

Digestion of solid matrices
Part 2: Microwave digestion with nitric acid
Evaluation study report

Kirsten Jebjerg Andersen

Eurofins A/S, Denmark

Acknowledgement

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

CONTENTS

SUMMARY	5
1. INTRODUCTION	7
2. DESCRIPTION OF THE EVALUATION STUDY	8
2.1 Ruggedness test – microwave oven digestion, nitric acid – Method A	8
2.1.1 Analytical principle	8
2.1.2 Ruggedness test - parameters to be tested	8
2.2 Microwave and autoclave digestion – nitric acid - Method A and C	10
2.3 Comparison of nitric acid digestion with digestions of mixtures of nitric acid and hydrochloric acid – Method A, Method B and Method D.	10
3. MATERIALS	12
4. RESULTS AND EVALUATION	13
4.1 Ruggedness test - Method A	13
4.2 Comparison of microwave and autoclave digestion - nitric acid	18
4.3 Comparison between nitric acid and mixtures of nitric acid and hydrochloric acid	20
4.3.1 Arsenic	21
4.3.2 Cadmium	22
4.3.3 Cobalt	23
4.3.4 Copper	24
4.3.5 Chromium	25
4.3.6 Manganese	27
4.3.7 Nickel	29
4.3.8 Lead	30
4.3.9 Zinc	31
4.3.10 Other elements	32
5. CONCLUSIONS AND RECOMMENDATIONS	33
5.1 Robustness	33
5.2 Comparison between microwave and autoclave methods	33
5.3 Comparison between nitric acid and mixtures of nitric acid and hydrochloric acid used as extraction media – microwave oven.	34
ANNEX 1	Results from ruggedness testing
ANNEX 2	Comparison of digestion efficiency and variations
ANNEX 3	Instruments and methods

LIST OF TABLES

Table 1	Conditions for ruggedness test.....	9
Table 2	Design for the eight experiments of the ruggedness test - Eight combinations of seven factors.....	10
Table 3	Description of samples used in the evaluation study.....	12
Table 4	Relative differences (%) related to experimental conditions – Barium.....	14
Table 5	Relative differences (%) related to experimental conditions – Vanadium.....	14
Table 6	Evaluation of effects in ruggedness study.....	16
Table 7	Comparison of microwave digestion and autoclave digestion.....	18
Table 8	Results from microwave oven digestion by methods A, B and D – Arsenic.....	20
Table 9	Results from microwave oven digestion by methods A, B and D – Cadmium...	22
Table 10	Results from microwave oven digestion by methods A, B and D – Cobalt.....	23
Table 11	Results from microwave oven digestion by methods A, B and D – Copper.....	24
Table 12	Results from microwave oven digestion by methods A, B and D – Chromium .	25
Table 13	Results from digestions by Methods A, B and D – Manganese.....	27
Table 14	Results from microwave oven digestion by methods A, B and D.....	29
Table 15	Results from microwave oven digestion by methods A, B and D – Lead.....	30
Table 16	Results from microwave oven digestion by methods A, B and D – Zinc.....	31
Table 17	Results from digestions by Methods A, B and D compared to the certified value for NRCC-PACS-2 sediment sample.....	32

SUMMARY

The present report contains an evaluation of a draft standard on a method for high-temperature microwave digestion for the extraction of elements by using nitric acid as extraction agent. It is the characteristic of the method principle that the preset temperature in the digestion mixture and the preset total heating time controls the digestion. The method has been evaluated and compared to other digestion methods by digestion and analyses of samples of soil, sludge, sediments and compost. The method corresponds to the nitric acid microwave oven digestion method in US EPA Method 3051A. The proposed method offers a quick and robust digestion method, where the digestion conditions are controlled and can be documented.

The draft method has been evaluated in a ruggedness study, which showed that the method is robust for the conditions and samples investigated. The ruggedness study indicated that elements like chromium and vanadium were affected by variations in energy input (temperature and duration of heating) during the digestion, which underlines a need for the control of conditions; however, the observed effect were weak. No changes of the conditions compared with US EPA 3051A have been introduced.

In general, the uncertainties obtained for the elements tested in the ruggedness study were low (1–8%). It is considered that these variations mimic the expected uncertainty component corresponding to the digestion process in a validation study (interlaboratory comparison).

The evaluation contains a comparison of the proposed microwave oven digestion method with an earlier proposed method on extraction of elements with nitric acid using autoclave heating. This method principle is widely used e.g. in the Nordic countries for digestion of elements from solid matrices. The results indicated that the extraction efficiencies for the two methods are, to a large extent, comparable. The results from the comparison on soil, sediments and sludge samples showed a good agreement of results between the two methods for arsenic, barium, cadmium, chromium, cobalt, copper, manganese, nickel, lead, strontium, vanadium and zinc. The results for compost samples showed good agreement for all the elements mentioned, except for chromium and nickel.

The nitric acid microwave digestion method was compared to aqua regia ($\text{HNO}_3 + \text{HCL} - 1+3$) digestion in microwave oven and to an alternative method using a different composition of nitric acid and hydrochloric acid ($\text{HNO}_3 + \text{HCL} - 3 + 1$). The extraction efficiency for arsenic, cadmium, cobalt, copper, lead and zinc were comparable for the three methods for sludge, soil, sediment and compost. A good comparability was also seen for nickel; however, results for some samples varied.

Extraction efficiency for the more refractory elements like aluminium, chromium, manganese and vanadium are for all three methods less than 80%. The extraction efficiency varied for the three methods - the higher the concentration of hydrochloric acid, the higher the extraction efficiency. The alternative method (with mixture of acid $\text{HNO}_3 + \text{HCL} - 3+1$) does not result in extraction efficiencies comparable to that of the aqua regia extraction for the refractory elements. Thus, a proposal to include an alternative extraction medium ($\text{HNO}_3 + \text{HCL} - 3+1$) in the proposed method (as is the case for US EPA 3051A) for the extraction of more refractory elements can not be justified by comparability to the aqua regia method. An alternative extraction method for refractory elements has therefore not been included in the proposed standard.

The results from the analyses of major ions (magnesium, calcium and sodium) indicate comparable results for the samples analysed using the three different digestion methods. Results for barium, strontium, silver, thallium, antimony, molybdenum and iron show that, to a varying extent, mixtures of nitric acid and hydrochloric acid have larger extraction efficiency than nitric acid alone. Comparison of results from different laboratories using the aqua regia methods suggests that relatively high variations between laboratories may be expected for some elements. An evaluation of the total variation for these elements from interlaboratory studies is needed to clarify to which extent the differences in extraction efficiency between methods are significant.

1. INTRODUCTION

The overall objective of the European project “Horizontal” is to develop horizontal and harmonized European standards in the fields of sludge, soil and biowaste and to facilitate regulation of these major streams in the multiple decisions related to different uses and disposal governed by EU directives.

The work on the development of horizontal and harmonized European standards is split into coherent work packages, of which the present subject belongs to WP 6: Inorganic parameters. The present report describes the results of an evaluation study (Phase II) under Project Horizontal WP 6 (topic 18): Inorganic Parameters: Evaluation of a standard on:

- Solid materials - Microwave digestion of sediment, sludge, soil and biowaste for the extraction of nitric acid soluble fraction of elements

A parallel study under WP 6, topic 18 is focused on an evaluation of aqua regia digestion methods. The results from this study is described in /8/.

In the previous desk study on digestion of solid matrices /1/ a detailed comparison of standards for the digestion prior to the determination of elements demonstrated the possibilities of preparing horizontal standards in this field. It was concluded that partial methods, which are most frequently used for digestion in these fields, are acceptable. More partial methods have been investigated, with a focus however, on digestion using aqua regia and digestion using nitric acid. It is important that the analyses of elements on sludge, soil and biowaste can be carried out in a reproducible manner with a sufficiently low variation between laboratories (high reproducibility). Furthermore, if different digestion methods are used, it is of importance that the methods provide statistical comparable results for the matrix and element in question.

The evaluation study is based on the recommendations as given in the desk study reports /1/ and suggestions from interested parties following the commenting period of Phase I of the Horizontal Project. The desk study report as well as a draft horizontal standard and a summary of comments are published at www.ecn.nl/horizontal. The proposed standard on digestion with nitric acid was based on autoclave heating /2/; however, the desk study suggested that also microwave digestion could be considered and pointed at a standard developed by US EPA /6/ using high-energy microwave oven digestion and nitric acid. The comments on the desk study supported a consideration of microwave oven digestion. A draft standard on microwave digestion has thereafter been developed: Solid materials – Microwave digestion of sediment, sludge, soil and biowaste for the extraction of nitric acid soluble fraction of elements/7/. The draft standard offers a method that is quick, the digestion conditions are controlled and can be documented and the acid used is less corrosive than methods containing hydrochloric acid.

An evaluation, which included a ruggedness test, has been carried out on the basis of this draft standard. The evaluation study included:

- Evaluation of the draft standard for conditions of microwave digestion using nitric acid - ruggedness study – evaluation of precision.
- Comparison of nitric acid digestion using microwave oven heating and autoclave heating
- Evaluation of the influence on the digestion efficiency of the draft standard by adding hydrochloric acid and comparison with methods using aqua regia

The present report describes the results of the evaluation study.

2. DESCRIPTION OF THE EVALUATION STUDY

A draft standard based on the principles described in US EPA method 3051A has been prepared /7/. The evaluation study focuses on the described draft standard (referred to as Method A in the following). Results of validation studies of US EPA 3051A have proven that the method is suitable for digestion of solid samples and oil samples for the determination of metals /6/. It is the characteristic of the principle that the preset temperature in the digestion mixture and the preset total heating time controls the digestion.

One objective of the evaluation study is to investigate the ruggedness of the digestion method described in the draft standard to small changes in the digestion condition. A second objective of the study is to compare the extractable fraction of elements when using the draft standard with the extractable fraction of elements when using the following standards and draft standards:

- B. Use of the same conditions (temperature and time) as in Method A, but with the use of a mixture of nitric acid and hydrochloric acid - HNO_3+HCl (3+1) as extraction medium /6/. Method B is included in US EPA method 3051A as an option for specified refractory elements.
- C. Heating in an autoclave in combination with the use of nitric acid as extraction medium /2/.
- D. Heating in microwave oven in combination with the use of aqua regia as extraction medium - HNO_3+HCl (1+3)/3/.

