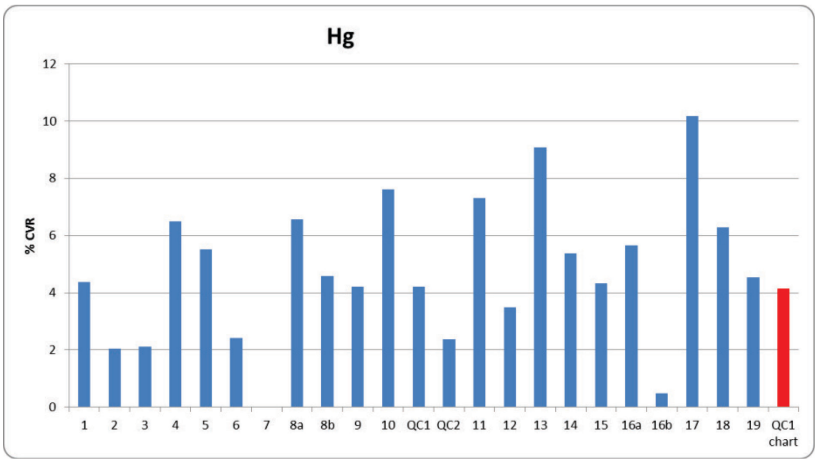

Figure 27 % CV_R of the 5 Hg results by sample (excl. aqua regia digestion)

In Figure 28 for each sample the ratio was calculated between the alternative methods and the reference method (2% HF – MW power). Although the value obtained with the reference method is also subjected to an measurement error, this value was considered as the 'true' value. In the evaluation process this has to be taken into account when drawing any conclusions. In case there would be a perfect match between both digestion results the calculated ratio would be 1. For sample 11 the Hg value obtained with the reference method (2% HF, MW power) was considered

as an outlier which is also confirmed when calculating the ratios; a similar low ratio of ± 0.6 for all other digestion methods related to the reference method was obtained. For all other samples comparable results are achieved using different digestion methods.

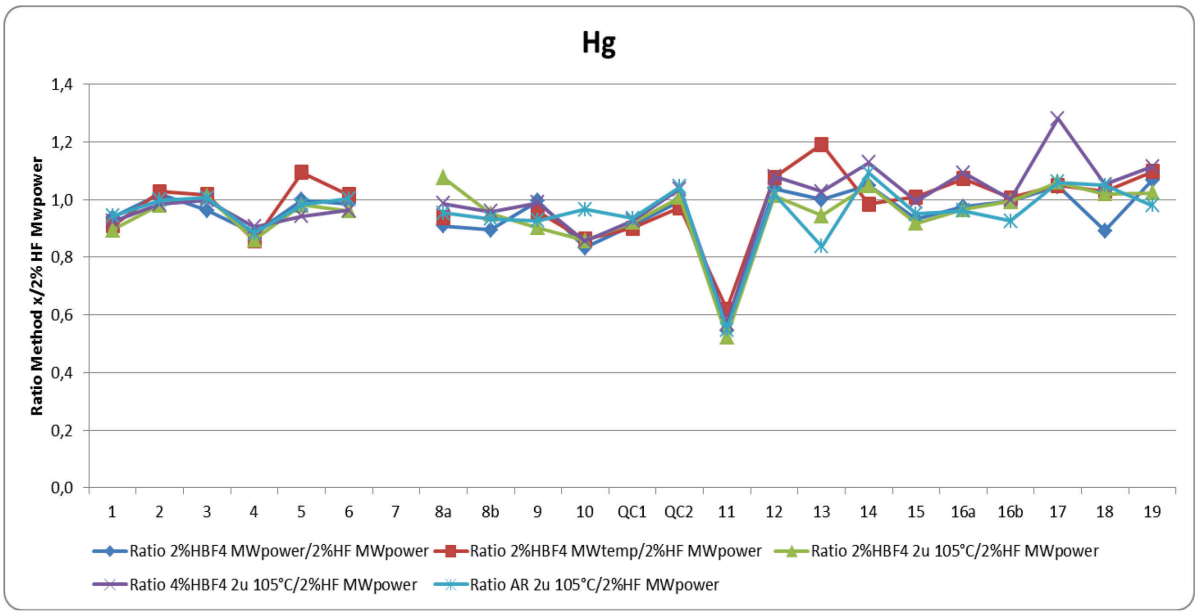

Figure 28 Ratio calculations of the alternative methods vs the reference method (2% HF – MW power) for Hg

5.1.9. ELEMENT ANTIMONY

In Figure 29 the Sb results of the different samples and the 2 quality control (QC) samples are presented. From the dataset 1 outlier was removed (sample 7: 2% HF, MW power controlled).

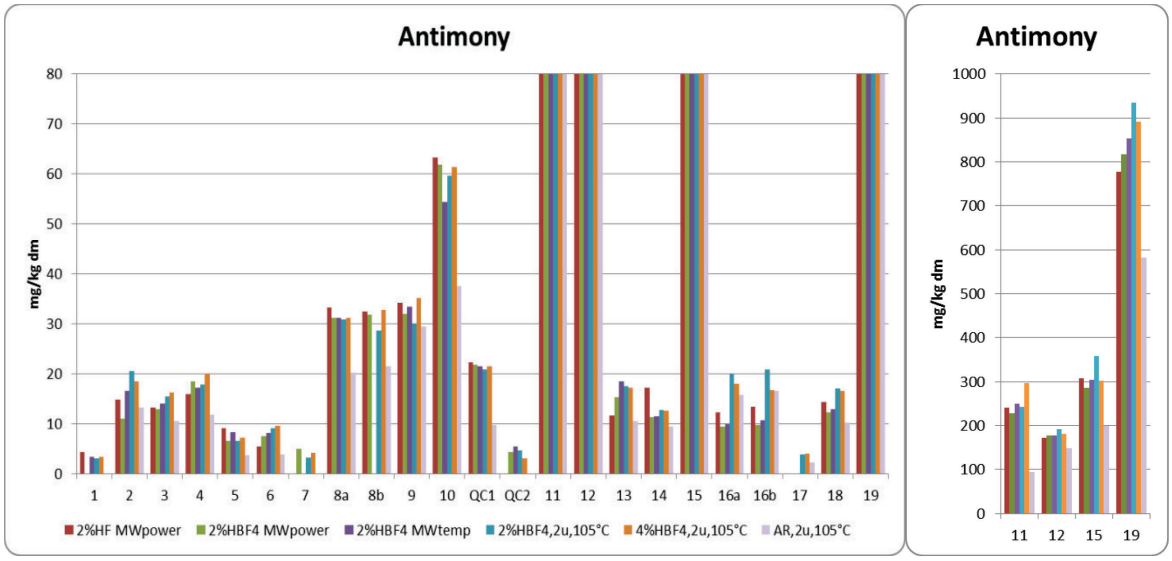

Figure 29 Sb results of the samples using the 6 digestion methods

The % coefficient of variation (CV_R) of the Sb results with the applied digestion methods (with the exception of the aqua regia digestion) was calculated per sample and is presented in Figure 30. This

figure also include the CV_R – red bar at the right side of the figure - obtained from the control chart of QC1 (HF digestion with power controlled microwave digestion). From all samples analysed the CV_R is situated below 35% and in most cases below 20%. The higher CVr values are often correlated with the low concentration value for Sb (concentration in the range of 10 to 20 mg/kg dm). The pooled CV_R of the 23 samples (including duplicates and QC samples) amounted 13.4%.

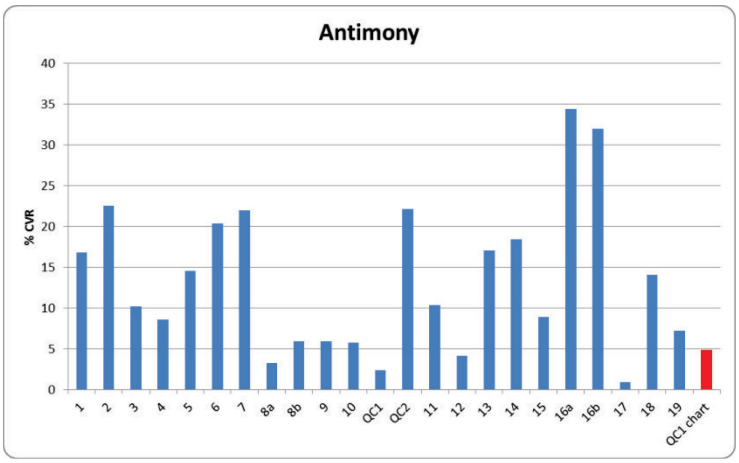

Figure 30 % CV_R of the 5 Sb results by sample (excl. aqua regia digestion)

In Figure 31 for each sample the ratio was calculated between the alternative methods and the reference method (2% HF – MW power). Although the value obtained with the reference method is also subjected to an measurement error, this value was considered as the 'true' value. In the evaluation process this has to be taken into account when drawing any conclusions. In case there would be a perfect match between both digestion results the calculated ratio would be 1. It is observed that the ratio factors are rather high due to the low concentration level of Sb for some samples. In general the data showed no significant difference between the different digestion methods, except for the aqua regia digestions. For the latter one a systematic underestimation of the Sb concentration could be detected.

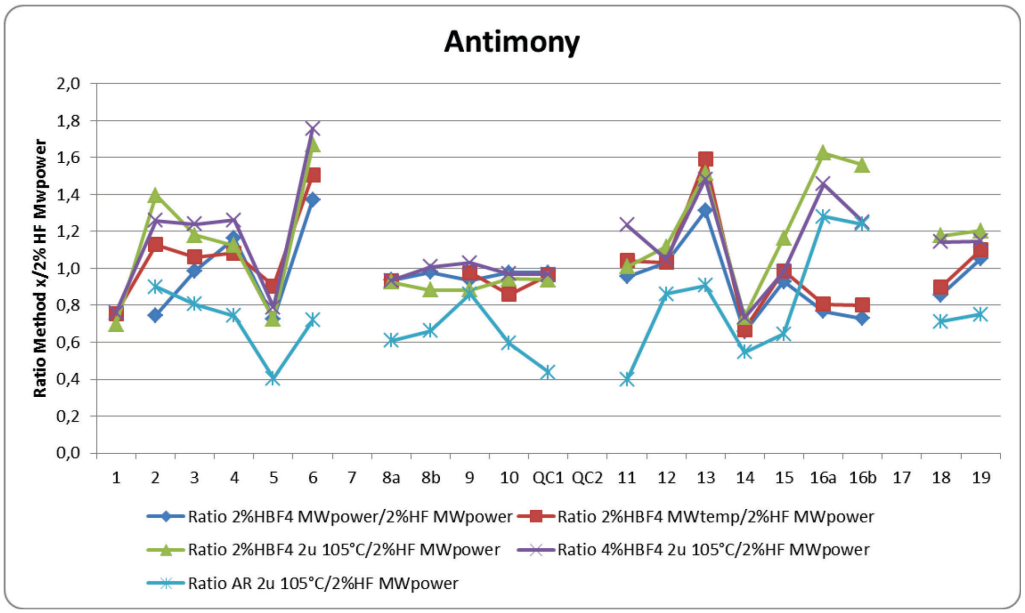

Figure 31 Ratio calculations of the alternative methods vs the reference method (2% HF – MW power) for Sb

5.1.10. ELEMENT BARIUM

In Figure 32 the Ba results of the different samples and the 2 quality control (QC) samples are presented. From the dataset 1 outlier was removed (sample 15: 2% HF, MW power controlled).

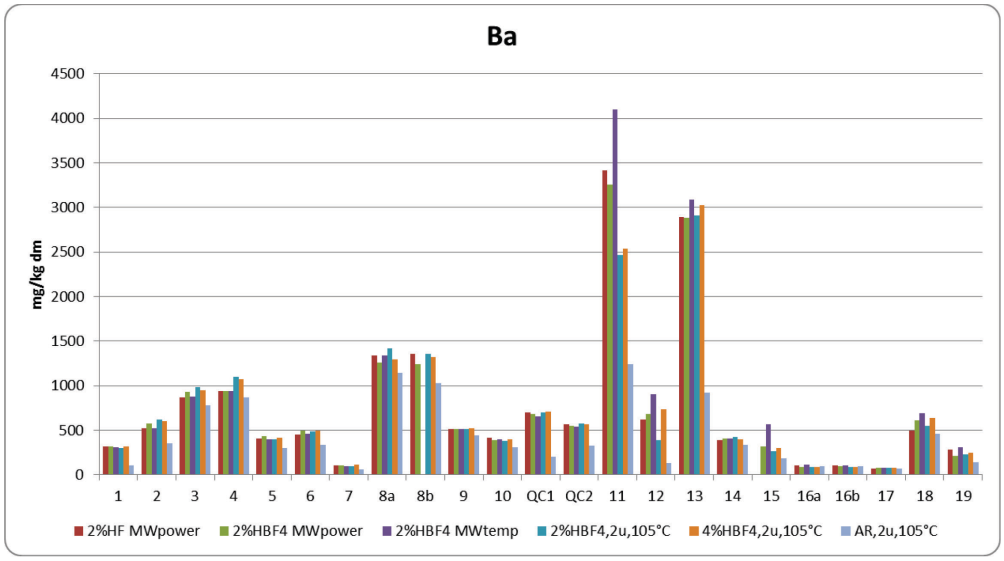

Figure 32 Ba results of the samples using the 6 digestion methods

The % coefficient of variation (CV_R) of the Ba results with the applied digestion methods (with the exception of the aqua regia digestion) was calculated per sample and is presented in Figure 33. This figure also include the CV_R – red bar at the right side of the figure - obtained from the control chart of QC1 (HF digestion with power controlled microwave digestion). From all samples analysed the CV_R is situated below 37% and in most cases below 15%. The pooled CV_R of the 23 samples (including duplicates and QC samples) amounted 8.9%.

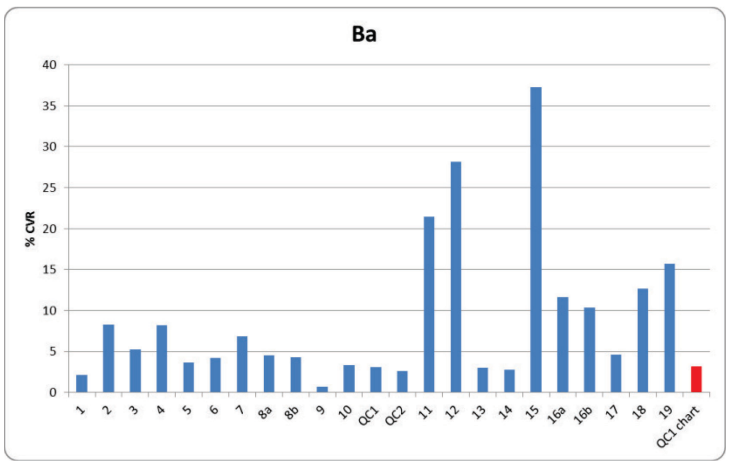

Figure 33 % CV_R of the 5 Ba results by sample (excl. aqua regia digestion)

In Figure 34 for each sample the ratio was calculated between the alternative methods and the reference method (2% HF – MW power). Although the value obtained with the reference method is also subjected to an measurement error, this value was considered as the 'true' value. In the evaluation process this has to be taken into account when drawing any conclusions. In case there would be a perfect match between both digestion results the calculated ratio would be 1.

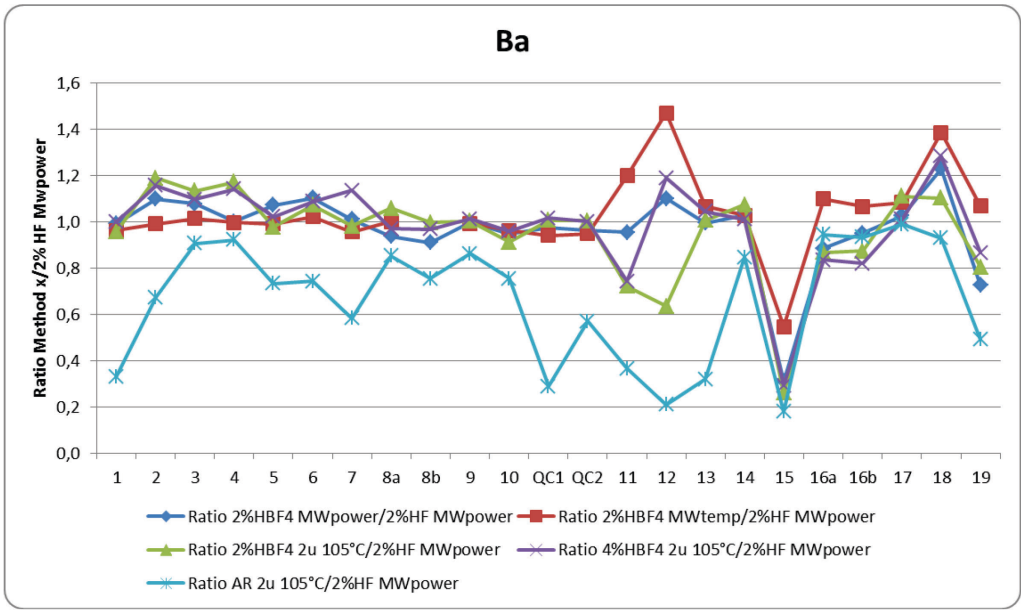

Figure 34 Ratio calculations of the alternative methods vs the reference method (2% HF – MW power) for Ba

For sample 15 the Ba value obtained with the reference method (2% HF, MW power) was considered as an outlier which is also confirmed when calculating the ratios; a low ratio of 0.2-0.5 for the other digestion methods related to the reference method was obtained. For all other samples comparable results are achieved using different digestion methods.
For sample 12 a lot of difference are obtained with the different digestion procedure. It might be that Ba is difficult to dissolve in this sample (sewage sludge) or heterogeneous distributed. The presented data show that the digestion with 2% HBF_4, 2 hrs 105°C resulted in a underestimation of the Ba value as compared with the reference method (ratio < 1). The use of 4% HBF_4 with digestion at 105°C, 2 hrs, on the other hand, shows a better recovery.
When evaluating the data obtained with the aqua regia digestion method, these data show for most of the samples a significant underestimation of the Ba results, with ratio factors down to 0.2.

5.1.11. ELEMENT COBALT

In Figure 35 the Co results of the different samples and the 2 quality control (QC) samples are presented.

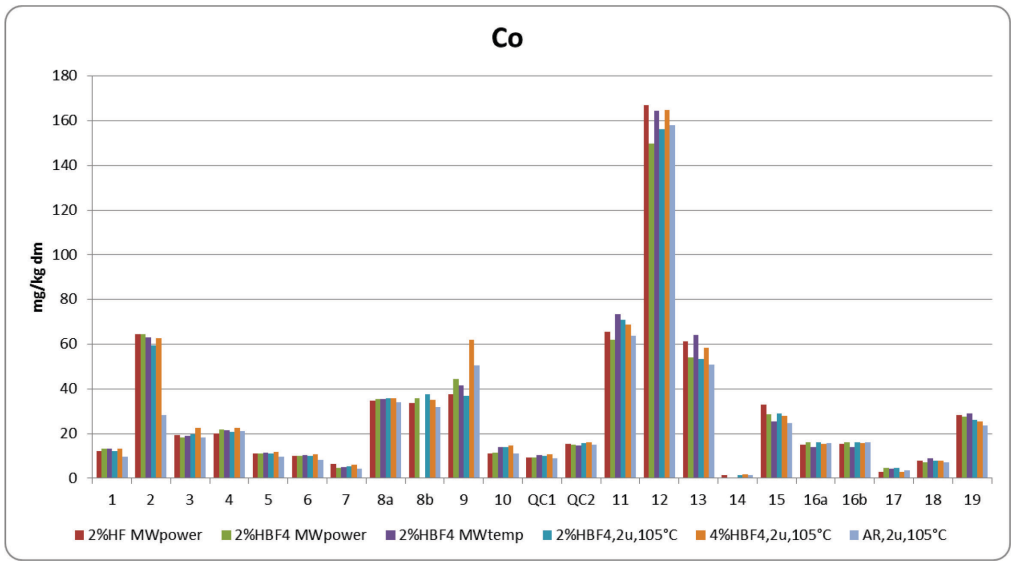

Figure 35 Co results of the samples using the 6 digestion methods

The % coefficient of variation (CV_R) of the Co results with the applied digestion methods (with the exception of the aqua regia digestion) was calculated per sample and is presented in Figure 36. From all samples analysed the CV_R is situated below 24% and in most cases below 15%. The pooled CV_R of the 23 samples (including duplicates and QC samples) amounted 8.2%.

In Figure 37 for each sample the ratio was calculated between the alternative methods and the reference method (2% HF – MW power). Although the value obtained with the reference method is also subjected to an measurement error, this value was considered as the 'true' value. In the evaluation process this has to be taken into account when drawing any conclusions. In case there would be a perfect match between both digestion results the calculated ratio would be 1.
When evaluating the data obtained with the aqua regia digestion method, these data show for a few samples an underestimation of the Co results, with ratio factors down to 0.4.

