

Digestion of Solid Matrices Desk Study - Horizontal

Kirsten J. Andersen
Monika I. Kisser

Eurofins A/S, Denmark
NÖ Umweltschutzanstalt, Austria



Acknowledgement

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

CONTENTS

LIST OF ANNEXES	3
LIST OF TABLES	4
LIST OF FIGURES	4
SUMMARY	6
1. INTRODUCTION	8
2. BACKGROUND AND PRINCIPLES	9
2.1 Overview of methods and principles	9
2.2 Partial digestion methods	13
2.3 Selection between methods	14
3. EXISTING STANDARDS OR DRAFT STANDARDS	17
3.1 Aqua regia digestion	17
3.1.1 Soil	17
3.1.2 Sludge	18
3.1.3 Soil improvers and growing media	19
3.1.4 Waste	20
3.1.5 Water (EN ISO 15587-1)	21
3.1.6 Sludge and sediments (DIN 38 414 S7)	22
3.2 Nitric acid digestion	23
3.2.1 Soil (SS 028311)	25
3.2.2 Water, sludge, and sediment	25
3.2.3 Sediment, sludge, soil and oil (US EPA 3051)	26
3.2.4 Water (EN ISO 15587-2)	26
4. EVALUATION OF DRAFTING A HORIZONTAL STANDARD	27
4.1 General	27
4.2 Aqua regia digestion methods	27
4.3 Nitric acid digestion	31
5. CRITICAL POINTS AND RECOMMENDATIONS	35
5.1 Aqua regia digestion method	35
5.2 Nitric acid digestion method	35
5.3 Conclusions and recommendations	36
6. DRAFT STANDARDS (SEPARATE CEN TEMPLATES)	37
REFERENCES	38
ANNEXES	40

LIST OF ANNEXES ANNEX 1 RECOVERY RATES OF ELEMENTS IN DIFFERENT MATRICES

ANNEX 2 COMPARISON OF RECOVERY RATES – HENRI CIESIELSKI, VALIDATION DATA EN 13657

ANNEX 3 RESULTS FROM INTERLABORATORY COMPARISON, DK

ANNEX 4 RESULTS FROM INTERLABORATORY COMPARISON, SF

LIST OF TABLES

Table 1	National and international standard methods - total and partial digestion	10
Table 2	Comparison of digestion methods – sand dust	11
Table 3	Comparison of digestion methods – melting dust	12
Table 4	Aqua regia digestion (International standards)	17
Table 5	Short description of the method ISO 11 466	17
Table 6	Short description of the method EN 13346	18
Table 7	Short description of the method EN 13650	19
Table 8	Short description of the methods in EN 13657	20
Table 9	Short description of the method EN ISO 15587-1	21
Table 10	Short description of the method DIN 38 414 S7	22
Table 11	Nitric acid digestion (National and International standards)	23
Table 12	Short description of the method SS 028311	25
Table 13	Short description of the method DS 259	25
Table 14	Short description of the method US EPA 3051	26
Table 15	Short description of the method EN ISO 15587-2	26
Table 16	Evaluation of available ISO and CEN standards resulting in a draft horizontal standard	30
Table 17	Evaluation of standards for nitric acid digestion in autoclave and proposal for horizontal standard	33
Table 18	Influence of sample particle size on aqua regia digestion method (Giove 2000)	52
Table 19	Results of the round robin test for validation of EN 13567	53
Table 20	Comparison of reproducibility for all the samples used in the round robin test for validation of EN 13567	55
Table 21	Data from interlaboratory comparison on two municipal sludge samples. Particle size < 4 mm. No of participants: 17.	56
Table 22	Data from interlaboratory comparison on two municipal sludge samples. Particle size < 2 mm. No of participants: 19 (Denmark, Norway and Sweden)	56
Table 23	Results in the Finnish PTs	57

LIST OF FIGURES

Figure 1	Solubility of silicium during digestion with different acids (van der Sloot, 2003)	14
Figure 2	Comparison of solubility of cadmium under different leaching/extraction conditions (van der Sloot 2003)	15
Figure 3	List of reference materials for which recovery rates were shown in Hofer, 1997	40
Figure 4	Recovery rate of Arsenic in different matrices by digestion with different acid mixtures (Hofer, 1997)	41
Figure 5	Recovery rate of Lead in different matrices by digestion with different acid mixtures (Hofer, 1997)	41
Figure 6	Recovery rate of Chromium in different matrices by digestion with different acid mixtures (Hofer, 1997)	42
Figure 7	Recovery rate of Cadmium in different matrices by digestion with different acid mixtures (Hofer, 1997)	42
Figure 8	RECOVERY RATE FOR CLOSED DIGESTION WITH HF/HNO ₃ /HCl (Hofer, 1997)	43
Figure 9	RECOVERY RATE FOR CLOSED DIGESTION WITH AQUA REGIA (Hofer, 1997)	43
Figure 10	Comparison Cd (HCl/HNO ₃) and Cd (HF)	44
Figure 11	Comparison Cr (HCl/HNO ₃) and Cr (HF)	45
Figure 12	Comparison Cu (HCl/HNO ₃) and Cu (HF)	45
Figure 13	Comparison Ni (HCl/HNO ₃) and Ni (HF)	46

Figure 14	Comparison Pb (HF) and Pb (HCl/HNO ₃)	46
Figure 15	Comparison Zn (HCl/HNO ₃) and Zn (HF)	47
Figure 16	Comparison Cd	48
Figure 17	Comparison Cr	49
Figure 18	Comparison Cu	49
Figure 19	Comparison Ni	50
Figure 20	Comparison Pb	50
Figure 21	Comparison Zn	51

SUMMARY

Choice of digestion methods

The report in hand concerns an evaluation of the potential for horizontal standardisation for the digestion of samples prior to the determination of trace elements covering sludge, soil, treated biowaste and neighbouring fields.

The detailed comparison of standards for the digestion prior to the determination of trace elements demonstrates the possibility of preparing horizontal standards in this field, however investigation has to be initiated prior to the establishment.

From an environmental impact evaluation perspective the composition derived from either "partial" or "total" digestion is hardly relevant, as the fraction which even under extreme environmental condition will be brought into solution (and made available for plants etc.) is several orders of magnitude lower. Thus for control purposes or for monitoring or evaluation of developments in element concentration, the use of "partial" methods are considered acceptable. However, it is of vital importance that the methods provide comparable results with a sufficiently high reproducibility for the elements and matter in question.

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 based on the use of nitric acid. The reason for this choice being the smaller interference effects from using nitric acids on some of the subsequent analytical procedures.

Aqua regia digestion methods

One major difference in the existing standards is 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) is proposed. Data exist for waste and sludge samples that suggest that comparable data can be obtained, but for other matrices more investigations are needed. Comparability of data is of high importance. An investigation of the optimum particle size of a test sample is needed for soil, sediment and biowaste.

A draft horizontal standard is described. Sediments, soil, sludge and waste are proposed to be included in the final scope of the horizontal standard.

Nitric acid digestion method

Autoclave digestion methods exist in the Nordic countries covering sludge and sediment (and water) and the same standards are generally prescribed for soil and biowaste. An equivalent method exists in Sweden covering soil samples. Microwave-assisted heating of nitric acid digests is validated as a US EPA method.

A draft horizontal standard covering nitric acid digestion in an autoclave equipment equivalent to the existing autoclave heating method has been prepared. It is proposed that sediments, soil, sludge and waste be included in the final scope of the horizontal standard.

It is suggested that investigations on the comparability of autoclave heating and microwave-assisted heating be carried out for consideration of a possible inclusion of microwave heating in the final standard, alternatively exchange of the autoclave assisted heating with microwave heating. Inclusion of the conditions given in the US EPA methods is suggested.

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 (WPs), 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.

The report in hand deals with a desk study under WP 6: Inorganic Parameters: Assessment of the feasibility of draft horizontal standards for:

- the digestion of samples prior to the determination of trace elements

covering sludge, soil, treated biowaste and neighbouring fields

Existing standards and/or draft standards are assessed and key points where possible differences exist are identified and the differences evaluated in order to prepare draft horizontal standards.

In addition, assessments of ongoing activities in the relevant CEN/TC workgroups are included in the project:

CEN/TC 292/WG 3 Waste

CEN/TC 308/WG 1, Sludge

CEN/TC 345, Soil (the TC is newly established)

CEN /TC 223, Soil improvers and growing media

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.

The report in hand covers an evaluation of both principles with a view to the development of horizontal standards.

2. BACKGROUND AND PRINCIPLES

2.1 Overview of methods and principles

In most cases, the determination of elements in solid matrices is a combination of a digestion procedure for dissolution of the elements and subsequent analyses/quantification of the dissolved elements. Various digestion methods are used for the analysis of elemental composition of soils, waste, sludge, sediments and biowaste. The digestion methods vary from "true" total determination using complete dissolution of the solid matrix to methods dissolving only part of the elements - "partial" digestion and leaves a residual fraction unaffected. Several of these methods have been developed and described in a prenormative research for the development of digestion standards for waste (Hofer, 1997). An extract of the evaluation of the influence of the acid mixtures on the recovery rates of different elements is shown in Annex 1.