2.1 Ruggedness test – microwave oven digestion, nitric acid – Method A

2.1.1 Analytical principle

The digestion procedure in Method A /7/ is described in the draft standard as follows:

.....10.2 Digestion

Weigh into the digestion vessel an amount equal to 0,25 – 0,5 g dried sample accurately at 0,001 g and transfer it into the digestion vessel. Add 10 mL \pm 0,1 mL of concentrated nitric acid to the digestion vessel with test portion. Swirl and allow the mixture to stand until any visible reaction has stopped.

.....

The temperature of each sample should rise to $175 \pm 0,5^\circ\text{C}$ in approximately $5,5 \pm 0,25$ minutes and remain at $175 \pm 0,5^\circ\text{C}$ for 4,5 minutes, or for the remainder of ten minute digestion period.

At the end of the microwave programme, allow the vessels to cool for a minimum of 5 minutes before removing them from the microwave system.Quantitatively transfer the sample to an acid-cleaned bottle. If the digested sample contains particles which may clog nebulizers or interfere with an injection of the sample into the instrument, the sample may be centrifuged, allowed to settle, or filtered /7/.

2.1.2 Ruggedness test - parameters to be tested

A ruggedness test according to the design described by Youden & Steiner /4/ was carried out for selected parameters of Method A /7/. An aim of the ruggedness test is to investigate factors influencing the digestion efficiency and variability of the tested method. If significantly sensitive factors are identified this indicates that further investigations prior to setting the conditions of the method might be needed.

The statistical design investigates the effect of seven experimental conditions. The conditions chosen are described in Table 1.

Table 1 Conditions for ruggedness test

Factor	Letter	Value for capital letter	Value for lower-case letter
Amount of sample	A, a	0,400 g	0,250 g
Amount of nitric acid	B, b	12,0 ml	8,0 ml
Reaction time prior to heating, room temperature	C, c	4 hours	No standing time
Temperature, heating	D, d	180°C	170°C
Heating time from room temperature to set temperature	E, e	9 minutes	5,5 minutes
Heating time at set temperature	F, f	5 min.	4 min.
Filtration/decanting	G, g	Settling until day after followed by decanting or direct analyses	Minimum settling time and filtration

The approach uses a systematic plan in which each factor can have two possible values. The values of four factors are changed in each digestion. The objectives of the ruggedness test are twofold. The test is designed to identify whether the method is sensitive to small changes in the factors concerned. Furthermore, the evaluation can provide an estimate of the variation likely to be expected between laboratories (and originating from the digestion procedure only). The changes are small and may well be compared to the small changes going from one laboratory to the other. It is underlined that the test does not investigate the effect of changing digestion conditions purposely – e.g. longer digestion time and lower temperature.

The experimental factors were combined in a total of eight experiments for each of 10 samples chosen for the ruggedness test. Blank tests were carried out to control contamination of acid and the cleaning procedure for the vials. To keep variations due to calibration insignificant, analyses of the same kind of samples/matrix were carried out in one batch. Each determination in the ruggedness test was performed according to the design described in Table 2.

Table 2 Design for the eight experiments of the ruggedness test - Eight combinations of seven factors

Experimental factor	Values for factors in determination no.							
	1	2	3	4	5	6	7	8
Amount of sample	A	A	A	A	a	a	a	a
Amount of nitric acid	B	B	b	b	B	B	b	b
Reaction time prior to heating, room temperature	C	c	C	c	C	c	C	c
Temperature, heating	D	D	d	d	d	d	D	D
Heating time from room temperature to set temperature	E	e	E	e	e	E	e	E
Heating time at set temperature	F	f	f	F	F	f	f	F
Filtration/decanting	G	g	g	G	g	G	G	g

The samples for the ruggedness tests represent a wide range of concentrations for most elements and represent soil (3 samples – SO1, SO4, SO9), sediment (2 samples - Lake Arresoe freshwater sediment and PACS-2, a harbour sediment), sludge (3 samples – SL4, SL11 and Solid 5 (2004-7) sample A) and compost (2 samples – CW1 and CW5). The materials used for testing are described in Chapter 3.

Method A is a performance-based method, designed to achieve or approach consistent leaching of the sample through achieving specific reaction conditions. It is fundamental to the method that the samples receive a predefined energy input during the microwave digestion; defined by preset heating time and temperature, and that the energy input is controlled. The conditions are specified as follows: *The temperature of each sample should rise to $175 \pm 5^\circ\text{C}$ in approximately 5.5 ± 0.25 minutes and remain at $175 \pm 5^\circ\text{C}$ for 4.5 minutes, or for the remainder of the ten minute digestion period /6/.* The combinations of heating and holding times chosen for ruggedness testing as described in Table 1 include the following total heating time (heating + holding) of 14 minutes, 13 minutes, 10.5 minutes and 9 minutes. Less than 9 minutes total heating time with the microwave oven used for the experiment were shown to compromise reaching 180°C in a reasonable time, thus leaving a too short period for holding time.

Results from the ruggedness testing are presented in Chapter 4.

2.2 Comparison of microwave and autoclave digestion – nitric acid - Method A and C

Triplicate digestions were carried out for the same samples as above following the digestion method A and following the autoclave digestion method – Method C /2/. The results from analyses of the digests allow a comparison of data obtained both from the conventional autoclave digestion method and from the microwave digestion method.

The digestion conditions for microwave digestion (Method A) are described in 2.1.1 and 2.2.2.

The digestion by using autoclave heating (**Method C**) is described in the draft standard /2/ as follows:

....10.2.1 Amount of sample and 10.2.2 digestion

Weigh into the digestion vessel an amount equal to 5 g dried sample, for samples rich in organic carbon a maximum of 2 g of the sample, accurately at 0.1 mg and transfer it into the vessel. Add 20 mL \pm 1 mL of HNO_3 to the digestion vessel with test portion. Run the autoclave. When it has reached 120°C , maintain the temperature for 30 minutes. Allow the digestion mixture to cool down to room temperature. Uncap and vent the digestion vessels in a fume hood. Decant the sample into the acid-cleaned volumetric flask /2/

Results of the analyses and comparison are presented in Chapter 4.

2.3 Comparison of nitric acid digestion with digestions of mixtures of nitric acid and hydrochloric acid – Method A, Method B and Method D.

Results from digestion and analyses of samples when using Method A are compared element by element with results from digestion and analyses of identical samples with two different mixtures of nitric acid and hydrochloric acid.

Method B: High temperature microwave digestions are carried out with a mixture of nitric acid and hydrochloric acid (3 + 1) according to EPA Method 3051A /6/. The set digestion conditions (apart from the extraction solution) are identical with the conditions for Method A.

...EPA Method 3051A: 2.0 Summary of method

A representative sample of up to 0.5 g is extracted and/or dissolved in 9 ml concentrated nitric acid and 3 ml concentrated hydrochloric acid for 10 minutes using microwave heating with a suitable laboratory unit. After cooling, the vessel contents are filtered, centrifuged, or allowed to settle and then diluted to volume and analysed by the appropriate determinative method.

The digestions in the present study were carried out in triplicate.

Method D: Duplicate digestions were performed in microwave oven with aqua regia following the procedure as described in /9/ and summarized as follows:

.....10.3 Microwave assisted digestion in closed vessels

Weigh between 0.2 g to 0.5 g of the sample, accurately at 0.1 mg and transfer it into the vessel (7.2). Then add separately 6 mL of HCl (6.3) and 2 mL of HNO₃ (6.4). Transfer the digestion vessels into the microwave oven (7.5) according to the manufactures instructions and start the following digestion procedure /9/.

Power programme

<i>Time (min.)</i>	<i>Power (W)</i>
2	250
2	0
5	250
5	400
5	500

The comparisons of results from microwave oven digestion with nitric acid and (Method A) and microwave oven digestion with aqua regia (Method D) include results carried out at Eurofins Danmark A/S. Aqua regia results produced in other laboratories have been included for selected elements.

Results from the described comparisons are presented in Chapter 4.

3. MATERIALS

Samples (so-called playground samples) for the evaluation study were samples made available through Horizontal Work package 1 and samples made available through the Eurofins proficiency-testing scheme. The general characteristics of the samples used in the evaluation study are described in /5/ and the respective reports of interlaboratory comparisons. A list of samples is given in Table 1.

Table 3 Description of samples used in the evaluation study

Sample ID	Sample description		C_{org} wgt. %
SO-1	Brown soil, Ispra, Italy	Ball-milled and sieved < 125 μ m	2,652
SO-4 (Equivalent to BCR-144)	Clay soil, Speyer, Germany	Ball-milled and sieved < 125 μ m	1,652
SO-7	Rice cultivation soil, Vercelli, Northern Italy	Ball-milled and sieved	
SO-9	Soil, Hagen, Germany	Ball-milled and sieved < 125 μ m	
Solid-9 (2003-5), sample B	Soil from soil recycling plant, Denmark	Sieved < 1 mm	
NRCC PACS-2	Marine sediment reference material		
Lake Arresoe	Fresh water sediment	< 250 μ m	
CW-1	Composted garbage, Munich, Germany	Dried and ball-milled	12,122
CW-5	Compost, Fulda, Germany		11,45
Compost – Sample KH	Compost, garden		
SL-4	Sewage sludge, domestic, Essen, Germany (= BCR 144)	Ball-milled and sieved < 125 μ m	29,035
SL-11	Sewage sludge, electronic industry, Turin, Italy	Ball-milled and sieved < 125 μ m	3,177
Solid-5 (2002-5), sample A	Municipal sludge from wastewater treatment plant	< 4 mm	
PP 1995-3, sample C	Harbour sediment	< 250 μ m	
Solid-5 (2004-7), Sample A	Sludge, wastewater treatment plant	Oven-dried at 40 °C, crushed, sieved < 1 mm	

4. RESULTS AND EVALUATION

4.1 Ruggedness test - Method A

The effects of the experimental conditions are investigated by calculation of the average differences as follows:

Factor	Average difference for determinations no.
Amount of sample	(1+2+3+4) - (5+6+7+8)
Amount of nitric acid	(1+2+5+6) - (3+4+7+8)
Reaction time prior to heating, room temperature	(1+3+5+7) - (2+4+6+8)
Temperature, heating	(1+2+7+8) - (3+4+5+6)
Heating time from room temperature to set temperature	(1+3+6+8) - (2+4+5+7)
Holding time at set temperature	(1+4+5+8) - (2+3+6+7)
Filtration/decanting	(1+4+6+7) - (2+3+5+8)

A total of 80 digestions were carried out during the ruggedness tests. The analyses of digests were performed using ICP-AES. Only data from samples containing an amount of the specific element well above the detection limit are taken into consideration. Some elements contained amounts above the calibration range. These data have also been excluded. Ruggedness test data have been evaluated for As, Ba, Cd, Cr, Co, Cu, Mn, Na, Ni, Pb, Sr and V. As would be expected, the size of the differences depends on the concentration of metal in the samples. For further analyses of data, the differences relative to average sample concentration are used. These differences are shown for each of the 12 elements in Annex 1 and the results are summarized in Table 6.