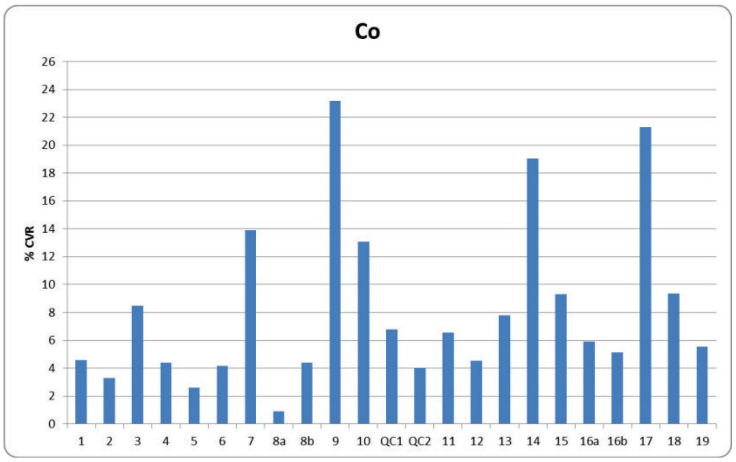

Figure 36 % CV_R of the Co results by sample (excl. aqua regia digestion)

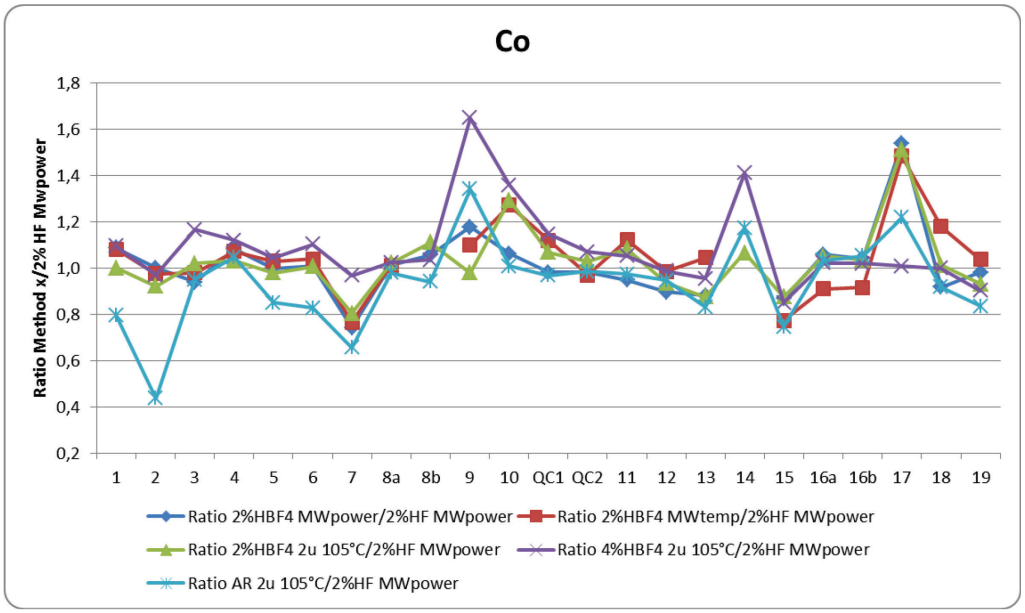

Figure 37 Ratio calculations of the alternative methods vs the reference method (2% HF – MW power) for Co

5.1.1. ELEMENT MANGANESE

In Figure 38 the Mn results of the different samples and the 2 quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the Mn results with the applied digestion methods (with the exception of the aqua regia digestion) was calculated per sample and is presented in Figure 39. This figure also include the CV_R – red bar at the right side of the figure - obtained from the control chart of QC1 (HF digestion with power controlled microwave digestion). From all samples analysed the CV_R is situated below 10%. The pooled CV_R of the 23 samples (including duplicates and QC samples) amounted 5.0%.

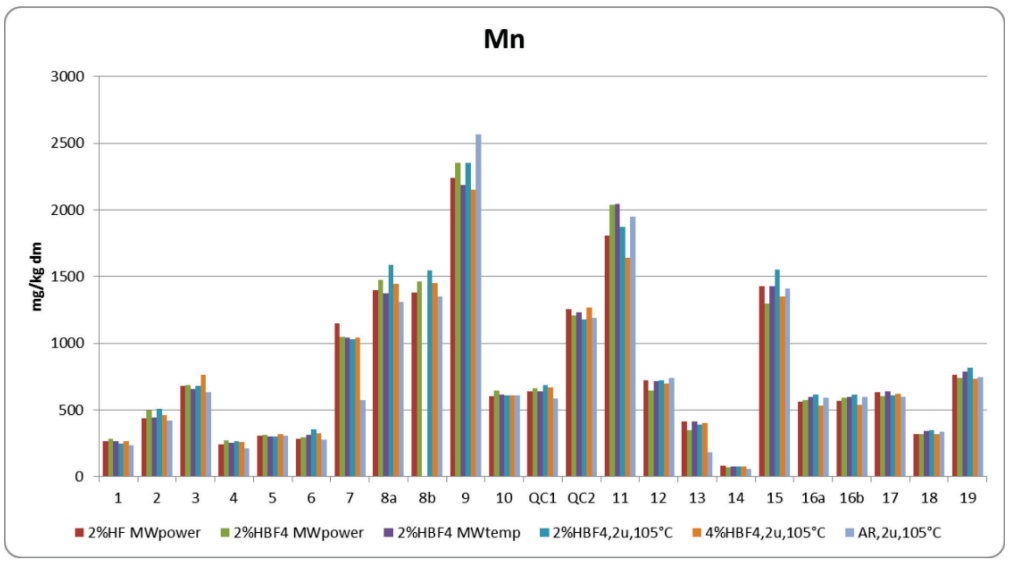

Figure 38 Mn results of the samples using the 6 digestion methods

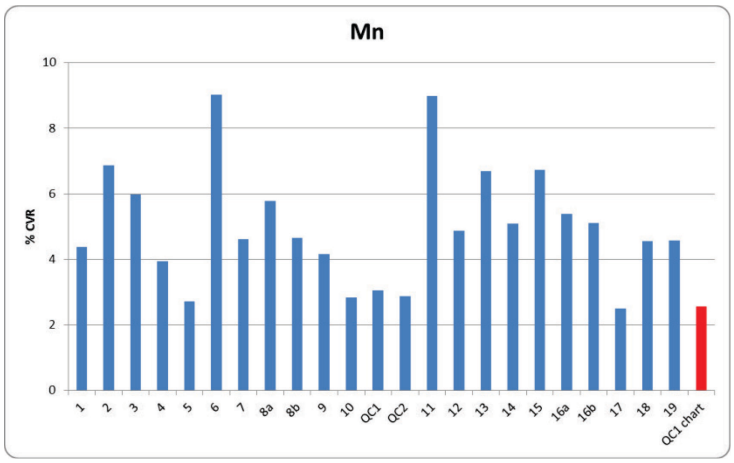

Figure 39 % CV_R of the 5 Mn results by sample (excl. aqua regia digestion)

In Figure 40 for each sample the ratio was calculated between the alternative methods and the reference method (2% HF – MW power). Although the value obtained with the reference method is also subjected to an measurement error, this value was considered as the 'true' value. In the evaluation process this has to be taken into account when drawing any conclusions. In case there would be a perfect match between both digestion results the calculated ratio would be 1.
For sample 7 and sample 13 a low ratio factor (0.4-0.5) was obtained when comparing the aqua regia data with de reference digestion method. This effect was also observed for the element Zn, as was shown before.

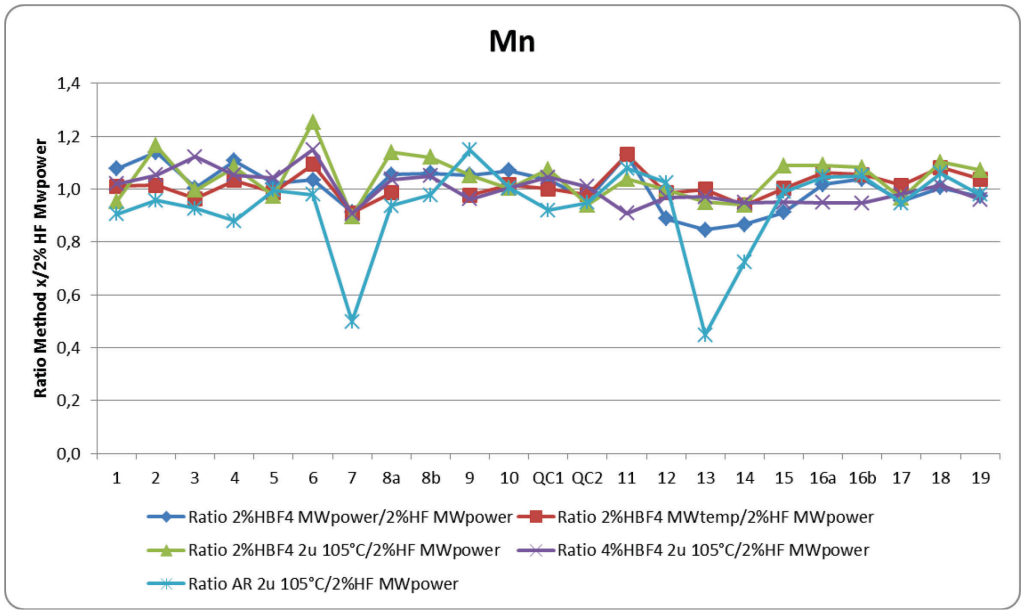

Figure 40 Ratio calculations of the alternative methods vs the reference method (2% HF – MW power) for Mn

5.1.2. ELEMENT MOLYBDENUM

In Figure 41 the Mo results of the different samples and the 2 quality control (QC) samples are presented. From the dataset 2 outliers were removed (sample 3 and 9: both 4% HBF_4, 2 hrs 105°C).

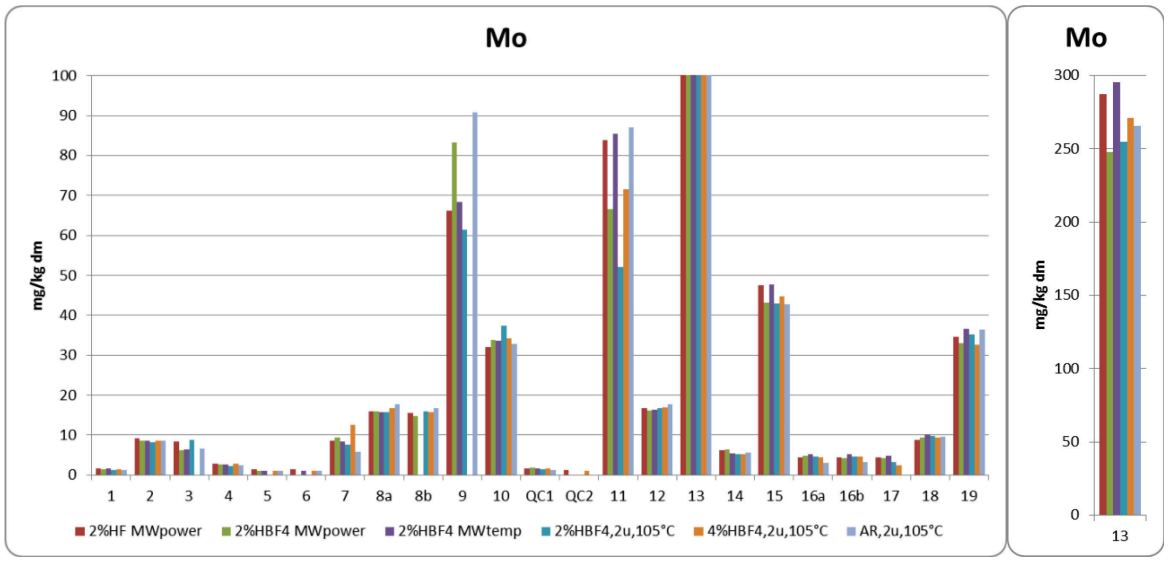

Figure 41 Mo results of the samples using the 6 digestion methods

The % coefficient of variation (CV_R) of the Mo results with the applied digestion methods (with the exception of the aqua regia digestion) was calculated per sample and is presented in Figure 42. From all samples analysed the CV_R is situated below 25%. The pooled CV_R of the 23 samples (including duplicates and QC samples) amounted 10.2%.

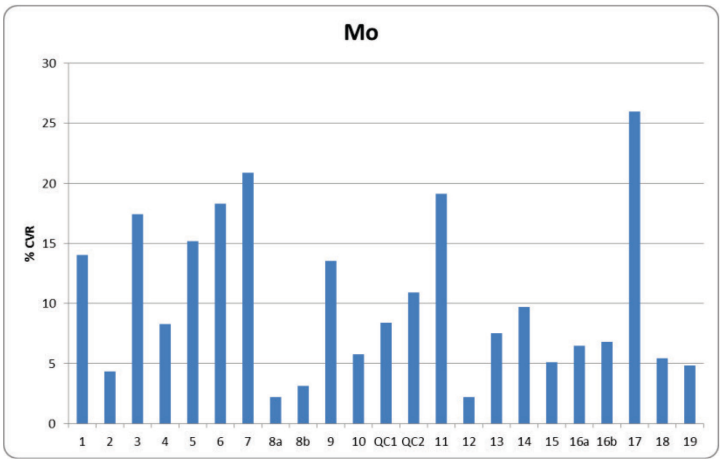

Figure 42 % CV_R of the 5 Mo results by sample (excl. aqua regia digestion)

In Figure 43 for each sample the ratio was calculated between the alternative methods and the reference method (2% HF – MW power). Although the value obtained with the reference method is also subjected to an measurement error, this value was considered as the 'true' value. In the evaluation process this has to be taken into account when drawing any conclusions. In case there would be a perfect match between both digestion results the calculated ratio would be 1.

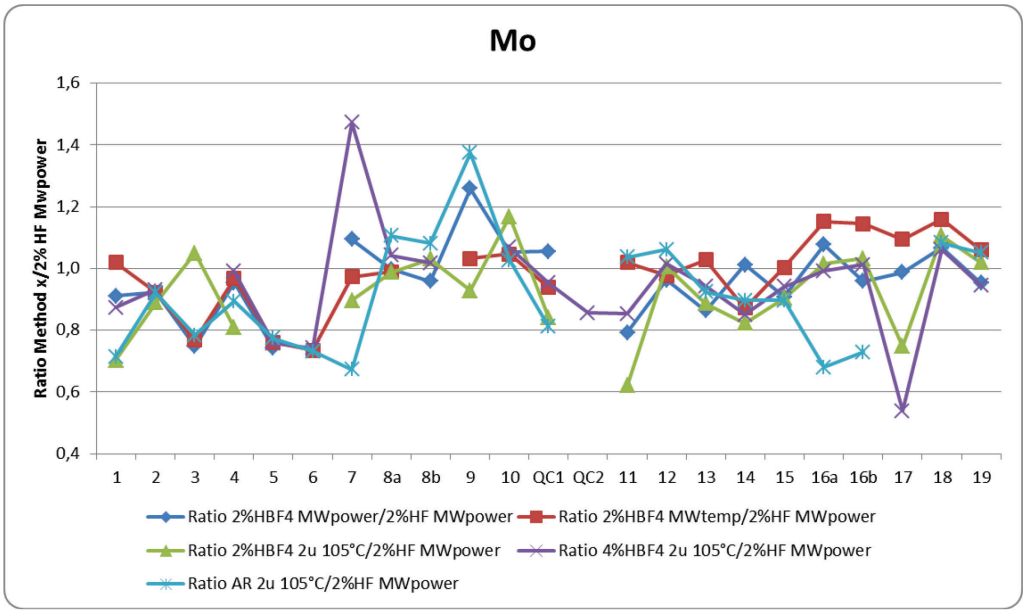

Figure 43 Ratio calculations of the alternative methods vs the reference method (2% HF – MW power) for Mo

5.1.3. ELEMENT TIN

In Figure 44 the Sn results of the different samples and the 2 quality control (QC) samples are presented. From the dataset 2 outliers were removed (sample 2 and 6: both 2% HBF_4, 2 hrs 105°C).

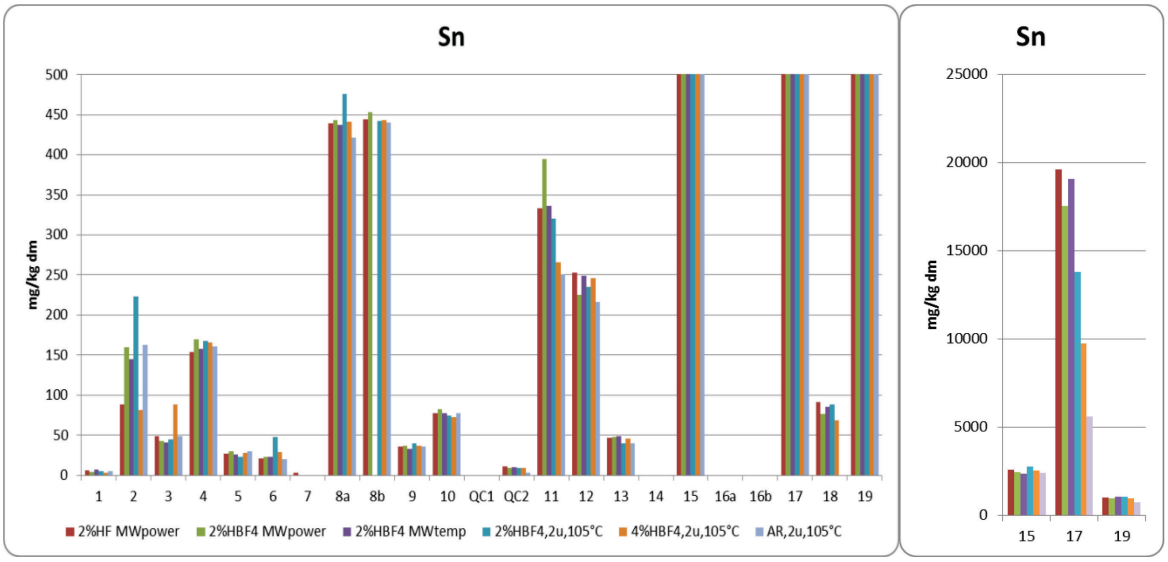

Figure 44 Sn results of the samples using the 6 digestion methods

The coefficient of variation (CV_R) of the Sn results with the applied digestion methods (with the exception of the aqua regia digestion) was calculated per sample and is presented in Figure 45. For some samples analysed the CV_R shows rather high values, even up to 42%. Very high values are sometimes observed for e.g. samples 2, 8a and 11, which could not be attributed to a certain digestion method. It is known that Sn is a difficult element to dissolve and often heterogeneously

distributed within a sample. The pooled CV_R of the 23 samples (including duplicates and QC samples) amounted 14.2%.

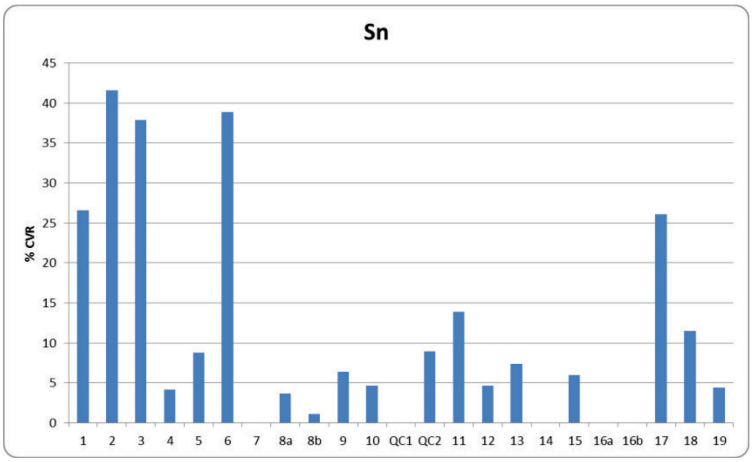

Figure 45 % CV_R of the 5 Sn results by sample (excl. aqua regia digestion)

In Figure 46 for each sample the ratio was calculated between the alternative methods and the reference method (2% HF – MW power). Although the value obtained with the reference method is also subjected to an measurement error, this value was considered as the 'true' value. In the evaluation process this has to be taken into account when drawing any conclusions. In case there would be a perfect match between both digestion results the calculated ratio would be 1. This figure also reflect some deviated positive results in comparison with the reference method, as already discussed above.