Alternative extraction methods are and may be developed in future to provide a quicker or easier dissolution of the matrix with less chemical consumption. Due to inherent limitations of the digestion/extraction fluids as opposed to instrumental analysis methods, the "partial" digestion methods, as well as the "true" total methods for that matter, will be adequate for some and may have limitations for some other elements.

In the following, the term "digestion" is used for the description of the process instead of terms that describe different grades of dissolution as extraction, dissolution and destruction. The process is a combination of oxidation/destruction of organic matter and dissolution of the mineral phase to a certain extent to bring the elements of interest into solution.

Selected standardized methods for partial and total digestion of metals from solid environmental matrices, such as soil, sludge and waste, are listed and described in Table 1. Digestion methods designed to extract the "bio-available" fraction or designed to simulate weathering conditions are not included. The list includes standards from international and national standardisation organisations (ISO, CEN, US EPA, ASTM, SS, and DS). The list includes total digestion methods that uses e.g. hydrofluoric acids and partial digestion methods that uses acid mixtures (e.g. aqua regia) or only nitric acid.

One alternative to the partial digestion by nitric acid or aqua regia (as focused on in this study) is digestion with a mixture of hydrofluoric acid (HF) and aqua regia ($\text{HCl} + \text{HNO}_3$), where, typically, the materials to be digested are boiled under pressure with acid solutions (e.g. EN 13656). The main advantage of these methods are that for most, but not all, inorganic components the results in the subsequent analysis are often good indicators of the total content of these components in the soil or mineral solid waste materials (Annex 1). The results may therefore, in contrast to the results based on partial digestion, be used for mass balance calculations and mass stream analyses. Among the disadvantages are, firstly, that only very small amounts of samples are digested and that, as a consequence, a representative sample may be difficult to collect and, secondly, that for safety reasons it is necessary to take special precautions when working with hydrofluoric acid.

Several other digestion methods are available, among which are digestions with other combinations of strong acids as well as fusion in different alkali solutions. A number of these methods are used for special purposes and for specific parameters. In addition, there is a number of non-destructive analytical methods for the determination of the total content of inorganic components in soil and waste residue matrices. Among these methods are neutron activation analysis (NAA) and various forms of x-ray fluorescence (XRF). Table 2 and Table 3 illustrate for a number of elements on 2 samples (sand dust and melting) the degree of solubility achieved by using different acids on digestion.

Table 1 National and international standard methods - total and partial digestion

Method and reference	Solid sample/Matrix	Approved or recommended elements
Total dissolution by acid		
ISO 14869-1:2001 Dissolution for determination of total trace element content. Part 1: Dissolution with hydrofluoric and perchloric acids	Soil, 0.25 g sample	The trace elements: Al, Ba, Cd, Cs, Cr, Co, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V, Zn
EN 13656:2003: Characterization of waste. Microwave assisted digestion with hydrofluoric (HF), nitric (HNO ₃) and hydrochloride (HCl) acid mixture for subsequent determination of elements in waste	Waste, 0.2-0.5 g sample	Al, Sb, As, B, Ba, Be, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Mo, Ni, P, K, Se, Ag, S, Na, Sr, Sn, Te, Ti, Tl, V, Zn
US EPA 3052: Microwave assisted acid digestion of siliceous and organically based matrices	Siliceous, organic and other complex matrices. Up to 0.5 g sample for soils, ash, sediments, sludges, and siliceous wastes	Al, Sb, As, B, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Mg, Mn, Hg, Mo, Ni, K, Se, Ag, Na, Sr, Tl, V, Zn
ASTM D 3683-94: Standard test method for trace elements in coal and coke ash by atomic absorption	Coal and coke ash (coal and coke ashed at 500°C), 0.2 g	Be, Cr, Cu, Mn, Ni, Pb, V, Zn
Partial dissolution by acid mixtures		
ISO 11466:1995: Soil quality – Extraction of trace elements soluble in <i>aqua regia</i>	Soil and similar materials, containing less than 20% organic carbon, 3 g sample	Trace elements, not further specified. Reference to: Cd, Cr, Co, Cu, Pb, Mn, Ni, Zn
EN 13657:2001: Characterization of waste. Digestion for subsequent determination of aqua regia soluble portion of elements in waste	Waste, 0.2-0.5 g sample	Al, Sb, As, B, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Mo, Ni, P, K, Se, Ag, S, Na, Sr, Sn, Te, Ti, Tl, V, Zn
US EPA 3050B: Acid digestion of sediments, sludges, and soils	Sediment, sludge, and soil, 1 g sample	Al, Ag, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, K, Pb, Se, Tl, V, and Zn.
EN 13650:2000: Soil improvers and growing media – Extraction of aqua regia soluble elements	Soil improvers and growing media	Interlaboratory trial included: P, K, Ca, Mg, Na, B, Cu, Fe, Mn, Mo, Zn, S, Cd, Pb, Cr, Ni
Partial dissolution by nitric acid		
Swedish Standard SS 02 83 11: Soil analysis – determination of trace elements in soils – extraction with nitric acid	Soil, up to 5 g sample	Not specified. Reference to: Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, (Cr), Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Si, Sn, (Sr), Ti, V, W, Zn, Zr
DS 259, DS 2210: Determination of metals in water, sludge and sediments	Sludge and sediments, up to 1 g (dry weight) samples	Not specified. Documentation found re: Ca, Li, Mg, Mn, Ni, Fe, Cr, Cu, Cd, Co, Pb Zn
US EPA 3051: Microwave assisted acid digestion of sediments, sludges, soils, and oils	Sediment, sludge, and soil, 0.25-0.50 g samples	Al, Ag, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, Pb, Se, Sr, Tl, V, and Zn
Nordic guidelines for Chemical Analysis of Contaminated Soil Samples . NT Techn report 329:1996	Soil	

Table 2 Comparison of digestion methods – sand dust
 Summary of the mean results in mg/kg for a sample of sand dust, obtained by use of different methods”. N denotes the number of replicates. From Laine-Ylijoki et al. (1999).

Lab.	N	Method	Concentrations, mg/kg sample							
			Al	As	Cd	Co	Cr	Cu	Pb	Zn
1	1	XRF (Philips PW2404): Semi-quantitative analysis	80000	<100	<100	<100	32000	880	380	1900
2	2	Decomposition by the use of HF, HNO ₃ + HCl + H ₂ O, HClO ₄ , Li ₂ CO ₃ + Li ₂ B ₄ O ₇ , K ₂ S ₂ O ₇	103000	NA	14	110	37000	830	460	2100
1	3	Decomposition by the use of Li ₂ B ₄ O ₇	87000	-	-	57	34000	700	-	1800
1	3	Microwave-assisted digestion (HNO ₃ + HF + H ₂ O ₂)	79000	5.7	3.6	53	19000	800	360	1700
9	3	Microwave-assisted digestion (HNO ₃ + HF + H ₂ O ₂) (EPA 3052/96)	48000	<13	9	36	18000	1020	560	2400
8	1	Microwave-assisted digestion (HNO ₃ + H ₂ O ₂)	17000	4	5	25	280	NA	350	1500
1	3	Aqua regia digestion	29000	6.4	4.1	24	970	780	350	1800
3	3	Aqua regia digestion (DIN38414/7)	28000	50	5	30	690	690	400	1700
4	3	Aqua regia digestion (ISO/DIS 11466)	22000	<15	<10	35	560	640	300	1500
5	3	Acid digestion (HNO ₃ + HF)	85000	3	2	44	34000	730	540	1900
6	3	Acid digestion (HNO ₃)	16000	3	4	20	340	580	310	1300
7	1	Acid digestion (HNO ₃)	20000	<10	4	22	320	730	380	1500

NA = not analysed

Table 3 Comparison of digestion methods – melting dust
 Summary of the mean results in mg/kg for a sample of melting dust by the use of different methods. N denotes the number of replicates. From Laine Ylijoki et al. (1999).

Lab.	N	Method	Concentrations, mg/kg sample							
			Al	As	Cd	Co	Cr	Cu	Pb	Zn
1	1	XRF (Philips PW2404): Semi-quantitative analysis	9700	<100	<100	<100	<100	1200	1900	89000
2	2	Decomposition by the use of HF, HNO ₃ + HCl + H ₂ O, HClO ₄ , Li ₂ CO ₃ + Li ₂ B ₄ O ₇ , K ₂ S ₂ O ₇	9400	NA	63	100	220	1800	2900	130000
1	3	Decomposition using Li ₂ B ₄ O ₇	7800	NA	NA	71	NA	1 400	NA	110000
1	3	Microwave-assisted digestion (HNO ₃ + HF + H ₂ O ₂)	7200	77	43	59	130	1 800	2700	130000
9	3	Microwave-assisted digestion (HNO ₃ + HF + H ₂ O ₂) (EPA 3052/96)	6000	110	81	79	150	2 200	3800	146000
8	1	Microwave-assisted digestion (HNO ₃ + H ₂ O ₂)	2400	55	61	37	33	NA	2600	130700
1	3	Aqua regia digestion	4900	77	44	51	71	1500	2000	120000
3	3	Aqua regia digestion (DIN38414/7)	4900	54	59	74	84	1600	2500	109000
4	3	Aqua regia digestion (ISO/DIS 11466)	4000	79	52	84	94	1500	2800	130000
5	3	Acid digestion (HNO ₃ + HF)	9600	64	66	63	240	1400	3100	120000
6	3	Acid digestion (HNO ₃)	2800	55	42	32	40	1300	2400	107000
7	1	Acid digestion (HNO ₃)	2900	64	47	31	38	1600	2800	140000

2.2 Partial digestion methods

One reason why for many years partial digestion methods have been used to describe element compositions in various solid matrices in preference to "total" digestion methods is pragmatism driven by a concern for the potential hazards of using hydrofluoric acids.