Table 4 illustrates the ruggedness calculations with barium results given as an example. Table 5 illustrates the ruggedness calculations with vanadium results given as an example.

Table 4 (barium) shows that for the choice of all the experimental conditions the sign of the differences spilt more or less evenly between plus and minus for barium. This implies that the differences observed are due to random variations. No significant effect from any of the tested conditions is identified.

Coefficients of variance (CV) of 1–6% are obtained for the eight samples. The observed variations (coefficient of variations) include variation components from sub-sampling, digestion and analyses. The analyses are carried out under repeatability conditions. Provided that the major uncertainty for the analyses of barium in the present study originates from the use of differing digestion conditions, an uncertainty component (attributed to the digestion procedure) corresponding to a maximum coefficient of variation of 1–6% may be expected in an interlaboratory comparison. This is considered satisfactory. The results show that the potential differing particle size of the materials does not significantly influence the variation of results.

Table 4 Relative differences (%) related to experimental conditions – Barium

Factor	SO-1 (<125 µm)	SO-4 (<125 µm)	SO-9 (<125 µm)	Lake sed. (<250 µm)	SL-4 (<125 µm)	Sludge Solid 5 (<4 mm)	SL-11 (<125 µm)	CW 5 n
Amount of sample	2	-5	-2	-4	3	-1	-2	1
Amount of nitric acid	0	0	0	6	0	3	0	0
Reaction time prior to heating, room temperature	-3	-8	0	-1	1	-1	0	0
Temperature, heating.	-1	1	-1	0	3	1	0	3
Heating time from room temperature to set temperature	-6	-2	-1	-3	1	0	1	-4
Heating time at set temperature	6	3	-1	4	2	1	3	2
Filtration/decanting	3	-5	0	3	1	-1	0	1
Coefficient of variation	5	6	1	5	3	2	2	3

n: no information

Table 5 Relative differences (%) related to experimental conditions - Vanadium

Factor	SO-1 (<125 µm)	SO-4 (<125 µm)	SO-9 (<125 µm)	PACS-2	Lake sed. (<250 µm)	SL-4 (<125 µm)	Sludge Solid 5 (<4 mm)	SL-11 (<125 µm)	CW 1 n	CW 5 n
Amount of sample	-1	-9	0	0	-9	6	-1	-2	-2	0
Amount of nitric acid	2	5	11	6	17	2	7	-1	8	7
Reaction time prior to heating, room temperature	-5	-13	-4	0	-6	3	-5	0	-7	-4
Temperature, heating.	1	0	6	3	3	8	2	-1	2	12
Heating time from room temperature to set temperature	-5	-4	-3	2	-8	1	0	3	-3	-4
Heating time at set temperature	5	5	5	1	12	6	1	1	3	5
Filtration/decanting	2	-8	0	-2	-2	5	1	2	-2	1
Coefficient of variation	5	10	8	4	13	7	5	3	6	9

n: no information

Table 5 (vanadium) shows that for the choice of all the experimental conditions the sign of the differences splits more or less evenly between plus and minus for vanadium. An exception to this is the effect from heating time, which indicates a small positive effect. This implies that most differences observed are due to random variations, however, that the differences in heating time may contribute to uncertainty. Coefficients of variation (CV) of 3–13% are obtained for the eight samples. In general, the uncertainties observed for vanadium are larger than for barium and, all in all, vanadium exhibits larger uncertainties than does the other elements (see later). A high coefficient of variation is achieved for lake sediment, which also exhibits the largest positive difference on duration of heating. The results show, as also seen for barium, that a potential differing particle size of the materials does not significantly influence the variation of results.

A summary of the evaluation of the ruggedness test and calculations of average values and coefficient of variations for the twelve elements is given in Table 6. For the elements **barium, cadmium, cobalt, copper, manganese, sodium, lead, strontium and zinc** no positive or negative effect on any of the tested conditions could be observed. Weak effects are seen for:

- the extracted amount of **chromium**, where the data could possibly indicate effects from amount of acid and energy input (combination of temperature and heating time). For **vanadium** the same possible positive effects are observed. The coefficient of variation for determination of chromium in eight experiments - all with slight changes in conditions - is relatively high for chromium in compost (14–20%) compared to 2–7% for other samples.
- the extracted amounts of **nickel**, where the data could possibly indicate effect from temperature and heating time (holding time). Variations for nickel are generally low in the analysed samples. The coefficient of variation for determination of nickel in eight experiments - all with slight relative changes in conditions – ranges from 1–8% in soil, sludge and sediment samples to 17% in one compost sample. The results indicate that control of temperature may possibly influence on the variations obtained for nickel.

According to the investigation cited in /6/ and results from the analyses of reference materials (see later), chromium and vanadium are only partly extracted by nitric acid or mixtures of nitric acid and hydrochloric acid. Therefore, it is most likely that a kind of steady state of the reaction has not been reached after digestion according to the applied procedure and the extraction of the elements are more sensitive to variations in energy input. For these elements it is considered most important to control the preset conditions of the digestion, i.e. in this case the acid and energy input. Changes (after further investigations) of the conditions may not necessarily improve variations due to these factors for the given elements.

As a consequence, the conditions as described in Method A are maintained and there are made no changes of conditions that describes the digestion in the draft standard (compared to the conditions in EPA 3051A).

Table 6 Evaluation of effects in ruggedness study

Element	Sample	Concentration mg/kg	CV (%) obtained in ruggedness study	Effects – Ruggedness tests
Arsenic	Soil - SO4	26	2	No effects identified (one sample)
Barium	Soil - SO1	116	5	No effects identified
	Soil - SO4	117	6	
	Soil - SO9	594	1	
	Lake Arresø	48	5	
	Sludge - SL 4	565	3	
	Sludge - Solid 5	303	2	
	Sludge - SL 11	78	2	
Cadmium	Compost CW 5	431	3	No effects identified
	Soil - SO9	107	1	
	Sludge - SL 4	3.2	6	
Chromium	Compost CW 1	5.3	5	Weak indication of effect of amount of acid, temperature and holding time.
	Soil - SO1	36	6	
	Soil - SO9	550	7	
	NRCC PACS-2	50	3	
	Sludge - SL 4	447	2	
	Sludge - Solid 5	27	6	
	Sludge - SL 11	59	6	
Cobalt	Compost CW 5	136	14	No effects identified
	Soil - SO1	11	8	
	Soil - SO9	16	4	
Copper	NRCC PACS-2	9	6	No effects identified
	Soil - SO1	37	6	
	Soil - SO4	12	6	
	Soil - SO9	187	1	
	NRCC PACS-2	302	4	
	Lake Arresø	7.6	6	
	Sludge - SL 4	672	2	
	Sludge - Solid 5	274	3	
	Compost CW 1	615	4	
Compost CW 5	66	3		
Manganese	Soil - SO1	697	6	No effects identified
	Soil - SO4	286	4	
	Soil - SO9	1028	1	
	NRCC PACS-2	249	2	
	Lake Arresø	607	4	
	Sludge - SL 4	425	2	
	Sludge - Solid 5	197	2	
	Sludge - SL 11	582	2	
	Compost CW 1	734	3	

	Compost CW 5	882	1	
Sodium	NRCC PACS-2	16785	3	No effects identified
	Lake Arresø	767	4	
	Sludge - SL 4	582	8	
	Sludge - SL 11	11404	2	
Nickel	Soil - SO1	37	8	Possibly no effect or a weak positive effect of temperature and holding time
	Soil - SO9	508	1	
	NRCC PACS-2	36	3	
	Sludge - SL 4	902	2	
	Sludge - Solid 5	28	4	
	Sludge - SL 11	1686	2	
	Compost CW 1	176	5	
	Compost CW 5	97	17	
Lead	Soil - SO9	273	1	No effects identified
	Lake Arresø	10	13	
	Sludge - SL 4	448	2	
	Sludge - Solid 5	92	4	
	Sludge - SL 11	9393	2	
	Compost CW 5	93	4	
Strontium	Soil - SO9	47	3	No effects identified
	NRCC PACS-2	74	4	
	Lake Arresø	333	2	
	Sludge - SL 4	98	2	
	Sludge - Solid 5	793	3	
	Sludge - SL 11	206	2	
	Compost CW 1	240	2	
	Compost CW 5	183	2	
Vanadium	Soil - SO1	43	5	Possibly positive effect indicated from acid, temperature and holding time
	Soil - SO4	30	10	
	Soil - SO9	33	8	
	NRCC PACS-2	80	4	
	Lake Arresø	13	13	
	Sludge - SL 4	11	7	
	Sludge - Solid 5	15	5	
	Sludge - SL 11	19	3	
	Compost CW 1	21	6	
	Compost CW 5	23	9	
Zinc	Soil - SO9	2251	1	No effects identified
	NRCC PACS-2	366	5	
	Sludge - Solid 5	1056	2	
	Sludge - SL 11	364	4	
	Compost CW 5	316	3	

4.2 Comparison of microwave and autoclave digestion - nitric acid

It was concluded in Chapter 4.1 that there is no indication of needs for adjustment of the conditions as described in Method A as a result of the ruggedness study and as the results can mimic the changes of conditions going from one laboratory to the other (and as a consequence mimic the uncertainty between laboratories). Therefore it is judged that the results fairly well describe the extractability using method A for the given samples. A comparison is therefore carried out with results obtained after digestion and analyses using Method C. The same samples as analysed in the ruggedness study were digested with nitric acid by the use of autoclave heating (Method C). Table 7 contains average values from the ruggedness study (Method A), the average values obtained from triplicate autoclave digestions (Method C) and the differences of the average values. Data for Sludge – solid 5 (2004-7) – autoclave digestion represent the assigned values from an interlaboratory comparison.

Table 7 Comparison of microwave digestion /7/ and autoclave digestion /2/.