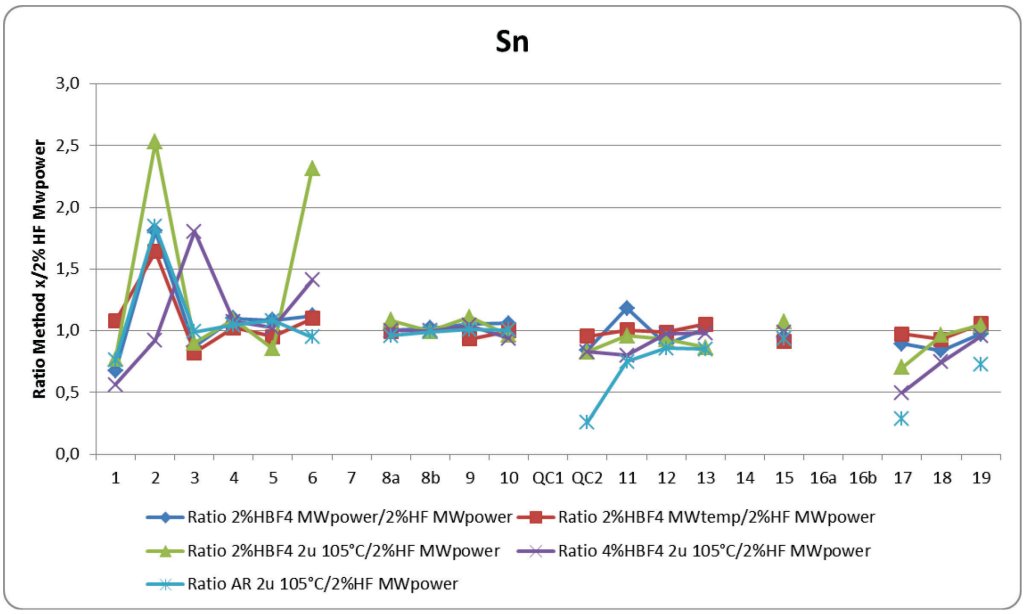

Figure 46 Ratio calculations of the alternative methods vs the reference method (2% HF – MW power) for Sn

5.1.4. ELEMENT VANADIUM

In Figure 47 the V results of the different samples and the 2 quality control (QC) samples are presented.

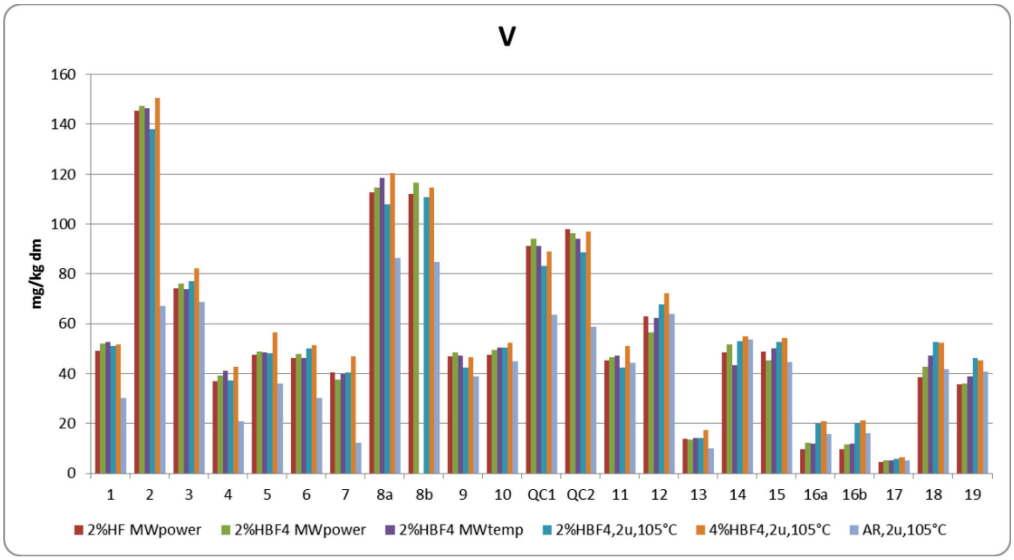

Figure 47 V results of the samples using the 6 digestion methods

The % coefficient of variation (CV_R) of the V results with the applied digestion methods (with the exception of the aqua regia digestion) was calculated per sample and is presented in Figure 48. This figure also include the CV_R – red bar at the right side of the figure - obtained from the control chart of QC1 (HF digestion with power controlled microwave digestion). From all samples analysed the CV_R is situated below 35% and in most cases below 15%. The pooled CV_R of the 23 samples (including duplicates and QC samples) amounted 9.3%. Only for sample 16 (a and b) a higher deviation is observed attributed to an elevated concentration obtained with the 2% and 4% HBF_4 digestion, 2hrs at 105°C.

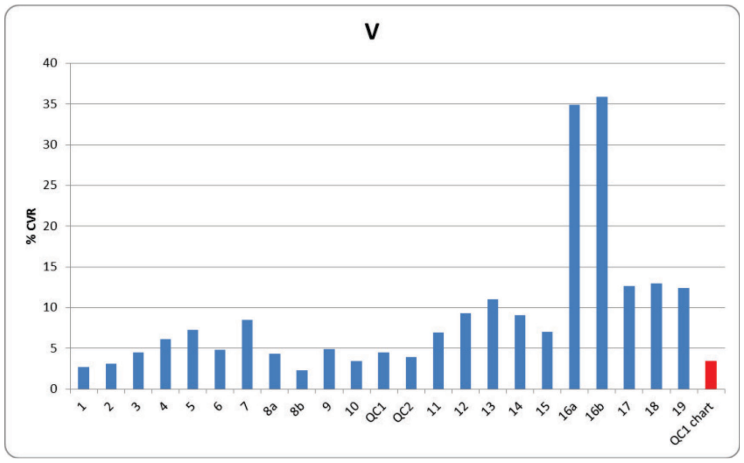

Figure 48 % CV_R of the 5 V results by sample (excl. aqua regia digestion)

In Figure 49 for each sample the ratio was calculated between the alternative methods and the reference method (2% HF – MW power). Although the value obtained with the reference method is also subjected to an measurement error, this value was considered as the 'true' value. In the

evaluation process this has to be taken into account when drawing any conclusions. In case there would be a perfect match between both digestion results the calculated ratio would be 1.
For sample 16 a and b all digestion methods show higher V values compared to the reference method. The highest ratios are observed for the 2% and 4% HBF_4 digestion, 2hrs at 105°C.
When evaluating the data obtained with the aqua regia digestion method, these data show for several samples a significant underestimation of the V results, with ratio factors down to 0.3. A similar trend, but more pronounced was observed for the element Cr.

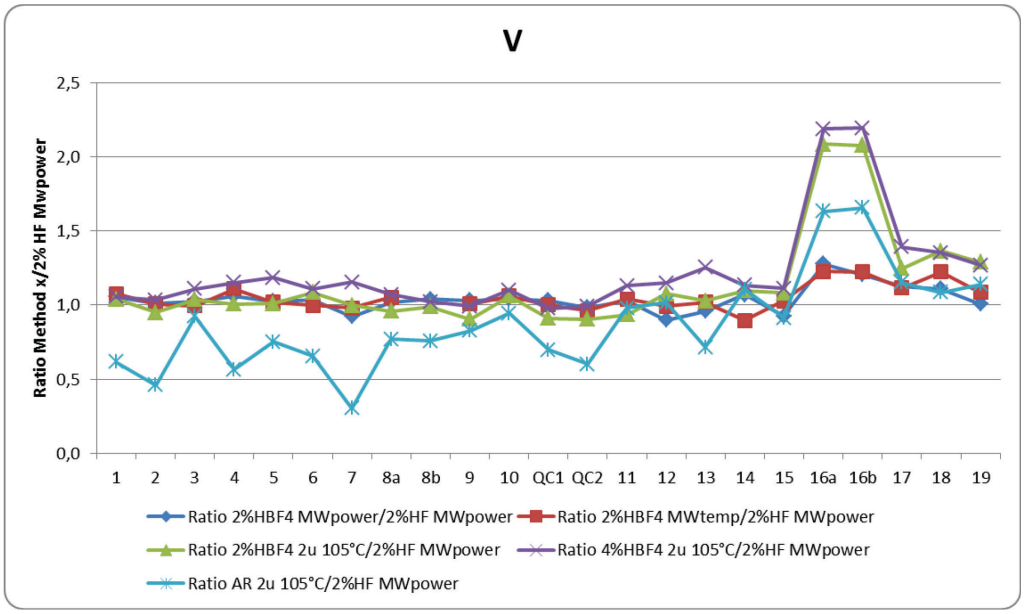

Figure 49 Ratio calculations of the alternative methods vs the reference method (2% HF – MW power) for V

5.2. RESULTS OF MAJOR ELEMENTS

5.2.1. ELEMENT SODIUM

In Figure 50 the Na results of the different samples and the 2 quality control (QC) samples are presented.

The % coefficient of variation (CV_R) of the Na results with the applied digestion methods (with the exception of the aqua regia digestion) was calculated per sample and is presented in Figure 51. This figure also include the CV_R – red bar at the right side of the figure - obtained from the control chart of QC1 (HF digestion with power controlled microwave digestion). From all samples analysed the CV_R is situated below 13%. The pooled CV_R of the 23 samples (including duplicates and QC samples) amounted 4.6%.

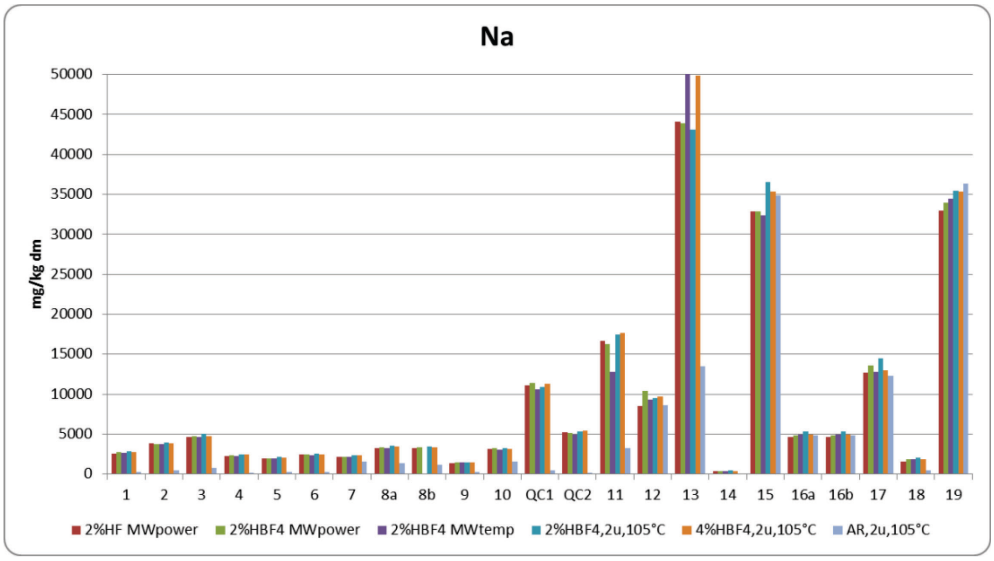

Figure 50 Na results of the samples using the 6 digestion methods

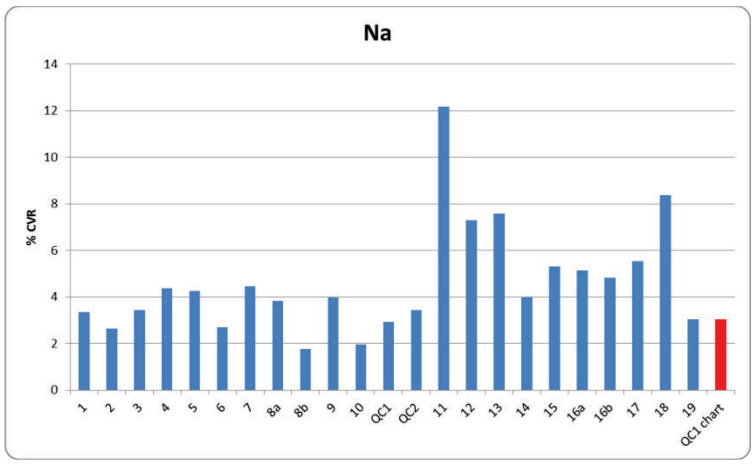

Figure 51 % CV_R of the 5 Na results by sample (excl. aqua regia digestion)

In Figure 52 for each sample the ratio was calculated between the alternative methods and the reference method (2% HF – MW power). Although the value obtained with the reference method is also subjected to an measurement error, this value was considered as the 'true' value. In the evaluation process this has to be taken into account when drawing any conclusions. In case there would be a perfect match between both digestion results the calculated ratio would be 1. It is clearly that aqua regia digestion results in an underestimation of the Na content compared to the other digestion methods.

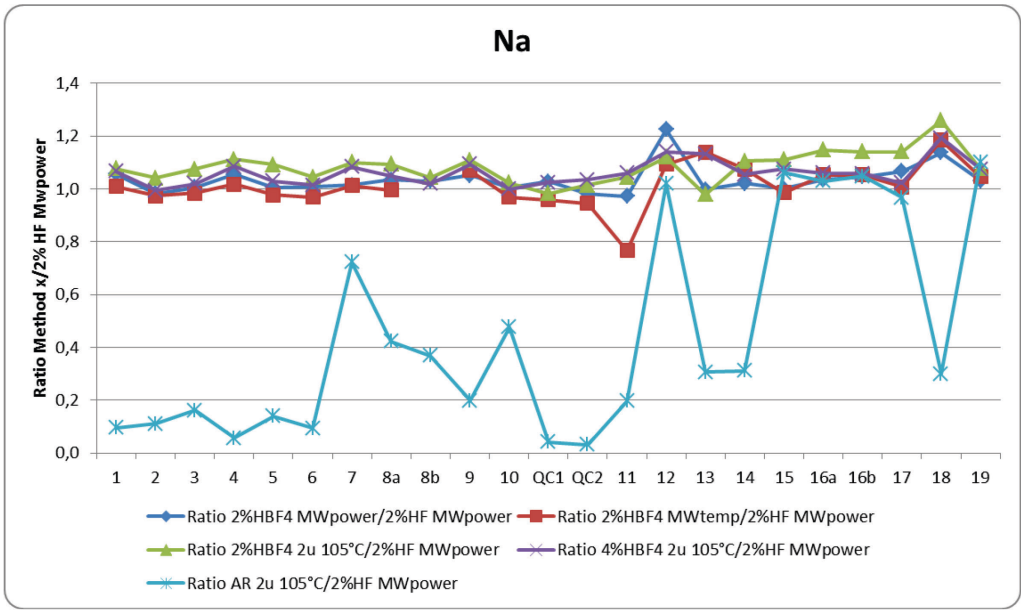

Figure 52 Ratio calculations of the alternative methods vs the reference method (2% HF – MW power) for Na

5.2.2. ELEMENT MAGNESIUM

In Figure 53 the Mg results of the different samples and the 2 quality control (QC) samples are presented.

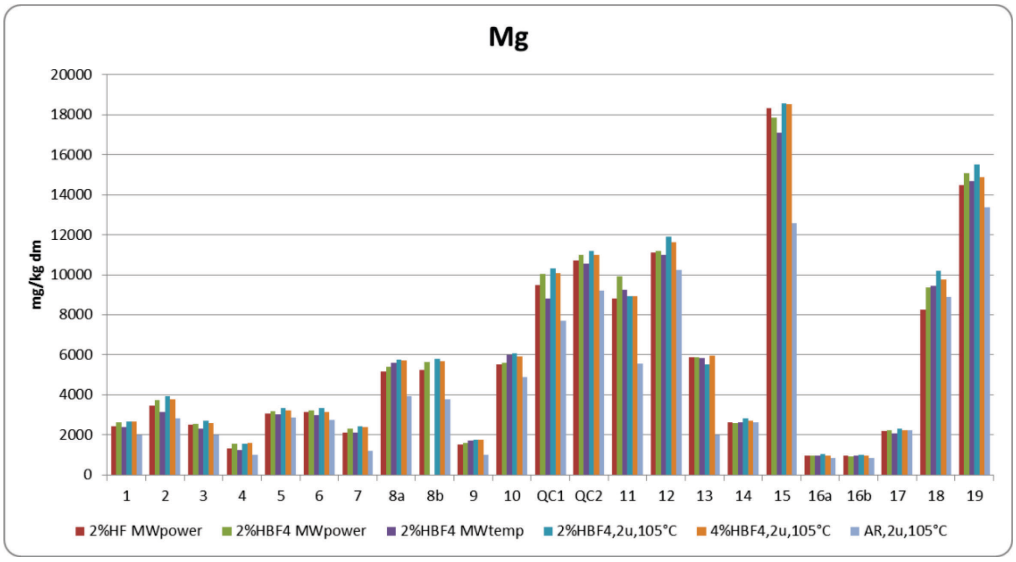

Figure 53 Mg results of the samples using the 6 digestion methods

The % coefficient of variation (CV_R) of the Mg results with the applied digestion methods (with the exception of the aqua regia digestion) was calculated per sample and is presented in Figure 54. This figure also include the CV_R – red bar at the right side of the figure - obtained from the control chart of QC1 (HF digestion with power controlled microwave digestion). From all samples analysed the CV_R is situated below 11%. The pooled CV_R of the 23 samples (including duplicates and QC samples) amounted 4.8%.

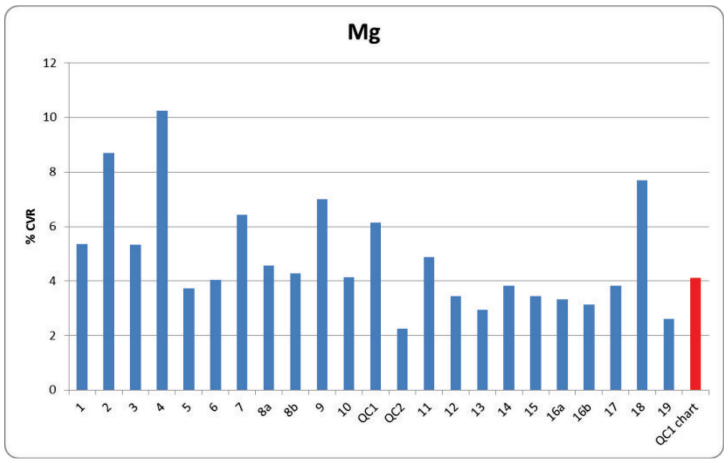

Figure 54 % CV_R of the 5 Mg results by sample (excl. aqua regia digestion)

In Figure 55 for each sample the ratio was calculated between the alternative methods and the reference method (2% HF – MW power). Although the value obtained with the reference method is also subjected to an measurement error, this value was considered as the 'true' value. In the evaluation process this has to be taken into account when drawing any conclusions. In case there would be a perfect match between both digestion results the calculated ratio would be 1. It is clearly that aqua regia digestion results in an underestimation of the Mg content compared to the other digestion methods.

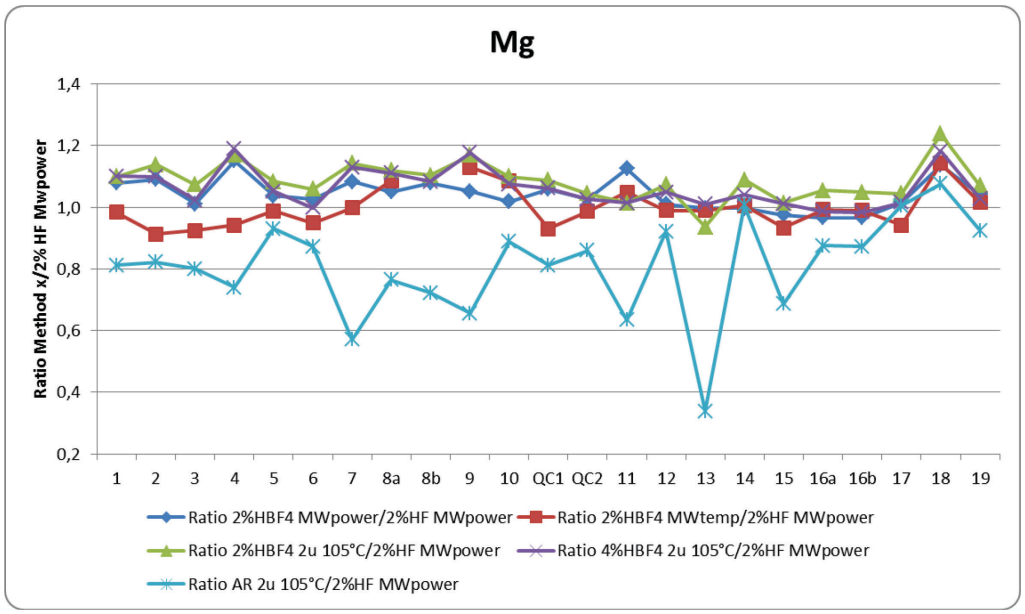

Figure 55 Ratio calculations of the alternative methods vs the reference method (2% HF – MW power) for Mg

5.2.3. ELEMENT ALUMINIUM

In Figure 56 the Al results of the different samples and the 2 quality control (QC) samples are presented.

