Digestion of solid matrices
Part 1: Digestion with Aqua Regia

Report of evaluation study

Monika I.Kisser

NUA-Umweltanalytik GmbH, Austria

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.

Cooperation in practical work has taken place with Fernwärme Wien, where the open microwave digestion has been conducted and UBA Vienna, where experiments with high temperature digestions were conducted. Cooperation with Ricarda Koopmann of "Landesbetrieb Hessisches Landeslabor, Kassel (LHL, Kassel)" had taken place by changing digested solutions.

CONTENTS

LIST OF TABLES

LIST OF FIGURES

SUMMARY

The present report describes the robustness study for aqua regia digestion in the project HORIZONTAL. The three methods for aqua regia digestion described in the horizontal draft standard (2), thermal heating, closed microwave digestion and open microwave digestion were used for the digestion of different samples of compost, sludge and soil prepared by JRC (4). Statistical evaluation of the data and comparison of the three methods within limits for deviation of 10% respectively 20% have been done. The influence of performance parameters as digestion time, temperature, mass of test portion and particle size has been evaluated in this study.

The experiments pointed out clearly that slight variations of performance parameters as well as the choice of the heating method have little influence on the analytic results for sludge and treated biowaste samples. But for some kinds of soil, especially clay soil, all these factors influence evidently the measured contents of elements. Similar effects have been found for refractory matrices during validation of EN 13657 and should be expected because of the chemical reaction taking place during digestion with aqua regia.

The aqua regia digestion method is empirical and it might not release elements completely. However, for most environmental applications, the result is fit for purpose. It is not suitable for the digestion of refractory compounds such as SiO_2, TiO_2 and Al_2O_3; therefore it is more likely an extraction procedure than a digestion. Nevertheless aqua regia dissolves organic matrix and metals to a large amount but not refractory minerals and is therefore useful for environmental analysis, where the mineral composition of soil is not of interest. If the total content of elements for refractory matrices has to be analysed other methods as XRF analysis or digestion methods by the use of HF (18,23) or alkali fusion (19,20) have to be used (26,28).

As aqua regia digestion is an empirical method digestion condition have to be laid down in detail in a standard method. Users should be aware that variations of performance characteristics may lead to deviations of the results for refractory matrices.

As consequence of the robustness study the Horizontal draft standard (2) has been changed in some details:

- Method C “open microwave digestion” has been removed from the draft standard, as some results for soil samples indicate lower recovery than the other two methods
- Reaction time with aqua regia before digestion has been defined to be as short as necessary to let vigorous reaction occur
- Particle size of test portion was fixed with < 250µm
- Mass of test portion has been reduced
- Specification of digestion temperature at about 110°C to 120°C

1. INTRODUCTION

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

The revision of the Sewage Sludge Directive 86/278/EEC, the upcoming Directive on the Biological Treatment of Biodegradable Waste and the Soil Monitoring Directive calls for standards on sampling, on hygienic and biological parameters and on methods for inorganic and organic contaminants and for mechanical properties of these materials.

The work for developing horizontal and harmonised European standards is split up in coherent Work Packages (WP), each of which addresses a main aspect of all relevant standards required, or likely to be required, in EU regulations regarding sludge, biowaste and soil.

In many European countries, digestion methods used for solid environmental samples such as waste, sludge and soil are based on the use of aqua regia in accordance with the relevant European and International standards for the different areas. However, in some European countries, e.g. the Nordic countries, the digestion methods are primarily based on the use of nitric acid.

In the previous desk study on digestion of solid matrices (1) a detailed comparison of standards for the digestion prior to the determination of trace 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, however with a focus on digestion using aqua regia and digestion using nitric acid. If results from different methods are used and compared it is of vital importance that the methods used provide comparable results with a sufficiently high reproducibility for the elements and matter in question.

The present report describes the results of an evaluation study (Phase II) under WP 6: Inorganic Parameters: Evaluation of the draft horizontal standards for:

- Digestion of solid matrices part 1: Digestion by Aqua regia

Covering sludge, soil, treated biowaste and neighbouring fields.

2. DESCRIPTION OF THE EVALUATION STUDY

In the desk study on digestion of solid matrices (1) one major difference in the existing standards was identified. The ISO standard on aqua regia digestion of soil and the EN standard on digestion of soil improvers and growing media include only digestion by the use of hot-plate heating, while the EN standards on digestion of waste and sludge also include methods for microwave heating. To take into account the developments that have taken place in many European laboratories, the development of a harmonised horizontal standard that includes both hot-plate heating and microwave-oven heating (open and closed heating) was proposed (2). Data exist for waste and sludge samples that suggest that comparable data can be obtained, but for other matrices more investigations are needed.

2.1 Procedures of Aqua regia digestion

In this evaluation study digestions of soil, sludge and treated biowaste were carried out by using the three different methods (thermal heating, closed microwave, open microwave) described in the proposed draft standard on aqua regia digestion (2). To evaluate the ruggedness of the proposed methods small variations of the digestion conditions have been made. The influence of particle size on the grade of digestion has been studied on a soil sample (SO16R Eurosoil), as it is known from previous studies that organic matrices as sludge and biowaste are digested rather totally (1).

2.1.1 Thermal heating digestion with Aqua regia:

The procedure of method A of the draft standard (2) was followed by using of 3 g of test portion (respectively 1,5g at LHL KASSEL) and 30 ml of Aqua regia. The mixture was heated 2h under reflux conditions with condensation zone 1/3 the height of the condenser. More details are described in Annex 1.

2.1.2 Closed Microwave digestion with Aqua regia:

The procedure of method B of the horizontal draft standard (2) was followed (unless it was not changed due to ruggedness testing) with 0,2 to 0,5 g of test portion and 4 to 8 ml of aqua regia. More details are described in Annex 1.

Programme for a batch of 6 samples:

Table 1 Programme for closed microwave oven

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

After digestion the vessels were allowed to cool down, transferred quantitatively to a volumetric flask and filled to 25 respectively 50ml with doubled deionised water. Before measurement the sample was allowed to settle down.

Recording of temperature and pressure was done during digestion.

2.1.3 Open Microwave digestion with Aqua regia:

Procedure:
The method C described in the horizontal draft standard (2) was followed by using 0,5 g of sample and 24 ml of aqua regia. More details are described in Annex 1.

Programme for a batch of 2 samples

Table 2 Programme for open microwave digestion

Time (min)	Temperature(°C)
3	103
12	103
3	103
12	103

After digestion the vessels were allowed to cool down, transferred quantitatively to a volumetric flask and filled to 50ml with doubled deionised water. Before measurement the sample was allowed to settle down.

Measurement:

Instrument: ICP-OES. Optima 3000XL, Perkin Elmer

Sample Preparation: sample dilution with aqua regia in following Steps 10,100, 1000
Internal Standardisation with Ytterbium
Calibration in aqua regia matrix

2.2 Design of ruggedness study for Aqua regia digestion

In the previous studies (1,8,9,15,16) the following factors proved to have an evident influence on the grade of digestion especially for refractory matrices:

- Particle size
- Digestion temperature
- Time of digestion
- Reaction time before digestion
- Mass of test portion - Solid/liquid ratio (sample to acid)

Therefore different digestions with variations of these factors were made for the method A – thermal heating - and method B – closed microwave digestion of Horizontal draft standard (2). Method C – open microwave digestion - proved to lead to rather not comparable results, therefore no further ruggedness tests were conducted for this method. The digestions were performed in different laboratories with different ovens, in order to lead to a rather realistic picture of possible variations of digestion conditions.

2.2.1 Comparison of aqua regia digestion carried out in different laboratories:

Variations of time, temperature and mass of test portions were performed in different laboratories.

Table 3 Performed aqua regia digestions at NUA

Number of digestions performed by NUA						
Samples	grain size	number of digestions/ method	closed microwave	open microwave	conventional heating	Internal sample number
SO4 clay soil	<125µm	5	5	5	5	UB0114
SO13 soil	<2mm	5	5		5	UB0117
SO16 R Eurosoil	< 2mm	5	5	5	5	UB0118
CW1 compost	<125µm	5	5	5	5	UB0109
CW5 compost	<125µm	3	3		3	UB0110
SL4 sludge	<125µm	3	3		3	UB0111
SL11S sludge	<125µm	3	3			UB0112
Reference materials:						
CRM 143R	<125µm		3	3	3	
WQB 1	<125µm		3	3	3	

Additional to these digestions carried out by NUA, digests made by LHL Kassel, another cooperation partner of project HORIZONTAL, were sent to NUA for analysis. Because the results of the round robin test for the validation of EN 13657 (6, 9) have indicated that the performance in different labs may influence reproducibility, this gives opportunity to check this possible influence.
At LHL Kassel thermal heating digestions and closed microwave digestions were carried out. Before thermal heating or microwave digestion the samples were standing at room temperature over night. Closed microwave digestions were conducted in Teflon tubes with a digestion time of 30 minutes.

Table 4 Performed aqua regia digestions in Kassel

Number of digestions performed by LHL KASSEL						
Samples	grain size	number of digestions/ method	closed microwave	open microwave	conventional heating	Internal sample number
SO4 clay soil	<125µm	3	3		3	UB0223
SO13 soil	<2mm	3	3		3	UB0226
SO16 R Eurosoil	< 2mm	3	3		3	UB0224
CW1 compost	<125µm	3	3		3	UB0225

At Eurofins too several digestions with aqua regia according to method 2 of Horizontal draft standard (2) in addition to the nitric acid digestions have been performed:

Table 5 Performed aqua regia digestions at Eurofins

Samples	grain size	number of digestions/ method	closed microwave	open microwave	conventional heating
SO4 clay soil	<125µm		2		
SO1 Italian soil	<125µm		2		
SO7 Italian soil			2		
SO9 German soil	< 2mm		2		
CW1 compost	<125µm		2		
CW5 compost	<125µm		2		
SL4 sludge	<125µm		2		
SL11S sludge	<125µm		2		

For further ruggedness testing additional digestions have been performed at UBA Vienna. Variations of mass of test portions and the influence of temperature on the digestion grade of soil samples have been investigated.

Table 6 Performed aqua regia digestions at UBA Vienna

Samples	grain size	number of digestions/ method	closed microwave	remarks
SO4 clay soil	<125µm	3	3	0,3 g sample, method B (2)
SO4 clay soil	<125µm	3	3	0,5 g sample, method B (2)
SO4 clay soil	<125µm	3	3	0,3 g sample, higher temperature
SO4 clay soil	<125µm	3	3	0,5 g sample, higher temperature
SO16 R Eurosoil	< 2mm	2	2	0,3 g sample, method B (2)
SO16 R Eurosoil	< 2mm	2	2	0,5 g sample, method B (2)
SO16 R Eurosoil	< 2mm	2	2	0,3 g sample, higher temperature
SO16 R Eurosoil	< 2mm	2	2	0,5 g sample, higher temperature

The main differences of the closed microwave digestion procedures performed in different labs are shown in the table below.

Table 7 Performance characteristics of closed microwave digestion procedures at different labs

Performance characteristics	NUA	Kassel	UBA	Eurofins
Mass of test portion	500 µg	200-400µg	300-500µg	250-400 µg
Amount of aqua regia	8 ml	4-8 ml	8 ml	8 ml
Digestion time	20 min	15 min standing over night	20 min resp. 30 min	20 min Let stand until no visible gas
Digestion temperature	100 – 120 °C		100 °C, resp.185 °C	

More details of used procedures, apparatus and materials are described in Annex 1.

2.2.2 Influence of particle size

Investigations were carried out for soil samples in order to estimate the necessary and sufficient pre-treatment for the different matrices, and to verify their applicability in terms of optimised reproducibility. Special emphasise is given to the necessary particle size. Coherence with the relevant horizontal standard on pre-treatment of soil, sludge and biowaste is secured.
Robustness tests for the validation of EN 13657 (8) as well as pre-normative research (15) have shown, that for aqua regia digestion an influence of the particle size for refractory matrices has to be supposed. The influence of particle size on digestion with aqua regia was evaluated by using one of the soil samples, as the matrix soil seems to be a more refractory matrix. Eurosoil SO-16R was chosen for measuring the influence of particle size on recovery rates as this is a sample with well known characterisation available and a particle size of <2mm. the sample was milled and sieved at NUA to a grain size of < 500µm and < 100 µm with a ball mill of inert material (achat) used routinely for trace analysis of heavy metals.