Element	Sample	Method A Microwave digestion /7/ mg/kg	Method C Autoclave digestion /2/, mg/kg	Differences of averages (%)
Arsenic	Soil SO4	26	24	-8
Barium	Soil - SO1	116	117	1
	Soil - SO9	594	589	-1
	Lake Arresoe	48	52	8
	Sludge - SL 4	565	552	-2
	Sludge - Solid 5 (2004-7)	303	290*	-4
	Sludge - SL 11	78	82	5
	Compost CW 5	431	416	-3
Cadmium	Soil - SO9	107	108	1
	Sludge - SL 4	3.2	3.4	6
	Compost CW1	5.3	5.2	-2
Chromium	Soil - SO1	36	36	0
	Soil - SO9	550	476	-13
	Sludge - SL 4	447	440	-2
	Sludge - Solid 5	27	25*	-7
	Sludge - SL 11	59	59	0
	Compost CW 1	136	95	-30
	Compost CW 5	133	53	-60
Cobalt	Soil – SO1	11	11	0
	Soil – SO9	16	17	6
Copper	Soil – SO1	37	36	-3
	Soil – SO4	12	12	0
	Soil – SO9	187	182	-3
	Lake Arresoe	7,6	8,6	13
	Sludge - SL 4	672	685	2
	Sludge - Solid 5	274	269*	-2
Manganese	Soil - SO1	697	676	-3
	Soil - SO9	1028	1007	-2
	Lake Arresoe	607	611	1
	Sludge - SL 4	425	428	1

Nickel	Soil – SO1	37	36	3
	Soil – SO9	508	506	
	Sludge - Solid 5	28	25*	0
	Compost CW 1	176	160	-11
	Compost CW 5	97	(47)	-9
				-
Lead	Soil - SO9	273	273	0
	Sludge - SL 4	448	449	0
	Sludge - Solid 5	92	92*	0
	Compost CW 5	93	91	-1
Strontium	Soil - SO9	47	47	0
	Lake Arresoe	333	333	0
	Sludge - SL 4	98	98	0
	Sludge - SL 11	206	200	-3
	Compost CW 1	240	242	1
	Compost CW 5	183	184	1
Vanadium	Soil - SO1	43	44	2
	Soil – SO4	30	34	13
	Soil – SO9	33	36	9
	Lake Arresoe	13	15	15
	Sludge - SL 4	11	11	0
	Sludge - Solid 5	15	14*	-7
	Sludge - SL 11	19	19	0
	Compost CW 1	21	22	5
	Compost CW 5	23	22	-4
Zinc	Soil - SO9	2251	2239	0
	Sludge - Solid 5	1056	1000*	-5
	Sludge - SL 11	364	368	1
	Compost CW 5	316	300	-5

* Results from interlaboratory studies - Assigned values

Significant differences between Method A and Method C are observed for chromium for two compost samples (CW1 and CW 5). The previous ruggedness tests pointed at effects on chromium extraction efficiency from slight differences in energy input. The microwave digestion method (Method A) exhibits 30% and 60 % higher extraction efficiency than the autoclave digestion method (Method C) for these two compost samples. There is no significant difference observed for the soil and sludge samples analysed for chromium. For the compost sample CW5 a significant lower extraction yield is seen for nickel, also. Similar differences are not seen for other samples. It is not clear whether the observed difference for compost is due to an in-homogeneity of samples. CW5 exhibits relative large variations for other elements as well.

4.3 Comparison between nitric acid and mixtures of nitric acid and hydrochloric acid

The extraction efficiency is compared from results of digestion and analyses of different sample types using three different microwave oven digestion techniques:

Method A: Nitric acid and high-temperature microwave oven digestion

Method B: Nitric acid and hydrochloric acid (3+1) and high temperature microwave oven digestion

Method D: Aqua Regia and microwave oven digestion

Tables 8 to 16 give an overview of results obtained from microwave digestion when using the three methods for digestion of the same samples for the following elements: **Arsenic, cadmium, cobalt, copper, chromium, manganese, nickel, lead and zinc**. The analyses were performed on ICPOES and ICPMS. Tables 8 to 16 include the average values and coefficient of variances. Digestions are carried out in triplicate for method A and B and in duplicate for method D. Analyses for a broad range of other elements are presented in Annex 2.

The comparison of results from the three applied digestion methods is valid for the analyses within one laboratory. The results do not investigate differences due to difference in calibration status between laboratories.

A comparison to results from using Method D in one other laboratory and the use of conventional heating with aqua regia is included for a few elements. Further information on the variances obtained when using different aqua regia methods principles are described in /8/.

4.3.1 Arsenic

The results from extraction of arsenic by the use of three different microwave oven methods (and different acid combinations) are in good agreement for the samples given in Table 8.

Table 8 Results from microwave oven digestion by methods A, B and D – Arsenic.

Sample ID	Average (mg/kg DM) Method			CV % Method			Results in % of B		
	A	B	D	A	B	D	A	B	D
SO-4	26.8	28.3	31.2	9	10	0	95	100	110
PACS-2 (26.2±1.5)	25.3	27.7	27.3	9	4	6	91	100	98
CW-1	23.9	19.7	22.9	11	3	-	121	100	116

PACS-2 – certified reference material – assigned value is indicated. The analyses are performed on ICPMS.

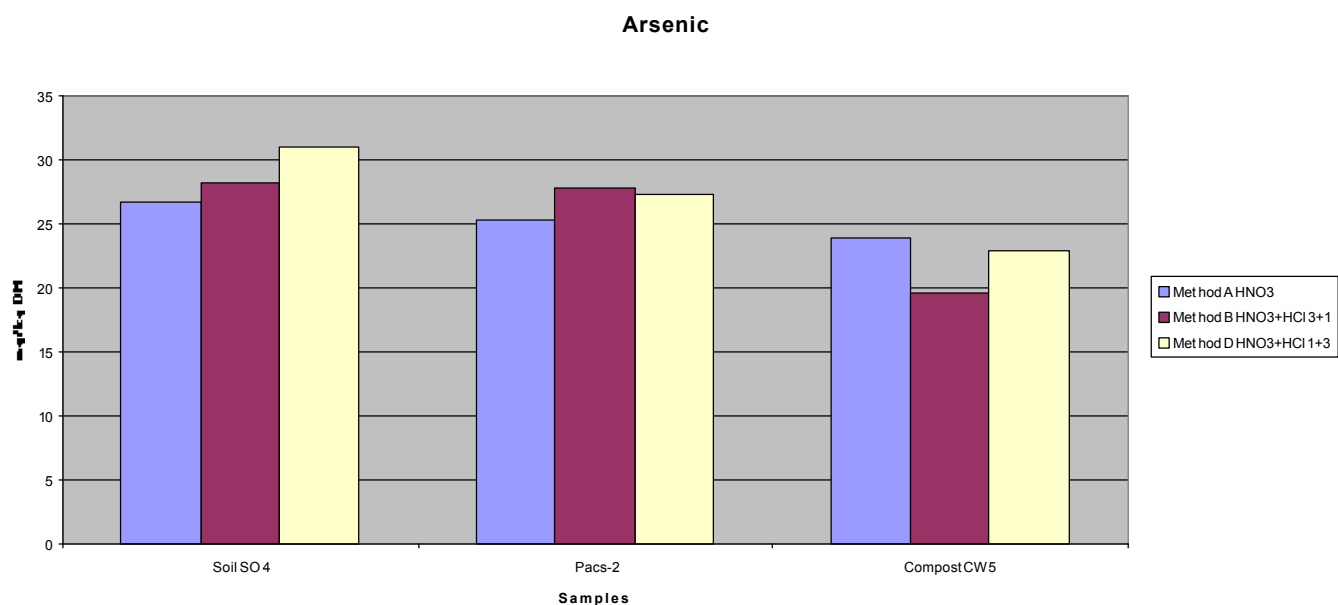


Fig 1. Comparison of microwave oven digestion methods: Method A (HNO₃), Method B (HNO₃+HCl – 3+1) and Method C (HNO₃+HCl – 1+3)

4.3.2 Cadmium

The results from extraction of cadmium when using three different microwave oven methods (and different acid combinations) are generally in good agreement. However, cadmium exhibits significantly different results for one sediment sample - sample PACS-2. The results from Method A-extractions are in line with the assigned value of the sample. None of the three methods extract 100 % of the assigned value for the reference material SL-4 (equivalent to BCR 144). However the results for the three methods are in agreement. Method A extracts 75 % of the assigned value. There is no significant difference observed for soil and compost samples.

The results can be seen from Table 9 and Figure 2.

Table 9 Results from microwave oven digestion by methods A, B and D – Cadmium.

Sample ID	Average (mg/kg DM) Method			CV % Method			Results in % of B		
	A	B	D	A	B	D	A	B	D
SO-1	0.53	0.60	0.61	8	10	13	88	100	103
SO-4	0.34	0.36	0.39	14	3	3	96	100	107
SO-7	1.33	1.55	1.58	7	1	2	86	100	102
SO-9	112	110	113	1	4	1	102	100	102
PACS-2 (2.11±0.15)	2.18	3.15	2.95	9	3	1	69	100	94
SL-4 (4.82±0.97)	3.61	3.38	3.24	3	5	16	107	100	96
Solid-5 (2004-7), Sludge 7	1.47	1.35	1.32	10	13	14	109	100	98
Solid-5 (2002-5), Sludge 5	1.41	1.43	1.22	16	41	2	98	100	85
CW-1	6.17	5.16	6.20	6	8		120	100	120
CW-5	1.03	1.01	1.06	9	8	10	102	100	105

PACS-2 and SL-4 – certified reference materials – assigned value are indicated. The analyses are performed using ICP-OES and ICPMS.