Partial digestion methods are empirical in the sense that the final results may be determined by a number of factors defining the method. They should at least dissolve the organic matter and the easily digestible inorganic compounds in the sample. Depending on the composition of the sample they can even lead to results similar to those of the "total" digestion methods for some matrices (Annex 2A) or correlation factors can be determined for the different elements (Annex 2B). There are various different partial digestion methods with different combinations of acids, amounts of acids, energy source for heating, time period for heating etc. The two groups of digestion methods (aqua regia methods and nitric acid methods) considered in the present study only represent part of the available methods; however, the nitric acid methods and the aqua regia methods are among the most frequent methods being standardized.

Considering the partial digestion methods. Some parts of the matrix may be left un-dissolved (e.g. silicates) leading to results differing from 100% dissolution and differing for each element considered (Annex 1). Elements are associated with different fractions of the solid sample (soil, sludge or waste), such as the silicate fraction, exchangeable fraction, carbonates, iron, manganese and organic matter. Therefore, a situation exists where different acids do not have the same potential for dissolution of all elements, so pragmatism is needed if there is a wish to use the same digest for the analyses of a broad range of elements. One acid or combination of acids preferable for some elements might be less appropriate for other elements.

Kind and amount of acids or combinations of acids used are key factors determining the rate of dissolution of refractory matrices. Another factor is the kinetic driving the reactions. In order to optimize the reactions and conditions, an external energy input to the system is generally necessary. It may be a hot-plate heating in either open or closed vessels combined with high pressure or it may be microwave-assisted heating in open or closed vessels. Conventionally, hot-plate heating was used, but recently, microwave-heating digestion systems have become more common and methods for this technique have been standardized during the last years.

As a consequence of more digestion methods having been standardized during the years and used on a routine basis, a horizontal and modular approach within the field of water analyses (wastewater, ground water, drinking water, etc.) was developed within CEN and ISO. The new approach aimed at defining in the standard the conditions for digestion that could take new and modern equipment into account. The standard (EN ISO 15587, part 1 and 2) defines the energy input to the system and defines the acid composition. Energy sources can then be selected, provided that the energy input for the given time period is achieved. The standard only makes distinctions between open digestion (at the boiling point – e.g. hot plate or microwave oven) or closed digestion (at high pressure – e.g. microwave oven or autoclave).

Two different principles for partial digestion are evaluated in the present study: Nitric acid and aqua regia (mixture of hydrochloric acid and nitric acid). Aqua regia standard methods are presently implemented for most of the matrices considered in most of the present EU countries; however, nitric acid is the method of choice for partial digestion in the Nordic countries. Thus, historic data are in many countries based on partial digestion using aqua regia and in others based on nitric acid digestion. For this reason, both acids and acid mixtures are evaluated for the present study.

2.3 Selection between methods

The key question in relation to judging the suitability of a specific method for a particular purpose is what type of information the method should provide. Another aspect is to identify the purpose of the method. If the intention is to judge the environmental properties of a material in relation to exposure of humans or the ecosystem to elevated concentrations of undesirable constituents, then neither the "partial" nor the "total" digestion methods are the proper assessment tools, as the total composition is in no way related to the release of substances from soil, sludge or biowaste under any given set of environmental exposure condition. In that case, the release of contaminants under simulated environmental conditions or test of bio-availability of constituents are more appropriate measures.

To put the latter aspect in a context for discussion, data on total and partial destruction methods applied to soil, sediment, compost, and sewage sludge (from the EU project on harmonization of leaching/extraction tests) have been plotted in linear and log scale relative to leaching as a function of pH (van der Sloot, 1998 and van der Sloot et al, 2003 - deskstudy no. 23). This has been done for a range of metals, oxyanions, major and minor components. The variability in composition of several constituents brought into solution is relatively small, even for different destruction methods, when judged in the broader context of environmental effects. There are some typical elements that are very sensitive to certain extractants (van der Sloot 1998). Silicate is very responsive to HF but silicium (Si) is to a minor extent brought into solution by using aqua regia and nitric acid. Because of their partial incorporation in the Silicate matrix, vanadium (V) and chromium (Cr) may vary with the extent to which Si is dissolved by a specific "partial" digestion method.

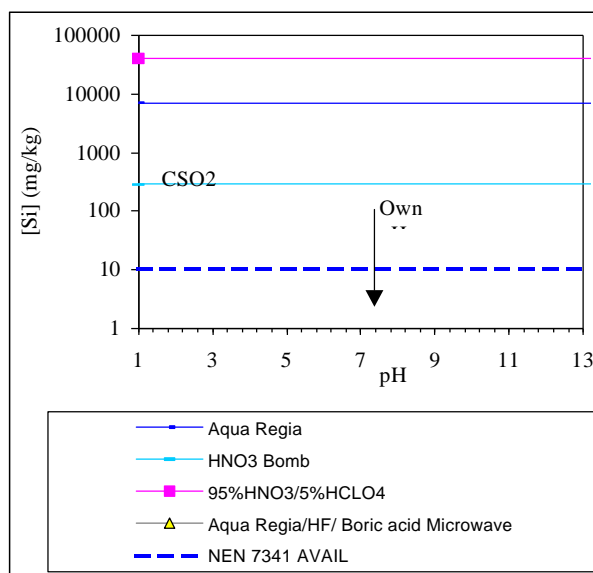


Figure 1 Solubility of silicium during digestion with different acids (van der Sloot, 2003)

Figure 2 illustrates the situation on solubility of cadmium from a sludge sample when a different extraction media is used, ranging from the stronger digestion media of hydrofluoric acid and perchloric acid to leaching tests that simulates natural leaching conditions. The stronger digestion methods show solubilities of up to 10^4 times the amounts brought into solution in leaching tests. The solubility obtained when aqua regia and nitric acid digestions are used are comparable to that of the "total" digestion when hydrofluoric acid is used. Data from extraction studies for other elements may be seen from the desk study on leaching tests (van der Sloot, 2003).

By comparing the potential total and partial leachable (extractable) and leaching with water at controlled pH, it is seen from that study that from an environmental impact evaluation perspective the total composition (and the composition derived from partial digestion) is hardly relevant, as several orders of magnitude difference may exist between the total composition (and partial composition) and fraction that under even extreme environmental conditions in the relevant pH range for the materials will be leached to the environment. From this perspective, the choice of the partial destruction method may be less critical than deciding what information is really important from an environmental impact evaluation perspective.

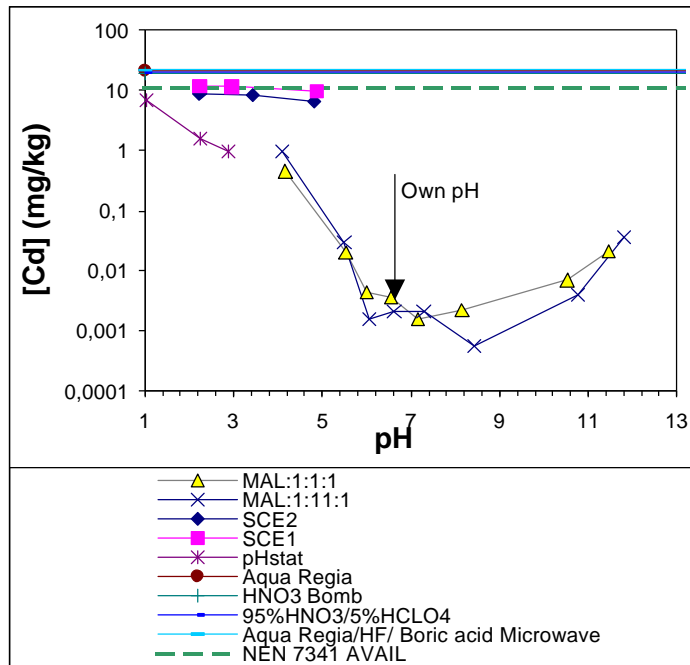


Figure 2 Comparison of solubility of cadmium under different leaching/extraction conditions (van der Sloot 2003)

For mass balance purposes or other cases, where the total content is of importance, “total” digestion methods or XRF has to be applied, otherwise the “partial” methods are judged sufficient. Different "partial" methods can be used provided that the methods lead to comparable results for given matrix.

Much data material shows that aqua regia and nitric acid digestions provide close to 100% of the total element composition depending on the matrix considered. (Exceptions are e.g. element bound to silicate matrix as shown above). For environmental analysis partial digestion fits for the purpose. To achieve comparable results by a certain method the conditions of the procedure should be defined clearly, in order to keep the reproducibility of the digestion step in a reasonable range.