Table 8 Particle size of soil SO-16R Eurosoil for digestion with aqua regia

Particle size	Number of digestions NUA/ thermal heating	Number of digestions NUA/ closed microwave	Number of digestions NUA/ open microwave	Number of digestions Kassel/ thermal heating	Number of digestions Kassel/ closed microwave
< 2mm	5	5	5	3	3
< 500 µm		5			
< 100 µm		5			

2.3 Comparison of three digestion methods

The focus of the study on aqua regia digestion was laid on the comparability of the three methods described in the draft Horizontal standard (2). These tests were mainly conducted at NUA, the samples used are visible in Table 3 Performed aqua regia digestions at NUA".
As the validation data of EN 13346 (7) and EN 13657 (6) have proven the comparability of the three methods for sludge samples and organic matrix(see validation data of EN 13657 in Annex 2), mainly soil and partly compost samples were used for these tests on comparison.

2.4 Statistical evaluation of data

The evaluation of the obtained analytical data was performed by statistical means. The elimination of outliers was done by Grubb's test, for each method the arithmetic mean, the standard deviation and the coefficient of variation were calculated by excel sheets. For the comparison of 2 different methods the F-test according to ISO 16489 with P-95% and the mean t-test were used. In case where comparison of 3 methods should be performed, analysis of variances proved to be applicable (25).

3. MATERIALS

Samples (so-called playground samples) for the evaluation study were samples made available through Work package 1. The general characteristics of the samples used in the evaluation study are described in (4) and the respective reports of interlaboratory comparisons (10, 14). A list of the samples used in this study is given in the following table:

Table 9 Characterisation of playground samples for aqua regia digestion

Sample id.		**Sample description**		**C_{org} wgt. %**
SO-4 (equivalent to BCR-144)		Clay soil, Speyer, Germany	Ball-milled and sieved < 125 µm	1,65
SO-13		Terra rossa, Spain	Air dried, identical to BCR-484, < 2 mm	1,69
SO-16R		uncontaminated soil, UK, EUROSOIL 3R, IRMM-433-3	Air dried, sieved < 2 mm	2,6
CW-1		Composted garbage, Munich, Germany	Dried and ball-milled	12,1
CW-5		Compost, Fulda, Germany		11,5
SL-4		Sewage sludge, domestic, Essen, Germany (= BCR 144)	Ball-milled and sieved < 125 µm	29
SL-11		Sewage sludge, electronic industry, Turin, Italy	Ball-milled and sieved < 125 µm	3,2

For control purposes and for checking the calibration status of the measurement device two additional certified reference materials, used normally for checking the routine analyses in the laboratory of NUA, were digested three times by each method and analysed. These reference materials are CRM-143R and WQB 1. The reference values are shown together with the results in Annex 2.

4. RESULTS:

4.1 Recovery rate of aqua regia digestion

The recovery rate of aqua regia digestion depends strongly on the matrix of the sample (1), it decreases the more refractory the matrix of the sample is. This fact has to be taken into account also when comparing different methods or the same method conducted in different labs. Small variations in pre-treatment or digestion conditions may influence the recovery rate especially in case of refractory matrices. This well known fact was also proven in the pre-normative research study and the robustness study of EN 13657 (6, 8) and can be seen by comparing the data obtained for aqua regia digestion with the results from characterisation study of the samples(4) too.

Table 10 Recovery rate of aqua regia digestion in comparison to total content measured by XRF

SO4 – Clay soil (Germany)				**SO13 – Terra Rossa (Spain)**			
Parameter	Aqua regia closed vessel	Total content – XRF*	Recovery rate %	Parameter	Aqua regia closed vessel	Total content – XRF*	Recovery rate
Cr mg/kg	26	110	23,6	Cr mg/kg	31	95	32,6
Cu mg/kg	13	77	16,9	Cu mg/kg	240	312	76,9
Hg mg/kg	0,25	0,64	39,1	Hg mg/kg	0,45	0,43	104
Ni mg/kg	14	75	18,7	Ni mg/kg	27	52	51,9
Pb mg/kg	41	81	50,6	Pb mg/kg	101	119	84,9
Zn mg/kg	52	290	17,9	Zn mg/kg	412	523	78,8
CW1 - Composted garbage				**SL4 – Sewage sludge**			
Parameter	Aqua regia closed vessel	Total content – XRF*	Recovery rate %	Parameter	Aqua regia closed vessel	Total content – XRF*	Recovery rate
Cr mg/kg	198	270	73,3	Cr mg/kg	445	729	61,0
Cu mg/kg	618	618	100	Cu mg/kg	636	645	98,6
Hg mg/kg	7,48	6,8	110	Hg mg/kg	1,57	1,39	113
Ni mg/kg	229	185	124	Ni mg/kg	872	956	91,2
Pb mg/kg	1661	1474	113	Pb mg/kg	476	580	82,1
Zn mg/kg	2002	1938	103	Zn mg/kg	2953	4033	73,2

* Results from characterisation study of JRC (4)

To check the trueness of the results obtained two certified reference materials were analysed at the same time together with the samples.

CRM 143 R (11) is a sewage sludge amended soil with certificates for total content as well as aqua regia soluble fractions. The results are in detail in Annex 2, Table A.2.4.2.

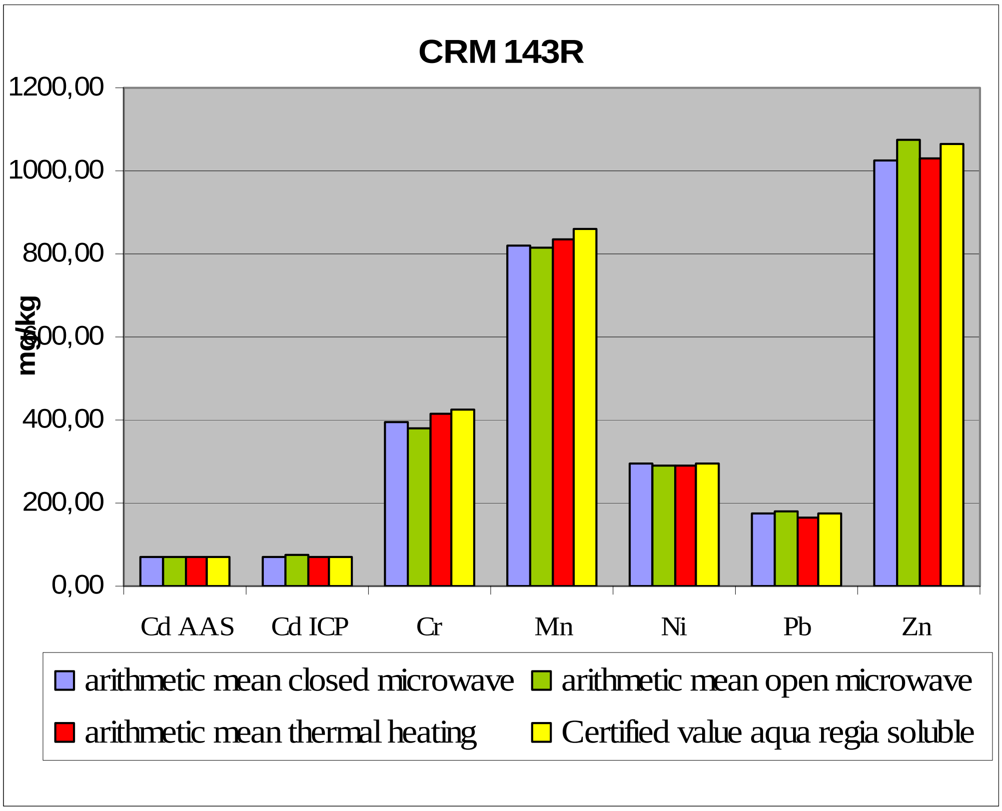

Figure 1 Recovery rate of certified reference material CRM 143R – a Sewage sludge Amended Soil

The second certified reference material used is Lake Ontario sediment of the National Water Research Institute of Canada (12). The results were compared with the "Recoverable" (or environmentally available) metals; according to the certificate are these data comparable to those produced by aqua regia methods and to those produced by EPA Method 3051.

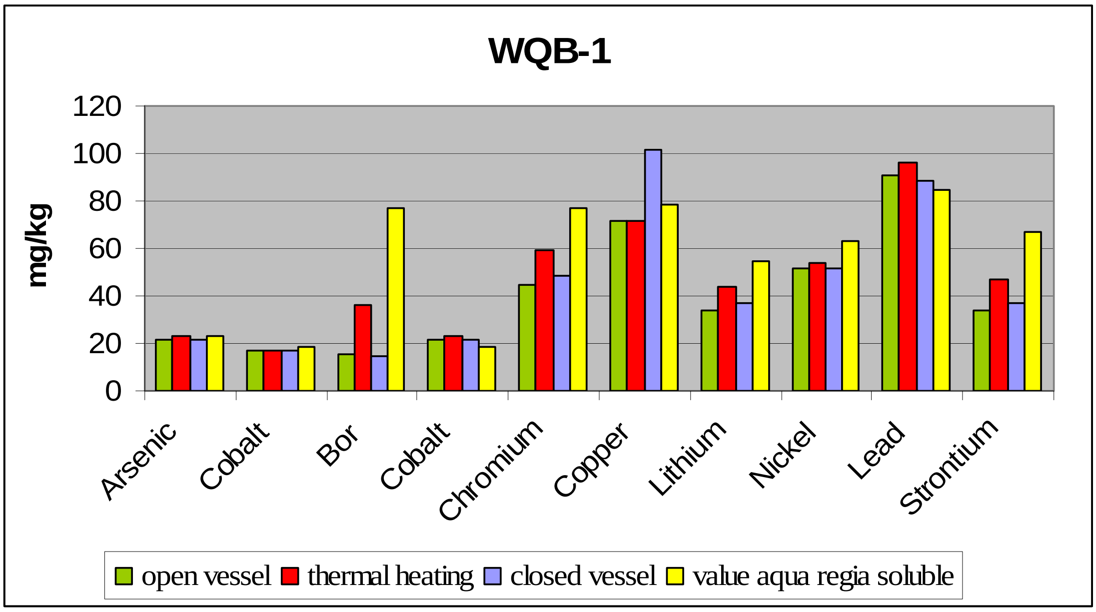

Figure 2 Recovery rate of certified reference material WQB-1 Lake Ontario Sediment

4.2 Results of ruggedness testing

As aqua regia digestion is not a method to obtain “true contents” of species, special care has to be taken to perform it as equal as possible in each laboratory to obtain equivalent results. In analysing digests produced in different labs with the same methods in one lab, it was tried to check these possible sources of error. Variations in sample pre-treatment - with exclusion of the influence of particle size for soil samples that proved to have an essential influence on recovery rate (8) - were not checked in this study, as this is another work item of project “Horizontal”.
As the thermal heating procedure is well known over years and the open microwave digestion proved to result in rather low recovery rates the ruggedness tests concentrated mainly on the closed microwave digestion (method B of draft horizontal standard, (2)).