Cadmium

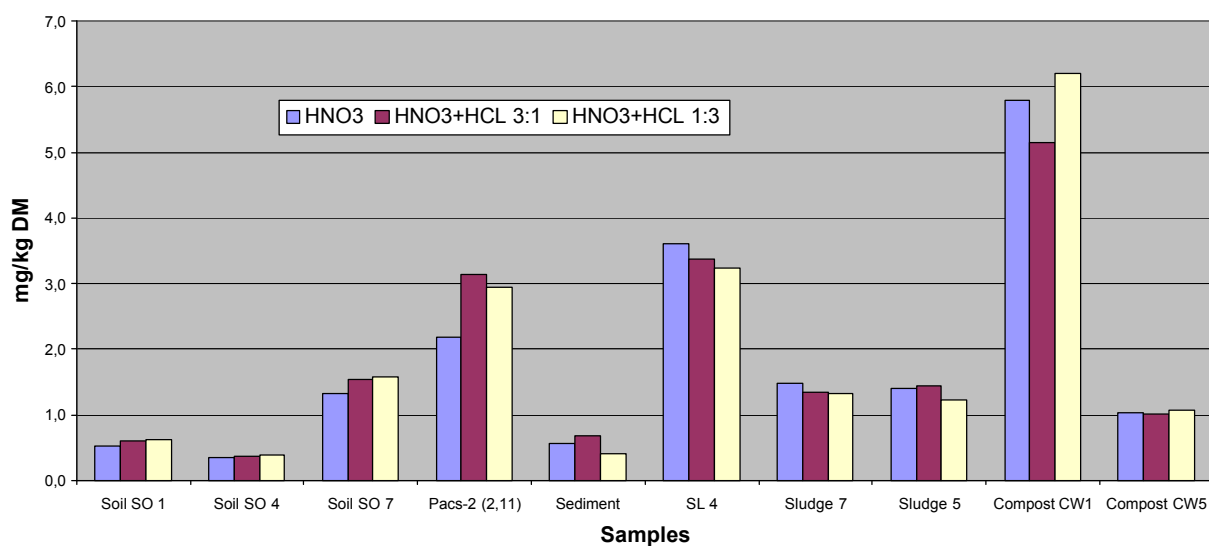


Fig 2. Comparison of microwave oven digestion methods: Method A (HNO₃), Method B (HNO₃+HCl – 3+1) and Method D (HNO₃+HCl – 1+3)

4.3.3 Cobalt

The results from extraction of cobalt by the use of three different extraction mixtures and methods generally show good agreement, however differences are seen. For two soil samples, SO-7 and SO-9, the results are significantly lower for the nitric acid extraction than for the hydrochloric acid and nitric acid mixtures. Method A gives results for SO-7 and SO-9 that are 17 and 13% lower than the results for the aqua regia method. For three other soil samples no significant differences are observed.

Method A extracts 13% less than the assigned value for one sediment reference material (PACS-2). The same is not the case for a second reference material SL-4 - sludge, where Method A extracts 17 more than the assigned value, however here the difference is not significant. One sludge sample (sludge 7) gives significantly higher results for Method A (nitric acid) than for Method D (aqua regia). The results for the compost samples do not reveal differences in extraction efficiency taking the uncertainty of the analyses into consideration.

Table 10 Results from microwave oven digestion by methods A, B and D – Cobalt.

Sample ID	Average (mg/kg DM) Method			CV % Method			Results in % of B		
	A	B	D	A	B	D	A	B	D
SO-1	12.1	10.3	10.6	6	2	3	117	100	103
SO-4	5.2	4.0	4.5	7	2	5	129	100	111
SO-7	19.7	20.8	23.8	3	1	1	95	100	115
SO-9	17.3	18.3	20.0	0	6	1	94	100	109
Solid 9 (2003-5), Soil 9	4.1	4.6	4.4	18	3	0	89	100	95
PACS-2 (11.5±0.3)	9.8	11.0	12.7	3	2	2	90	100	116
SL-4 (9.06±0.6)	10.6	9.1	8.8	6	6	4	116	100	97
SL-11	4.6	4.3	4.1	7	17	16	109	100	95
Solid-5 (2004-7), Sludge 7	7.8	6.6	6.8	4	1	1	120	100	103
Solid-5 (2002-5), Sludge 5	2.9	3.0	3.3	6	35	21	97	100	112
CW-1	10.4	11.4	13.4	3	5		92	100	118
CW-5	8.9	9.3	9.6	3	4	3	96	100	104
Compost KH	5.3	5.8	5.4	6	8	17	91	100	93

PACS-2 and SL-4 – certified reference materials – assigned value are indicated. The analyses are performed on ICP-OES and ICPMS.

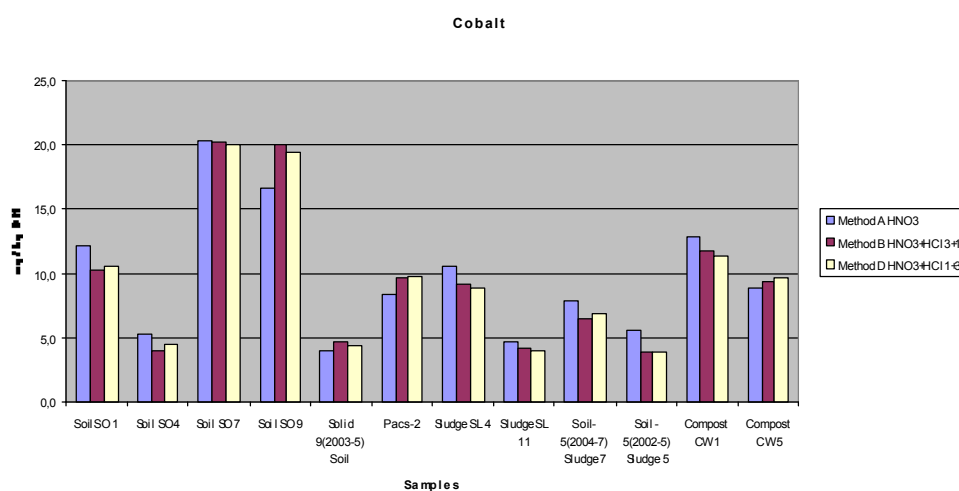


Fig 3. Comparison of microwave oven digestion methods: Method A (HNO_3), Method B ($HNO_3+HCl-3+1$) and Method D ($HNO_3+HCl-1+3$)

4.3.4 Copper

The results from extraction of copper by the use of the three different extraction mixtures and methods generally show good agreement. All three methods extract 100% compared to the assigned value for one sediment reference material (PACS-2) and close to 100 % for one sludge reference material (SL-4). For the one compost sample (CW5), the results are significantly lower for nitric acid extraction than for aqua regia. The results for the other compost samples, however, are in good agreement.

Table 11 Results from microwave oven digestion by methods A, B and D – Copper. .

Sample ID	Average (mg/kg DM) Method			CV % Method			Results in % of B		
	A	B	D	A	B	D	A	B	D
SO-1	35.9	37.3	36.0	1	3	1	96	100	97
SO-4	12.6	12.6	13.75	1	1	4	100	100	110
SO-7	70.8	71.6	70.5	2	1	0	99	100	99
SO-9	193	194	197	1	4	1	99	100	101
Solid-9 (2003-5), Sample B	20.6	19.2	20.2	6	4	0	108	100	106
PACS-2 (310±12)	304	308	305	2	1	0	99	100	99
PP 1995-3, sample C Sediment	21.7	22.4	21.3	1	4	0	97	100	95
SL-4 (713±26)	677	701	680	1	7	0	97	100	97
SL-11	107687	100228	107449	2	0	0	107	100	107
Solid-5 (2004-7), Sludge 7	293	288	299	1	1	2	102	100	104
Solid-5 (2002-5), sludge 5	597	607	596	3	26	5	98	100	98
CW-1	661	637	662	2	2		104	100	104
CW-5	67.3	73.7	75.3	1	1	3	91	100	102
Compost KH	91.8	86.7	99.5	9	3	24	106	100	115

PACS-2 and SL-4 – certified reference materials – assigned value are indicated. The analyses are performed on ICP-OES.

Zinc

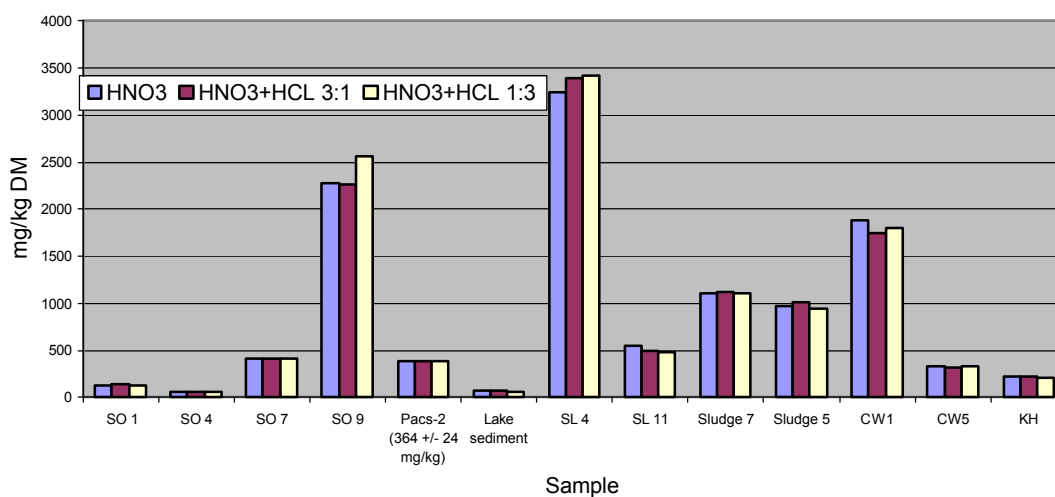


Fig 4. Comparison of microwave oven digestion methods: Method A (HNO₃), Method B (HNO₃+HCl – 3+1) and Method D (HNO₃+HCl – 1+3)

4.3.5 Chromium

Extraction efficiency for chromium for Method A, Method B and Method D was 55%, 63% and 73% for the certified reference material PACS-2 (Sediment). Method A gives significantly lower results than Method B and significantly lower results than does Method D - aqua regia for all samples, except one sludge sample (SL4).

Figure 6 show the results for soil (SO-4), sludge (SL4) and compost (CW1 and CW5) samples where another laboratory (NUA) is involved in the digestion and analyses. Results from NUA are reported in /8/. Compared to figure 5 analyses from using closed vessel microwave digestion (here referred to as Method D) and conventional aqua regia thermal heating are added. The between laboratory uncertainty component (from both digestion and analyses) need to be taken into account for the judgement if the differences in the overall results. For SO4 (soil) it is seen that the significant difference between nitric acid and aqua regia digestion as observed above may not be “visible” when chromium results from more laboratories are involved or when other heating procedures are used (e.g. thermal heating). In other words a laboratory comparison with more laboratories may show that the differences as seen when all procedures are carried out in one laboratory may not be significant when the total reproducibility is taken into account.

Table 12 Results from microwave oven digestion by methods A, B and D – Chromium.