Among other factors, the uncertainty of the determination step is influenced by the composition of the digestion solution and also depends on the method of determination. In general, the determination of trace elements by the use of graphite furnace atomic absorption (HGAAS) or inductively coupled mass spectrometry (ICPMS) exhibits major interference effect for a number of elements, whereas flame atomic absorption (FAAS) and optical emission spectrometry (ICP-AES) generally exhibit less effects (but have higher detection limits). However, the consideration of interference effect differs from element to element. For digestion solutions the major interferences originates from the acids used for digestion. An important interference, which is related to aqua regia in particular, is the interference from high chloride concentrations in the extract on ICPMS and HGAAS determinations. Thus the choice of digestion method is

not only a question of the digestion itself; proper consideration also needs to be given to the subsequent determination step.

The uncertainties on the measurement of trace element composition in solid matrices consist of uncertainty from the digestion step and the uncertainty from the determination step. The combined uncertainties may be seen from the results from interlaboratory studies, however, often the data do not leave the possibility to determine the size of uncertainty coming from the digestion and the uncertainty attributed to the determination. The distinction between the two uncertainty elements is only possible in interlaboratory studies where the participating laboratories receive both a solid sample and the same digested sample (Annex 2E) or in studies where the laboratories conduct the digestion step and analysis is done by one central laboratory with the same method for all samples.

3. EXISTING STANDARDS OR DRAFT STANDARDS

3.1 Aqua regia digestion

Aqua regia is an acid mixture containing three volumes of concentrated hydrochloric acid and one of nitric acid. It is commonly used for digestion of solid samples and subsequent analysis of elements as it has a strongly oxidising effect. Nevertheless, the analysed concentration after aqua regia digestion cannot be called "total content" for the dissolution is not complete for all kinds of matrices. Especially elements bound to the silicate matrix will not be totally solubilized. Therefore, some experts speak of aqua regia extraction for the subsequent analysis of the aqua regia soluble portion of elements.

The organic matrix is usually totally dissolved by aqua regia, proven by several studies (validation data EN 13346 and EN 13657) where a comparison of analytical data of sewage sludge digested with aqua regia and hydrofluoric acid (mixture) – normally regarded as total dissolution – was conducted.

For aqua regia digestion of different materials, the following international standards have been identified:

Table 4 Aqua regia digestion (International standards)

Soil	Sludge	Biowaste	Waste	Water
ISO 11466	EN 13346	EN 13650	EN 13657	EN ISO 15587-1

The degree of dissolution of the solid sample with aqua regia depends on the input of energy and the reaction time as well as on the matrix and grain size of the sample. The cited methods differ in some of these parameters. They were prepared for different matrices and use different energy sources: ISO 11 466 and EN 13650 describe only methods by thermal heating while in EN 13346, EN 13657 and EN ISO 15587-1 it is allowed to use either thermal heating or energy supply by a microwave oven. The main points are described in the following short descriptions of the different methods:

3.1.1 Soil

Reference: ISO 11466 Soil quality – Extraction of trace elements soluble in aqua regia

Table 5 Short description of the method ISO 11 466

	ISO Standard: Soil quality – extraction of trace elements soluble in aqua regia (ISO, 1995)
Country	ISO member countries world-wide
Materials/matrices	Soil and similar materials, containing less than 20% organic carbon
Pre-treatment	According to ISO 11464 or mill and sieve through the 150 µm sieve
Sample size	3 g milled sample with particle size less than 0,115 mm
Reagents	H ₂ O HCl (12.0 mol/L, density ≈ 1.19 g/L) HNO ₃ (15.8 mol/L, density ≈ 1.42 g/L)
Procedure	Weigh sample into reaction vessel, moisten with 0.5 – 1.0 mL of water add, while mixing 21 mL HCl followed by 7 mL HNO ₃ drop by drop. Add 15 mL dilute HNO ₃ (0.5 mol/L) to the absorption vessel and connect with reaction vessel and allow to stand for 16 h at room temperature. Raise temperature until reflux conditions and maintain for 2 h, then allow to cool, add contents of the absorption vessel to reaction vessel via

	condenser, rinse with further 10 mL dilute HNO ₃ (0.5 mol/L), decant relatively sediment-free supernatant carefully through filter and collect filtrate in volumetric flask. Wash insoluble residue onto the filter paper with nitric acid, collect this filtrate with the first.
Modifications/ alternatives	Materials containing more than about 20% organic carbon require treatment with additional HNO ₃
Approved elements	Trace elements not further specified. Reference to Cd, Cr, Co, Cu, Pb, Mn, Ni, Zn
Analysis method Other comments	AAS techniques

Updated and supplemented from Nordtest techn. report 446 (Hjelmar et al, 1999)

For soil samples, usually the fraction <2 mm is used for further sample preparation (air drying, grinding, sieving). A note in paragraph 3 Principle states that for some soil types experience has shown that there is little difference between the results before and after grinding.

3.1.2 Sludge

Reference: EN 13346 Characterisation of sludge – Determination of trace elements and phosphorus – Aqua regia extraction methods

The standard describes 4 different methods for digestion, two using conventional heating, and two using microwave oven.

Table 6 Short description of the method EN 13346

	Characterisation of sludge – Determination of trace elements and phosphorus – Aqua regia extraction m
Materials/matrices	Sludge and sludge products
Pre-treatment	Weigh a representative amount of the wet sample, to give a sufficient dry mass for the method used, in a porcelain dish and prepare it according to EN 12880. Take the dried sample and grind with contaminant free pestle and mortar or mill. Keep the sample under dry conditions. Variations: air-drying or freeze-drying
Sample size	Method A: Approximately 3 g, weighed to the nearest 0.001 g Method B: Approximately 0.5 g, weighed to the nearest 0.001 g Method C: Approximately 0.3 g to 1 g, weighed to the nearest 0.001 g Method D: Approximately 0.5 g to 1 g, weighed to the nearest 0.001 g
Reagents	Deionized or distilled water purity grade 2 of EN ISO 3696 HCl (12.0 mol/L, about 37% (m/m), __ 1.18 g/mL) HNO ₃ (15.8 mol/L, about 65% (m/m), __ 1.42 g/mL)
Procedure	Method A: Transfer sample to the 250 mL reaction vessel. Moisten with about 0.5 mL to 1.0 mL of water and add 21 (± 0.1) mL of HCl followed by 7 (± 0.1) mL of HNO ₃ . Connect the condenser to the reaction vessel, leave at room temperature until any effervescence has almost settled (?). Transfer to the heating device and raise the temperature of the reaction mixture slowly to reflux conditions and maintain for 2 h ensuring that the condensation zone is lower than 1/3 of the height of the condenser, then allow to cool. Rinse the condenser into the reaction vessel with 10 mL of water. Method B: Transfer the sample to the 50 mL glass tube. Add 1.0 (± 0.1) mL of water to wet the sample. Carefully run 6 (± 0.1) mL of HCl down the side of the tube followed by 2.0 (± 0.1) mL of HNO ₃ . Place the tube in the heating apparatus and adjust the control so that the sample gently refluxes. After 10 (± 2) min., wash down the sides of the tube with about 5 mL of water. Reflux for a further 5 (± 1) min., then remove the tube from

	<p>the block. Allow cooling and make up to volume with water. Stopper the tube and mix by inversion. Transfer the digested sample into a suitable-sized volumetric flask and dilute to the mark with water.</p> <p>Method C: Transfer the sample to the vessel. Add (2 ± 0.1) mL HNO₃ and 6 (± 0.1) mL of HCl. Place cover and spring on the top of the vessel. Weigh the reaction vessel to the nearest 0.1 g. Place it in the rotor. Place the rotor in the microwave oven and start the digestion programme. Cool the rotor to room temperature. Check the mass of the vessel and the condition of the safety membrane or cover. Control that the loss of mass does not exceed 10% (<i>m/m</i>) of the initial mass. Open the vessel slowly under fume extraction. Transfer the digested sample into a suitable-sized volumetric flask and dilute to the mark with water.</p> <p>Method D: Transfer the sample into the vessel, add the acids according to the programme chosen, cap the vessel with the reflux column and place the vessel in the microwave unit and run the programme. At the end of the microwave programme, allow the vessel to cool to room temperature. Uncap and vent under fume extraction. Transfer the digested sample into a suitable-sized volumetric flask and dilute to the mark with water.</p>
Modification/ alternatives	4 methods in the standard
Approved elements	As, Cd, Cr, Cu, Hg, Ni, Pb, Se, Zn and P
Analysis method	Spectrometric techniques: AAS, ICP-OES, ICP-MS
Other comments	

Updated and supplemented from Nordtest techn. report 446 (Hjelmar et al, 1999)

3.1.3 Soil improvers and growing media

Reference: EN 13650 Soil improvers and growing media – Extraction of aqua regia soluble elements