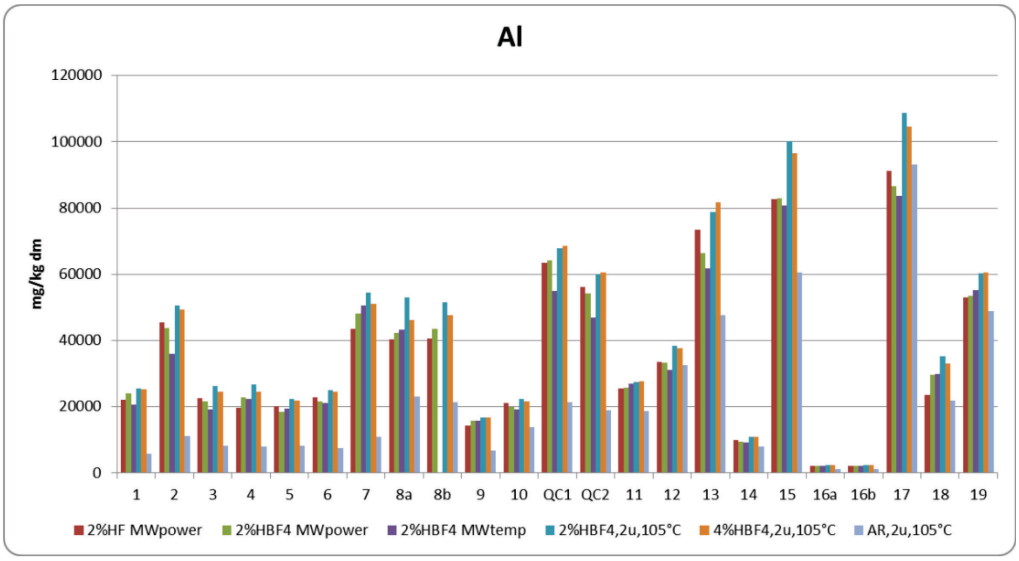

Figure 56 Al results of the samples using the 6 digestion methods

The % coefficient of variation (CV_R) of the Al results with the applied digestion methods (with the exception of the aqua regia digestion) was calculated per sample and is presented in Figure 57. This figure also include the CV_R – red bar at the right side of the figure - obtained from the control chart of QC1 (HF digestion with power controlled microwave digestion). From all samples analysed the CV_R is situated below 15%. The pooled CV_R of the 23 samples (including duplicates and QC samples) amounted 9.1%.

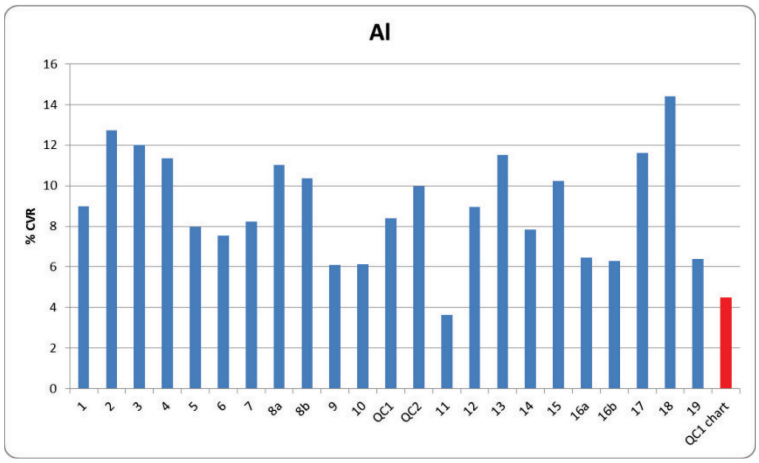

Figure 57 % CV_R of the 5 Al results by sample (excl. aqua regia digestion)

In Figure 58 for each sample the ratio was calculated between the alternative methods and the reference method (2% HF – MW power). Although the value obtained with the reference method is also subjected to an measurement error, this value was considered as the 'true' value. In the evaluation process this has to be taken into account when drawing any conclusions. In case there would be a perfect match between both digestion results the calculated ratio would be 1. It is clearly that aqua regia digestion results in an underestimation of the Al content compared to the other digestion methods.

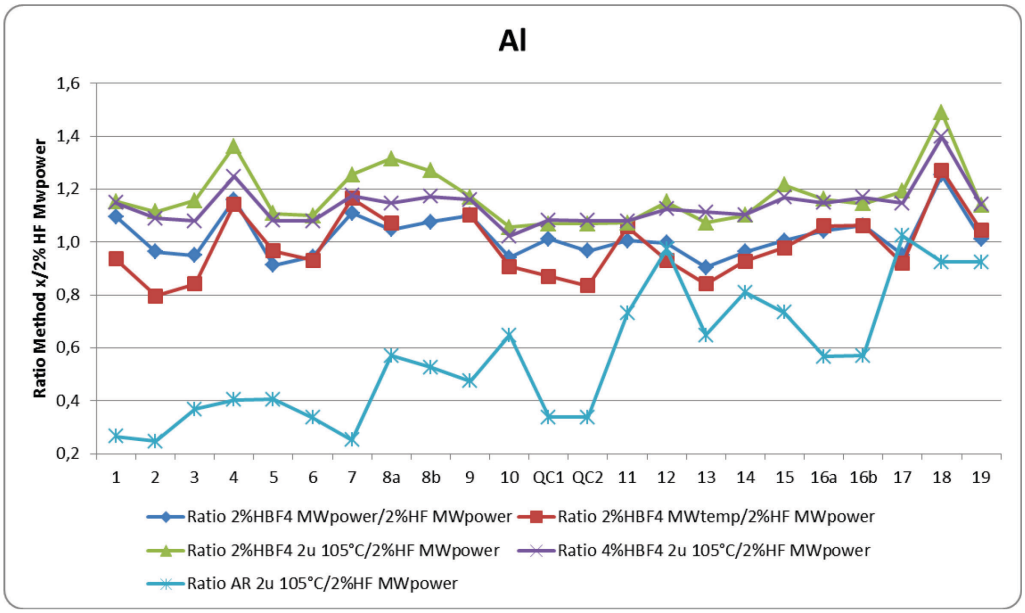

Figure 58 Ratio calculations of the alternative methods vs the reference method (2% HF – MW power) for Al

5.2.4. ELEMENT POTASSIUM

In Figure 59 the K results of the different samples and the 2 quality control (QC) samples are presented.

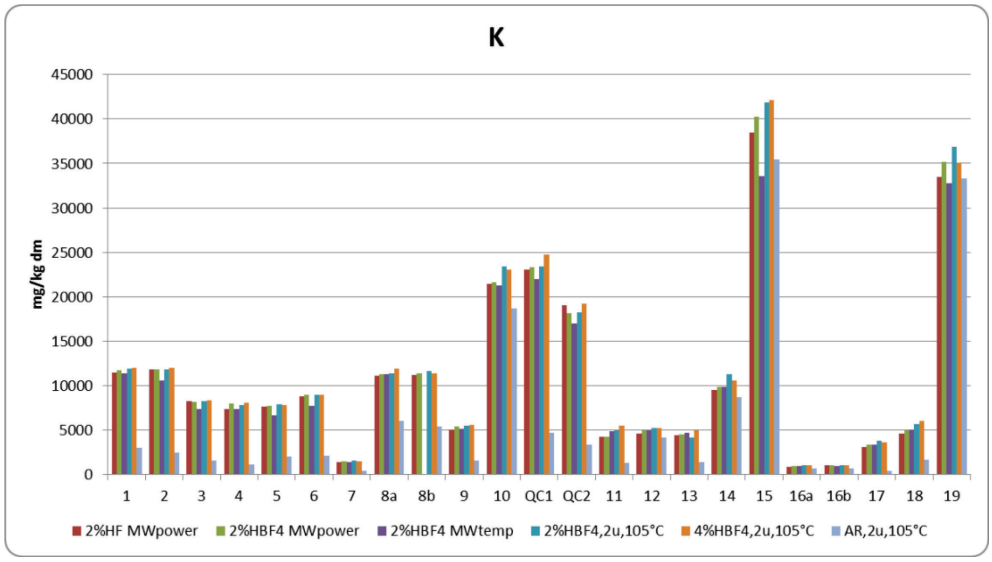

Figure 59 K results of the samples using the 6 digestion methods

The % coefficient of variation (CV_R) of the K results with the applied digestion methods (with the exception of the aqua regia digestion) was calculated per sample and is presented in Figure 60. This figure also include the CV_R – red bar at the right side of the figure - obtained from the control chart of QC1 (HF digestion with power controlled microwave digestion). From all samples analysed the CV_R is situated below 12%. The pooled CV_R of the 23 samples (including duplicates and QC samples) amounted 5.8%.

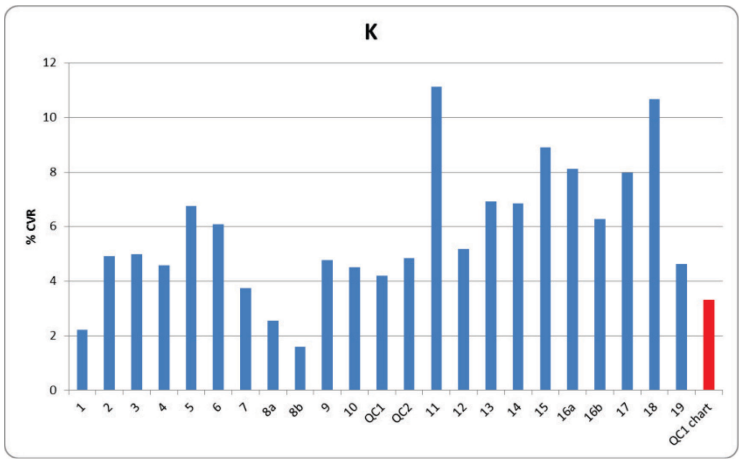

Figure 60 % CV_R of the 5 K results by sample (excl. aqua regia digestion)

In Figure 61 for each sample the ratio was calculated between the alternative methods and the reference method (2% HF – MW power). Although the value obtained with the reference method is also subjected to an measurement error, this value was considered as the 'true' value. In the evaluation process this has to be taken into account when drawing any conclusions. In case there would be a perfect match between both digestion results the calculated ratio would be 1. It is clearly that aqua regia digestion results in an underestimation of the K content compared to the other digestion methods.

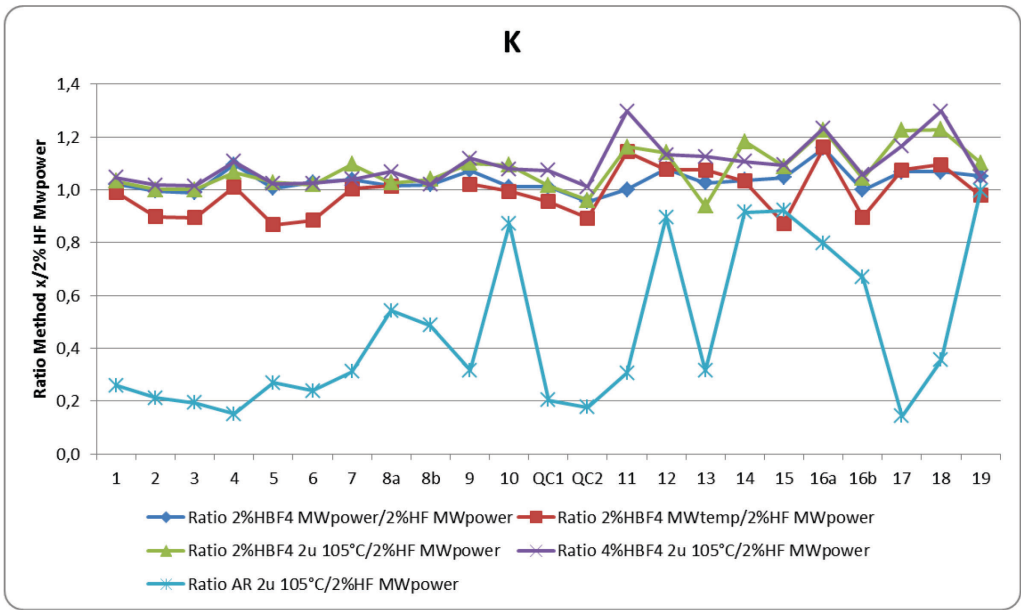

Figure 61 Ratio calculations of the alternative methods vs the reference method (2% HF – MW power) for K

5.2.5. ELEMENT CALCIUM

In Figure 62 the Ca results of the different samples and the 2 quality control (QC) samples are presented.

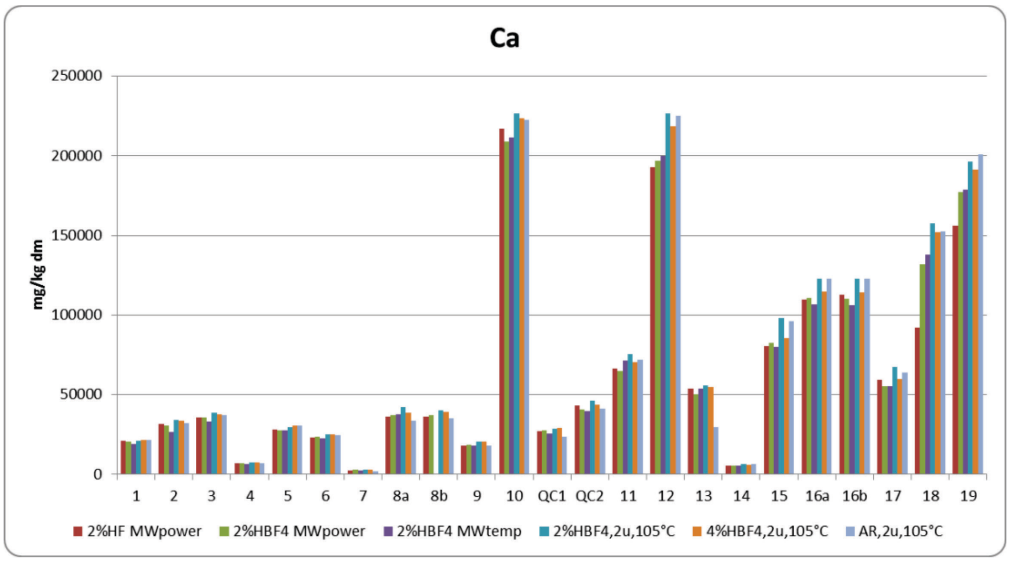

Figure 62 Ca results of the samples using the 6 digestion methods

The % coefficient of variation (CV_R) of the Ca results with the applied digestion methods (with the exception of the aqua regia digestion) was calculated per sample and is presented in Figure 63. This figure also include the CV_R – red bar at the right side of the figure - obtained from the control chart of QC1 (HF digestion with power controlled microwave digestion). From all samples analysed the CV_R is situated below 10%, except for sample 18 with a CV_R of 19%. The higher CV_R is attributed to a low Ca content obtained with the reference method in comparison with the other digestion methods. The pooled CV_R of the 23 samples (including duplicates and QC samples) amounted 6.7%.

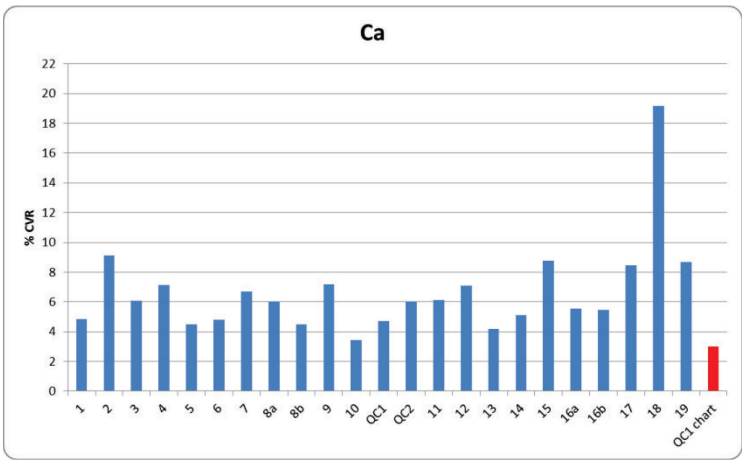

Figure 63 % CV_R of the 5 Ca results by sample (excl. aqua regia digestion)

In Figure 64 for each sample the ratio was calculated between the alternative methods and the reference method (2% HF – MW power). Although the value obtained with the reference method is also subjected to an measurement error, this value was considered as the 'true' value. In the evaluation process this has to be taken into account when drawing any conclusions. In case there would be a perfect match between both digestion results the calculated ratio would be 1. As already stated above for sample 18 an underestimation is observed for the Ca content using the reference method, this can also be deduced from the figure as for this sample all the ratios from the different digestion methods in relation with the reference method are between 1.4 and 1.7.

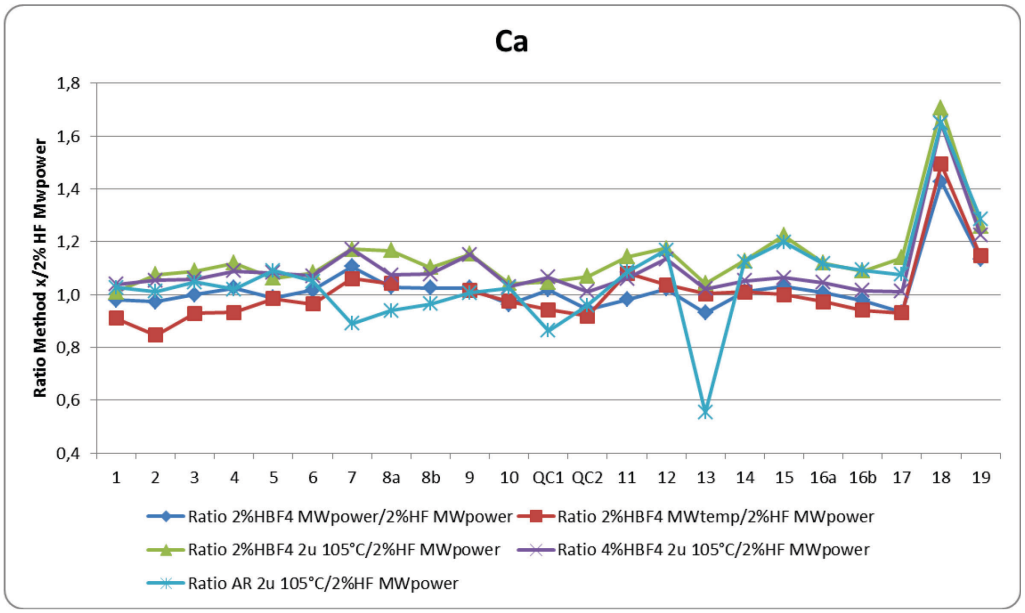

Figure 64 Ratio calculations of the alternative methods vs the reference method (2% HF – MW power) for Ca

5.2.6. ELEMENT TITANIUM

In Figure 65 the Ti results of the different samples and the 2 quality control (QC) samples are presented.

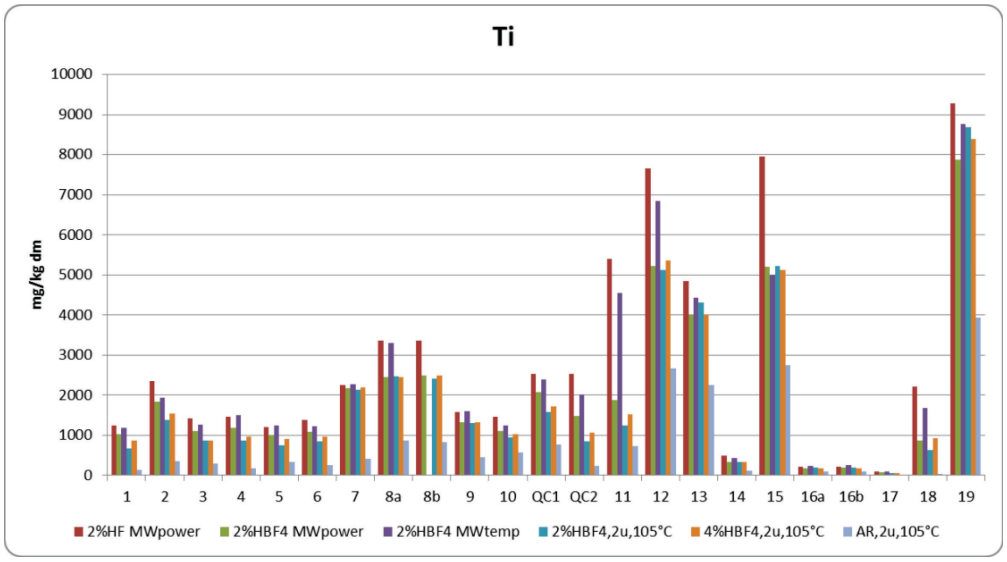

Figure 65 Ti results of the samples using the 6 digestion methods

The % coefficient of variation (CV_R) of the Ti results with the applied digestion methods (with the exception of the aqua regia digestion) was calculated per sample and is presented in Figure 66. This figure also include the CV_R – red bar at the right side of the figure - obtained from the control chart of QC1 (HF digestion with power controlled microwave digestion). In comparison with other elements a high CV_R is obtained for the different samples. For most samples the CV_R fluctuates

around 20%, with outliers of 40 to 65% for sample QC2, 11 and 18. The pooled CV_R of the 23 samples (including duplicates and QC samples) amounted 22%.