4.2.1 Ruggedness testing of method A of horizontal draft standard, thermal heating digestion – influence of reaction time before heating

For the thermal heating procedure (method A of horizontal draft standard, (2)) only the influence of immediate digestion (NUA) versus overnight standing (Kassel) before heating were evaluated with the help of the statistical means of variance analysis:

Table 11 Thermal heating digestion of CW1 – Influence of letting sample stand overnight

Element		**Results in mg/kg**					**Statistic evaluation**
Cadmium	NUA	6,1	6,1	5,8	6,0	6,0	
	Kassel	5,8	6,1	6,0			
Cobalt	NUA	14,7	15,1	14,4	14,3	14,9	
	Kassel	14,7	13,8	13,6			
Chromium	NUA	194,1	193,3	195,3	199,8	194,7	
	Kassel	201,1	205,3	205,5			significant difference
Copper	NUA	644,0	709,3	720,0	706,7	622,0	
	Kassel	592,7	581,7	706,7			
Nickel	NUA	238,7	246,7	244,0	250,0	248,0	
	Kassel	253,3	252,7	240,7			
Lead	NUA	1653,3	1626,7	1673,3	1680,0	1660,0	
	Kassel	1720,0	1746,7	1746,7			significant difference
Zinc	NUA	1838,0	2028,7	2033,3	1940,0	1793,3	
	Kassel	1573,3	1413,1	1720,0			significant difference

Table 12 Thermal heating digestion of SO13 – Influence of letting sample stand overnight

Element		Results in mg/kg					Statistic evaluation
Cadmium	NUA	1,05	0,91	0,99	1,03	1,00	
	Kassel	1,34	1,24	1,46			significant difference
Cobalt	NUA	10,33	10,60	10,33	10,67	10,27	
	Kassel	7,80	6,47	7,47			significant difference
Chromium	NUA	33,33	33,67	34,53	33,87	33,67	
	Kassel	33,33	30,80	33,27			
Copper	NUA	252,00	240,67	246,00	246,00	240,00	
	Kassel	251,00	217,23	209,67			
Nickel	NUA	29,87	29,87	29,13	30,07	28,33	
	Kassel	27,10	23,27	28,20			significant difference
Lead	NUA	131,33	102,00	99,33	114,87	102,00	
	Kassel	261,90	105,80	130,17			
Zinc	NUA	457,07	444,67	434,00	450,60	433,33	
	Kassel	430,00	386,67	406,67			significant difference

The time how long the material is standing with aqua regia has an evident influence on the grade of digestion in compost and soil samples. **In consequence the time how long the acid/sample mixture is standing before heating has to be fixed in the draft standard.**

4.2.2 Ruggedness testing of method B of horizontal draft standard, closed microwave digestion

4.2.2.1 Influence of mass of test portion:

The differences for the same methods performed in different laboratories are shown in the tables in Annex 2 for the three types of matrices. In table A.2.5.1 comparison data of digestions in two labs for the sludge sample SL4 with mass of test portions of 0,5 g respectively 0,25-0,4 g is shown. As conclusion of the results of the sludge sample in this table it can be stated, that the relevant metals show little differences, only B, Na and K differ evidently, which may also be due to analytical differences, as the solutions were analysed in the respective labs.

Table 13 Closed microwave digestion of compost CW 1 - Influence of mass of test portion

Compost CW 1	**NUA 0,5 g**		**Kassel * 0,4 g**		**Eurofins 0,25-0,4 g**		
	arithmetic mean	**standard deviation**	**arithmetic mean**	**standard deviation**	**arithmetic mean**	**standard deviation**	**statistic evaluation**
Cadmium	5,47	0,22	6,10	0,77	5,09	1,57	
Copper	612	16,87	596	54	551	111	
Chromium	192	7,04	188	34	195	34,4	
Lead	1622	68,8	1451	604	1369	343	
Nickel	235	8,19	227	9,34	208	56	
Zink	1781	163	2372	43	1511	416	significant difference

*digestion time 15 minutes instead of 20 minutes, but power 850 W

The statistic evaluation of data was performed by variance analysis as shown for one parameter in this example:

Table 14 Example for variance analysis – compost sample CW1, Cadmium

CW1: results of the parameter Cadmium in mg/kg					
NUA ICP	5,81	5,35	5,28	5,32	5,58
Kassel ICP	6,92	5,97	5,41		
Eurofins ICP	3,99	6,20			

Variance analysis

Groups	*number*	*Sum*	*mean*	*Variance*
NUA ICP	5	27,34217	5,46843	0,050612
Kassel ICP	3	18,30119	6,1004	0,585262
Eurofins ICP	2	10,18663	5,09331	2,45448

differences	*(SS)*	*degrees of freedom (df)*	*(MS)*	*(F)*	*P-value*	*critical F-value*
between groups	1,34831	2	0,67415	**1,232957**	0,34776	**4,737414**
within groups	3,827452	7	0,54678			
overall	5,175762	9				

As the F-value lies under the critical F-value, no significant difference can be determined.

The mass of test portion for this experiment was varied in this way:
For the matrices sludge and compost no significant differences can be noticed for most elements even if the digestion is not carried out in the same way in the different labs.
For soil samples this is not the case in the same extent, as the following example shows:

Table 15 Mass of test portion for soil samples

	Mass of test portion in g
NUA	0,5
Kassel	0,4
Eurofins	0,25-0,4
UBA 1	0,3 / 0,5

Table 16 Variance analysis of closed microwave digestion of clay soil SO4 - Influence of mass of test portion

Soil SO 4	**Chromium mg/kg**				
NUA-0,5 g	21,4	22,4	21,7	21,7	23,0
Kassel-0,4 g*	31,9	33,6	34,5		
Eurofins- 0,25-0,4 g	35,9	33,2			
UBA 1-0,3 g	22,0	21,7	21,0		
UBA 1 – 0,5 g	24,0	22,5	24,3		

Variance analysis

Groups	*number*	*Sum*	*Mean*	*Variance*
NUA	5	110	22,0	0,4
Kassel	3	100	33,3	1,8
Eurofins	2	69	34,5	3,6
UBA 1 0,5 g	3	65	21,6	0,3
UBA 1 0,3 g	3	71	23,6	0,9

ANOVA

differences	*(SS)*	*(df)*	*(MS)*	*(F)*	*P-Value*	*critical F-Value*
between groups	460,7070287	4	115,1767572	**112,3321226**	7,67059E-09	**3,356690021**
within groups	11,27855773	11	1,02532343			
overall	471,9855865	15				

*digestion time 15 minutes instead of 20 minutes, but power 850 W

For most of the metals of clay soil SO4 the data of the different digestion procedures are not comparable. **As consequence the mass of test portion has to be fixed in a smaller range than in the draft Horizontal standard (2).**

4.2.2.2 Closed microwave digestion – Influence of digestion time and temperature

As described before and in more detail in Annex 1 the digestion time was varied at the different experiments performed in this study. While at NUA, Eurofins and at UBA for procedure 1 the instructions of method B of Horizontal draft standard were followed strictly and therefore a digestion time of 20 minutes was maintained, the digestion time in Kassel was 15 minutes and at UBA for procedure 2 it was 30 minutes.

In order to check the influence of digestion temperature it was measured where possible and varied at UBA to reach about 185°C (for mass of test portion=0,3 g) till 200°C for mass of test portion=0,5g).

The following figures show the temperature/pressure diagram of method B for the three sample types characterised in this study.

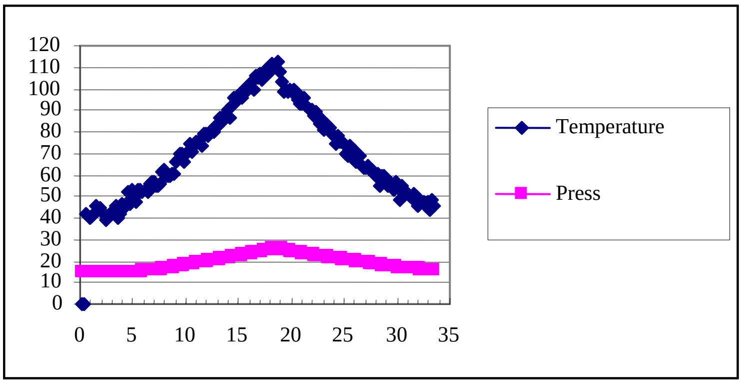

Figure 3 Example of temperature/pressure diagram of method B for the matrix composted garbage, CW1 (UB0109)

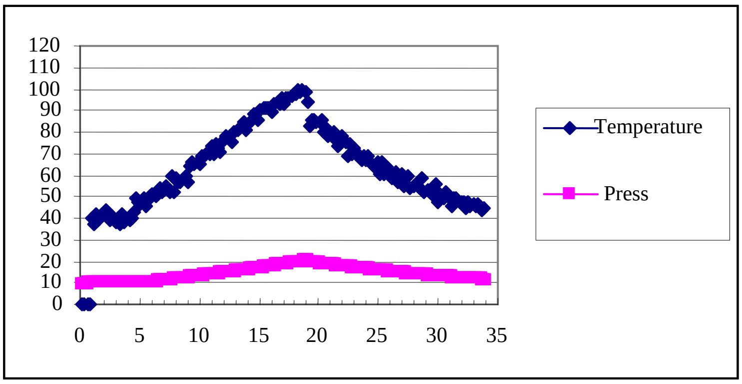

Figure 4 Example of temperature/pressure diagram for clay soil, SO4 (UB0114)

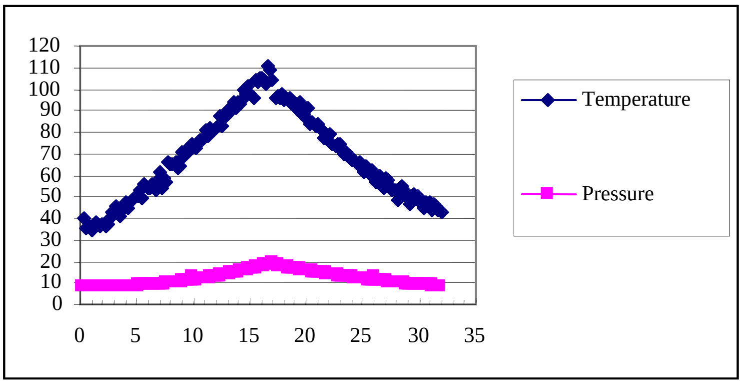

Figure 5 Example of temperature/pressure diagram for sludge, SL4 (UB0111)

For the exercises with high temperature following diagrams apply:

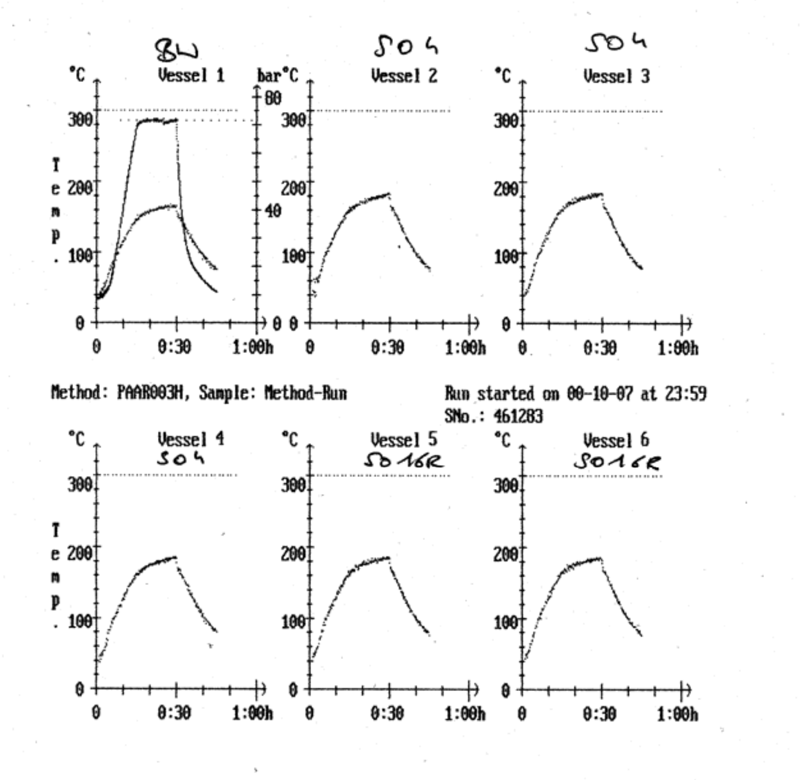

Figure 6 Temperature diagrams for soil samples digested at high temperatures (UBA procedure 2) with a mass of test portion of 0,3 g

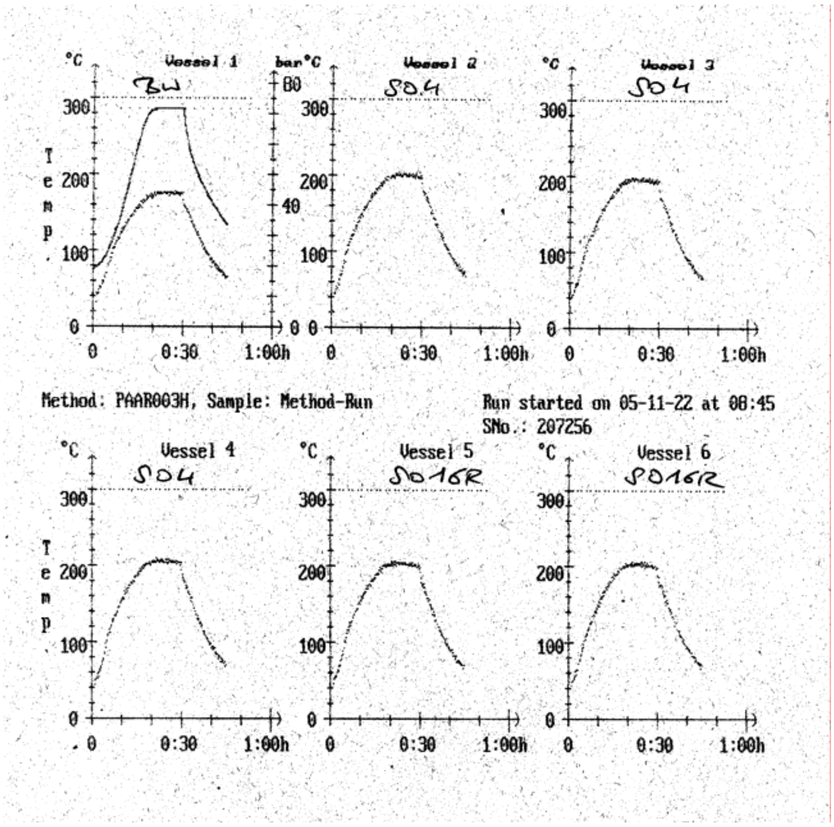

Figure 7 Temperature diagrams for soil samples digested at high temperatures (UBA procedure 2) with a mass of test portion of 0,5 g

The results of these exercises are listed in detail in Annex 2. In the following diagrams the single results for the relevant metals are shown in comparison with the thermal heating procedure.