Sample ID	Average (mg/kg DM) Method			CV % Method			Results in % of B		
	A	B	D	A	B	D	A	B	D
Soil SO 1	33	41	47	2	4	1	80	100	114
Soil SO 4	22	28	35	3	4	5	79	100	124
Soil SO 7	172	198	224	2	2	2	87	100	113
Soil SO 9	536	611	678	2	12	6	88	100	111
Pacs-2 (90.7)	51	57	66	3	5	6	89	100	115
PP 1995-3, sample C Sediment	9	10	13	3	3	18	89	100	134
SL 4	468	480	466	1	7	1	97	100	97
SL 11	65	77	81	5	2	5	83	100	104
Solid-5 (2004-7), Sludge 7	29	35	35	2	14	2	83	100	99
Solid-5 (2002-5), Sludge 5	26	32	33	2	29	4	81	100	104
CW-1	138	212	230	6	2		65	100	108
CW-5	98	299	316	23	2	6	33	100	106
Compost KH	14	20	22	19	13	27	69	100	108

The analyses are performed on ICP-OES.

Chromium

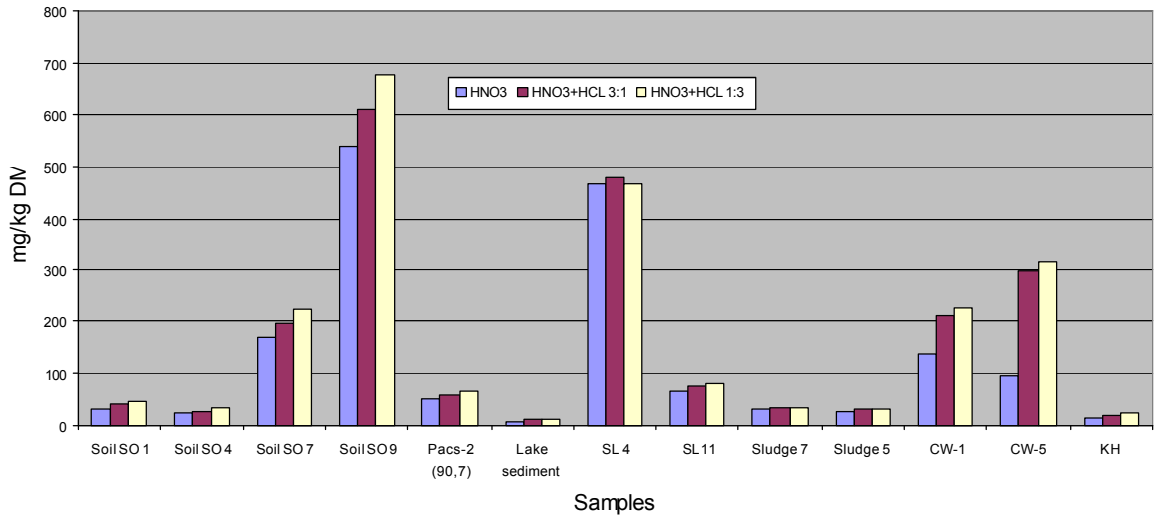


Fig 5. Comparison of microwave oven digestion methods: Method A (HNO₃), Method B (HNO₃+HCl-3+1) and Method D (HNO₃+HCl-1+3)

Chromium nitric acid - aqua regia, different energy input

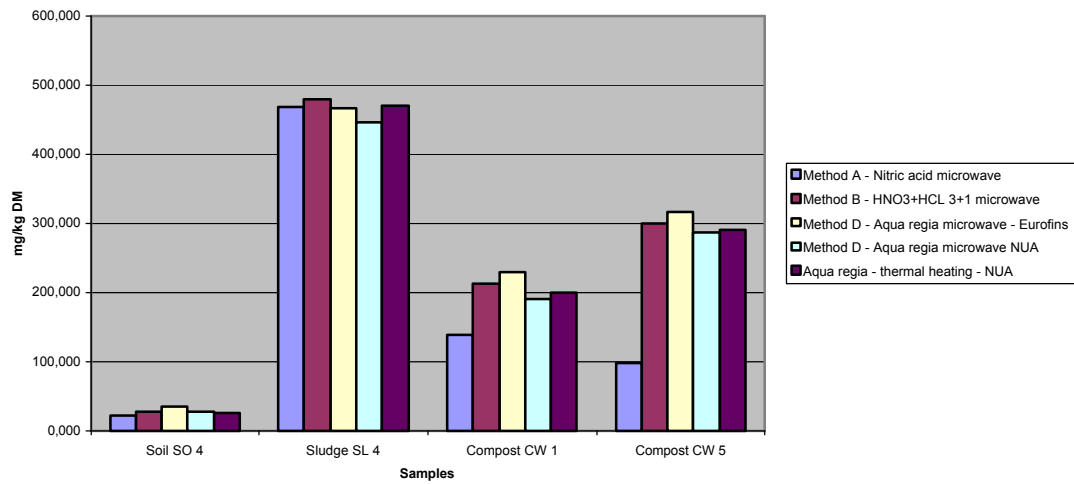


Fig 6. Comparison of different microwave oven digestion methods: Method A, Method B and Method D and conventional aqua regia thermal heating. Results from Method D are shown for two different laboratories.

4.3.6 Manganese

Method A, Method B and Method D extract what corresponds to 60%, 68% and 79%, respectively, of the assigned value for the certified reference material PACS-2 (Sediment). For three of the four soil samples, Method A extracts significantly less than Method D (aqua regia). Method B extract less than Method D (aqua regia). This can be seen from Table 5 and is illustrated in Figure 7 (the first 6 sample). When results from one other laboratory is included for soil sample SO4 the significant difference “disappears”, indicating that differences may not be encountered or may not be significant when comparing results from more laboratories. This is illustrated in Figure 8.

The results from extraction of manganese by the three different extraction mixtures and methods generally show good agreement for the sludge and compost samples. For the sludge reference material (SL-4) the three methods extract corresponding to 100 % of the assigned value. The Figure 8 illustrates that the results from using Method D (aqua regia) may exhibit variations in the order of magnitudes encountered when comparing results from using different methods. The variations are further investigated in the coming interlaboratory comparison.

Table 13 Results from digestions by Methods A, B and D – Manganese. Digestions are carried out in triplicate for Methods A and B and in duplicate for Method D. Analyses are carried on ICP-OES.

Sample ID	Average (mg/kg DM) Method			CV % Method			Results in % of B		
	A	B	D	A	B	D	A	B	C
SO-1	695	745	818	1	2	0	93	100	110
SO-4	314	316	358	1	1	3	99	100	113
SO-7	857	877	955	2	1	1	98	100	109
SO-9	1075	1078	1110	1	4	2	100	100	103
PACS-2 (440±19)	266	289	340	1	3	3	92	100	117
PP 1995-3, sample C Sediment	61	66	105	6	3	25	92	100	160
SL-4	448	457	439	1	7	1	98	100	96
SL-11	620	606	611	2	1	3	102	100	101
Solid-5 (2004-7), Sludge 7	219	217	224	0	1	1	101	100	104
Solid-5 (2002-5), sludge 5	407	418	412	3	28	1	97	100	99
CW-5	854	891	884	1	2		96	100	99
CW-1	1013	968	1034	1	2	5	105	100	107
Compost KH	722	668	864	9	6	10	108	100	129

Manganese

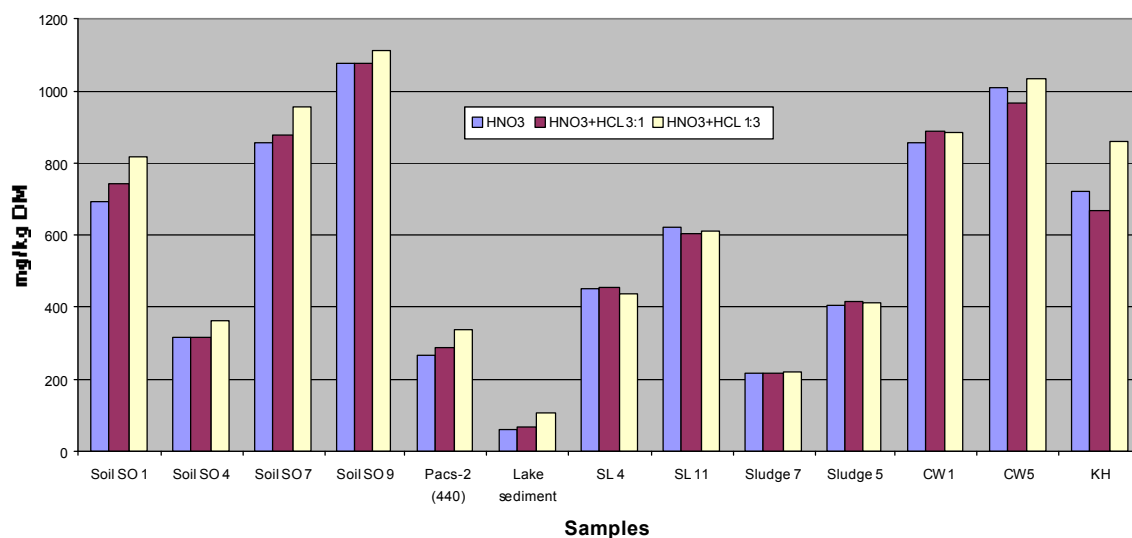


Fig 7. Comparison of microwave oven digestion methods: Method A (HNO₃), Method B (HNO₃+HCL-3+1) and Method D (HNO₃+HCL-1+3)

Manganese - nitric acid - aqua regia, different energy input

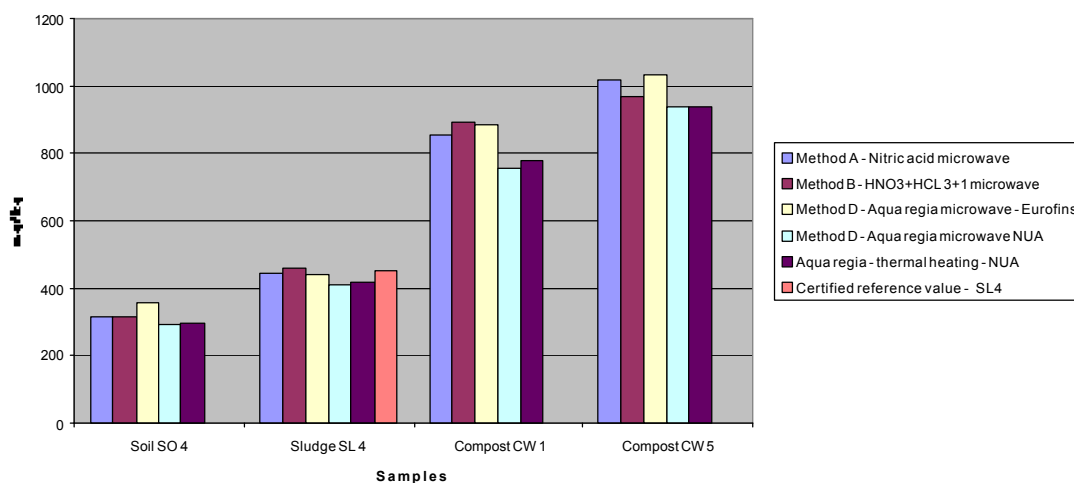


Fig 8. Comparison of different microwave oven digestion methods: Method A, Method B and Method D and conventional aqua regia thermal heating. Results from Method D are shown for two different laboratories

4.3.7 Nickel

The extraction efficiency of Method A is apparently slightly less, in general, than the extraction efficiency for Method B and D for nickel. The three methods extracts what corresponds to 100% of the assigned value for the sediment reference material PACS-2 and the sludge reference material SL-4 (it is anticipated that the laboratory uncertainty is slightly larger than actually measured). The differences seen for the soil samples are significant, but this is not the case for the other sample types. The results for the soil samples for Method A and D deviates less than 20 %.