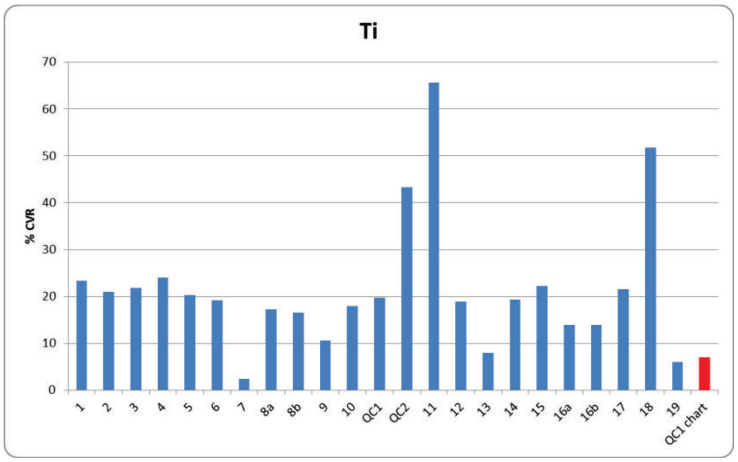

Figure 66 % CV_R of the 5 Ti results by sample (excl. aqua regia digestion)

In Figure 67) for each sample the ratio was calculated between the alternative methods and the reference method (2% HF – MW power). Although the value obtained with the reference method is also subjected to an measurement error, this value was considered as the 'true' value. In the evaluation process this has to be taken into account when drawing any conclusions. In case there would be a perfect match between both digestion results the calculated ratio would be 1.

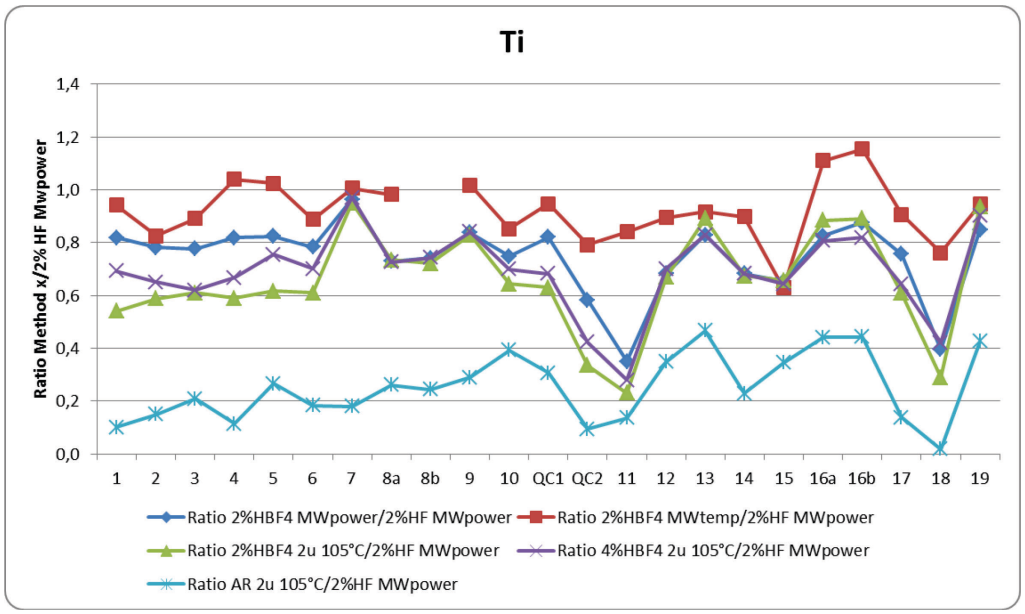

Figure 67 Ratio calculations of the alternative methods vs the reference method (2% HF – MW power) for Ti

For the Ti results differences are observed between the different digestion methods and the reference method. The highest Ti values are obtained with the reference digestion method of 2% HF and power controlled microwave digestion. Only a slight reduction in Ti concentration values (by average ± 8%) is observed when applying the HBF_4 digestion with the temperature controlled microwave digestion. Applying the 2% HBF_4 digestion with the power controlled microwave digestion, resulted in a systematic underestimation of about 25% by average. Digestion with 2% or

4% HBF_4 digestion at 105°C, 2 hrs, resulted in a systematic underestimation of about 30% by average. Using aqua regia digestion even resulted in a recovery with respect to the reference method of only 25% by average.
Although the element Ti is not included in the legislation it gives a fairly good overview about the impact a certain digestion method can have on the obtained results.

5.2.7. ELEMENT IRON

In Figure 68 the Fe results of the different samples and the 2 quality control (QC) samples are presented.

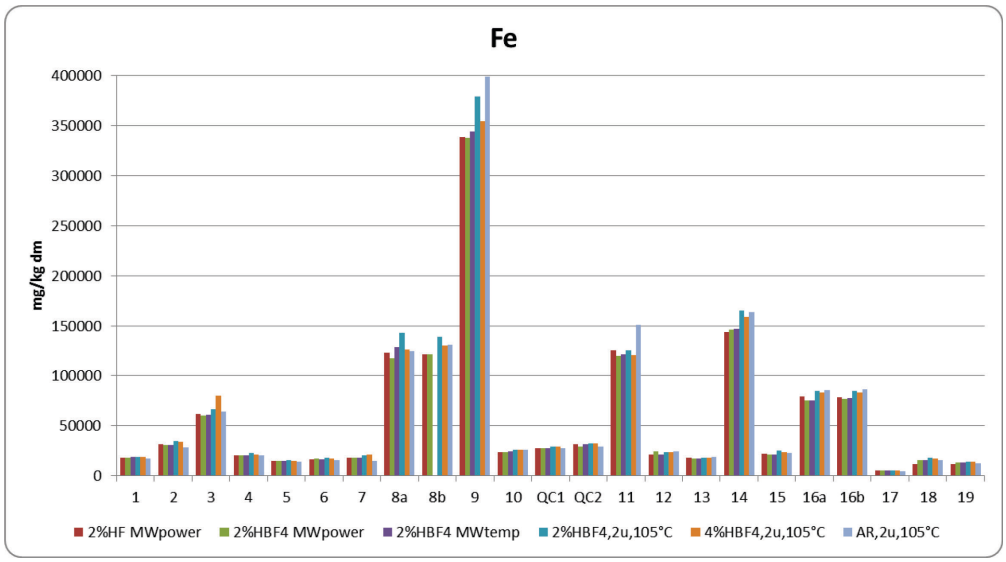

Figure 68 Fe results of the samples using the 6 digestion methods

The % coefficient of variation (CV_R) of the Fe results with the applied digestion methods (with the exception of the aqua regia digestion) was calculated per sample and is presented in Figure 69. This figure also include the CV_R – red bar at the right side of the figure - obtained from the control chart of QC1 (HF digestion with power controlled microwave digestion). From all samples analysed the CV_R is situated below 15%. The pooled CV_R of the 23 samples (including duplicates and QC samples) amounted 5.8%.

In Figure 70 for each sample the ratio was calculated between the alternative methods and the reference method (2% HF – MW power). Although the value obtained with the reference method is also subjected to an measurement error, this value was considered as the 'true' value. In the evaluation process this has to be taken into account when drawing any conclusions. In case there would be a perfect match between both digestion results the calculated ratio would be 1.
For sample 18 an underestimation is observed for the Fe content using the reference method, this can also be deduced from the figure as for this sample all the ratios from the different digestion methods in relation with the reference method are between 1.3 and 1.5. A similar effect was also observed for the element Ca.

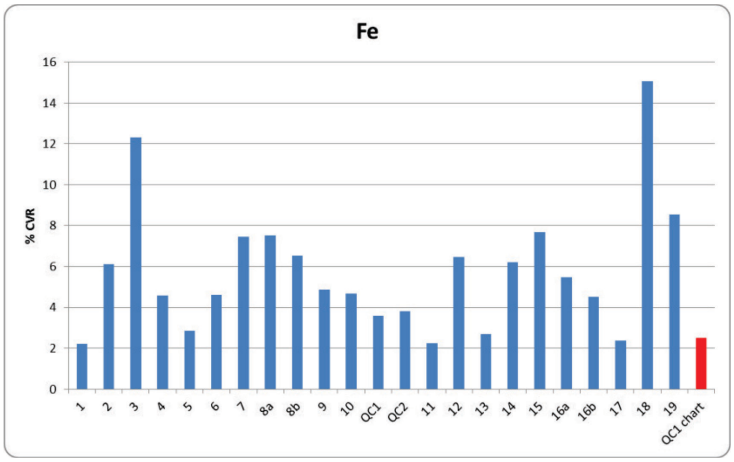

Figure 69 % CV_R of the 5 Fe results by sample (excl. aqua regia digestion)

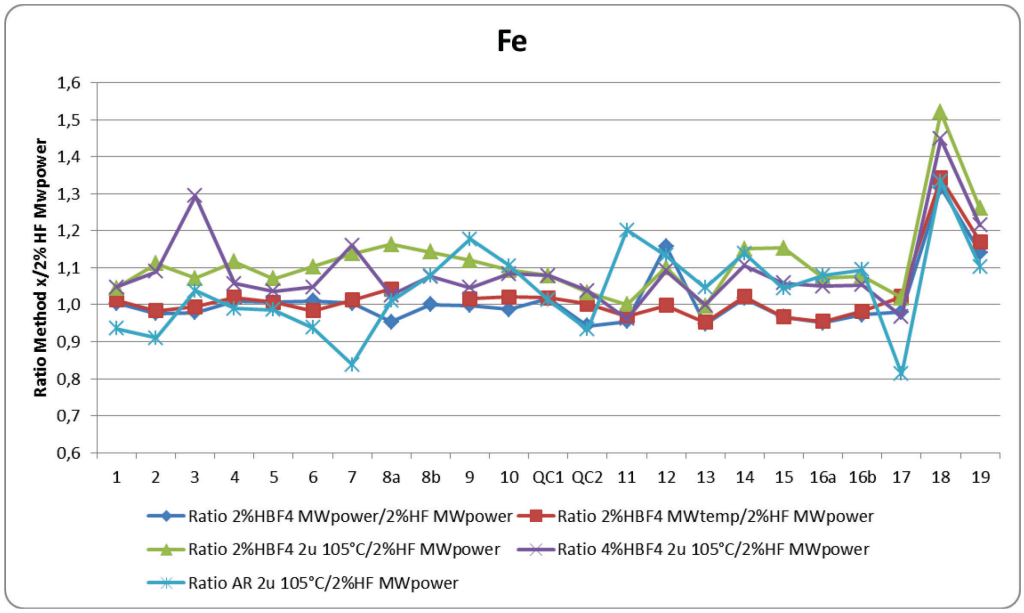

Figure 70 Ratio calculations of the alternative methods vs the reference method (2% HF – MW power) for Fe

5.3. 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 samples. As control samples a certified soil samples (NIST 2711) – QC 1 – and a round robin soil sample (SETOC 701) – QC2 - , distributed by Wageningen, were included in the analytical process. The obtained results and their recovery are presented in Table 4.

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 for the 3 applied digestion methods using microwave digestion (with 2 ml of HF or HBF_4) is limited to about 90%. Digestion with a heated block digestion resulted in a recovery of QC1 84% / QC2 78% for the

2% HBF_4 digestion and QC1 87% / QC2 84% for the 4% HBF_4 digestion. Using an aqua regia digestion the recovery is reduced to 56% for QC1 and to 66% for QC2.

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:

- 2%HF MWpower: digestion using 2% HF with power controlled digestion procedure
- 2%HBF_4 MWpower: digestion using 2% HBF_4 with power controlled digestion procedure
- 2%HBF_4 MWtemp: digestion using 2% HBF_4 with temperature controlled digestion procedure
- 2%HBF_4,2u,105°C: digestion using 2% HBF_4 with heated block digestion at 105°C during 2 hours
- 4%HBF_4,2u,105°C: digestion using 4% HBF_4 with heated block digestion at 105°C during 2 hours
- AR,2u,105°C: digestion using aqua regia with heated block digestion at 105°C during 2 hours

Table 4 Overview of the performance of the QC samples

		QC1 mg/kg dm	Ref. value mg/kg dm	Recovery %	QC2 mg/kg dm	Ref. value mg/kg dm	Recovery %
Al	2%HF MWpower	63365	65300	97%	56148		
	2%HBF4 MWpower	64150	65300	98%	54291		
	2%HBF4 MWtemp	55086	65300	84%	46866		
	2%HBF4,2u,105°C	67776	65300	104%	60005		
	4%HBF4,2u,105°C	68535	65300	105%	60662		
	AR,2u,105°C	21357	65300	33%	18998		
Sb	2%HF MWpower	22,2	19,4	115%	<2		
	2%HBF4 MWpower	21,7	19,4	112%	4,3		
	2%HBF4 MWtemp	21,5	19,4	111%	5,4		
	2%HBF4,2u,105°C	21	19,4	107%	4,6		
	4%HBF4,2u,105°C	22	19,4	111%	3,0		
	AR,2u,105°C	9,7	19,4	50%	<2		
As	2%HF MWpower	104	105	100%	35	33,6	105%
	2%HBF4 MWpower	104	105	99%	35	33,6	103%
	2%HBF4 MWtemp	100	105	95%	35	33,6	103%
	2%HBF4,2u,105°C	103	105	98%	31	33,6	93%
	4%HBF4,2u,105°C	110	105	105%	32	33,6	96%
	AR,2u,105°C	103	105	98%	31	33,6	94%
Ba	2%HF MWpower	698	726	96%	570		
	2%HBF4 MWpower	681	726	94%	550		
	2%HBF4 MWtemp	657	726	90%	541		
	2%HBF4,2u,105°C	703	726	97%	573		

		QC1 mg/kg dm	Ref. value mg/kg dm	Recovery %	QC2 mg/kg dm	Ref. value mg/kg dm	Recovery %
	4%HBF4,2u,105°C	710	726	98%	571		
	AR,2u,105°C	201	726	28%	324		
Cd	2%HF MWpower	39	41,7	95%	2,5	2,6	95%
	2%HBF4 MWpower	41	41,7	98%	2,5	2,6	94%
	2%HBF4 MWtemp	40	41,7	96%	2,5	2,6	96%
	2%HBF4,2u,105°C	42	41,7	100%	2,6		
	4%HBF4,2u,105°C	43	41,7	104%	2,5		
	AR,2u,105°C	44	41,7	106%	2,5		
Ca	2%HF MWpower	27403	28800	95%	43121		
	2%HBF4 MWpower	27876	28800	97%	40661		
	2%HBF4 MWtemp	25820	28800	90%	39587		
	2%HBF4,2u,105°C	28691	28800	100%	46105		
	4%HBF4,2u,105°C	29188	28800	101%	43571		
	AR,2u,105°C	23662	28800	82%	41313		
Cr	2%HF MWpower	42	*47*	89%	121	131,8	92%
	2%HBF4 MWpower	43	*47*	91%	117	131,8	89%
	2%HBF4 MWtemp	42	*47*	90%	122	131,8	92%
	2%HBF4,2u,105°C	40	*47*	84%	103	131,8	78%
	4%HBF4,2u,105°C	41	*47*	87%	111	131,8	84%
	AR,2u,105°C	26	*47*	56%	87	131,8	66%
Co	2%HF MWpower	9,3	*10*	93%	15,2		
	2%HBF4 MWpower	9,1	*10*	91%	14,9		
	2%HBF4 MWtemp	10,4	*10*	104%	14,7		
	2%HBF4,2u,105°C	10	*10*	99%	16		
	4%HBF4,2u,105°C	11	*10*	106%	16		
	AR,2u,105°C	9,0	*10*	90%	15		
Fe	2%HF MWpower	27283	28900	94%	31217		
	2%HBF4 MWpower	27721	28900	96%	29419		
	2%HBF4 MWtemp	27800	28900	96%	31254		
	2%HBF4,2u,105°C	29415	28900	102%	32261		
	4%HBF4,2u,105°C	29425	28900	102%	32403		
	AR,2u,105°C	27624	28900	96%	29117		
K	2%HF MWpower	23068	24500	94%	19041		
	2%HBF4 MWpower	23299	24500	95%	18182		
	2%HBF4 MWtemp	22023	24500	90%	16980		
	2%HBF4,2u,105°C	23436	24500	96%	18272		
	4%HBF4,2u,105°C	24760	24500	101%	19231		
	AR,2u,105°C	4702	24500	19%	3374		
Cu	2%HF MWpower	119	114	105%	103	103,9	99%
	2%HBF4 MWpower	115	114	101%	100	103,9	96%
	2%HBF4 MWtemp	116	114	102%	101	103,9	97%
	2%HBF4,2u,105°C	108	114	95%	99	103,9	95%
	4%HBF4,2u,105°C	110	114	97%	100	103,9	97%

		QC1 mg/kg dm	Ref. value mg/kg dm	Recovery %	QC2 mg/kg dm	Ref. value mg/kg dm	Recovery %
	AR,2u,105°C	107	114	94%	92	103,9	88%
Pb	2%HF MWpower	1102	1162	95%	167	171,5	97%
	2%HBF4 MWpower	1124	1162	97%	167	171,5	98%
	2%HBF4 MWtemp	1134	1162	98%	170	171,5	99%
	2%HBF4,2u,105°C	1126	1162	97%	166	171,5	97%
	4%HBF4,2u,105°C	1174	1162	101%	176	171,5	102%
	AR,2u,105°C	1248	1162	107%	172	171,5	100%
Mg	2%HF MWpower	9487	10500	90%	10711		
	2%HBF4 MWpower	10041	10500	96%	11005		
	2%HBF4 MWtemp	8828	10500	84%	10574		
	2%HBF4,2u,105°C	10324	10500	98%	11185		
	4%HBF4,2u,105°C	10069	10500	96%	10992		
	AR,2u,105°C	7699	10500	73%	9200		
Mn	2%HF MWpower	638	638	100%	1257		
	2%HBF4 MWpower	660	638	103%	1209		
	2%HBF4 MWtemp	638	638	100%	1231		
	2%HBF4,2u,105°C	686	638	107%	1181		
	4%HBF4,2u,105°C	666	638	104%	1268		
	AR,2u,105°C	586	638	92%	1191		
Mo	2%HF MWpower	1,7	*1,6*	105%	1,3		
	2%HBF4 MWpower	1,8	*1,6*	111%	<1		
	2%HBF4 MWtemp	1,6	*1,6*	98%	<1		
	2%HBF4,2u,105°C	1,4	*1,6*	88%	<1		
	4%HBF4,2u,105°C	1,6	*1,6*	100%	1,1		
	AR,2u,105°C	1,4	*1,6*	85%	<1		
Na	2%HF MWpower	11093	11400	97%	5240		
	2%HBF4 MWpower	11403	11400	100%	5143		
	2%HBF4 MWtemp	10630	11400	93%	4949		
	2%HBF4,2u,105°C	10887	11400	95%	5315		
	4%HBF4,2u,105°C	11351	11400	100%	5421		
	AR,2u,105°C	467	11400	4%	164		
Ni	2%HF MWpower	21	20,6	101%	46	46,6	98%
	2%HBF4 MWpower	22	20,6	106%	45	46,6	98%
	2%HBF4 MWtemp	20	20,6	99%	45	46,6	97%
	2%HBF4,2u,105°C	20	20,6	99%	46	46,6	99%
	4%HBF4,2u,105°C	20	20,6	95%	45	46,6	96%
	AR,2u,105°C	18	20,6	87%	42	46,6	90%
Sn	2%HF MWpower	<2			11		
	2%HBF4 MWpower	<2			9,3		
	2%HBF4 MWtemp	<2			10		
	2%HBF4,2u,105°C	<2			9,1		
	4%HBF4,2u,105°C	<2			9		
	AR,2u,105°C	<2			3		

		QC1 mg/kg dm	Ref. value mg/kg dm	Recovery %	QC2 mg/kg dm	Ref. value mg/kg dm	Recovery %
Ti	2%HF MWpower	2522	3060	82%	2534		
	2%HBF4 MWpower	2067	3060	68%	1477		
	2%HBF4 MWtemp	2388	3060	78%	2005		
	2%HBF4,2u,105°C	1587	3060	52%	849		
	4%HBF4,2u,105°C	1721	3060	56%	1071		
	AR,2u,105°C	772	3060	25%	237		
V	2%HF MWpower	91	81,6	112%	98		
	2%HBF4 MWpower	94	81,6	115%	96		
	2%HBF4 MWtemp	91	81,6	112%	94		
	2%HBF4,2u,105°C	83	81,6	102%	89		
	4%HBF4,2u,105°C	89	81,6	109%	97		
	AR,2u,105°C	64	81,6	78%	59		
Zn	2%HF MWpower	365	350,1	104%	487	515	95%
	2%HBF4 MWpower	381	350,4	109%	492	515	95%
	2%HBF4 MWtemp	356	350,4	102%	490	515	95%
	2%HBF4,2u,105°C	344	350,4	98%	532	515	103%
	4%HBF4,2u,105°C	366	350,4	104%	551	515	107%
	AR,2u,105°C	371	350,4	106%	538	515	105%
Hg	2%HF MWpower	6,7	6,25	107%	1,1	1,17	97%
	2%HBF4 MWpower	6,1	6,25	98%	1,1	1,17	97%
	2%HBF4 MWtemp	6,0	6,25	97%	1,1	1,17	95%
	2%HBF4,2u,105°C	6,2	6,25	99%	1,1	1,17	98%
	4%HBF4,2u,105°C	6,2	6,25	99%	1,2	1,17	101%
	AR,2u,105°C	6,3	6,25	100%	1,2	1,17	102%

Italic: indicative value

5.4. OVERVIEW OF ALL ELEMENTS

Per element and per sample the ratio was calculated between the alternative methods and the reference method. The distribution for the different elements is presented by a Box and Whisker plot, as shown in Figure 71 till Figure 82. Note that the evaluation is based on the comparison of single measurement results.