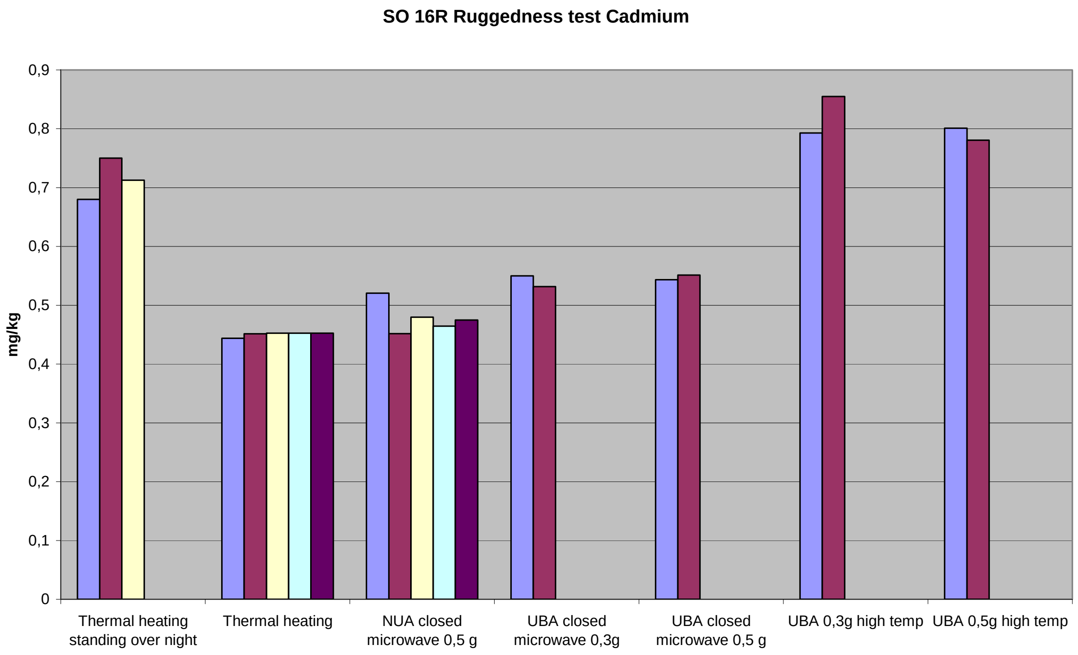

Figure 8 Comparison of different digestion methods for soil sample SO16R –Cadmium

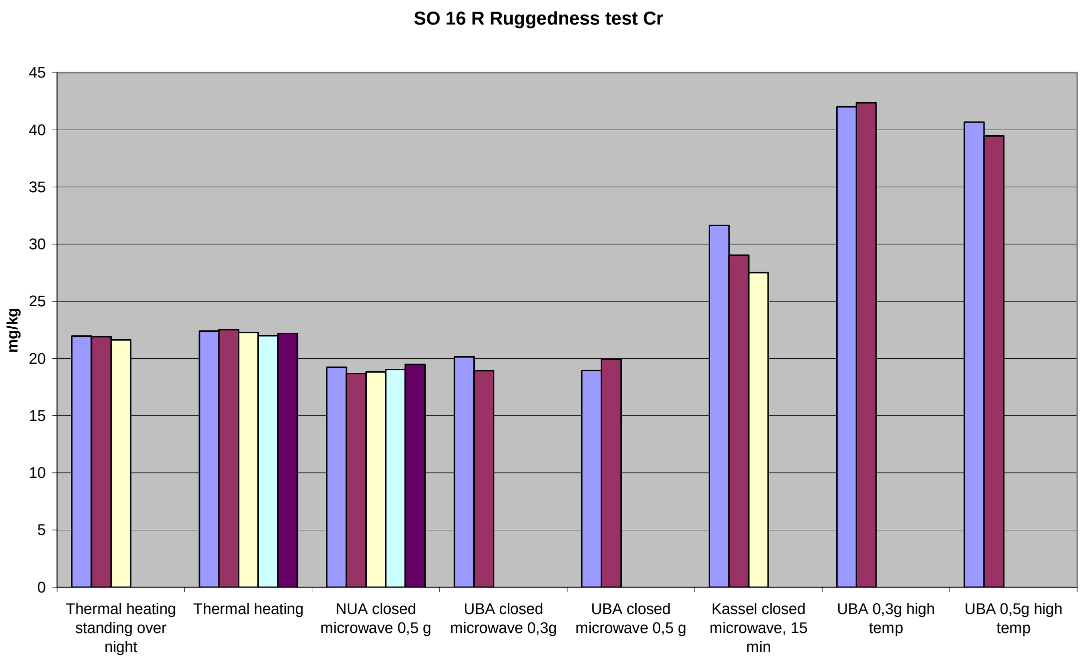

Figure 9 Comparison of different digestion methods for soil sample SO16R - Chromium

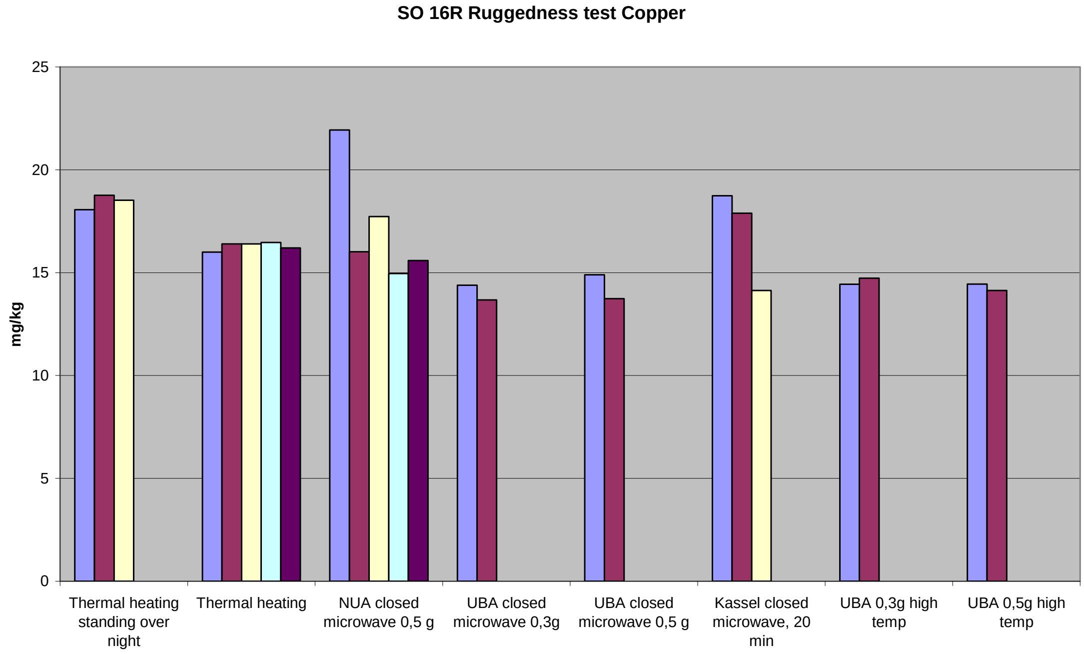

Figure 10 Comparison of different digestion methods for soil sample SO16R – Copper

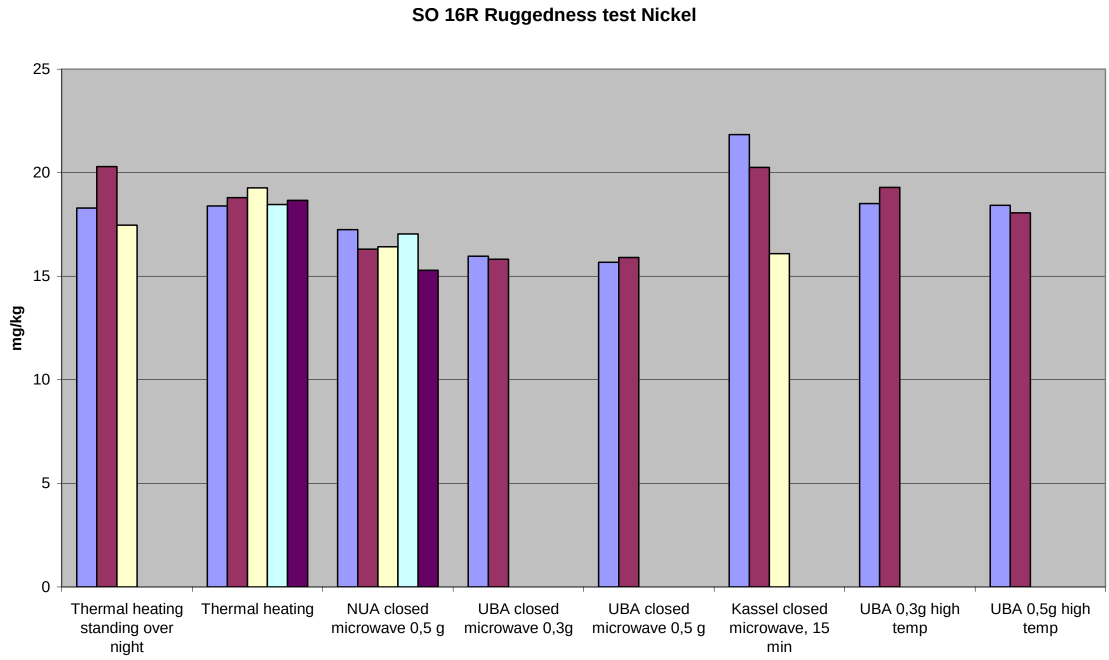

Figure 11 Comparison of different digestion methods for soil sample SO16R - Nickel