Table 7 Short description of the method EN 13650

	Soil improvers and growing media – Extraction of aqua regia soluble elements
Materials/matrices	Soil improvers or growing media
Pre-treatment	Take approximately 5 g of the sample prepared in accordance with EN 13040:1999, clause 9, and grind the sub-sample by using a mill until all the sub-sample has passed through a 500 µm sieve
Sample size	Approximately 1 g to 3 g, to the nearest 0.001 g
Reagents	HCl (12 mol/L; 1.18 g/mL; 37% mass/volume) HNO ₃ (15 mol/L; 1.42 g/mL; not less than 65% mass/volume)
Procedure	Weigh the test sample into the reaction vessel. Moisten with about 0.5 mL to 1.0 mL water. Add while mixing, 21 mL of HCl followed by 7 mL HNO ₃ . Leave at room temperature for 16 h. Add a few roughened glass beads and place the reaction vessel on a cool heating apparatus. Raise the temperature of the reaction mixture slowly until reflux conditions are reached and maintain for 2 h ensuring that the condensation zone is lower than 1/3 of the height of the condenser, then allow to cool. Transfer the contents of the reaction vessel to a 100 mL volumetric flask. Wash the reaction vessel at least three times with water by decanting each washing into the volumetric flask before adding the next. Dilute to the mark with water and mix. Leave until most of any insoluble residue settles out of suspension. Decant the relatively sediment-free supernatant onto a filter paper discarding at least the first 10 mL of filtrate.
Modification/ alternatives	If there is more than 0.85 g of organic matter (corresponding to about 0.5 g of organic carbon) in the test sample, then reduce the quantity of sample

	analysed or proceed as follows. Leave the first reaction with aqua regia to subside. Then add an extra 1 mL of nitric acid only to every 0.17 g of organic matter above 0.85 g. Do not add more than 10 mL of nitric acid at any time, and leave any reaction to subside before proceeding further. If there is any doubt about the amount of organic matter present, carry out a determination according to EN 13039.
Approved elements	Elements not further specified. Reference to P, K, Ca, Mg, Na, B, Cu, Fe, Mn, Mo, Zn, S, Cd, Pb, Cr, Ni
Analysis method Other comments	ICP-AES, AAS, flame emission spectrometry, photometry

Updated and supplemented from Nordtest techn. report 446 (Hjelmar et al, 1999)

3.1.4 Waste

Reference: EN 13657 Characterisation of waste – Digestion for subsequent determination of aqua regia soluble portion of elements

Table 8 Short description of the methods in EN 13657

	Characterisation of waste – Digestion for subsequent determination of aqua regia soluble portion of elements in waste (European Standard, 2002)
Materials/matrices	Waste
Pre-treatment	The test portion without any pre-treatment, if possible. Only if the test portion is representative for the laboratory sample and the effectiveness of the digestion is proven. If not, pre-treatment of the laboratory sample without changing the concentration of the elements of interest. Pre-treatment should include drying or grain size reduction to a particle size below 250 µm for solid waste or homogenizing by the use of a high-speed mixer or sonification for liquid samples.
Sample size	0.2 – 0.5 g for closed microwave digestion 0.2 - 1.0 g for semi-open microwave digestion 1 - 10 g for thermal heating in reflux system
Reagents	H ₂ O HCl (35 – 37% (m/m)) HNO ₃ (65 – 70% (m/m))
Procedure	<p>Microwave-assisted digestion in closed vessels: Weigh sample into vessel, if necessary moisten with minimum of water, add 6 mL of HCl and 2 mL of HNO₃, close and transfer vessel into microwave unit and heat for 2 min. at 250 W, 2 min. at 0 W, 5 min. at 250 W, 5 min. at 400 W and 5 min. at 500 W. Let vessel cool to room temperature. Confirm that no loss of digestion solution occurred during the procedure (e.g. by control of burst membrane, referring to the manufacturer's specifications or control of mass). Otherwise, the samples have to be discarded. Uncap and vent each vessel in a fume hood, then transfer into a volumetric flask and fill to the mark.</p> <p>Microwave-assisted digestion in semi-open vessels: Transfer the digestion vessels into the microwave-unit cavity according to the manufacturer's instructions and start the following digestion procedure. Add 9 mL HCl and 3 mL HNO₃ and heat for 15 min. at 40 W, then add again 9 mL HCl and 3 mL HNO₃ and heat for 15 min. at 40 W. Leave the vessels to cool down to room temperature. Transfer into a suitable-sized volumetric flask and dilute to the mark.</p> <p>Thermal heating digestion in reflux system: Add HCl followed by nitric acid. The mass: volume ratio between sample and acid mixture shall be 1:10. Connect the condenser to the reaction</p>

	vessel, fill the absorption vessel with aqua regia. Connect the absorption vessel to the condenser and leave at room temperature until effervescence has settled. Raise the temperature of the reaction mixture slowly to reflux conditions and maintain for 2 h, then allow to cool. Add the content of the absorption vessel to the reaction vessel via the condenser, rinsing both the absorption vessel and condenser with further 10 mL of diluted nitric acid. If the digested mixture contains particles, the sample may be centrifuged, allowed to settle or be filtered. In the case of filtration, dilute the content of the vessel before filtering, rinse and then dilute to the mark of the volumetric flask.
Modification/ Alternatives	3 methods in the standard
Approved elements	Al, Sb, As, B, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Mo, Ni, P, K, Se, Ag, S, Na, Sr, Sn, Te, Ti, Tl, V, Zn
Analysis method Other comments	AAS-methods, ICP-OES and ICP-MS

Updated and supplemented from Nordtest techn. report 446 (Hjelmar et al, 1999)

3.1.5 Water (EN ISO 15587-1)

Reference: EN ISO 15587-1 Water quality – Digestion for the determination of selected elements in water – Part 1: Aqua regia digestion

Table 9 Short description of the method EN ISO 15587-1

	Water quality – Digestion for the determination of selected elements in water – Part 1: Aqua regia digestion
Materials/matrices	Water
Sample size	25 mL
Reagents	H ₂ O HCl (35 – 37% (m/m) HNO ₃ (65 – 70% (m/m)
Procedure	2 digestion principles: Digestion in an open system Digestion in a closed system
Modification/ Alternatives	4 methods of energy input given as informative annexes: Digestion in an open system by the use of electrical heating Digestion in an open system by the use of microwave-assisted heating Digestion in a closed system by the use of microwave-assisted heating Digestion in a closed system by the use of an autoclave
Approved elements	Ag, Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Se, Sn, Sr, Tl, V, Zn
Analysis method Other comments	- Equation for the ratio between digestion period and digestion temperature

This standard describes 2 methods for aqua regia digestion of water samples – closed vessel and open vessel. The method is developed for water of low content of suspended solids and may not prove comparable to methods developed for solid samples, due to dilution of digestion solution. The digestion in open vessels prescribe a digestion time period of ? hours. For the closed vessel digestion, an equation describes a relation between the temperature of the digestion vessel and the time needed for digestion, thus enabling laboratories to choose. No information has been identified as to the applicability of this method (or the principle in it) for solid environmental samples.

Additional to the mentioned international standards there are several national standards on aqua regia digestion available in the member states. One example is DIN 38 414 S7 from 1983 for sludge and sediments.

3.1.6 Sludge and sediments (DIN 38 414 S7)

Reference: DIN 38 414 S7: Sludge and Sediments (Group S). Digestion using aqua regia for subsequent determination of the acid-soluble portion of metals (S7)(DIN,1983)

Table 10 Short description of the method DIN 38 414 S7

Method DIN 38 414 S7	German standard method: Sludge and Sediments (Group S). Digestion using aqua for subsequent determination of the acid-soluble portion of metals (S7) (DIN, 1983)
Country	Germany
Materials/matrices	Sludge and sediment samples
Pre-treatment	
Sample size	3 g milled sample with particle size less than (0.1 mm)
Reagents	H ₂ O HCl (density = 1.19 g/mL) HNO ₃ (density = 1.40 mg/L)
Procedure	Weigh sample into reaction vessel, moisten with little H ₂ O, add while mixing 21 mL HCl, followed by 7 mL HNO ₃ , add 10 mL dilute HNO ₃ to the absorption vessel and connect with reaction vessel and leave for several hours at room temperature. Raise temperature until boiling conditions and maintain for 2 h, then allow cooling. Add contents of the absorption vessel to reaction vessel via condenser, rinse with further 10 mL dilute HNO ₃ , decant relatively sediment-free supernatant carefully through filter and collect filtrate in volumetric flask for analysis
Modification/ alternatives	Materials containing more than about 20% organic carbon require treatment with additional HNO ₃
Approved elements	Elements not further specified. Reference given to other DIN Standards
Approved elements Other comments	Reference given to other DIN Standards

Updated and supplemented from Nordtest techn. report 446 (Hjelmar et al, 1999)

3.2 Nitric acid digestion

Nitric acid digestion results in dissolution of many common metals and is especially useful for oxidation of organic matter. Nitric acid is manufactured in very pure form with a very low content of trace element. Furthermore, nitric acid is the acid of choice considering the low interference effect in respect to many subsequent analytical methods. This makes it very suitable for analytical chemistry purposes. Due to the strong oxidising effect and low interference effect in the subsequent analysis it is commonly used for digestion of solid samples. Since this method is a partial method and not intended to accomplish total decomposition of the sample, the extracted element concentration may not reflect the total content in the sample. Like aqua regia, especially silicate matrix will not be totally solubilized. The fraction dissolved may be described as the "nitric acid soluble portion" of elements in a given matrix.