Table 14 Results from microwave oven digestion by methods A, B and D.

Sample ID	Average (mg/kg DM) Method			CV % Method			Results in % of B		
	A	B	D	A	B	D	A	B	D
SO-1	36.1	39.0	37.9	5	3	0	92	100	110
SO-4	14.7	14.7	17.6	6	4	2	101	100	113
SO-7	198	208	217	2	1	1	95	100	109
SO-9	541	562	581	1	5	2	96	100	103
PACS-2 (39.5±2.3)	39.2	39.7	42.1	1	3	1	99	100	117
PP 1995-3, sample C Sediment	6.4	6.3	5.6	11	26	2	102	100	160
SL-4 (942±22)	983	993	948	1	6	0	99	100	96
SL-11	1788	1847	1700	6	0	2	97	100	101
Solid-5 (2004-7), Sludge 7	33.6	34.0	34.3	3	8	2	99	100	104
Solid-5 (2002-5), Sludge 7	17.6	19.2	19.3	6	24	3	92	100	99
CW-5	189	233	248	2	1		81	100	99
Compost KH	14.6	18.4	19.3	14	8	26	79	100	129

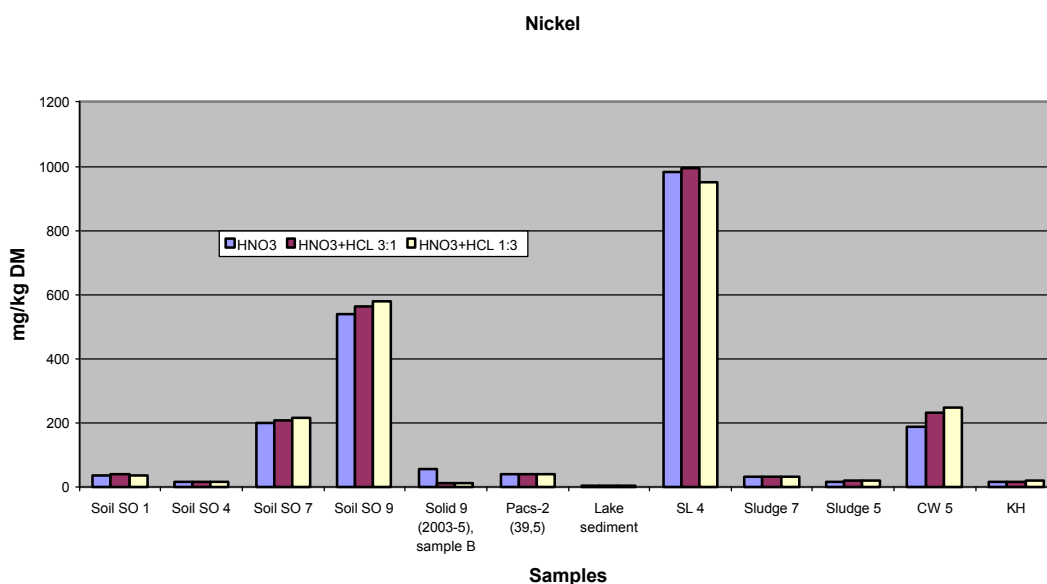


Fig 9. Comparison of microwave oven digestion methods: Method A (HNO₃), Method B (HNO₃+HCl- 3+1) and Method D (HNO₃+HCl- 1+3)

4.3.8 Lead

The results from extraction of lead using the three different extraction mixtures and methods show in general good agreement. All three methods extract close to 100 % compared to the assigned value for one sediment reference material (PACS-2) and one sludge reference material (SL-4).

Table 15 Results from microwave oven digestion by methods A, B and D – Lead.

Sample ID	Average (mg/kg DM) Method			CV % Method			Results in % of B		
	A	B	D	A	B	D	A	B	D
SO-1	47.8	47.6	47.4	2	2	2	101	100	100
SO-4	34.6	33.7	40.8	3	7	17	103	100	121
SO-7	82.5	82.6	80.9	4	3	2	100	100	98
SO-9	286	285	284	1	4	0	100	100	100
Solid-9 (2003-5), Sample B	29.0	31.6	33.4	5	10	2	92	100	106
PACS-2 (183±8)	187	182	181	2	2	1	103	100	99
PP 1995-3, sample C Sediment	18.9	16.8	16.9	2	16	1	112	100	100
SL-4 (495±19)	477	489	462	1	7	1	98	100	95
SL-11	10151	9924	10277	2	0	2	102	100	104
Solid-5 (2004-7), Sludge 7	103	105	106	2	5	0	98	100	101
Solid-5 (2002-5), sludge 5	87.1	76.3	87.3	6	18	2	114	100	114
CW-1	1704	1629	1611	1	1		105	100	99
CW-5	106	94.9	102	9	4	1	112	100	107
Compost KH	44.6	46.4	45.4	6	7	12	96	100	98

Lead

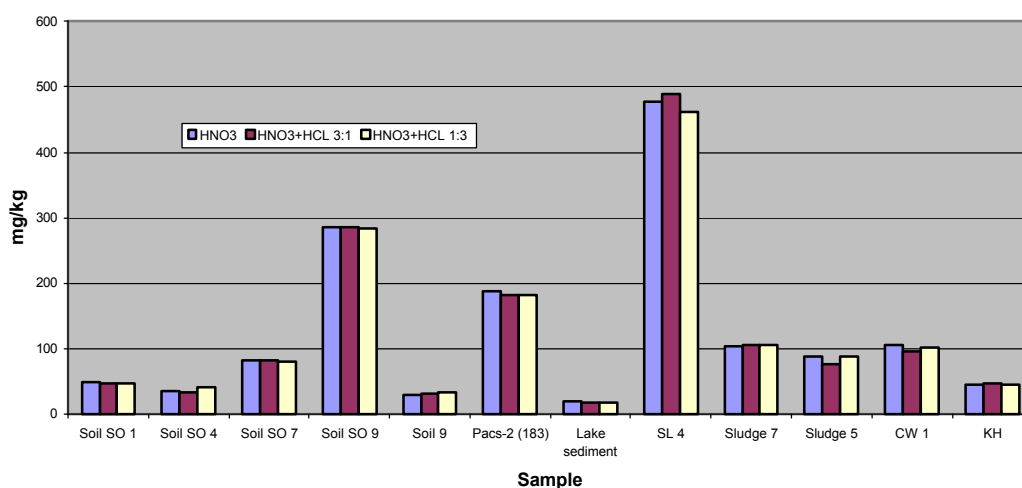


Fig 10. Comparison of microwave oven digestion methods: Method A (HNO₃), Method B (HNO₃+HCl – 3+1) and Method D (HNO₃+HCl – 1+3)

4.3.9 Zinc

The results from extraction of zinc using the three different extraction mixtures and methods show in general good agreement. The three methods extract close to 100 % (104 to 110 %) compared to the assigned values for one sediment sample (PACS-2) and for one sludge reference material SL-4 (103 to 108 %).

Table 16 Results from microwave oven digestion by methods A, B and D – Zinc.

Sample ID	Average (mg/kg DM) Method			CV % Method			Results in % of B		
	A	B	D	A	B	D	A	B	D
SO-1	126	137	124	1	8	0	92	100	90
SO-4	56	58	60	2	6	1	96	100	103
SO-7	415	420	413	2	0	0	99	100	98
SO-9	2283	2259	2558	1	4	2	101	100	113
PACS- 2(364±23)	392	387	384	2	4	1	101	100	99
PP 1995-3, sample C Sediment	70	70	65	8	6	3	100	100	93
SL-4 (3143±103)	3247	3397	3421	2	6	0	96	100	101
SL-11	550	495	476	2	1	3	111	100	96
Solid-5 (2004-7), Sludge 7	1107	1115	1109	1	1	1	99	100	99
Solid-5 (2002-5), Sludge 5	969	1016	944	2	28	2	95	100	93
CW-1	1884	1740	1805	1	1		108	100	104
CW-5	337	317	331	2	2	5	106	100	104
Compost KH	218	220	216	11	1	22	99	100	98

Zinc

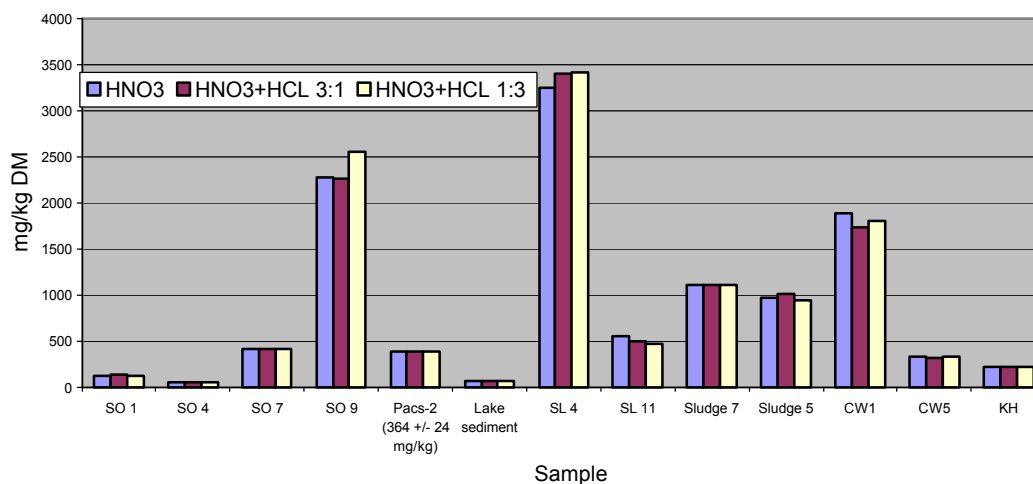


Fig 11. Comparison of microwave oven digestion methods: Method A (HNO_3), Method B ($HNO_3+HCl-3+1$) and Method D ($HNO_3+HCl-1+3$)

4.3.10 Other elements

Results from the analyses of other elements than mentioned above can be seen in Annex 2 and are summarized below.