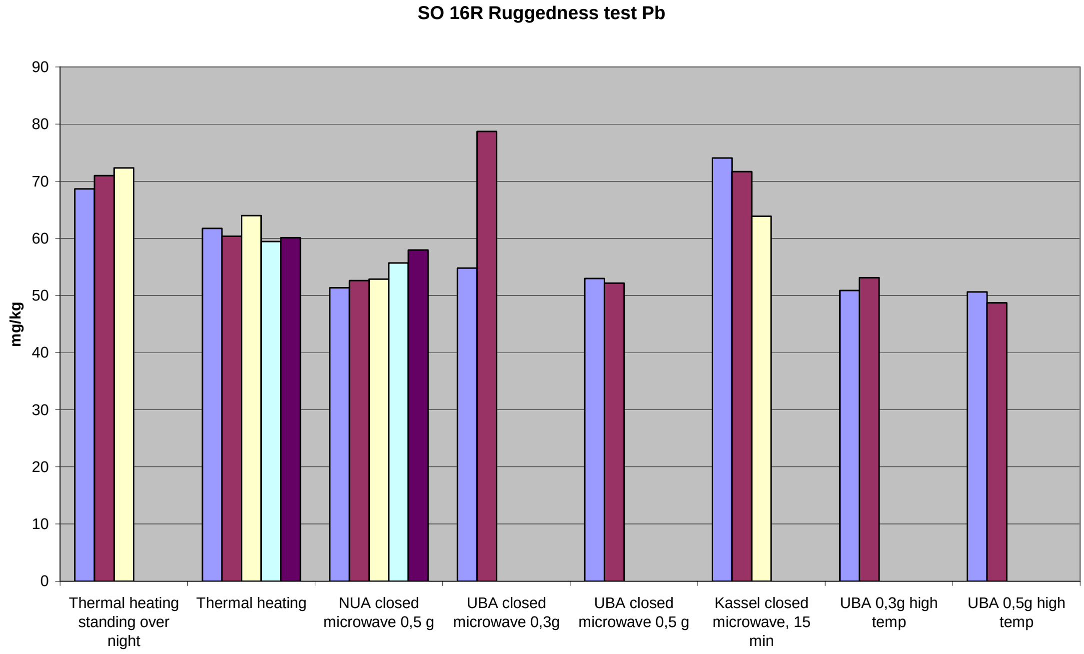

Figure 12 Comparison of different digestion methods for soil sample SO16R – Lead

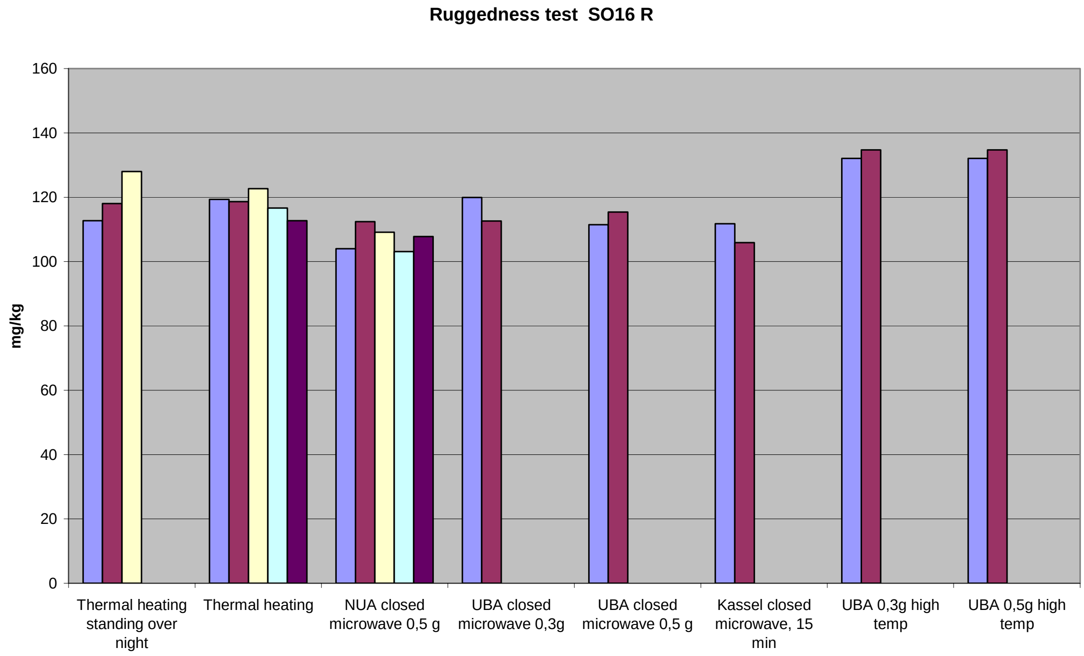

Figure 13 Comparison of different digestion methods for soil sample SO16R – Zink

As the aqua regia extraction is an empirical method that releases more or less the environmentally relevant metals and shall be used for comparison reason with limit values, main focus in drafting a standard was laid on the robustness on the one hand and the comparability of the results of microwave digestion with the thermal heating procedure on the other hand. This was the reason why this empirical microwave procedure with a fixed power programme had been drafted in TC 292. Validation data of several European standards (6,7,8,9) had proven this comparability more or less for many waste and sludge matrices and a broad range of elements.

Nevertheless exists a contradiction between this empirical microwave method and the theoretical approach as pointed out for aqua regia digestion of water and soil samples (17,24): ISO TC 190/SC3/WG1 N 0326:

"4 Principle

The test portion is digested with aqua regia at a defined temperature and time. The temperature is at least the boiling point (103 °C at 101,3 kPa) and at most 175 °C. At the boiling point, the minimum duration to release the digestible fraction is 120 min at 103°C. The maximum duration is set at four times the minimum duration at that temperature. By convention, both the required minimum and maximum duration is assumed to halve with every 15°C increase in temperature above the boiling point

...

NOTE 1: Given the digestion period Δt, expressed in minutes, the digestion temperature Td, expressed in degrees Celsius, shall meet the following condition:

206,2 – 21,64 x In(Δt)< Td<236,6 – 21,64 x In(Δt)

Boundary conditions in equation (1) reflect the assumption of clause 4 on release kinetics and duration time."

Calculation of digestion time and temperature according to this formula results in the following table:

Table 17 Calculation of digestion time/temperature according to ISO 15587-1

Time (minutes)	**ln(t)x 21,64**	**T_{min} (°C)**	**T_{max} (°C)**
		206,6	236,6
5	34,8	171,8	201,8
10	49,8	156,8	186,8
15	58,6	148,0	178,0
20	64,8	141,8	171,8
30	73,6	133,0	163,0
60	88,6	118,0	148,0
120	103,6	103,0	133,0

T_{min} in the last line of this table gives the condition as they are usually reached in the thermal heating procedure (method A of draft standard, 103 °C is the boiling temperature of aqua regia and atmospheric pressure and it is hold for 2 hours). Method B of draft standard results in digestion of about 5 min at 110°C as can be seen in Figure 3 Example of temperature/pressure diagram of method B for the matrix composted garbage, CW1 (UB0109) and Figure 5 Example of temperature/pressure diagram for sludge, SL4 (UB0111).

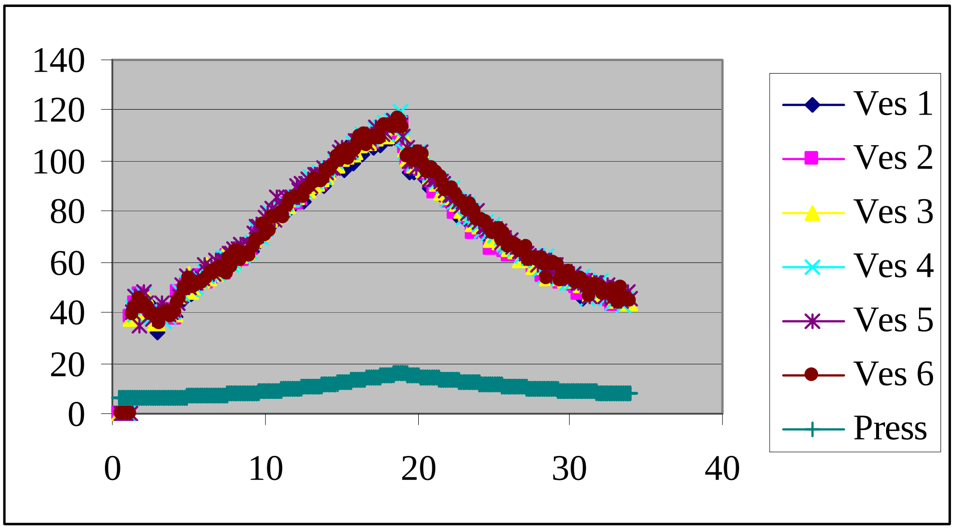

Figure 14 Temperature/pressure diagram for soil sample SO 13 terra rossa (UB0117)

The results obtained by using method B indicate no significant differences for many parameters and matrices (see 4.3 and 4.4) compared with thermal heating procedure. Theoretically heating temperatures about 160°C to 185°C for about 10 minutes should lead to comparable results as indicated in the theoretic formula of ISO. The experiments at UBA Vienna maintain this range of temperature of about 10 minutes, but result in evident higher recovery for some parameters compared to thermal heating for soil sample SO16.

Different is the situation for clay soil sample SO4: the temperatures reached with method B are laying about the boiling point of 103°C as can be seen in Figure 4 Example of temperature/pressure diagram for clay soil, SO4 (UB0114). In consequence the recovery rate of method B is for some parameters evidently lower than the one of thermal heating. But the closed vessel digestion at high temperature does not lead to comparable results, too, as can be seen in the tables of Annex 2 and in the next figure.

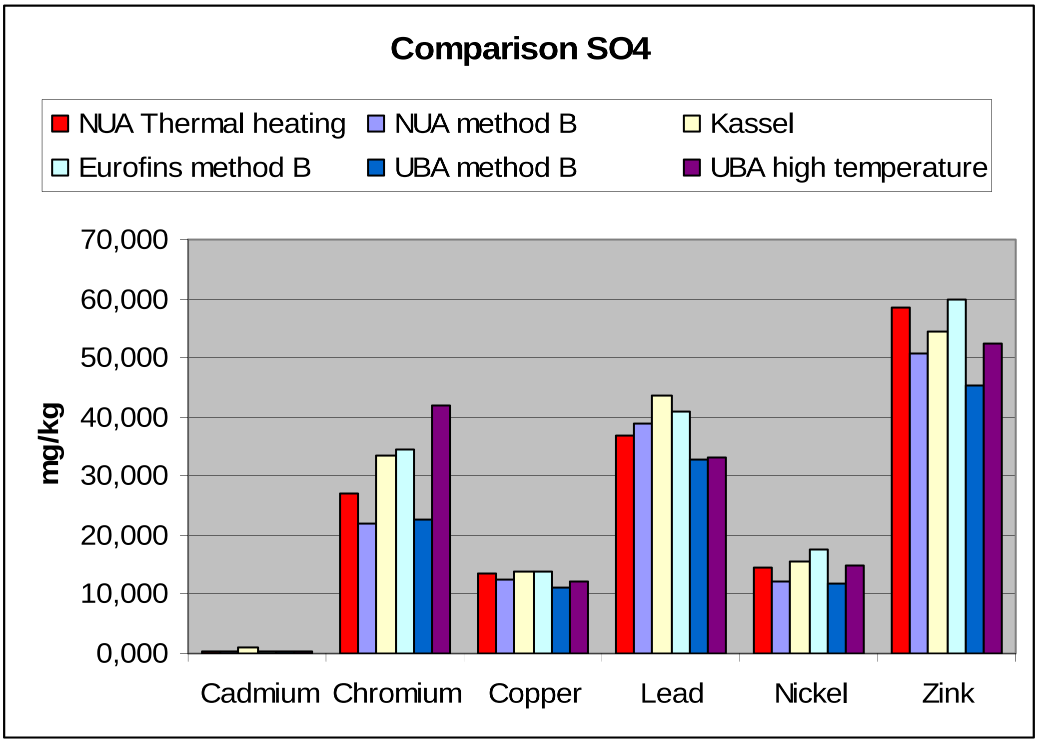

Figure 15 Comparison of different digestion methods for soil sample SO4

In consequence of these data the empirical method of method B of Horizontal draft standard can be used, but it was noted that the user should take care to hold a temperature of at least 110-120°C about 5 minutes.

4.3 Statistical evaluation – comparison of the three digestion methods

The results of the different methods were evaluated by statistical means according to ISO 16489 by comparing method per method. Outliers were eliminated by Grubb's test in case of at least 5 results per parameter and method available.

Excel sheets with detailed results and statistical evaluation of all samples are amended as annex named. For the matrix compost playground sample CW 1, for the matrix soil the samples SO-4, SO-13 and SO-16R were evaluated extensively according 16489. For the matrix sludge has been validated for previous standards (6,7), only a comparison of the means has been done to check if any deviation occurred.

As typical example for the results, the evaluation of the data of EUROSOIL SO-16R has been chosen. Statistical evaluation (F-test, mean-t-test) indicate equality only for some parameters, but these parameters vary from each pair of compared methods to the next.