For nitric acid digestion of different environmental matrices the following international and national standards have been identified:

Table 11 Nitric acid digestion (National and International standards)

Soil	Sludge	Sediment	Water
SS 02 83 11 US EPA 3051 US EPA 3050B	SS 02 81 50, 2.ed. DS 259, DS 2210 + equivalent Norwegian and Finnish standards. US EPA 3051 US EPA 3050B	SS 02 81 50, 2.ed. DS 259, DS 2210 + equivalent Norwegian and Finnish standards. US EPA 3051 US EPA 3050B	EN ISO 15587-2 SS 02 81 50 DS 259, DS 2210 + equivalent Norwegian and Finnish standards

Updated and supplemented from Nordtest techn. report 446 (Hjelmar et al, 1999)

A majority of the presented methods for nitric acid digestion as shown in Table 11 is based on the use of autoclave heating at 120°C or 200 kPa (closed vessel digestion). However, during the last years microwave techniques have been taking over. The EN ISO 15587-2 is a modular international standard in which the digestion is defined from the energy input (defined for open and closed digestion by the temperature and the digestion time period), coming from e.g. autoclave digestion, open vessel on a heating block or digestion in a microwave oven.

US EPA 3051 describes a method on microwave digestion of soil, sludge and sediment using nitric acid. It provides a rapid multielement digestion technique and an alternative to methods using hydrochloric acid (such as US EPA 3050 A or equivalent EN standards). It is developed due to the analytical problems encountered in the analysis of hydrochloric acid based digest by the subsequent analytical procedures – graphite furnace atomic absorption (GFAAS) and inductively coupled plasma mass spectrometry (ICPMS). The use of GFAAS and ICPMS are especially relevant for solid samples of low content of elements (e.g. clean soil) requiring low detection limits and for the analyses of arsenic and selenium in solid samples. USA EPA 3050B is a hot plate digestion method, in which there is a choice between nitric acid and hydrochloric acid digestion, depending on the detection limit requirements. For arsenic and selenium only nitric acid digestion is prescribed. The method again reflects that nitric acid is superior for elements requiring GFAAS and ICPMS determination.

The nitric acid digestion method by the use of autoclave has been selected as the method of choice in "Nordic guideline for chemical analyses of contaminated soil samples". Prior to publication, the method was validated in an interlaboratory comparison with 26 participants from the Nordic countries. The method was validated for As, Cd, Cr, Cu, Pb, Hg, Ni, and Zn. (Karstensen, 1996).

Numerous data based on the digestion with nitric acid in combination with autoclave digestion are available from interlaboratory comparisons and can be used for characterization of the method in respect to analyses of soil, sludge, and sediment. Fewer data exist for waste.

3.2.1 Soil (SS 028311)

Reference: SS 028311 Soil analysis – determination of trace elements in soils – extraction with nitric acid.

Table 12 Short description of the method SS 028311

	Swedish Standard: Soil analysis – determination of trace elements in soils – extraction with nitric acid (Swedish Standards Institute SSI, 1997)
Materials/matrices	Soil with low content of trace elements
Pre-treatment	Reference to ISO 11 464
Sample size	Up to 5 g, organic rich samples maximum 2 g
Reagents	H ₂ O HNO ₃
Procedure	Weigh sample into vessel, add 20 mL 7 M HNO ₃ , heat in autoclave at 200 kPa or 120°C for 30 minutes. Cool at room temperature, filter or centrifuge solution into volumetric flask
Modification	
Approved elements	Trace elements, not further specified. Reference to 33 elements: Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Si, Sn, Sr, Ti, V, W, Zn, Zr.
Analysis method	ICP and AAS techniques
Other comments	

Updated and supplemented from Nordtest techn. report 446 (Hjelmar et al, 1999) (Pre-treatment added)

3.2.2 Water, sludge, and sediment

Reference: DS 259: Determination of metals in water, sludge and sediments. General guidelines for determination by atomic absorption spectrophotometry in flame (Technical equivalent to Finnish Standard SFS 3044, Norwegian Standard NS 4770 and Swedish Standard SS 02 81 50)

Table 13 Short description of the method DS 259

	Danish Standard: Determination of metals in water, sludge and sediments. General guidelines for determination by atomic absorption spectrophotometry in flame (Danish Standard, 1982)
Materials/matrices	Water, sludge and sediments
Pre-treatment	
Sample size	Up to 1 g (dry weight) or equivalent wet sample size
Reagents	H ₂ O HNO ₃
Procedure	Weigh sample into vessel, add 20 mL 7 M HNO ₃ , heat at 200 kPa pressure (120°C) for 30 min. Cool at room temperature, decant sediment-free supernatant, if necessary through filter, and collect filtrate in volumetric flask. Dilute to 100 mL.
Modification	Different procedure described for water samples
Approved elements	Not specified
Analysis method	AAS flame, but generally used in combination with other AAS techniques (equivalently described in DS 2210), ICP and ICPMS methods.

Other comments	The content of the standard is technically equivalent to Finnish Standard SFS 3044, Norwegian Standard NS 4770 and Swedish Standard SS 02 81 50
----------------	---

Updated and supplemented from Nordtest techn. report 446 (Hjelmar et al, 1999)

3.2.3 Sediment, sludge, soil and oil (US EPA 3051)

Reference: US EPA 3051. Microwave-assisted acid digestion of sediments, sludges, soils, and oils (US EPA, revised 1998)

Table 14 Short description of the method US EPA 3051

	Microwave assisted acid digestion of sediments, sludges, soils, and oils.
Materials/matrices	Sediments, sludges, soils and oils
Pre-treatment	
Sample size	Up to 0.5 g
Reagents	H ₂ O Concentrated HNO ₃
Procedure	Weigh sample into vessels, add 10 mL conc. HNO ₃ , close and place vessel in microwave unit. Heat to 175°C within 5.5 min., maintain 175°C for remaining part of 10 min. Uncap and vent, transfer sample to acid-cleaned bottle and centrifuge, allow to settle or filter, dilute with H ₂ O to known volume
Modification	-
Approved elements	26 elements: Ag, Al, Sb, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, Pb, Se, Sr, Tl, V, and Zn
Analysis method	AAS flame and graphite furnace, ICP-AES and ICP-MS
Other comments	Options for improving the performance for certain analytes, such as antimony, iron, aluminium, and silver by addition of hydrochloric acid, when necessary.

3.2.4 Water (EN ISO 15587-2)

Reference: EN ISO 15587-2 Water quality – Digestion for the determination of selected elements in water – Part 2: Nitric acid digestion

Table 15 Short description of the method EN ISO 15587-2

	Water quality – Digestion for the determination of selected elements in water – Part 2: Nitric acid digestion
Materials/matrices	Water
Sample size	25 mL
Reagents	H ₂ O HNO ₃ (65 – 70% (m/m))
Procedure	2 digestion principles: Digestion in an open system Digestion in a closed system
Modification/alternatives	4 methods of energy input given as informative annexes: Digestion in an open system by the use of electrical heating Digestion in an open system by the use of microwave-assisted heating Digestion in a closed system by the use of microwave-assisted heating Digestion in a closed system by the use of an autoclave
Approved elements	Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, P, Pb, Se, Sr, Tl, V, Zn (Not suitable for Sb and Sn)
Analysis method	-
Other comments	Equation for the ratio between digestion period and digestion temperature

4. EVALUATION OF DRAFTING A HORIZONTAL STANDARD

4.1 General

Two general principles of partial digestion have been evaluated: Methods using aqua regia and methods using nitric acid. Among each group of methods more principles are described. There are e.g. slight modifications in regard to amount of sample, reagent composition and heating time, many of which can be explained by the matrices that the standards are intended to describe and each of which theoretically could lead to different extraction ability and thereby different results. One general observation in regard to variability of methods is the different heating principle described in the methods. The principles range from conventional heating in open vessels for 2 hours, heating in autoclave (under pressure) for 30 minutes and heating in a microwave oven (open or closed) for 15 to 30 minutes.

One of the driving forces for development of more digestion techniques rather than using the conventional heating block technique is the demand on analytical methods that are in accordance with the development of modern laboratory techniques. For the development of a horizontal and modular standard it is proposed to continue this effort, however in due consideration to the comparability to more conventional and tedious methods.

As is the case with the horizontal standard EN ISO 15587 (part one and two) for digestion of water samples, it is suggested to develop the nitric and aqua regia standards for the solid matrices in a parallel manner, except for the acid mixtures used.

Aqua regia methods are the conventional group of methods in many EU countries. Nitric acid based methods are the methods of choice in e.g. the Nordic countries. Thus the majority of data (e.g. monitoring data) are based on these methods, respectively. Aqua regia, composed of three parts of hydrochloric acid and one part of nitric acid, increases the difficulties of detection with some analytical techniques or influences the limit of detection and potentially results in data of lower reproducibility – compared to the use of nitric acid alone (data from evaluation of US EPA 3051). Nitric acid on the other hand shows lower extractability for certain element (e.g. aluminium (Al), silver (Ag) and antimony (Sb)). The choice of method in a given situation should be based on consideration of the quality requirement needed for the particular purpose and it is questionable if one digestion method alone is suitable for all elements considered.

4.2 Aqua regia digestion methods

For the drafting of a horizontal standard the following existing standards have been taken into account:

ISO 11466	Soil quality – extraction of trace elements soluble in aqua regia (ISO, 1995)
EN 13346	Characterisation of sludge – Determination of trace elements and phosphorus – Aqua regia extraction
EN 13650	Soil improvers and growing media – Extraction of aqua regia soluble elements
EN 13657	Characterisation of waste - Digestion for subsequent determination of aqua regia soluble portion of elements in waste (European Standard, 2002)

For the evaluation of the different standards they were compared in detail chapter by chapter and the text that seems to be more general or best fitting for a broad variety of matrices was selected as proposal for the common draft standard as described in the table below.