The results of the following elements were not considered in this evaluation due to there low concentration: As: results < 15 mg/kg dm; Sb, Co, Pb, Mo, Sn, V: results < 10 mg/kg dm

Legend

R1 Ratio 2% HBF_4, microwave power controlled versus 2% HF, microwave power controlled

R2 Ratio 2% HBF_4 microwave temperature controlled versus 2% HF digestion, microwave power controlled

R3 Ratio 2% HBF_4, heated digestion block 2 hrs at 105°C versus 2% HF, microwave power controlled

R4 Ratio 4% HBF_4, heated digestion block 2 hrs at 105°C versus 2% HF, microwave power controlled

R5	Ratio aqua regia, heated digestion block 2 hrs at 105°C versus 2% HF, microwave power controlled

For the element As in soil and waste sample the median values of the ratios ranges between 0.88 and 0.98. The lowest value is obtained using 2% HBF_4 digested at 105°C during 2 hrs with the heated block digestor. Increasing the acid concentration to 4% HBF_4 results in an increased median value of 0.95 which is comparable with the other digestion methods.

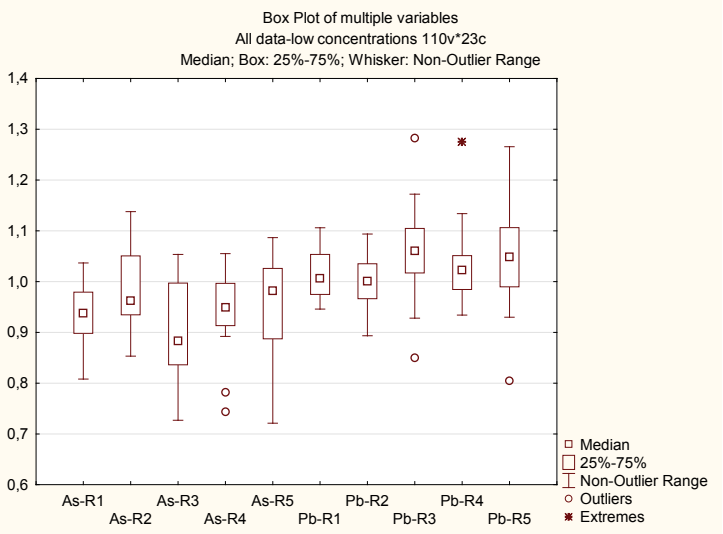

Figure 71 Overview ratio alternative methods vs the reference method for the elements As and Pb in soil and waste samples

For the elements Cd, Cu, Pb, Zn and Hg in soil and waste samples the median values of the ratios fluctuate around 1, indicating that comparable results are obtained with the reference method and the alternative methods. Globally, for most of the data the non-outlier range is situated between a ratio of 0.8 and 1.2, which can be expected from replicate measurements. For these elements also the data obtained by aqua regia digestion (R5) show comparable results, but for the elements As and Pb a broader distribution profile is observed.

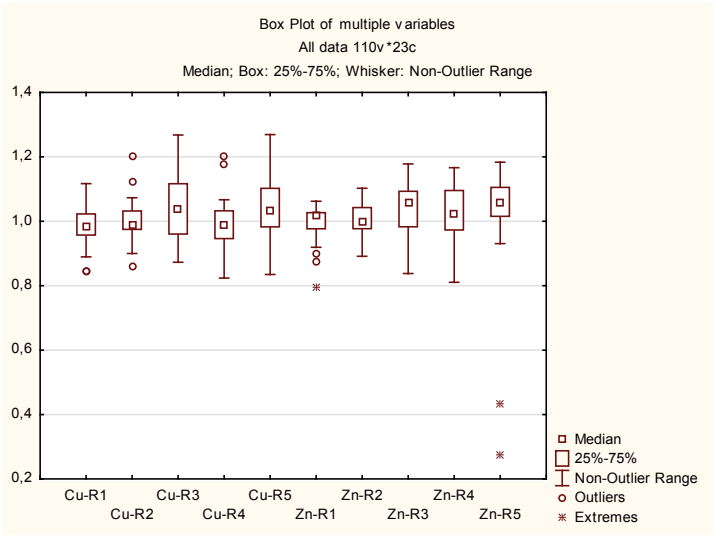

Figure 72 Overview ratio alternative methods vs the reference method for the elements Cu and Zn in soil and waste samples

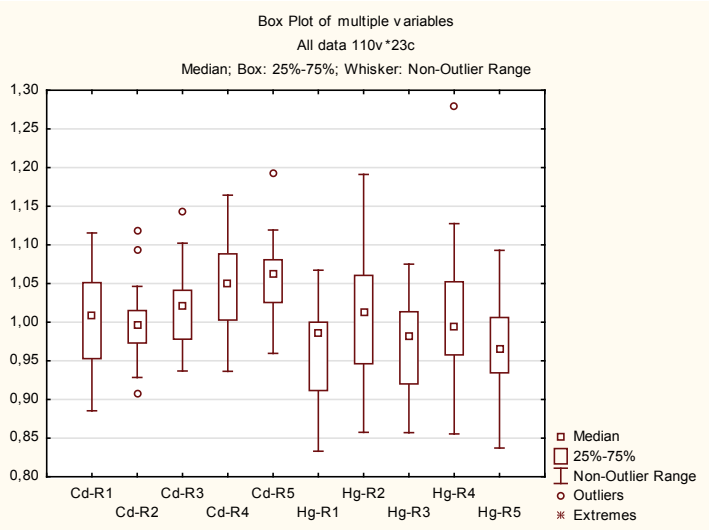

Figure 73 Overview ratio alternative methods vs the reference method for the elements Cd and Hg in soil and waste samples

For the elements Cr and Ni more differences between the applied digestion procedures are observed. For the element Cr using the aqua regia digestion (R5) results in a median value of the ratio of 0.86 and a broad non-outlier range is obtained. Digestion with the heated block digestion using 2% HBF_4 results in a median value of the ratio of 0.92 which increases up to 0.99 by using 4% of HBF_4. The 4% HBF_4 digestion at 105°C during 2 hrs gives comparable results in the evaluation of the ratios compared to the microwave digestion methods. For the element Ni the aqua regia digestion results in a median value of the ratio of 0.90, while all other digestion methods results in a median value of the ratios around 1.

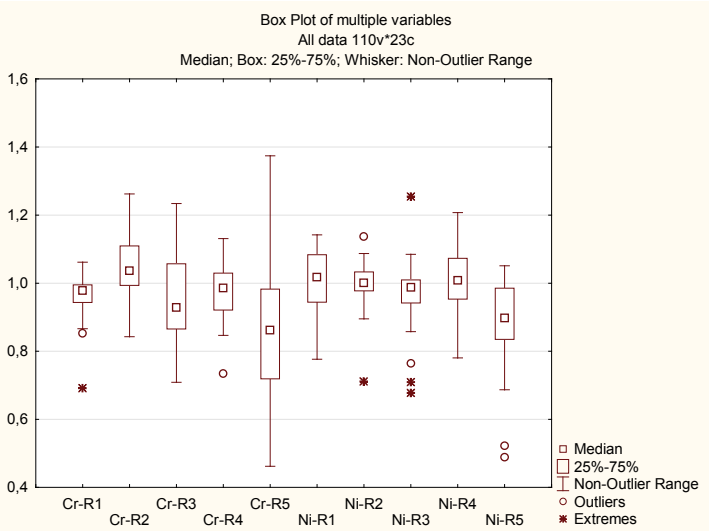

Figure 74 Overview ratio alternative methods vs the reference method for the elements Cr and Ni in soil and waste samples

For the trace element Sb the measured concentration are in general low introducing a broader distribution profile of the obtained ratio factor. For the HF and HBF_4 digestions the median value of the ratio varies between 0.95 and 1.14. The non-outlier range is situated between 0.7 and 1.5

which is broader due to the low concentration levels. For the aqua regia digestion, on the other hand, the median value is reduced down to 0.74 and the non-outlier range is situated between 0.4 and 1.2.
For the element Ba also a reduced median value of the ratio (0.75) is observed for the aqua regia digestion, while for the other digestion methods these values fluctuates around 1 with a non-outlier range between 0.8 and 1.2.

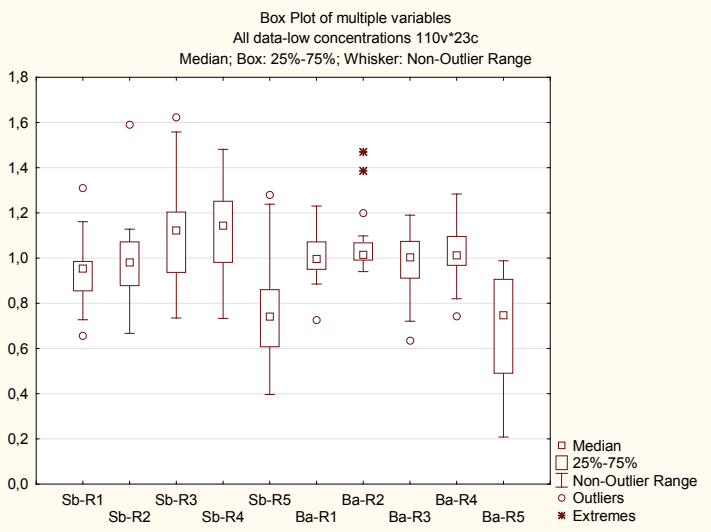

Figure 75 Overview ratio alternative methods vs the reference method for the elements Sb and Ba in soil and waste samples

For the elements Co and Mo for all digestion methods the median value of the ratio fluctuates around 1 with a non-outlier range between 0.8 and 1.2. Several outliers are detected, attributed to the low concentration values of these elements.

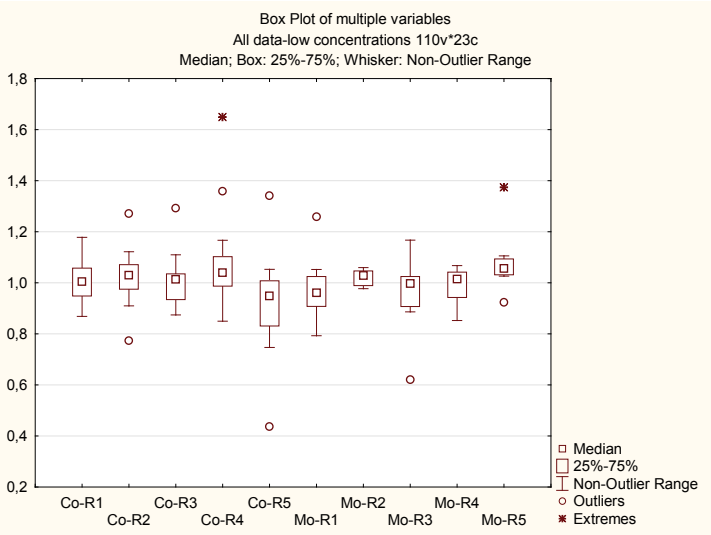

Figure 76 Overview ratio alternative methods vs the reference method for the elements Co and Mo in soil and waste samples

For the element V the median value of the ratios is for all digestion methods, except aqua regia, around 1. For the aqua regia digestion this value is reduced down to 0.8. The detected extreme values can be assigned to sample 16. For the element Mn all digestion results in a median ratio factor of 1. Only when applying the aqua rgeia digestion some outliers and extremes are observed.

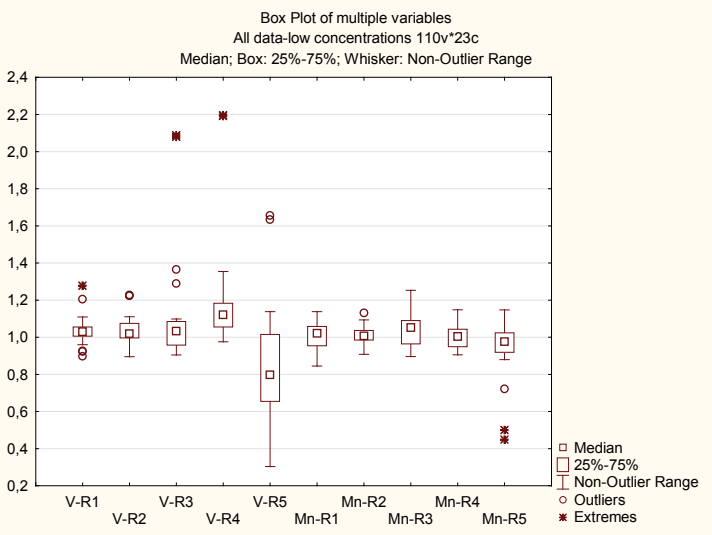

Figure 77 Overview ratio alternative methods vs the reference method for the elements V and Mn in soil and waste samples

For the element Sn all median values of the ratio fluctuates around 1 with a non-outlier range between 0.8 and 1.2. Nevertheless a lot of extreme values are present. The high extreme values are attributed to sample 2 (4 out of 7), sample 3 (1 out of 7) and sample 6 (2 out of 7). For sample 2 it might be attributed to the heterogeneity of the sample, while for sample 3 and 6 no systematic is observed. The low extreme values are attributed to sample 17. A lower result with aqua regia digestion might occur, but the reduced result obtained with 4% HBF_4, 2 hrs at 105°C is not reasonable as this is not detected with the 2% HBF_4, 2 hrs at 105°C.

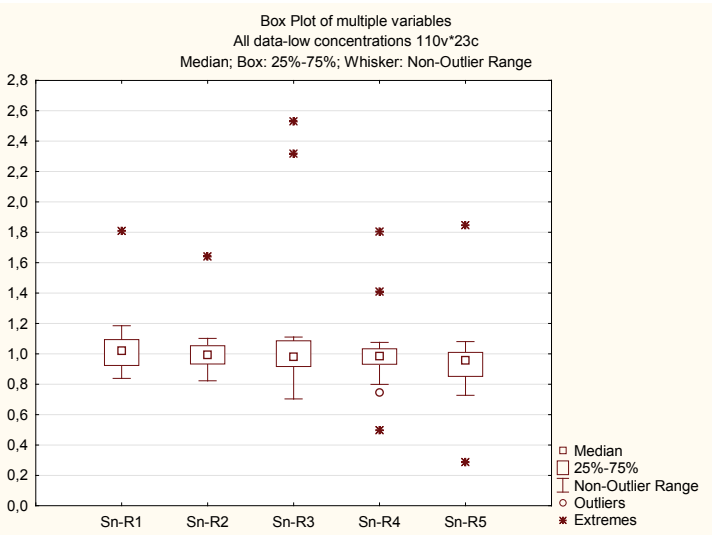

Figure 78 Overview ratio alternative methods vs the reference method for the elements Sn in soil and waste samples

For the major elements Na, Mg, Al, K, Ca and Fe in soil and waste samples the median values of the ratios are situated around 1 is for the different digestion methods, except for the aqua regia digestion. Comparable results are obtained for the analysed samples with the different digestion methods (R1, R2, R3 and R4).
On the other hand, for the elements Na, Mg, Al and K the median value of the ratio for the aqua regia digestion (R5) is significant lower than 1, indicating a significant difference of this digestion method with the reference method (2% HF, MW power). Also a broad distribution profile of the ratio factor is observed, indicating that the recovery for these elements are sample dependant.

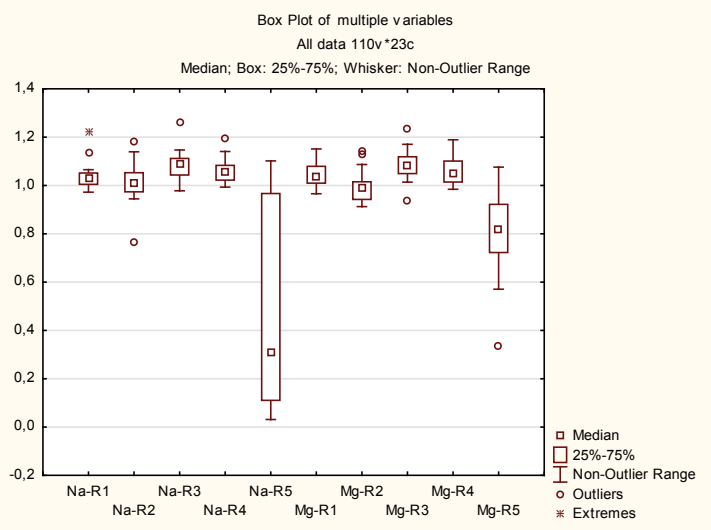

Figure 79 Overview ratio alternative methods vs the reference method for the elements Na and Mg in soil and waste samples

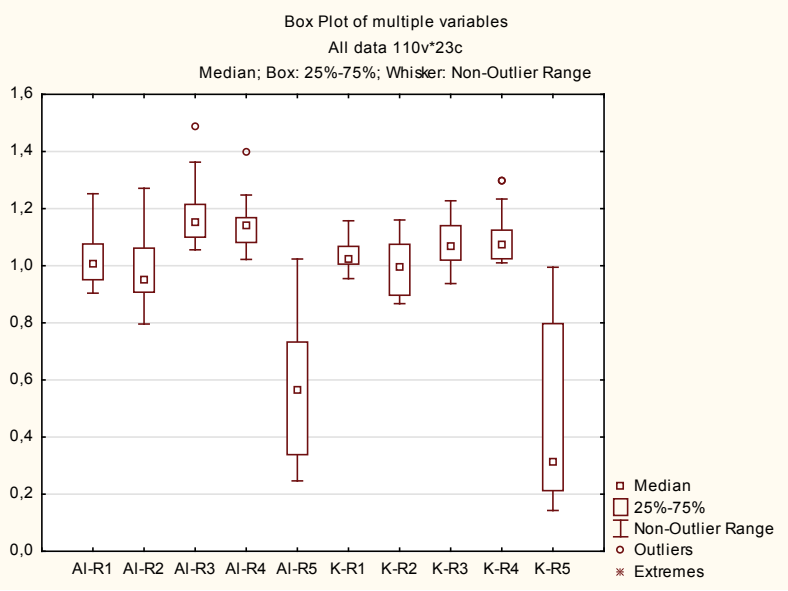

Figure 80 Overview ratio alternative methods vs the reference method for the elements Al and K in soil and waste samples

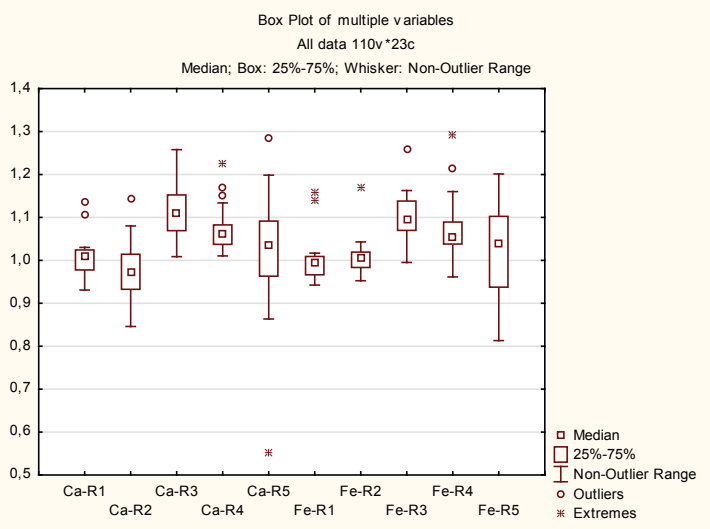

Figure 81 Overview ratio alternative methods vs the reference method for the elements Ca and Fe in soil and waste samples

For the element Ti the obtained results are different depending on the applied digestion method. Digestion with 2% HBF_4 using the microwave power controlled programme results in a median ratio value of 0.78, while the microwave temperature controlled programme has a value of 0.91. These results indicate that within the range of microwave digestions the recovery of Ti can also be different. Digestion using the heated block digestor 2 hrs at 105°C results in a median ratio value of 0.64 for the 2% HBF_4 digestion and 0.70 for the 4% HBF_4 digestion method. Using aqua regia digestion even resulted in a median ratio value of only 0.24.
Although the element Ti is not included in the legislation it gives a fairly good overview about the impact a certain digestion method can have on the obtained results.