Table 18 Statistical evaluation of open and closed microwave digestion for soil sample SO16R

SO 16R	methode of reference closed microwave		methode of comparison open microwave						methode of reference	methode of comparison
	arithmetic mean	coefficient of variation	arithmetic mean without outlier	coefficient of variation	recovery %	F-test result	arithmetic mean -t-test	"average" standard deviation	standard deviation without outlier	standard deviation without outlier
Arsenic	8,71	2,98	8,93	6,01	2,53	not equal	equal	0,39	0,10	0,54
Mercury	0,14	14,66	0,11	14,35	-19,96	not equal	not equal	0,02	0,02	0,01
Cadmium	0,48	5,43	0,45	3,33	-6,14	equal	equal	0,02	0,03	0,01
Cobalt	7,48	6,32	7,25	8,50	-3,16	equal	equal	0,55	0,47	0,62
Aluminium	14386,96	42,62	7385,57	6,27	-48,66	not equal	not equal	4348,15	6131,74	463,25
Calcium	1420,22	8,01	1292,14	3,23	-9,02	not equal	not equal	85,66	113,71	41,77
Chromium	22,94	23,85	15,00	4,80	-34,60	not equal	not equal	3,87	5,47	0,15
Copper	17,12	14,64	15,70	3,66	-8,28	not equal	equal	1,27	1,71	0,57
Iron	22563,11	7,67	21772,68	7,72	-3,50	equal	equal	1515,99	1331,97	1679,97
Potassium	2794,28	77,54	755,26	6,07	-72,97	not equal	equal	1532,41	2166,67	45,87
Magnesium	2906,16	21,40	1989,25	4,23	-31,55	not equal	not equal	353,24	492,42	84,17
Manganese	997,72	13,82	1001,21	2,76	0,35	not equal	equal	57,67	76,71	27,68
Nickel	17,56	12,93	14,39	5,01	-18,06	equal	not equal	1,24	1,59	0,72
Lead	60,02	14,79	55,36	4,94	-7,75	not equal	equal	6,32	8,88	1,09
Sulphur	1504,10	11,15	1158,09	1,60	-23,00	not equal	not equal	119,26	167,64	18,50
Zink	120,16	29,44	104,12	3,82	-13,36	equal	not equal	3,81	3,63	3,98
Phosphor	2481,15	11,61	1992,51	3,23	-19,69	not equal	not equal	208,66	288,01	64,27

Table 19 Statistical evaluation of open microwave and thermal heating digestion for soil sample SO16R

	methode of reference open microwave		methode of comparison thermal heating						methode of reference	methode of comparison
	arithmetic mean without outlier	coefficient of variation	arithmetic mean without outlier	coefficient of variation	recovery %	F-test result	arithmetic mean -t-test	"average" standard deviation	standard deviation without outlier	standard deviation without outlier
Arsenic	8,93	6,01	8,87	0,67	-0,73	not equal	equal	0,38	0,54	0,06
Mercury	0,11	14,35	0,11	3,98	-2,76	equal	equal	0,01	0,01	0,00
Cadmium AAS	0,45	3,33	0,45	0,84	0,41	not equal	equal	0,01	0,01	0,00
Cobalt AAS	7,25	8,50	7,55	4,58	4,15	equal	equal	0,50	0,62	0,35
Aluminium	7385,57	6,27	12993,83	6,89	75,94	equal	not equal	712,82	463,25	895,33
Bor	3,61	17,16	12,68	76,86	251,45	not equal	equal	8,96	0,62	12,66
Barium	74,47	4,17	85,73	3,70	15,11	equal	not equal	3,14	3,10	3,17
Calcium	1292,14	3,23	1466,33	3,28	13,48	equal	not equal	45,29	41,77	48,54
Cobalt ICP	9,91	59,74	10,46	10,67	5,49	not equal	equal	0,79	0,11	1,12
Chromium	15,00	4,80	22,11	1,33	47,41	equal	not equal	0,23	0,15	0,29
Copper	15,70	3,66	17,10	6,68	8,91	equal	not equal	0,90	0,57	1,14
Iron	21772,68	7,72	24232,50	5,62	11,30	equal	not equal	1529,10	1679,97	1361,60
Potassium	755,26	6,07	2299,67	2,87	204,49	equal	not equal	57,08	45,87	66,42
Lithium	8,56	6,39	17,15	10,23	100,49	not equal	not equal	1,25	0,21	1,75
Magnesium	1989,25	4,23	3109,50	5,25	56,32	equal	not equal	129,87	84,17	163,25
Manganese	1001,21	2,76	1049,28	4,12	4,80	equal	equal	36,30	27,68	43,24
Nickel	14,39	5,01	18,48	4,39	28,41	equal	not equal	0,77	0,72	0,82
Lead	55,36	4,94	64,71	8,05	16,89	not equal	not equal	3,76	1,09	5,21
Sulphur as SO4	1158,09	1,60	1508,29	7,31	30,24	not equal	not equal	79,02	18,50	110,21
Zink	104,12	3,82	117,24	4,28	12,60	equal	not equal	4,56	3,98	5,07
Phosphor as P2O5	1992,51	3,23	2385,08	8,03	19,70	not equal	not equal	142,92	64,27	191,63

Table 20 Statistical evaluation of closed microwave and thermal heating digestion for soil sample SO16R

	methode of reference closed microwave		**methode of comparison thermal heating**						methode of reference	methode of comparison
	arithmetic mean without outlier	**coefficient of variation**	**arithmetic mean without outlier**	**coefficient of variation**	**recovery %**	F-test result	arithmetic mean -t-test	"average" standard deviation	standard deviation without outlier	standard deviation without outlier
Arsenic	**8,60**	**2,98**	**8,87**	**0,67**	**3,09**		not equal	0,07	0,10	0,00
Mercury	**0,14**	**14,66**	**0,11**	**3,98**	**-22,17**	not equal	not equal	0,01	0,02	0,00
Cadmium	**0,48**	**5,43**	**0,45**	**0,84**	**-5,75**	not equal	equal	0,02	0,03	0,00
Cobalt	**7,48**	**6,32**	**7,55**	**4,58**	**0,85**	equal	equal	0,41	0,47	0,35
Aluminium	**14386,96**	**42,62**	**12993,83**	**6,89**	**-9,68**	not equal	equal	4381,77	6131,74	895,33
Calcium	**1420,22**	**8,01**	**1466,33**	**3,28**	**3,25**	not equal	equal	84,32	113,71	35,93
Chromium	**22,94**	**23,85**	**22,11**	**1,33**	**-3,59**	not equal	equal	3,87	5,47	0,29
Copper	**16,43**	**14,64**	**17,10**	**6,68**	**4,07**	equal	equal	1,45	1,71	1,14
Iron	**22992,45**	**7,67**	**24232,50**	**5,62**	**5,39**	equal	equal	1346,87	1331,97	1361,60
Potassium	**2794,28**	**77,54**	**2299,67**	**2,87**	**-17,70**	not equal	equal	1532,49	2166,67	51,17
Magnesium	**2756,59**	**21,40**	**3109,50**	**5,25**	**12,80**	not equal	equal	366,83	492,42	163,25
Manganese	**955,95**	**13,82**	**1049,28**	**4,12**	**9,76**	equal	equal	62,27	76,71	43,24
Nickel	**16,95**	**12,93**	**18,48**	**4,39**	**9,01**	not equal	equal	1,19	1,59	0,55
Lead	**60,02**	**14,79**	**64,71**	**8,05**	**7,83**	equal	equal	7,28	8,88	5,21
Sulphur as SO4	**1504,10**	**11,15**	**1508,29**	**7,31**	**0,28**	equal	equal	141,86	167,64	110,21
Zink	**107,72**	**29,44**	**117,24**	**4,28**	**8,84**	equal	equal	3,62	3,63	3,62
Phosphor as P2O5	**2481,15**	**11,61**	**2385,08**	**8,03**	**-3,87**	equal	equal	244,61	288,01	191,63

For clarification of the magnitude of the differences for each kind of matrix - compost, sludge and soil – some examples are pointed out in the following tables and figures. Results in the diagrams are showing some parameters of similar content in the respective sample showing the means, in some cases with or without standard deviation.

One obvious result of these comparisons is that there is no tendency in one special direction, the variation of the results for the single parameters indicates that none of the three method checked lead to significant higher results.

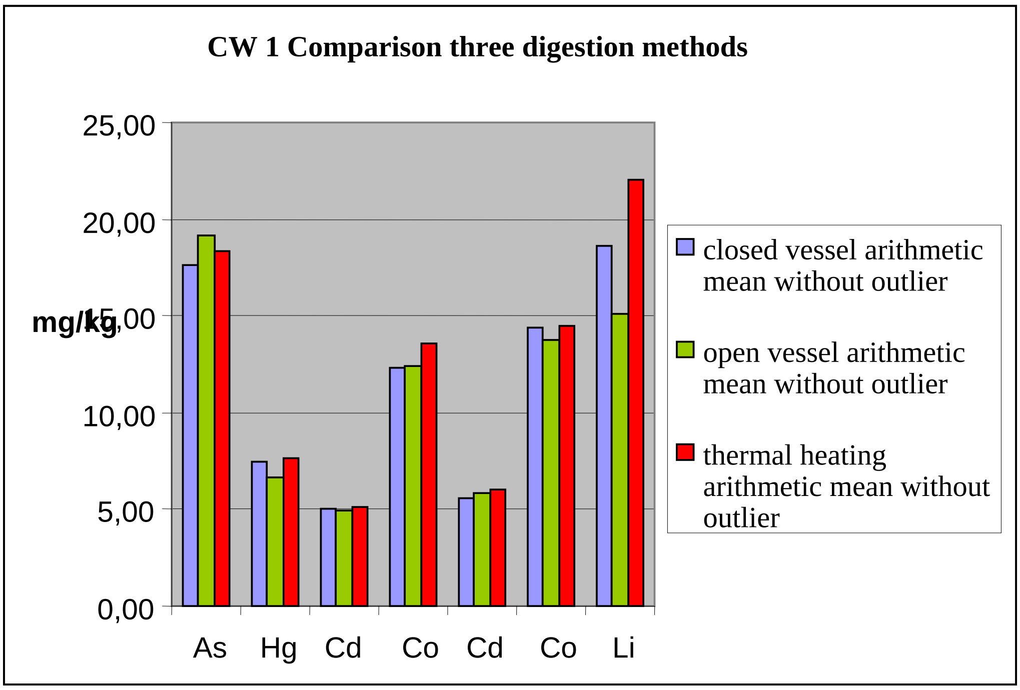

Figure 16 Comparison of three digestion methods of aqua regia digestion for compost CW1

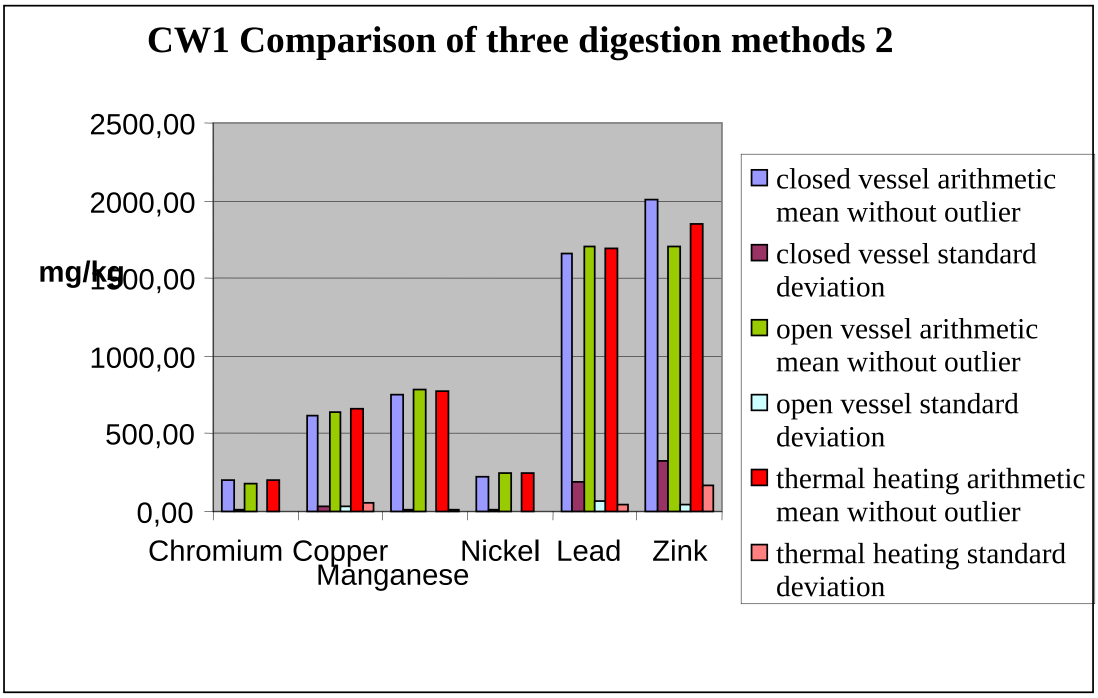

Figure 17 Comparison of three digestion methods of aqua regia digestion for compost CW1 with standard deviation