Scope

The scope is rewritten as a common scope for all matrices covered by the standard. As there are

not enough validation data available for all kinds of materials, elements and analytical methods that should be covered by this draft horizontal standard, the elements and analytical measurement standards for elemental analysis are not mentioned in the scope.

Normative references

References were made to the digestion standards and one general measurement standard – more detailed references can only be made after the results of the project HORIZONTAL on analysis of elements, TOC and dry residue are available.

Definitions

Definitions are very poor in most of the cited standards, in this case the broadest definitions seemed to be useful.

Safety remarks

A chapter on safety remarks is included due to e.g. the potential hazards on the use of strong acids.

Reagent and equipment

For reagents and equipment the most detailed descriptions in the different standards were chosen.

Interferences

A chapter containing interference is included.

Pre-treatment of samples

A critical point is the way the samples are treated before digestion. In addition to many possibilities of loss and contamination during drying, milling, grinding and sieving the particle size proved to be crucial for the grade of digestion, especially for refractory matrices (Giove 2000). As a compromise between the varying requirements, a particle size of 250 µm is proposed for the horizontal draft standard, as this proved to be the minimum requirement of the cited robustness test. It may be supposed that for sludge and some kind of soils the particle size may not have that influence on the grade of digestion as for other matrices. Especially for silicates the recovery rates depend on the particle size (Annex 2C), a standardized particle size is thus a precondition for comparable data.

A robustness study on this issue for the matrices covered in the project "Horizontal" is necessary before any concrete specification on particle size and grade of milling as well as on the possible influence of drying methods will be fixed. The rather general statements in this chapter of the draft standard are only proposals for further investigation.

Procedure

Three procedures were selected for the draft standard, as it seemed to be the most pragmatic way to lay down concrete conditions not only for conventional heating but also for microwave digestion. As many labs use microwave digestion in their every day practice anyway, it makes no sense to standardise only the best-known conventional heating method and leave the conditions of microwave digestion open for the labs. However, many routine labs use microwave digestion anyway and if they make in-house validation to prove comparability with the standardized heating method, many different power programs/temperatures will be used all over Europe and will potentially lead to more varying results, than if power settings/temperature is prescribed in the standard. But more research work has to be done and results of interlaboratory trials for all the different matrices must be available before the procedures are fixed.

The decision of choosing the three already standardized methods was taken due to pragmatic reasons as they are well known, broadly used and a lot of validation data are already available (Annex 2D). In the round robin test for validation of the standard on waste reproducibility

proved to be in a rather wide range, because the participating labs were free to use their own analytical methods (Annex 2E). The draft horizontal standard must be validated by separating the variation of the analytical step from the digestion step in a joint validation of these two modules, digestion and analysis. Additional robustness studies are necessary for investigation of the influence of specific digestion conditions, especially the influence of temperature as mentioned in ISO 15587-1.

In the sludge standard a fourth method with heating in a tube is mentioned. This procedure should be taken into account for the research and validation studies. Till now only validation data for sludge are available, but it may prove to be applicable also for other matrices.

Precision and accuracy

Validation data were available from several existing standards. As the proposed methods in the draft horizontal standard – as it is now – do not differ remarkably from the original standards, the validation data may be used as an annex to the draft. But for the finalized version, additional data should be available.

Table 16 Evaluation of available ISO and CEN standards resulting in a draft horizontal standard

Paragraphs	ISO 11466	EN 13346	EN 13650	EN 13657	Proposal Horizontal
Foreword	yes	yes	yes	yes	
Introduction	no	yes	no	yes	
Scope	soil	sludges	soil improvers and growing media	waste	Soil, sludge, soil improvers and growing media, waste
References	ISO 3696 (1987), ISO 10694 (1995)-TOC, ISO 11464 (1994), ISO 11465 (TS),	EN 1233, EN 1483, EN 12880 (TS), EN ISO 3696, EB ISO 5961, EN ISO 11885, EN IOS 11969, ISO 5725-2, ISO 8288	EN ISO 3696, EN 13039 (TOC), EN 13040	EN ISO 3696 (1995), ENV 12506	EN ISO 3696, EN 12506 TOC and dry matter – proposal Horizontal
Definitions	---	Aqua regia, TS (EN 12880)	Defintions as in EN 13039, 13040	Aqua regia, TS, digestion, sample, ...	As in EN 13657
Principle	Short description (1 method) + Note (pre-treatment)	Short description 4 methods	Short description 1 method pretreatment	---	---
Safety remarks	as foreword	---	in foreword + (8) procedure	(4) Safety remarks	As (4) in EN 13657
Reagents	(4): H ₂ O, HCl c in mol/L, , HNO ₃ conc.+diluted (0,5 mol/L)	(5) H ₂ O, HCl, HNO ₃ conc + 1% c in mol/L + %	(5): H ₂ O in general, HCl, HNO ₃ conc. + dil. 0,5 mol/L	(7): H ₂ O in general, HCl, HNO ₃ conc in % + dil. 0,5 mol/L	As (5) in EN 13650
Apparatus	(5): all for 1 method, gen: cleaning incl. pretreatment	(6) gen: cleaning vessel, oven, filter, for 4 methods	(6): Gen cleaning + note, pretreatment, vessel + all for 1 method	(6): oven + vessel for 3 methods + general equipment	As in EN 13346
Interferences	---	---	---	(8)	As in EN 13657
Sample/pre-treatment	(6) air dry, ISO 11464 or mill 150 µm (or NOTE 2) – 20 g water content of milled sample	(7) dry at 105°C (EN 12880) Homogenization with mortar + pistil or Annex A freeze dry	(7) EN 13040 (9), mill 500 µm particle size	(5) if possible without pretreatment, dry, 250 µm, >200 mg test portion	Air dry (or freeze dry), mill if necessary 250 µm particle size
Procedure blank test	-	(9)	(8.3)	(9.1)	
A) Conventional Heating	(7) 3 g sample test portion 250 mL vessel + 0,5 – 1 mL H ₂ O + 21 mL HCl + 7 mL HNO ₃ Reflux + absorption vessel 16 h room temperature 2 h reflux	(8.1) 3 g 250 mL vessel + 0,5 – 1 mL H ₂ O 21 (± 0,1) mL HCl + 7 (± 0,1) mL HNO ₃ Reflux at room temperature until no reaction 2 h reflux	(8.2) 1 g – 3 g 250 mL vessel + 0,5 – 1 mL H ₂ O + 21 mL HCl + 7 mL HNO ₃ if TOC > 0,85 g add HNO ₃ 16 h at room temperature 2 h reflux	(9.4): 1 g – 10 g m:v = 1:10 reflux + absorption vessel if TOC > 0,5 g (30 mL a.r.) add HNO ₃ 2 h reflux	A) Conventional heating 3 g (if necessary 1-10g) procedure as in EN 13 346 Plus TOC as in EN 13650
B) Closed microwave	---	(8.3) 0,3 – 1 g + 2 mL HNO ₃ + 6 mL HCl Note: power prog: 2 min – 250 W; 2 min.0W; 5 min – 250 W, 5 min – 400 W; 5 min 500 W (calibration in Annex B)	---	(9.2) 0,2 g – 0,5 g + 6 mL HCl + 2 mL HNO ₃ power prog.: 2 min – 250 W; 2 min – OW; 5 min – 250 W; 5 min – 400 W; 5 min – 500 W (calibration in Annex A	B) Closed microwave 0,2g –1 g procedure as (9.2) in EN 13657
C) Open microwave	---	(8.4) 0,5 - 1 g + reflux Note: power prog: 15 min – 40 W 3 mL HNO ₃ + 9 mL HCL 15 min – 40 W 3 mL + 9 mL HCl	---	(9.3) 0,2 g – 1 g power prog: 9 mL HCl + 3 mL HNO ₃ – 15 min – 40 W + 9 mL HCl + 3 mL HNO ₃ – 15 min – 40 W	C) Open microwave 0,2 g– 1 g procedure as (9.3) in EN 13657
D) Glass tube	---	(8.2) 0,5 g 50 mL glass tube + 6 mL HCl + 2 mL HNO ₃ an room temp. until no reaction reflux 10 min + 5 mL H ₂ O reflux 5 min	---	---	---
Analysis	inf. Annex A scope: atomic spect. techn.	(10) references to analytical standards informative Annex C with possible interference	(9) Annex B informative ISO standards	methods in scope, literature	Infomative annex as Annex C in EN 13346
Test report	(8)	(12)	(12)	(10)	As (12) of EN 13346 combined with (10) of EN 13657
Precision/Validation	--	(13) Round robin test + Annex D (for 8.3, 8.4) certified reference mat.)	(11) + Annex A	Annex B: Round robin test + Robustness + certified reference mat.	Validation data for method A: (13) in EN 13346, Annex A in EN 13650, Annex B in EN 13657 Validation data for method B) and C): (13) and Annex D in EN 13346, Annex B in EN 13657

4.3 Nitric acid digestion

For the drafting of a horizontal standard the following existing standards have been taken into account:

SS 02 83 11	Soil analysis – determination of trace elements in soils – extraction with nitric acid.
DS 259, DS 2210 and equivalent Nordic standards (SFS 3044/ NS 4770/ SS 02 81 50)	Determination of metals in water, sludge and sediments . General guidelines for determination by FAAS/HGAAS
US EPA 3051, revised 1998	Microwave-assisted acid digestion of sediments, sludges, soils, and oils

The two first mentioned standards are technically equivalent, except for the scope of the standard. The third method is a method where the heating is accomplished by the use of microwave digestion. For the proposal of a horizontal standard the two first standards are compared in details and further compared to the text of the proposed horizontal standard for aqua regia. As it is proposed that the text of the two draft horizontal standards on digestion be harmonized the draft horizontal standard on aqua regia is taken into account. The comparison and proposal for a horizontal standard is given in Table 16.