Magnesium and calcium: The results indicate that the magnesium and calcium results from the three different digestion techniques are comparable.

Sodium and potassium: Especially for potassium, the results exhibit large variations, which partly invalidate a clear conclusion. The results indicate that the use of nitric acid alone and the use of mixtures of nitric acid and hydrochloric acid give no significant differences.

Barium and strontium: It is likely that a slight acid effect (hydrochloric acid) can be seen for some of the soil sample analyses. However, for the other matrices the results are comparable. The extraction efficiencies for strontium are 28%, 33% and 40% for one PACS-2 sediment reference material.

Vanadium, aluminium and chromium and strontium: An effect of hydrochloric acid is seen; higher results are shown when hydrochloric acid is added to nitric acid (nitric acid:hydrochloric acid 3:1) compared to nitric acid alone. There is a tendency towards even higher results (however, not significant for all samples) for some samples, when aqua regia is applied (nitric acid:hydrochloric acid 1:3) – compared to nitric acid:hydrochloric acid 3:1. The extraction efficiencies for vanadium are 55%, 66% and 80% for one PACS-2 sediment reference material. These are comparable with the figures obtained for chromium (Section 4.3.5).

Silver, thallium, antimony, molybdenum and iron: The results show according to /6/ that, for these elements, mixtures of nitric acid and hydrochloric acid have a larger extraction efficiency than nitric acid alone. For thallium, the nitric acid:hydrochloric acid 3:1 mixture has a higher extraction efficiency than the aqua regia method using the nitric acid:hydrochloric acid 1:3 mixture.

Table 17 gives an overview of results obtained from analyses of certified reference material (Harbour sediment) for all three methods applied (Methods A, B and D). The results are in accordance with the similarities and differences stated above.

Table 17 Results from digestions by Methods A, B and D compared to the certified value for NRCC-PACS-2 sediment sample.

	A Microwave- Nitric acid	B Microwave- Nitric acid + hydrochloric acid	D Microwave- Nitric acid + hydrochloric acid	Certified value
Ag	1.69	1.62	1.22	1.22±0.14
As	25	28.5	27	26.2±1.5
Cd	2.18	3.15	2.95	2.11±0.15
Co	10	11	13	11.5±0.3
Cr	51	57	66	90.7±4.6
Cu	304	308	305	310±12
Mn	266	289	340	440±19
Ni	39	40	42	39.5±2.3
Pb	187	182	181	183±8
Sr	79	91	110	276±30
V	79	95	115	144±5
Zn	392	387	384	364±23

5. CONCLUSIONS AND RECOMMENDATIONS

The present report contains an evaluation of a draft standard (herein named Method A) describing a high-temperature microwave digestion method for the extraction of elements by using nitric acid as extraction agent. The method has been compared to one other method using nitric acid as extraction medium – “the autoclave method (herein referred to as Method C). Furthermore, the extraction efficiency of Method A has been compared to the extraction efficiency for two other microwave digestion methods: Method B using a mixture of nitric acid and hydrochloric acid (3+1) and Method D using aqua regia (nitric acid and hydrochloric acid (1+3)). The conclusions and recommendations of the study are as follows.

5.1 Robustness

The proposed high-temperature microwave digestion method, with the use of nitric acid, is shown to be robust for the conditions and elements investigated. The uncertainties observed in the ruggedness study are for the major part due to random error. The elements **barium, cadmium, cobalt, copper, manganese, sodium, lead, strontium and zinc** showed neither positive nor negative effect from any of the tested conditions. **Chromium and vanadium** showed for some samples a possibly weak effect depending on amount of acid, temperature and heating time. Chromium and vanadium are only partly extracted by nitric acid and it is considered that these elements may be more sensitive to variations in the extraction conditions than other element. For the major part of the samples, the variations encountered in the ruggedness study for chromium and vanadium were considered satisfactory. For **nickel**, weak positive effects could possibly also be observed for temperature and heating time; however, the variations for nickel were generally small. The results indicate that control of temperature may possibly influence the variations for nickel.

The digestion method (Method A) is considered to be a robust method for the elements tested. The results did not indicate a need for changes to the conditions described in the method. However, as slight indications of effects for some elements were possibly detected, it is the recommendation that the conditions as described in the method be followed.

The uncertainties seen for the elements tested in the ruggedness study were, with a few exceptions, low (1–8%). As the ruggedness tests mimic the conditions expected varying from one laboratory to the other, total digestion uncertainties of the same magnitude for the proposed method examined are expected. A study of the digestion uncertainty can be accomplished by including digested solid samples along with the solid samples in an interlaboratory comparison.

5.2 Comparison between microwave and autoclave methods

A number of soil, sludge, sediment, and compost samples were digested using the previously proposed nitric acid - autoclave digestion method (Herein referred to as Method C). The digests were analysed for a number of elements and the results are compared to the results from digestion of the same samples using the proposed microwave digestion method, Method A.

The results indicate that there is a fairly good agreement between Method A and Method C data. The results for arsenic, barium, cadmium, chromium, cobalt, copper, manganese, nickel, lead, strontium, vanadium and zinc show no significant differences of the average values. Exceptions to this conclusion are chromium results in two compost samples and nickel results in one compost sample.

5.3 Comparison between nitric acid and mixtures of nitric acid and hydrochloric acid used as extraction media – microwave oven

A number of soil, sludge, sediment and compost samples were digested by microwave oven technique using nitric acid (Method A), a mixture of nitric acid and hydrochloric acid ($\text{HNO}_3 + \text{HCl } 3+1$) (Method B) and aqua regia (Method D) as extraction media. The analyses were carried out in one single laboratory.

The results from digestion of arsenic by the use of the three different microwave oven techniques and different acid combinations are in good agreement for the samples investigated for **arsenic, cadmium, cobalt, copper, lead and zinc**.

The extraction efficiency for **nickel** is apparently lower for Method A and B than for Method D. This is not confirmed for the analyses of the certified reference materials, where all the three methods extract 100% of the assigned values. When results from extraction of analyses in a different laboratory are taken into account the apparent differences disappear, as the uncertainty between analyses in different laboratories is higher than the apparent differences in extraction efficiency.

The extraction efficiency for **chromium, manganese and vanadium** are significantly less than the assigned values for one sediment reference material. Extraction efficiency for chromium for Method A, Method B and Method D were 55%, 63% and 73% for one certified sediment reference material. The corresponding extraction efficiency for manganese were 60%, 68% and 79% and the corresponding extraction efficiency for vanadium were 55%, 66% and 80%. The results indicate that the higher the concentration of hydrochloric acid compared to nitric acid concentration, the higher yield. However, all three methods only extract a partial amount of the total content of the elements (Less than 80%). The same hydrochloric acid effects are also observed for **aluminium**. The addition of hydrochloric acid in a lower concentration (Method B) compared to aqua regia does not result in extracted amounts of these elements that are comparable to aqua regia extraction. Thus an argument of implementing a method B to compensate for the lower extraction efficiency for the nitric acid method (Method A) compared to the aqua regia method (Method D) can not be justified for the analyses carried out for those elements in this study.

The elements chromium, manganese, vanadium and aluminium are only partly extracted by nitric acid or aqua regia. The ruggedness test pointed at a higher sensitivity for chromium and vanadium to small differences in temperature and holding time (i.e. energy input). It is most likely, that this effect will also influence the overall uncertainty when digestion is being carried out in different laboratories – thus resulting in a larger uncertainty component from digestion for these elements than for other elements. This may be expected when the same heating principles are used (and controlled); however, the energy effects (and corresponding uncertainty) are expected to be higher when different heating principles are used (different energy input and different acid combinations).

For **barium and strontium** slight hydrochloric acid effects as mentioned above can be seen for some samples (soil samples) but not for sludge and compost samples.

The results from using the three different microwave techniques for extraction of the major components, **magnesium, calcium and sodium**, indicate that the extracted amounts are comparable.

The results for **silver, thallium, antimony, molybdenum and iron show that** mixtures of nitric acid and hydrochloric acid have larger extraction efficiencies than nitric acid alone. For thallium, the nitric acid:hydrochloric acid 3+1 mixture has a higher extraction efficiency than the aqua regia method.

6. REFERENCES

1. K.J.Andersen and M.I Kisser. “Digestion of Solid Matrices – Desk study Horizontal” March 2004. www.ecn.nl/horizontal.
2. Chemical Analyses – Digestion of sediment, sludge, soil, biowaste and waste for the extraction of nitric acid soluble fraction of elements. www.ecn.nl/horizontal. - draft desk studies 1st set.
3. Chemical Analyses – Digestion of soil, sludge and biowaste and waste for the extraction of aqua regia soluble fraction of elements. www.ecn.nl/horizontal draft desk studies 1st set.
4. Youden, W.J. & E.H. Steiner: Statistical manual of the AOAC, Published by AOAC International. 1975.
5. Gawlik, B.M., F. Bo, F. Sena, L. Roncari, G. Locoro & R. Vivian: Characterisation of “Playground” samples to be used in the context of Project “Horizontal”. Part 1: Inorganic parameters. SWCR-Report No 03/07/2004.
6. EPA metode 3051A. Microwave assisted acid digestion of sediments, sludges, soils and oils.
7. Solid materials – Microwave digestion of sediment, sludge, soil and biowaste for the extraction of nitric acid soluble fraction of elements. www.ecn.nl/horizontal [consultation](#) phase II
8. M.I Kisser. “Digestion of solid matrices – Part 1: Digestion with aqua regia – Report of evaluation study. December 2005. www.ecn.nl/horizontal/
9. Solid materials – Digestion of sludge, soil, bio waste and waste for the extraction of aqua regia soluble fraction of elements. www.ecn.nl/horizontal - [consultation](#) phase II
10. Certificate of BCR-144 (SL-4), Community Bureau of Reference, Commission of the European Communities