Table 21 Comparison of two methods of aqua regia digestion for sludge

SL4	closed microwave mg/kg		thermal heating mg/kg	
	arithmetic mean	standard deviation	arithmetic mean	standard deviation
As	5,99	0,27	5,88	0,04
Hg	1,57	0,06	1,41	0,03
Cd	3,24	0,03	3,30	0,07
Co	7,47	0,69	6,92	0,10
Ag	16,21	0,45	16,67	0,29
Al	8575,53	450,38	9070,67	409,44
B	28,99	0,48	35,30	2,50
Ba	476,05	35,44	518,44	21,42
Be	3,02	0,07	3,01	0,05
Ca	36168,75	639,01	36731,11	308,42
Cd	3,91	0,19	3,90	0,04
Co	13,33	0,34	12,84	0,10
Cr	445,41	8,35	470,07	19,62
Cu	636,47	22,10	722,22	32,89
Fe	46638,65	1273,71	68688,89	7915,20
K	935,11	35,55	1155,56	30,96
Li	5,41	0,17	5,86	0,13
Mg	4529,30	75,33	4610,22	64,24
Mn	409,79	11,81	416,44	6,05
Na	1242,67	21,03	1280,22	24,13
Ni	871,53	50,93	906,67	37,12
Pb	476,37	7,96	479,22	17,60
SO4	15505,10	423,53	13982,22	274,25
Sr	103,04	1,48	86,44	0,77
Zn	2953,42	138,48	3406,67	41,63
P2O5	45901,03	2947,16	48688,89	2059,49

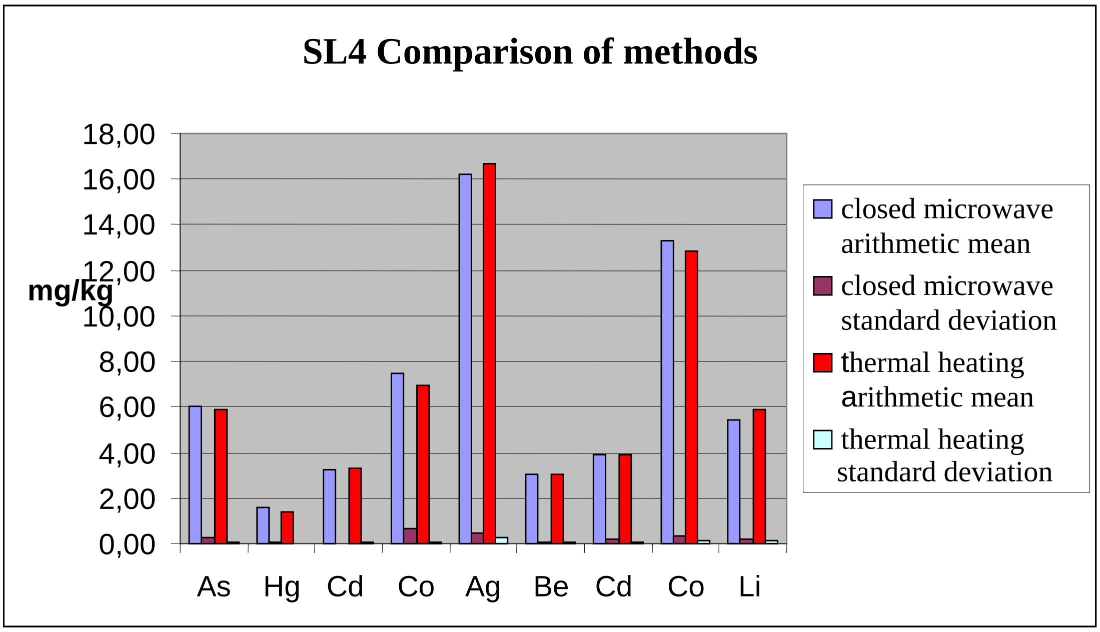

Figure 18 Comparison of thermal heating and closed microwave digestion for sludge SL4

Table 22 Comparison of three methods of aqua regia digestion for clay soil SO4

SO4	closed vessel microwave		open vessel microwave		thermal heating	
mg/kg	arithmetic mean	standard deviation	arithmetic mean	standard deviation	arithmetic mean	standard deviation
As	28,32	1,16	28,07	0,87	30,45	0,91
Hg	0,25	0,05	0,21	0,01	0,20	0,00
Cd (AAS)	0,24	0,00	0,23	0,00	0,23	0,01
Co (AAS)	3,45	0,07	3,17	0,08	4,00	0,08
Al	11780,88	4281,39	4484,65	100,77	11732,83	833,39
B	6,28	4,41	3,70	1,01	18,68	7,00
Ba	111,00	10,53	97,13	2,34	113,14	2,06
Ca	4735,92	435,33	3993,67	114,31	4801,42	113,35
Cr	26,27	5,91	17,58	0,50	26,34	1,04
Cu	12,77	0,56	12,66	0,70	14,74	2,38
Fe	15035,17	780,16	11775,19	505,02	14559,00	895,05
K	1442,41	1164,18	512,25	18,28	1770,33	19,68
Li	11,94	3,85	5,26	0,18	13,17	0,77
Mg	1630,79	361,85	952,46	29,59	1763,00	78,29
Mn	288,29	13,42	273,08	6,10	294,54	10,32
Na	170,16	44,63	179,37	7,63	209,00	73,15
Ni	13,52	1,65	10,37	0,32	14,58	0,33
Pb	39,47	2,05	37,93	4,35	38,92	4,69
SO4	2492,16	79,16	2147,10	29,21	2576,58	88,78
Sr	29,39	10,12	16,91	0,49	28,43	1,12
Zn	51,26	1,93	40,18	4,08	50,42	11,22
P2O5	1319,74	41,71	1196,53	36,75	1419,71	58,24

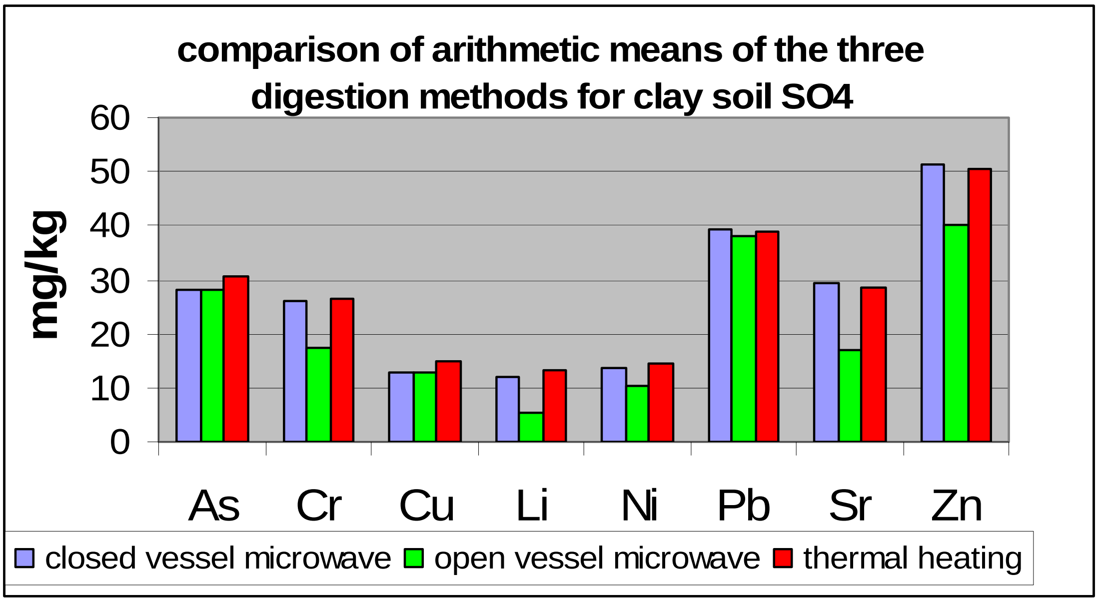

Figure 19 Comparison of three methods for clay soil SO4

4.4 Comparison of the three digestion methods

In order to summarise the results and to check the magnitude of eventual deviations, additional evaluation of the data has been done by comparing the means of all methods with each other and with the overall mean. Limits were defined with ±5% and ±10% deviation of the overall mean and checked for what type of sample, for which method and which parameter deviations bigger than ±5% (in the table shown as >10%) or ±10% (in the table shown as >20%) could be detected.

Table 23 Comparison of different digestion methods

Element analytical method	**Compost CW1 results/ deviation**	**Compost CW 5 deviation**	**Sludge SL4 results/ deviation**	**Soil SO4 results/ deviation**	**Soil SO13 deviation**	**Soil SO16R results/ deviation**
As-AAS	ov>th>cv/ <10%	<10%	cv>th <10%	th>cv>ov <10%	<10%	ov>th>cv <10%
Hg-AAS	th>cv>>**ov/** >10%,<20%	>10%, <20%	-	cv>ov>th >20%	<10%	cv>ov=th >10%
Cd-AAS	th>cv>ov/ <10%	<10%	th>cv <10%	cv>ov=th <10%	<10%	cv>ov=th <10%
Cd-ICP	th>ov>cv/ <10%	-	cv>th <1%	cv>th(>>AAS) <10%	<10%	-
Co-AAS	**th>>ov>cv/** **>10%,<20%**	<10%	cv>th <10%	**th>>cv>>ov** >10%,<20%	<10%	th>cv>ov <10%
Co-ICP	th=cv>ov/ <10%	<10%	cv>th <10%	th>cv <10%	<10%	th>ov>cv >10%
Cr-ICP	th>cv>>**ov/** >10%,<20%	<10%	th>cv <10%	**th>>cv>>ov** **>20%**	<10%	cv>th>ov >20%
Cu-ICP	th>ov>cv <10%	<10%	th>cv >10%, <20%	**th>>cv>>ov** **>20%**	<10%	cv>th>ov >10%,<20%
Ni-ICP	th>ov>cv/ <10%	<10%	th>cv <10%	**th>>ov>cv** **>20%**	<10%	th>cv>ov >20%
Pb-ICP	ov>th>cv/ <10%	<10%	th>cv <1%	cv>ov>th <10%	>20%	th>cv>ov >10%,<20%
Zn-ICP	**cv>>th>ov**/ >10%,<20%	<10%	th>cv >10%, <20%	**th>>cv>>ov** **>20%**	<10%	cv>th>ov >10%,<20%

Explanations: cv = microwave closed vessel; ov = microwave open vessel; th = thermal heating
th>cv means: mean of all results obtained by thermal heating digestion is bigger than means of all results obtained by digestion with closed vessel microwave

Discussion of data evaluation in detail for each sample:

CW1 (compost):
In general good correlation, Hg, Co-AAS, Cr, Zn >10%, but <20% deviation
Results of Cd- ICP >10% higher than Cd-AAS
Results of Co-ICP >10% higher than Co-AAS

CW5 (compost):
Comparison of closed microwave and thermal heating only;
Very good correlation, only Hg and K>10%, Al >20%, standard deviation very small

SL4 (sludge):
Comparison of closed microwave and thermal heating only;
Correlation of Cu, Zn >10%, other heavy metals <10%, deviation of results between the two methods of B, Fe, K
Results of Cd- ICP >10% higher than Cd-AAS
Results of Co-ICP >10% higher than Co-AAS

SO4 (clay soil):
In general deviation in many cases > 20%, e.g. Cr deviation >20% (cv/ov/th=17,6/22/26,9), standard deviation strongly influenced by different labs performing digestion

SO13 (soil):
Comparison of closed microwave and thermal heating only;
Very good correlation, only B (maybe error) does not correlate, K and Na >10% and Pb >20%, standard deviation strongly influenced by different labs performing digestion

4.5 Influence of particle size

In order to check the influence of particle size one soil sample available with a grain size of <2mm, SO-16R, was milled to a particle size of <500µm and <100µm and digested 5 times for each particle size by closed microwave digestion. Evaluation of data was done by comparing mean and standard deviation of the analysed parameters.