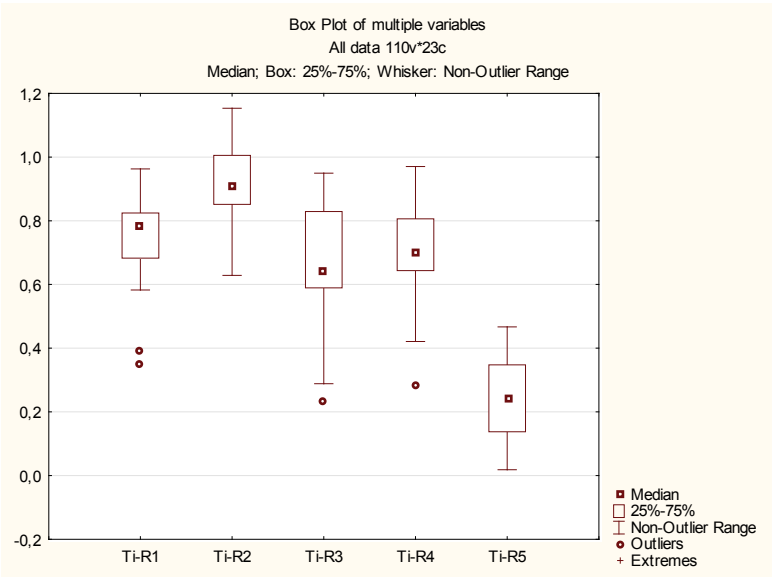

Figure 82 Overview ratio alternative methods vs the reference method for the element Ti in soil and waste samples

CHAPTER 6 OVERALL EVALUATION OF THE DIGESTION METHODS

The overall measurement variation which can be expected when different digestion procedures are applied, is summarized in Figure 83 for the VLAREBO elements and in Figure 85 for the VLAREMA elements.

For the Vlarebo elements (As, Cd, Cr, Cu, Pb, Ni, Zn and Hg) the ratio calculations (R0, R1, R2, R3, R4, R5 see legend) were pooled. It should be noted that low concentration values[i] for As (< 15 mg/kg dm) and for Pb (< 10 mg/kg dm) were excluded. In this evaluation also an R0 ratio was calculated consisting of the data of the control chart of QC1 (N= ± 30 per element) normalised towards the average value. This R0 ratio gives an idea about the distribution/deviation of results you can obtain within the reference method (2% HF, MW power). Compared to the other ratio calculations the distribution profile of this ratio factor R0 is an underestimation because only 1 type of sample is considered in comparison with the other ratio values where 23 samples are considered.
Figure 83 includes the pooled results for R0, R1, R2, R3, R4 and R5. The median 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 when all elements are considered. The non-outlier range is, in general, situated between a ratio of 0.8 and 1.2, which can also be expected from replicate/duplo measurements. For the digestion with 2% HBF_4 at 105°C, 2 hrs the non-outlier range is slightly larger compared to the microwave digestions (R1 and R2). But this effect is reduced when 4% of HBF_4 (R4) is used. For the aqua regia digestion the non-outlier range is more extended (from 0.7 to 1.3) in combination with several outliers and extreme values. Introducing the aqua regia digestion would have an impact on the recovery of the different Vlarebo elements in soil and waste samples, while the microwave digestions methods and the digestion with the heated block digestor using 4% HBF_4 at 105°C, 2 hrs would reveal comparable data.

Legend

R0	Data of control chart of QC1 normalised towards the average value
R1	Ratio 2% HBF_4, microwave power controlled versus 2% HF, microwave power controlled
R2	Ratio 2% HBF_4 microwave temperature controlled versus 2% HF digestion, microwave power controlled
R3	Ratio 2% HBF_4, heated digestion block 2 hrs at 105°C versus 2% HF, microwave power controlled
R4	Ratio 4% HBF_4, heated digestion block 2 hrs at 105°C versus 2% HF, microwave power controlled
R5	Ratio aqua regia, heated digestion block 2 hrs at 105°C versus 2% HF, microwave power controlled

[i] Soil remediation value for As is 45 mg/kg dm and for Pb 200 mg/kg dm.

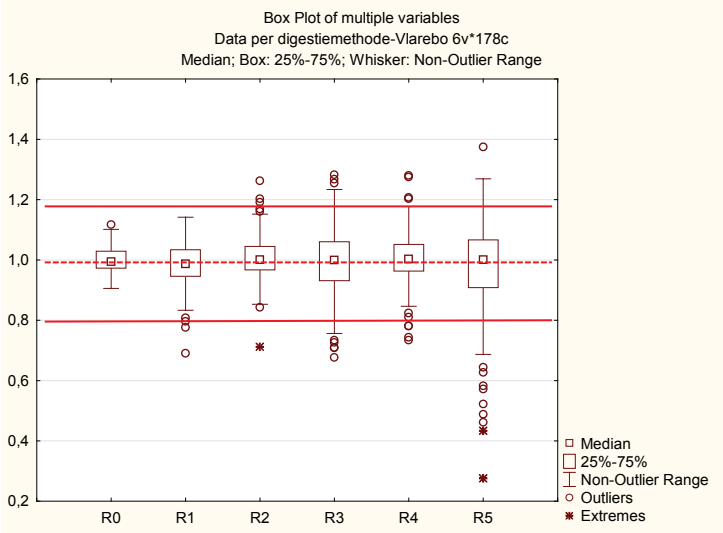

Figure 83 Overview ratio alternative methods vs the reference method in soil and waste samples (elements included are Vlarebo elements)

It is well known that the selection of digestion method would have the most influence on the recovery of the elements Cr and Ni. Therefore, the data of the elements Ni and Cr were pooled for the different digestion procedures as shown in Figure 84. The same conclusions could be drawn as above. Similar results are achieved with the microwave digestion methods and the digestion with the heated block digestor using 4% HBF_4 at 105°C, 2 hrs. Also a narrower non-outlier range is observed for the 4% HBF_4 at 105°C, 2 hrs digestion compared to the 2% HBF_4 digestion.

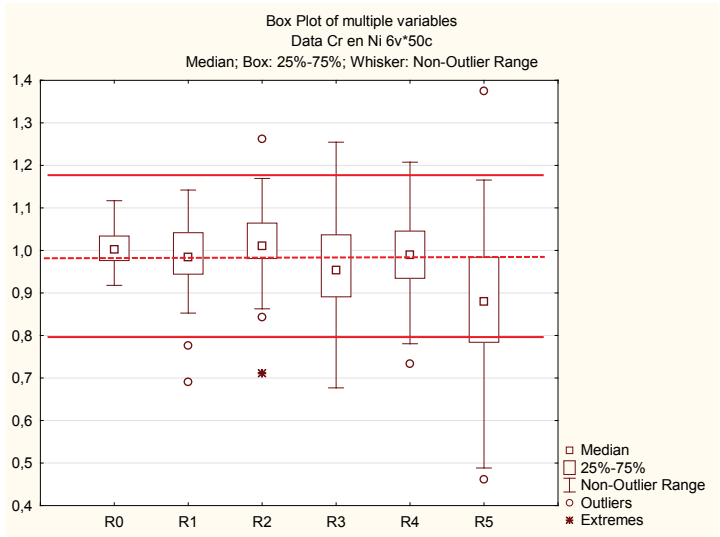

Figure 84 Overview ratio alternative methods vs the reference method in soil and waste samples (elements included are Ni and Cr)

For the Vlarema elements (As, Cd, Cr, Cu, Pb, Ni, Zn, Hg, Sb, Ba, Co, Mo, Sn and V) and Mn the ratio calculations (R0, R1, R2, R3, R4 and R5, see legend) were pooled. It should be noted that low concentration values for As, Sb, Co, Pb, Mo, Sn and V (in the range of less then 10 mg/kg dm) were excluded. Figure 85 includes the pooled results for R0, R1, R2, R3, R4 and R5.

Note: Results of Se were not included as all data are below the limit of determination.

The median value of the ratios is always closely related to 1, indicating a good correspondence between the alternative methods and the reference method. The observed extreme values are attributed to Sb, Co, V due to their low content and to Sn probably due to the sample heterogeneities. The non-outlier range is in general situated between a ratio of 0.8 and 1.2, which can also be expected from replicate/duplo measurements. For the digestion with 2% HBF_4 at 105°C, 2 hrs (R3) the non-outlier range is slightly larger compared to the microwave digestions (R1 and R2). But this effect is reduced when 4% of HBF_4 (R4) is used. For the aqua regia digestion the non-outlier range is more extended (from 0.6 to 1.4) in combination with several outliers in the lower range (underestimation of the concentration).

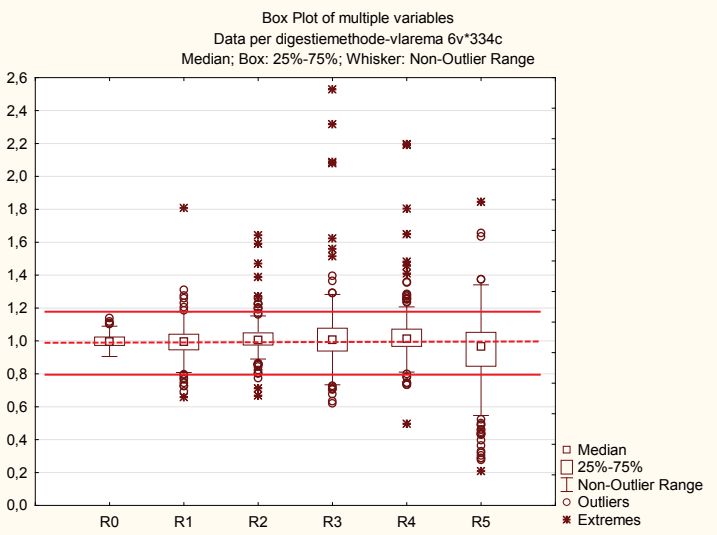

Figure 85 Overview ratio alternative method vs the reference methods in waste samples (elements included are Vlarema elements)

CHAPTER 7 CONCLUSION

In this study 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 digestion 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 (2% HBF_4) as replacement for the two-steps digestion with 2%HF + H_3BO_3*
   The procedure involves a one-step digestion, while maintaining the same power of digestion of the silicate matrix, by using 2% 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 2% HBF_4 digestion using power controlled microwave oven was compared with a temperature controlled digestion.
3. *Evaluation of the implementation of the heated block digestion as an addition to microwave systems*
   The 2% HBF_4 and 4% HBF_4 digestion was compared with the results obtained with the previous digestion methods using a microwave system. The heated block digestion was performed at 105°C during 2 hours.
4. *Evaluation of the aqua regia digestion using the heated block digestion*
   The aqua regia digestion was compared with the results obtained with the previous digestion methods. The heated block digestion was performed at 105°C during 2 hours.

In 2014 task 1 and task 2 were already investigated and the digestion using 2% of HBF_4 was included in CMA/2/II/A.3, describing the digestion procedures for soil and waste samples. Also the temperature controlled microwave digestion was successfully validated and accepted as applicable digestion method.

In 2015 task 3 and task 4 were investigated and the following conclusion can be formulated.

Evaluation of the Vlarebo elements (As, Cd, Cr, Cu, Pb, Ni, Zn and Hg)

For the 8 VLAREBO elements (As, Cd, Cr, Cu, Pb, Ni, Zn and Hg) the results obtained with the microwave digestion methods and the heated block digestion using 4% HBF_4 (38 wt%) are comparable with the results of the reference method (2% HF, MW power controlled digestion). In CHAPTER 6 on page 60 it is shown that the measurement variation for these digestion methods is situated in a range of < 20%, which can also be expected from replicate/duplo analyses. For the digestion with 2% HBF_4 (38 wt%) at 105°C, 2 hrs the measurement variation is slightly higher (about 25%) compared to the microwave digestions. But this effect is reduced when 4% of HBF_4 is used when digesting at 105°C during 2 hours.
For the aqua regia digestion the measurement variation is more extended (about 30%) in combination with several outliers and extreme values. Introducing the aqua regia digestion would have an impact on the recovery of the different Vlarebo elements in soil and waste samples, while the microwave digestions methods and the digestion with the heated block digestor using 4% HBF_4 (38 wt%) at 105°C, 2 hrs would reveal comparable data.

Evaluation of the Vlarema elements (As, Cd, Cr, Cu, Pb, Ni, Zn, Hg, Sb, Ba, Co, Mo, Se, Sn and V)

For the VLAREMA elements (As, Cd, Cr, Cu, Pb, Ni, Zn, Hg, Sb, Ba, Co, Mo, Se, Sn and V) the results obtained with the microwave digestion methods and the heated block digestion using 4% HBF_4 (38 wt%) corresponds with the results of the reference method (2% HF, MW power controlled digestion). For all digestion methods high deviated values for Sb, Se en V are observed which could be assigned to their low content, and for Sn probably due to the sample heterogeneities. In CHAPTER 6 on page 60 it is shown that the measurement variation is in general situated in a range of <20%, which can also be expected from replicate/duplo measurements. For the digestion with 2% HBF_4 at 105°C, 2 hrs the measurement variation is slightly higher (about 30%) compared to the microwave digestions. But this effect is reduced when 4% of HBF_4 is used when digesting at 105°C during 2 hours.
For the aqua regia digestion the measurement variation is more extended (about 40%) in combination with several outliers in the lower range (underestimation of the concentration). Introducing the aqua regia digestion would have an impact on the recovery of the different Vlarema elements in soil and waste samples, while the microwave digestions methods and the digestion with the heated block digestor using 4% HBF_4 (38 wt%) at 105°C, 2 hrs would reveal comparable data.

Evaluation of the major elements

For the major elements (Na, Mg, Al, K, Ca, Ti and Fe) a good correspondence is observed between the results of the alternative methods (except the aqua regia digestion) and the reference method, except for Ti.
For the Ti results differences are observed between the different digestion methods and the reference method. The highest Ti values are obtained with the reference digestion method using 2% HF and power controlled microwave digestion. Only a slight reduction in Ti concentration values (by average ± 8%) is observed when applying the 2% HBF_4 digestion with the temperature controlled microwave digestion. Applying the 2% HBF_4 digestion with the power controlled microwave digestion, resulted in a systematic underestimation of about 25% by average. Digestion with 2% or 4% HBF_4 digestion at 105°C, 2 hrs, resulted in a systematic underestimation of about 30% by average. Using aqua regia digestion even resulted in a recovery with respect to the reference method of only 25% by average. Although the element Ti is not included in the legislation it gives a fairly good overview about the impact a certain digestion method can have on the obtained results.

ANNEX A ANALYTICAL RESULTS OF THE SOIL AND WASTE SAMPLES FOR CR, NI, TI AND ZN USING DIFFERENT DIGESTION PROCEDURES

	2%HF MW-power mg/kg dm	2%HBF4 MW-power mg/kg dm	2%HBF4 MW-temp mg/kg dm	2%HBF4 105-2u mg/kg dm	4%HBF4 105-2u mg/kg dm	2%HBF4 105-4u mg/kg dm	4%HBF4 105-4u mg/kg dm
Cr							
Sample 2	115	109	114	100	105	104	107
Sample 4	58	61	66	56	59	59	60
Sample 7	856	742	762	455		918	851
Sample 10	153	149	163	147	146	151	145
Sample 15	294	251	326	226	235	239	232
Sample 17	78	73	81	76	77	81	75
QC1	42	40	42	39	39	40	40
QC2	125	121	133	113	116	114	117
Ni							
Sample 2	128	133	125	120	123	131	128
Sample 4	105	118	108	111	112	114	113
Sample 7	68	53	61	39	74	59	92
Sample 10	110	118	110	119	112	122	112
Sample 15	111	108	105	112	111	117	107
Sample 17	1709	1599	1687	1774	1692	1780	1695
QC1	21	22	24	20	20	21	20
QC2	47	43	47	46	45	47	45
Ti							
Sample 2	2358	1841	1944	1423	1664	1471	1669
Sample 4	1454	1191	1510	930	1055	920	1031
Sample 7	2257	2173	2269	2362	2337	2364	2421
Sample 10	1471	1099	1252	1034	1118	977	1095
Sample 15	7963	5209	5006	4709	5337	4806	5119
Sample 17	98	74	89	64	71	64	64
QC1	2522	2092	2424	1589	1971	1663	1992
QC2	2601	1363	2700	969	1443	962	1303
Zn							
Sample 2	1854	1939	1743	1788	1831	2290	1775
Sample 4	4973	5029	5238	5138	5023	5323	5277
Sample 7	101	102	111	108	115	119	115
Sample 10	2595	2653	2610	2804	2898	3054	2869
Sample 15	26852	27524	25782	27004	26493	28528	25893
Sample 17	244	220	241	202	194	205	196
QC1	365	344	381	370	362	372	363
QC2	505	570	527	574	562	568	575

ANNEX B ANALYTICAL RESULTS OF THE SAMPLES USING DIFFERENT DIGESTION PROCEDURES

	1	2	3	4	5	6	7	8a	8b	9	10	QC1	QC2	11	12	13	14	15	16a	16b	17	18	19
	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds
Al																							
2%HF MWpower	22058	45361	22695	19646	20212	22780	43413	40381	40560	14427	21218	63365	56148	25605	33464	73485	9892	82588	2163	2150	91099	23618	52955
2%HBF4 MWpower	24186	43686	21536	22787	18451	21525	48178	42296	43646	15873	19961	64150	54291	25731	33367	66418	9532	82993	2252	2283	86638	29570	53612
2%HBF4 MWtemp	20636	36101	19111	22461	19539	21215	50543	43257		15890	19249	55086	46866	27087	31168	61841	9177	80759	2292	2282	83729	30020	55227
2%HBF4,2u,105°C	25443	50579	26255	26768	22403	25057	54436	53078	51521	16883	22399	67776	60005	27453	38538	78831	10893	100326	2513	2461	108608	35166	60246
4%HBF4,2u,105°C	25320	49422	24493	24507	21861	24563	51045	46287	47555	16728	21685	68535	60662	27637	37641	81824	10907	96475	2481	2511	104511	33018	60482
AR,2u,105°C	5859	11180	8351	7922	8173	7647	10945	22996	21323	6849	13756	21357	18998	18676	32580	47615	8005	60520	1226	1227	93246	21823	48913
Sb																							
2%HF MWpower	4,3	14,7	13,1	15,9	9,1	5,4	-	33,3	32,5	34,2	63,3	22,2	<2	240	172	12	17	308	12	13	<2	14	776
2%HBF4 MWpower	<2	11,0	12,9	18,4	6,6	7,4	4,9	31,2	31,8	32,0	61,9	21,7	4,3	229	178	15	11	286	9,4	9,7	<2	12	816
2%HBF4 MWtemp	3,3	16,6	13,9	17,2	8,2	8,2	<2	31,1		33,3	54,3	21,5	5,4	250	178	18	11	304	9,9	11	<2	13	853
2%HBF4,2u,105°C	3,0	21	16	18	6,6	9,1	3,1	31	29	30	60	21	4,6	242	192	18	13	359	20	21	3,9	17	935
4%HBF4,2u,105°C	3,3	19	16	20	7,2	9,5	4,2	31	33	35	61	22	3,0	296	181	17	13	302	18	17	3,9	16	890
AR,2u,105°C	<2	13	11	12	3,7	3,9	<2	20	22	29	38	9,7	<2	95	148	11	9,4	198	16	17	2,3	10	583
As																							
2%HF MWpower	13	71	28	133	29	34	3,4	29	28	71	13	104	35	33	70	42	687	89	6,1	6,3	5,2	7,5	56
2%HBF4 MWpower	11	66	28	122	23	32	3,5	27	25	74	11	104	35	29	61	36	675	88	4,5	5,2	6,5	8,6	54
2%HBF4 MWtemp	13	68	27	120	24	29	2,4	29		75	12	100	35	31	70	47	642	95	6,2	5,6	6,0	9,4	60
2%HBF4,2u,105°C	11	63	23	126	25	29	3,1	25	21	58	11	103	31	34	65	30	708	90	4,8	4,8	3,9	8,5	59
4%HBF4,2u,105°C	19	67	27	122	28	32	3,5	26	26	53	12	110	32	26	69	42	655	92	5,2	5,3	4,7	9,1	56
AR,2u,105°C	12	68	25	123	27	28	<2	29	28	75	13	103	31	24	71	-	691	97	7,7	7,7	<2	8,0	59
Ba																							
2%HF MWpower	319	523	864	940	405	453	103	1339	1360	517	415	698	570	3415	618	2894	393	*1033*	102	103	74	495	287
2%HBF4 MWpower	316	575	931	941	434	500	104	1256	1238	516	394	681	550	3256	681	2881	405	319	90	98	76	610	208
2%HBF4 MWtemp	307	519	877	936	401	463	99	1340		514	399	657	541	4095	908	3084	404	563	112	110	80	687	306
2%HBF4,2u,105°C	305	622	980	1102	396	485	101	1417	1357	518	378	703	573	2462	392	2913	422	268	88	90	83	546	231
4%HBF4,2u,105°C	319	605	948	1073	414	493	117	1298	1317	524	398	710	571	2535	736	3025	397	302	85	84	75	636	248
AR,2u,105°C	105	352	784	866	297	336	60	1141	1027	446	313	201	324	1245	129	924	333	184	96	96	73	461	141
Cd																							
2%HF MWpower	<0.5	13	2,6	3,4	21	27	<0.5	1,6	1,6	1,7	9,5	39	2,5	45	25	24	8,6	565	<0.5	<0.5	<0.5	18	218
2%HBF4 MWpower	<0.5	13	2,4	3,6	22	28	<0.5	1,7	1,6	1,9	10,0	41	2,5	47	22	22	9,4	538	<0.5	<0.5	<0.5	18	205
2%HBF4 MWtemp	0,5	13	2,9	3,5	21	25	<0.5	1,5		1,7	9,5	40	2,5	44	25	25	9,4	513	<0.5	<0.5	<0.5	19	220
2%HBF4,2u,105°C	<0.5	13	2,6	3,2	21	27	<0.5	1,7	1,7	1,8	10	42	2,6	43	25	24	8,4	646	<0.5	0,5	<0.5	19	240
4%HBF4,2u,105°C	<0.5	13,7	2,8	3,8	23	30	<0.5	1,9	1,8	<0.5	10	43	2,5	42	25	24	8,4	567	<0.5	<0.5	<0.5	18	219
AR,2u,105°C	<0.5	12,5	2,6	3,6	23	29	<0.5	1,5	1,8	2,1	10	44	2,5	44	26	26	9,2	599	<0.5	<0.5	<0.5	20	229
Ca																							
2%HF MWpower	20916	31761	35648	6882	28167	23312	2478	36128	36447	17911	217327	27403	43121	66325	192900	53831	5686	80344	109974	112738	59368	*92356*	156348
2%HBF4 MWpower	20479	30885	35618	7053	27808	23698	2737	37114	37328	18347	209124	27876	40661	65066	197116	50115	5751	82776	110620	110221	55306	131819	177344
2%HBF4 MWtemp	19036	26869	33111	6418	27704	22488	2625	37620		18168	211662	25820	39587	71646	199863	54018	5738	80227	106958	106100	55270	137852	179043
2%HBF4,2u,105°C	21099	34169	38835	7699	29895	25219	2902	42132	40184	20642	226480	28691	46105	75744	226479	56049	6413	98284	123115	122804	67616	157717	196675
4%HBF4,2u,105°C	21697	33478	37722	7487	30491	24963	2902	38794	39257	20626	223726	29188	43571	70279	218706	55004	5983	85455	114827	114318	60056	152231	191527
AR,2u,105°C	21478	32137	37290	7015	30699	24471	2206	33899	35105	18020	222771	23662	41313	71978	225247	29750	6396	96282	122759	123052	63780	152423	200964