Table 24 Influence of particle size

SO 16R	**< 2mm**			**< 0,5mm**			**< 0,1mm**		
Parameter	**arithmetic mean**	standard deviation	coefficient of variation	**arithmetic mean**	standard deviation	coefficient of variation	**arithmetic mean**	standard deviation	coefficient of variation
Cadmium	**0,48**	0,03	5,43	**0,49**	0,01	1,72	**0,58**	0,01	2,12
Cobalt	**7,48**	0,47	6,32	**5,41**	0,23	4,21	**6,34**	0,26	4,07
Aluminium	**10026,93**	729,31	7,27	**10179,14**	740,23	7,27	**11996,27**	1706,30	14,22
Barium	**84,24**	3,13	3,71	**79,48**	2,01	2,52	**80,50**	39,73	49,36
Calcium	**1405,11**	79,03	5,62	**1497,21**	92,15	6,15	**1838,63**	80,72	4,39
Cobalt	**9,77**	1,74	17,82	**6,60**	0,31	4,71	**8,26**	0,16	1,99
Chromium	**19,06**	0,32	1,66	**18,85**	0,53	2,81	**23,09**	0,92	3,97
Copper	**17,24**	2,82	16,33	**14,62**	0,64	4,39	**19,42**	1,02	5,27
Iron	**22603,73**	1259,70	5,57	**23362,71**	1288,82	5,52	**26422,93**	913,81	3,46
Potassium	**1236,71**	66,46	5,37	**1274,81**	51,20	4,02	**1638,81**	155,23	9,47
Lithium	**12,32**	0,44	3,56	**13,32**	0,35	2,59	**16,30**	0,93	5,71
Magnesium	**2504,56**	141,48	5,65	**2597,48**	69,93	2,69	**3145,48**	134,24	4,27
Manganese	**1027,12**	147,68	14,38	**1020,89**	21,73	2,13	**1243,14**	58,14	4,68
Nickel	**16,46**	0,77	4,66	**15,46**	1,02	6,61	**20,66**	0,83	4,04
Lead	**54,10**	2,69	4,96	**56,86**	5,81	10,21	**76,39**	2,92	3,83
Sulphur as SO4	**1435,94**	46,85	3,26	**1521,58**	63,67	4,18	**1783,75**	35,12	1,97
Strontium	**7,70**	0,88	11,45	**8,39**	0,39	4,60	**9,71**	0,63	6,44
Zink	**107,27**	3,81	3,55	**97,08**	49,30	50,78	**130,73**	4,19	3,20
Phosphor as P2O5	**2480,92**	153,62	6,19	**2591,18**	162,05	6,25	**3059,10**	86,46	2,83

To point out possible differences the results of selected parameters are shown in a diagram (figure 11). This makes the influence of smaller particle size for rather refractory matrix visible. This fact was already shown in previous studies (15, 16) for waste and soil materials, but it cannot be detected for sewage sludge and other organic matrices.

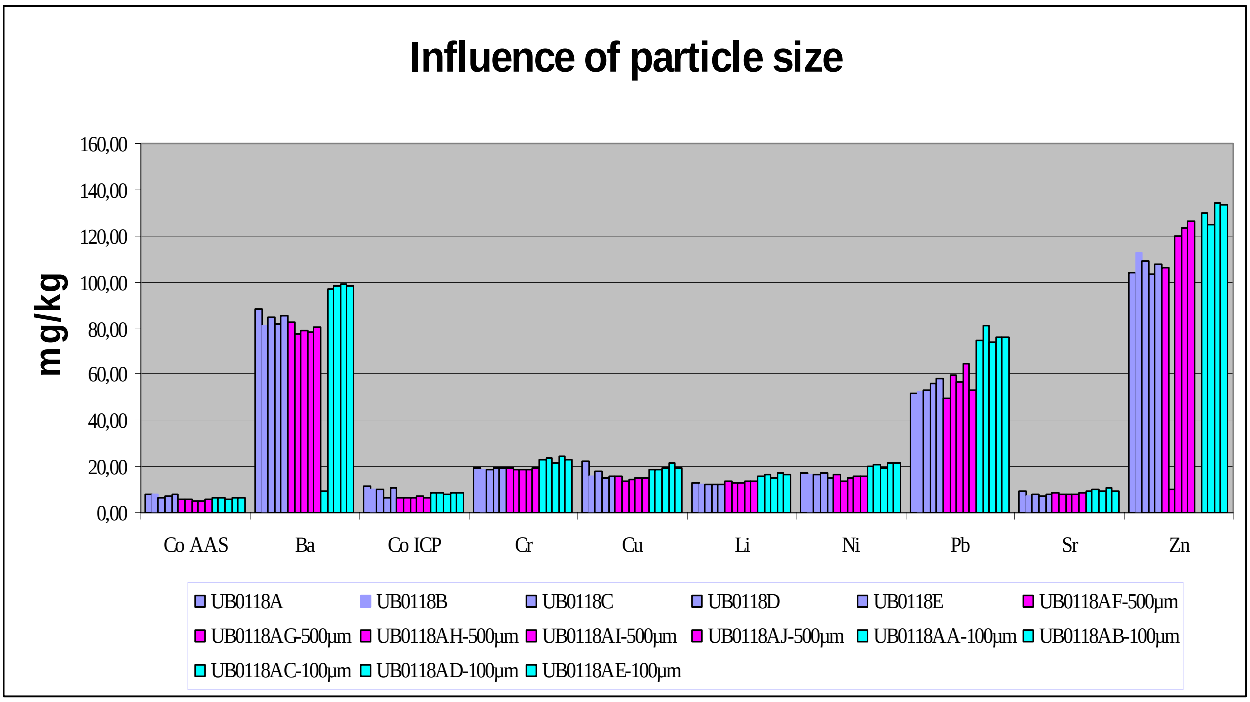

Figure 20 Influence of particle size on closed microwave digestion of SO-16R

The influence of particle size on the grade of digestion (recovery rate) and therefore the representativity of results is visible for refractory matrix. Therefore it has to be laid down in the standard; the proposal is to prescribe the particle size with <250µm, as a particle size of <100µm leads to evidently higher results that may influence the robustness of the method.

5. CONCLUSIONS

Evaluation of the analytical results of this robustness study in combination with previous pre-normative research and validation of the two standards EN 13346 and EN 13657 lead to these conclusions:

- The comparison of the three aqua regia digestion methods shows in most cases deviations of smaller than 10%, several times till <20%. Only for very refractory matrices as clay soil, deviations of over 20% are possible for selected parameters, mainly because of lower results of method C. Results for organic matrix as sludge and compost correlate in most cases.
- One obvious result of the statistical evaluation of the data of the three digestion methods is that there is no evident tendency in one special direction for the two methods “Thermal heating” and “Closed microwave digestion”. The method C of Horizontal draft standard “Open microwave digestion” may lead especial for soil samples to lower recovery rates see table 24); therefore it was taken out of the final version of the Horizontal draft standard. This method may be used as well as other methods for this kind of matrices, for which the equivalency is proven (7,9,13,26,27,28,29).
- The differences obtained by using the same method in different labs with small variations of performance conditions lead for both methods checked in that way - closed microwave and thermal heating digestion – to one important conclusion: They are in the same order of magnitude as the differences obtained by different methods of aqua regia digestion in the same lab.
- The influence of particle size on the grade of digestion (recovery rate) and therefore the representativity of results is visible for refractory matrix. Therefore it has to be laid down in the standard; the proposal is to prescribe the particle size with smaller than 250µm, as a particle size of 100µm leads to higher results that may influence the robustness of the method.
- Pre-treatment and performance parameters of digestion have to be prescribed in very detail to succeed in comparable results:
  The time how long the material is standing with aqua regia has an evident influence on the grade of digestion in compost and soil samples. In consequence the time how long the acid/sample mixture is standing before heating has to be fixed in the draft standard.
  Mass of test portion and time and temperature of digestion have an evident influence on the results and therefore they have to be fixed in the draft standard in a rather small range. Only for not refractory matrices where aqua regia extraction leads to a rather “total” digestion, these influences may be negligible.

REFERENCES

1. K.J.Andersen and M.I Kisser. “Digestion of Solid Matrices – Desk study Horizontal” March 2004. www.ecn.nl/library/horizontal.
2. K.J.Andersen and M.I Kisser. “Digestion soil, sludge, biowaste and waste for the extraction of aqua regia soluble elements – Horizontal Draft Standard” March 2004. www.ecn.nl/library/horizontal
3. K.J.Andersen and M.I Kisser. “Chemical Analysis - Digestion sediment, sludge, soil, biowaste and waste for the extraction of nitric acid soluble fraction of trace elements – Horizontal Draft Standard” March 2004. www.ecn.nl/library/horizontal
4. 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.
5. Youden, W.J. & E.H. Steiner: Statistical manual of the AOAC, Published by AOAC International. 1975.
6. EN 13657: Characterisation of waste – Digestion for subsequent determination of aqua regia soluble portion of elements, 2002
7. EN 13346 Characterisation of sludge – Determination of trace elements and phosphorus – Aqua regia extraction methods 2000
8. Giove,A.; Politi,M.; Cavallo,G.: Robustness study on standard methods developed by CEN TC 292/WG3, Italy 2000
9. Muntau, H.; Kisser, M. I.; Yuste, C.; Giove, A.; Bianchi, M.: The validation of CEN draft standards for the analysis of waste, Joint Research Centre, European Commission EUR 19680 EN, European Communities 2000
10. Certificate of BCR-144 (SL4), Community Bureau of Reference, Commission of the European Communities
11. Certificate of BCR-143, Community Bureau of Reference, Commission of the European Communities
12. Certificate of WQB-1, National Water Research Institute, Ontario, Canada
13. Roy, R.; Kainrath, P.: The EPA 3050 B Soil Digestion Method Versus EN 13346 Method Using a Graphite Digestion System, Soil Digestion Poster, Winter Conference, 2002
14. Gawlik, B.M., Crößmann, G., Bianchi, M., Muntau, H. (1999) In: B. M. Gawlik and H. Muntau (Eds.), EUROSOILS II – Laboratory reference materials for soil-related studies. EUR 18983 EN
15. Kisser, M.I.; Hollensteiner,C: Pre-normative research for EN 13657, “Vergleich von Königswasserauszügen mit und ohne Mikrowelle an 4 konkreten Abfallarten im Hinblick auf die Erstellung von Normen”, study for the Austrian Ministry of Environment, Ma. Enzersdorf, 1998
16. Dreher, P.; Kisser, M.I.; Peticka. R.; Scharf, W.: “Erden aus Abfällen”, study for the Austrian Ministry of Environment, Austria, 2000
17. EN ISO 15587-1 Water quality – Digestion for the determination of selected elements in water – Part 1: Aqua regia digestion, 2002

18. EN 13656: Characterisation of waste – Microwave assisted digestion with hydrofluoric (HF), nitric (HNO_3) and hydrochloric (HCI) acid mixture for subsequent determination of elements, 2002

19. ISO/FDIS 14869-2 Soil quality – dissolution for the determination of total element content – Part 2: Dissolution by alkaline fusion, 2002

20. CEN TC 292/WG 3 WI 292042 "Characterisation of waste – Digestion of waste samples using alkali-fusion techniques"

21. EPA method 3015 A: Microwave assisted acid digestion of aqueous samples and extracts, Revision 1, 1998

22. EPA method 3051 A: Microwave assisted acid digestion of sediments, sludges, soils and oils, Revision 1,1998

23. EPA method 3052 A: Microwave assisted acid digestion of siliceous and organically based matrices, 1996

24. ISO TC 190/SC3/WG1 N 0326: Microwave assisted aqua regia digestion for the determination of selected elements

25. Rosenberg, E.: oral information, Technical University Vienna, November 2005

26. Lo, J.M.; Sakamoto, H.: Comparison of the Acid Combinations in Microwave assisted Digestion of Marine Sediments for Heavy Metal Analysis, Analytical Sciences, Vol 21, 1181-1184, October 2005

27. Lacort, G.; Camarero, L.: Characterisation of Lake Sediments – Extraction Method of Elements Soluble in Aqua Regia, University of Barcelona,

28. Chen, M; MA, L.Q.: Comparison of three Aqua Regia Digestion Methods for Twenty Florida Soils, Soil Science Society of America Journal *65:491-499 (2001)*

29. Riebe,G.; Pritzkow, W.; Vogl,J.: A Comparative Study in the Field of Soil Analysis, Federal Institute for Material Research and Testing (BAM), 2004