	1	2	3	4	5	6	7	8a	8b	9	10	QC1	QC2	11	12	13	14	15	16a	16b	17	18	19
	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds
Cr																							
2%HF MWpower	40	115	177	58	59	63	856	199	196	673	153	42	121	504	278	1024	50	294	3577	3588	78	170	284
2%HBF4 MWpower	40	109	167	61	58	60	742	195	193	653	149	43	117	533	247	708	50	251	3527	3536	73	181	279
2%HBF4 MWtemp	45	114	173	66	63	65	762	202		567	163	42	122	635	289	883	53	326	3512	3570	81	199	329
2%HBF4,2u,105°C	37	87	214	51	57	56	684	183	189	582	181	40	103	421	255	726	53	272	3848	3887	75	210	295
4%HBF4,2u,105°C	40	104	180	59	58	62	-	220	198	-	142	41	111	437	251	751	52	249	3745	3694	76	193	270
AR,2u,105°C	26	53	138	47	51	51	490	171	174	-	135	26	87	692	241	597	49	211	3912	3949	78	199	254
Co																							
2%HF MWpower	12,1	64,5	19,3	20,1	11,2	9,8	6,4	34,8	33,8	37,6	10,9	9,3	15,2	65	167	61	1,2	33	15	15	2,9	7,7	28
2%HBF4 MWpower	13,1	64,6	18,1	21,7	11,2	9,9	4,7	35,3	35,7	44,3	11,6	9,1	14,9	62	150	54	<1	29	16	16	4,5	7,0	28
2%HBF4 MWtemp	13,0	62,9	18,9	21,5	11,5	10,2	4,9	35,2		41,3	13,8	10,4	14,7	73	165	64	<1	25	14	14	4,3	9,0	29
2%HBF4,2u,105°C	12	59	20	21	11	10	5,1	36	38	37	14	10	16	71	156	53	1,3	29	16	16	4,4	7,8	26
4%HBF4,2u,105°C	13	63	23	22	12	11	6,2	36	35	62	15	11	16	69	165	58	1,8	28	15	16	3,0	7,7	25
AR,2u,105°C	9,6	28	18	21	9,5	8,1	4,2	34	32	50	11	9,0	15	64	158	51	1,5	25	16	16	3,6	7,0	23
Fe																							
2%HF MWpower	18371	31287	61756	20300	14631	16714	18184	123050	121243	338601	23848	27283	31217	125696	21414	18092	143802	22052	79179	78833	5538	11795	11448
2%HBF4 MWpower	18445	30563	60413	20485	14727	16879	18255	117356	121272	338101	23555	27721	29419	119987	24790	17148	146223	21310	75286	76673	5430	15539	13059
2%HBF4 MWtemp	18596	30768	61386	20691	14733	16443	18409	128351		344186	24334	27800	31254	121806	21372	17236	146947	21307	75544	77457	5663	15837	13394
2%HBF4,2u,105°C	19187	34758	66200	22657	15652	18423	20694	143070	138576	379050	26077	29415	32261	125793	23566	18005	165517	25432	84957	84936	5644	17930	14430
4%HBF4,2u,105°C	19233	34079	79890	21468	15158	17501	21096	126272	130536	354309	25839	29425	32403	120839	23380	18073	159154	23326	83091	83014	5362	17086	13908
AR,2u,105°C	17194	28480	64094	20090	14424	15670	15246	124274	130730	398762	26348	27624	29117	150988	24250	18919	163809	23019	85381	86263	4503	15735	12620
K																							
2%HF MWpower	11510	11843	8235	7338	7666	8769	1433	11120	11173	5037	21415	23068	19041	4277	4605	4407	9546	38505	865	1029	3116	4646	33509
2%HBF4 MWpower	11754	11795	8143	8036	7708	9002	1488	11291	11379	5405	21646	23299	18182	4281	4964	4519	9884	40275	1001	1028	3329	4960	35200
2%HBF4 MWtemp	11397	10620	7358	7414	6649	7759	1439	11268		5142	21263	22023	16980	4894	4956	4737	9851	33558	1003	922	3351	5086	32806
2%HBF4,2u,105°C	11879	11846	8232	7829	7874	8940	1572	11403	11615	5542	23392	23436	18272	4968	5252	4131	11289	41877	1060	1073	3815	5702	36904
4%HBF4,2u,105°C	12032	12042	8354	8116	7842	8982	1490	11883	11376	5632	23095	24760	19231	5548	5213	4956	10570	42079	1066	1087	3633	6024	35110
AR,2u,105°C	2977	2516	1598	1110	2066	2088	446	6027	5432	1590	18657	4702	3374	1312	4124	1387	8729	35481	689	687	446	1646	33329
Cu																							
2%HF MWpower	41	1573	1696	710	139	150	85	6685	6613	1490	526	119	103	9163	2019	769	21	1315	12640	12491	99213	813	1068
2%HBF4 MWpower	34	1751	1430	715	155	153	84	6178	6384	1325	504	115	100	8804	2105	768	22	1248	12548	12597	95184	833	1056
2%HBF4 MWtemp	40	1416	1603	716	145	143	84	6618		1461	505	116	101	-	2262	926	18	1411	12540	12892	98234	793	1106
2%HBF4,2u,105°C	36	-	2151	757	141	139	79	7232	6898	1432	514	108	99	9088	2373	895	19	1385	14189	13949	113808	896	1102
4%HBF4,2u,105°C	37	1380	2040	733	144	145	85	6559	6653	1267	521	110	100	8670	2376	821	17	1290	12905	12824	101871	851	1048
AR,2u,105°C	34	-	1681	790	149	147	73	7158	7289	1377	626	107	92	-	2232	859	22	1332	13071	13193	107769	1032	1091
Pb																							
2%HF MWpower	159	918	468	817	610	971	8,2	852	828	863	531	1102	167	5570	1076	71	200	11746	6038	5922	9943	583	4033
2%HBF4 MWpower	170	976	444	904	584	940	6,5	869	875	909	555	1124	167	6055	1049	71	202	11598	5856	5912	9405	569	4181
2%HBF4 MWtemp	157	951	443	849	551	867	8,5	860		907	580	1134	170	5576	1072	76	202	10883	5789	5880	9609	609	3938
2%HBF4,2u,105°C	151	1019	516	914	566	1088	8,7	914	884	906	554	1126	166	-	1094	60	217	13769	6206	6279	9765	644	5172
4%HBF4,2u,105°C	203	904	477	864	588	1101	7,6	853	868	846	555	1174	176	-	1091	74	187	12157	6174	6016	9779	569	4257
AR,2u,105°C	167	922	482	983	577	961	3,5	834	884	850	604	1248	172	5180	1139	57	202	13083	6354	6238	10437	645	5105

	1	2	3	4	5	6	7	8a	8b	9	10	QC1	QC2	11	12	13	14	15	16a	16b	17	18	19
	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds
Mg																							
2%HF MWpower	2436	3445	2518	1342	3071	3159	2125	5166	5245	1511	5519	9487	10711	8808	11099	5889	2612	18309	982	979	2213	8254	14468
2%HBF4 MWpower	2627	3758	2545	1545	3185	3246	2303	5423	5662	1589	5619	10041	11005	9911	11204	5870	2603	17854	948	946	2247	9378	15069
2%HBF4 MWtemp	2397	3144	2327	1264	3035	2996	2121	5615		1707	5986	8828	10574	9242	10978	5830	2626	17079	975	969	2083	9429	14689
2%HBF4,2u,105°C	2678	3921	2702	1571	3326	3343	2427	5780	5788	1767	6069	10324	11185	8929	11905	5511	2846	18571	1036	1027	2312	10213	15495
4%HBF4,2u,105°C	2682	3785	2574	1596	3230	3153	2399	5738	5683	1780	5936	10069	10992	8934	11640	5944	2716	18523	968	964	2246	9751	14886
AR,2u,105°C	1979	2831	2015	993	2857	2757	1213	3949	3789	991	4905	7699	9200	5582	10232	1992	2632	12577	859	854	2224	8880	13369
Mn																							
2%HF MWpower	263	437	682	244	307	284	1150	1396	1380	2238	605	638	1257	1806	724	411	80	1424	563	568	631	317	762
2%HBF4 MWpower	283	497	685	270	314	293	1048	1472	1461	2354	647	660	1209	2038	642	347	69	1298	572	590	602	318	740
2%HBF4 MWtemp	266	443	657	252	303	310	1045	1375		2185	614	638	1231	2042	713	411	75	1427	599	599	640	343	790
2%HBF4,2u,105°C	250	508	679	264	299	355	1030	1590	1546	2354	607	686	1181	1873	723	391	75	1551	614	615	609	349	816
4%HBF4,2u,105°C	268	460	765	257	320	326	1041	1445	1448	2152	607	666	1268	1640	701	399	76	1352	534	538	619	321	731
AR,2u,105°C	237	418	632	215	306	278	573	1307	1347	2568	607	586	1191	1946	741	184	58	1409	589	596	597	336	745
Mo																							
2%HF MWpower	1,7	9,3	8,4	2,8	1,5	1,6	8,6	16,0	15,5	66,2	32,1	1,7	1,3	84	17	287	6,3	48	4,5	4,5	4,4	8,9	35
2%HBF4 MWpower	1,5	8,6	6,3	2,7	1,1	<1	9,4	16,0	14,8	83,3	33,7	1,8	<1	67	16	248	6,3	43	4,9	4,3	4,3	9,5	33
2%HBF4 MWtemp	1,7	8,6	6,4	2,7	1,1	1,1	8,3	15,8		68,3	33,5	1,6	<1	86	16	296	5,5	48	5,2	5,2	4,8	10	37
2%HBF4,2u,105°C	1,2	8,3	8,8	2,3	<1	<1	7,7	16	16	61	37	1,4	<1	52	17	255	5,2	43	4,6	4,7	3,3	10	35
4%HBF4,2u,105°C	1,4	8,7	-	2,8	1,1	1,2	13	17	16	-	34	1,6	1,1	72	17	271	5,3	45	4,5	4,6	2,4	9,4	33
AR,2u,105°C	1,2	8,6	6,6	2,5	1,2	1,1	5,8	18	17	91	33	1,4	<1	87	18	265	5,6	43	3,1	3,3	<1	9,6	36
Na																							
2%HF MWpower	2604	3830	4670	2238	1965	2416	2129	3274	3274	1345	3191	11093	5240	16692	8484	44082	383	32912	4676	4645	12731	1598	32962
2%HBF4 MWpower	2751	3759	4695	2358	1976	2437	2158	3384	3369	1414	3207	11403	5143	16230	10393	43938	391	32913	4837	4859	13567	1818	33985
2%HBF4 MWtemp	2627	3729	4592	2278	1920	2340	2154	3261		1437	3091	10630	4949	12794	9272	50222	412	32398	4918	4891	12833	1892	34464
2%HBF4,2u,105°C	2804	3988	5019	2488	2144	2523	2343	3576	3416	1491	3265	10887	5315	17431	9499	43109	423	36507	5363	5300	14517	2011	35460
4%HBF4,2u,105°C	2776	3803	4762	2426	2021	2447	2307	3438	3338	1469	3185	11351	5421	17672	9678	49900	403	35371	4956	4909	13013	1905	35399
AR,2u,105°C	249	423	753	127	272	228	1537	1386	1207	267	1522	467	164	3286	8645	13529	119	34907	4810	4866	12309	478	36317
Ni																							
2%HF MWpower	23	128	141	105	28	31	68	114	110	431	110	21	46	443	126	592	10	111	23	22	1709	68	116
2%HBF4 MWpower	24	133	133	118	28	31	53	118	120	404	118	22	45	506	116	542	12	108	26	25	1599	67	109
2%HBF4 MWtemp	24	125	141	108	27	31	61	113		306	110	20	45	458	127	530	11	105	25	25	1687	72	116
2%HBF4,2u,105°C	22	121	177	106	26	31	48	108	110	292	-	20	46	339	119	508	10	118	24	24	1771	68	115
4%HBF4,2u,105°C	24	126	170	117	27	32	73	128	111	-	119	20	45	346	124	564	9	123	24	24	1728	66	108
AR,2u,105°C	16	67	127	111	22	26	33	105	105	-	109	18	42	412	113	483	9	97	23	23	1690	68	102
Sn																							
2%HF MWpower	6,4	88	49	154	27	21	3,2	439	444	36	77	<2	11	333	253	46	<2	2569	<2	<2	19626	92	1005
2%HBF4 MWpower	4,3	160	43	170	30	23	<2	443	453	37	82	<2	9,3	395	225	47	<2	2447	<2	<2	17566	77	978
2%HBF4 MWtemp	6,9	145	41	158	26	23	<2	437		33	77	<2	10	336	249	49	<2	2344	<2	<2	19098	85	1064
2%HBF4,2u,105°C	4,9	*224*	44	168	23	*48*	<2	476	442	39	75	<2	9,1	320	235	40	<2	2750	<2	<2	13802	88	1052
4%HBF4,2u,105°C	4	82	89	166	28	29	<2	441	443	37	73	<2	9	266	246	45,6	<2	2536	<2	<2	9735	68	962
AR,2u,105°C	5	163	49	161	30	20	<2	421	440	36	78	<2	3	251	217	40	<2	2409	<2	<2	5609	<2	731

	1	2	3	4	5	6	7	8a	8b	9	10	QC1	QC2	11	12	13	14	15	16a	16b	17	18	19
	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds	mg/kg ds
Ti																							
2%HF MWpower	1251	2358	1412	1454	1211	1390	2257	3367	3356	1572	1471	2522	2534	5402	7652	4841	486	7963	215	217	98	2203	9279
2%HBF4 MWpower	1023	1841	1095	1191	997	1089	2173	2453	2484	1316	1099	2067	1477	1886	5224	4014	332	5209	177	190	74	872	7875
2%HBF4 MWtemp	1178	1944	1257	1510	1241	1233	2269	3307		1600	1252	2388	2005	4543	6836	4436	437	5006	239	251	89	1677	8766
2%HBF4,2u,105°C	677	1386	859	857	746	848	2143	2474	2419	1303	946	1587	849	1243	5119	4310	328	5223	190	194	60	636	8693
4%HBF4,2u,105°C	866	1531	875	970	914	973	2190	2443	2493	1321	1027	1721	1071	1511	5361	4013	332	5126	173	178	63	928	8381
AR,2u,105°C	126	352	295	167	323	254	404	875	819	455	576	772	237	732	2660	2260	111	2741	95	96	14	41	3944
V																							
2%HF MWpower	49	146	74	37	48	46	41	113	112	47	48	91	98	45	63	14	48	49	10	10	4,6	39	36
2%HBF4 MWpower	52	147	76	39	49	48	37	115	116	48	50	94	96	46	57	13	52	45	12	12	5,2	43	36
2%HBF4 MWtemp	53	146	74	41	49	46	40	119		47	51	91	94	47	62	14	43	50	12	12	5,1	47	39
2%HBF4,2u,105°C	51	138	77	37	48	50	40	108	111	42	51	83	89	42	68	14	53	53	20	20	5,7	53	46
4%HBF4,2u,105°C	52	150	82	43	56	51	47	121	115	47	52	89	97	51	72	17	55	54	21	21	6	52	45
AR,2u,105°C	30	67	69	21	36	30	12	87	85	39	45	64	59	44	64	10	54	45	16	16	5	42	41
Zn																							
2%HF MWpower	159	1854	1553	4973	1591	1924	101	4047	4030	1660	2595	365	487	16690	3245	908	227	26852	1259	1269	244	2913	16572
2%HBF4 MWpower	169	1939	1428	5029	1558	2011	102	4118	4108	1704	2653	381	492	17100	3170	723	199	27524	1244	1282	220	2810	17326
2%HBF4 MWtemp	169	1743	1523	5238	1577	1928	111	4163		1736	2610	356	490	18290	3244	809	204	25782	1312	1311	241	2861	16192
2%HBF4,2u,105°C	171	1861	1733	5392	1557	1991	99	4767	4602	1615	2817	344	532	16904	3434	782	223	30989	1330	1334	205	3267	18005
4%HBF4,2u,105°C	178	1762	1511	5265	1607	2133	117	4553	4412	1819	2781	366	551	16188	3317	815	222	27743	1242	1229	198	3042	16797
AR,2u,105°C	168	1855	1577	5458	1722	2088	44	4470	4570	1894	2870	371	538	19754	3430	251	212	29273	1323	1327	236	3308	17512
Hg																							
2%HF MWpower	77	0,58	0,99	0,39	2,5	2,6	<0.1	1,1	1,2	65	0,58	6,7	1,1	*6,2*	3,2	2,2	12	33	1,6	1,7	0,13	7,7	1,3
2%HBF4 MWpower	72	0,59	0,95	0,35	2,5	2,6	<0.1	1,0	1,0	65	0,48	6,1	1,1	3,4	3,3	2,2	13	30	1,6	1,7	0,14	6,9	1,4
2%HBF4 MWtemp	70	0,60	1,01	0,34	2,8	2,6	<0.1	1,0		63	0,50	6,0	1,1	3,9	3,4	2,7	12	33	1,8	1,7	0,14	8,0	1,5
2%HBF4,2u,105°C	69	0,57	1,00	0,34	2,5	2,5	<0,1	1,2	1,1	59	0,50	6,2	1,1	3,3	3,2	2,1	13	30	1,6	1,7	0,14	7,9	1,4
4%HBF4,2u,105°C	71	0,57	0,99	0,36	2,4	2,5	<0,1	1,1	1,1	65	0,50	6,2	1,2	3,6	3,4	2,3	14	32	1,8	1,7	0,17	8,2	1,5
AR,2u,105°C	72	0,58	1,00	0,35	2,5	2,6	<0,1	1,1	1,1	61	0,56	6,3	1,2	3,4	3,3	1,9	14	31	1,6	1,6	0,14	8,1	1,3

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