The Swedish standard SS 02 83 11 is based on the digestion principle given in the Nordic standard DS 259/ DS 2210/ SFS 3044/ NS 4770/ SS 02 81 50 for determination of metals in water, sludge and sediment. Thus there is a great deal of similarity, but SS 02 83 11 is a more modern standard due to its recent development. However, information such as safety remarks, interferences, quality control and test report is not covered in any of the standards.

US EPA 3051 is a method revised in 1998 covering nitric acid digestion in microwave oven. The method is precise and well described and is validated for sediment, sludge, soil and oil samples. It is validated for 26 elements. The method includes an alternative digestion solution with the addition of concentrated hydrochloric acid to the nitric acid. The alternative solution is used for the stabilisation of certain elements, such as silver, barium and antimony and high concentrations of iron and aluminium in solution.

The US EPA 3051 method gives quality control proper attention. Regular duplicate analyses, regular spike addition and the use of reference material are covered. Furthermore, the standard precisely prescribes in detail procedures for calibration of the microwave oven. The digestion is controlled via requirements on the temperature, but calibration methods for instruments with power control are given. Further it gives due attention to interferences, safety precautions, equipment requirement, calibration and standardisation.

The method of choice, for those European countries in which nitric acid digestion is preferred, is the autoclave digestion. Therefore, priority has been given to the description of a horizontal autoclave digestion procedure, which should undergo further developments/validation during the present study. However, it is foreseen that, in future, laboratories will be using microwave digestion techniques. As numerous data already exist on the validation of the EPA 3051 on various matrices and on the comparison between this method and methods using hydrochloric acid, it is suggested that the method is compared to the autoclave method during the coming study, with the possibility to include the microwave digestion method in the horizontal method.

The following evaluation is limited to an evaluation of the autoclave method and is referring to the overview given in Table 16.

Scope

The scope shall be rewritten as a common scope for all matrices that are to be included. So far there is not enough validation data available for all kinds of materials and elements that could be covered.

References

Detailed references are to be made to the relevant modular horizontal standards on the analysis of elements. Further more references are given to the horizontal standard on dry matter.

Definitions

Definitions are given in none of the evaluated standards. The definitions, as proposed in the parallel standard on aqua regia, are suggested for this standard on nitric acid digestion.

Safety remarks

Safety is not covered in SS 02 83 11, nor is it properly mentioned in the other nitric acid standards. For the use of strong acid it is recommended to use a text equivalent to the text used in the parallel aqua regia standard.

Principle

Are to summarize the final method.

Interferences

A chapter containing interference similar to the chapter proposed for the aqua regia methods, where relevant, is proposed. Interferences are to be in accordance with results of the further evaluation of the method.

Pre-treatment

Pre-treatment before digestion is critical, as variability of results may be attributed to different procedure in regard to drying, milling, grinding and sieving. It is recommended that the text in regard to pre-treatment be harmonised with the parallel methods using aqua regia. Further investigations are needed, see also chapter 4.2.

Apparatus

The requirements regarding apparatus, vessels etc. are equivalent to the text in SS 02 83 11, except for the addition on requirement of an analytical balance.

Procedure

The procedure is limited to a method that prescribes autoclave heating at 120 or 200 kPa for 30 minutes.

The argumentation for the aqua regia digestion method mentioned in the previous chapter may also partly be used for the choice of a microwave oven digestion as opposed to autoclave digestion. However, it is recommended to await data on comparability of a microwave procedure to that of the autoclave method before implementation of the description in the standard.

Precision

Validation data are to be included in the final version of the standard. Validation data from proficiency tests are presently available and included in Annex 3 and 4.

Table 17 Evaluation of standards for nitric acid digestion in autoclave and proposal for horizontal standard

Paragraphs	Swedish standard SS 02 83 11	DS 259/DS2210/ SFS 3044/NS 4770/ SS 02 81 50	US EPA 3051A	Proposal Horizontal
Introduction	Yes	-	-	Given for horizontal standards
Scope	Soil	Water, sludge and sediment (include digestion as well as the analyses of the digests)	Sediments, sludges, soils, and oils Note on validated elements and subsequent analytical methods	Soil, sludge, soil improvers and growing media, waste
References	EN ISO 3696 ISO 11 464 + reference to various Swedish standards on determination of elements in the digested solution	National standards on: Sampling Dry matter Analysis of digests	-	EN ISO 3696 Horizontal standards for TOC and dry matter Horizontal standards for determination of elements in the digested solution Horizontal standard for pre-treatment of relevant matrices
Definitions	-	-	Reference to EPA definitions	Definition according to EN 13657 (equivalent to horizontal standard on aqua regia)
Principle	Given as a summary	Given as a summary	Given as a summary	Short description/summary
Safety remarks	-	-	Given as precaution notes throughout the text	Equivalent to horizontal standard on aqua regia
Reagents	<ul style="list-style-type: none"> Water (grade 2) or better HNO₃ conc.+diluted (7 mol/l) 	Water (grade 1) HNO ₃ conc.+diluted (7 mol/l) (quarts distilled, if accuracy demands requires) HNO ₃ diluted (7 mol/l)	HNO ₃ conc. HCl conc Water Requirement, that the reagent blank is less than MDL	<ul style="list-style-type: none"> Water (grade 2) or better HNO₃ conc.+diluted (7 mol/l)
Apparatus	Digestion vessels, autoclave, volumetric flasks and filter paper	Digestion vessels, autoclave, volumetric flasks and filter and filter paper	Microwave apparatus with temperature monitoring and feed back control (temperature sensor within ± 2°C) (alternatively, programmable power, controlled to within ± 12 W) A rotating turntable or equivalent Volumetric flasks Filter paper, filter funnel Analytical balance	<ul style="list-style-type: none"> Digestion vessels Autoclave Volumetric flasks and filter paper Analytical balance with an accuracy of 0,1 mg or better
Interferences	-	Interferences in regard to the subsequent analysis are covered	High pressure upon digestion Refractory sample matrix Corrosion from vessels	Equivalent to horizontal standard on aqua regia
Sample/pre-treatment	Reference to ISO 11 464	No requirements, except for storage		Reference to horizontal standard for pre-treatment of relevant matrices
Procedure blank test E) Conventional Heating F) Closed microwave G) Open microwave H) Glass tube	Max. 5 g (2g) sample test portion- Add 20,0 mL HNO ₃ (7 mol/l) Allow to stand until visible reaction has stopped Heat in autoclave for 30 min. at 200 kPa or 120°C Allow to cool Filter or centrifuge the digest Transfer the filtrate to 50 mL volumetric flask and fill to mark with water ---	Test portion equivalent to max. 1 g dried sample Add 20.0 mL HNO ₃ (7 mol/l) Heat in autoclave for 30 min. at 200 kPa or 120°C Allow to cool Filter or centrifuge the digest, if needed. Transfer the filtrate to 100 mL volumetric flask and fill to mark with water.	Requirement on temperature control Washing procedure for vessel Digestion procedure: Max. 0,5 g sample test portion- Add 10,0 mL HNO ₃ (alternatively 9 mL HNO ₃ + 3 mL HCL) Allow to stand until visible reaction has stopped Heat in microwave oven for 10 min. at 175°C Allow to cool Let settle, filter or centrifuge the digest Transfer the filtrate to volumetric flask and fill to mark with water	Blank test + Max. 5 g (2g) dry sample test portion- Add 20,0 mL HNO ₃ (7 mol/l) Allow to stand until visible reaction has stopped Heat in autoclave for 30 min. at 200 kPa or 120°C Allow to cool Decant or filter the digest Transfer the filtrate to volumetric flask and fill to mark with water

			Requirements on <ul style="list-style-type: none"> • digestion of quality control samples • periodic duplicate sample • spike samples • maintenance of quality control data • validation of temperature control • power calibration 	
Analysis	Reference to SS 02 81 50 (AAS flame) SS 02 81 83 (AAS graphite furnace) ISO 11885 (ICP-OES) DIN 38 406 Teil 22 1988 (ICP) EPA 200.7 (ICP)	Reference to: National standards	Literature on microwave digestion and on validation data	Reference to be given as normative reference
Test report	-	On digestion: Information on digestion procedure with reference to the method.		Equivalent to horizontal standard on aqua regia
Precision/validation	-	No information related to digestion	Validated on soil, sediment and oil reference materials.	Results from interlaboratory comparisons

5. CRITICAL POINTS AND RECOMMENDATIONS

5.1 Aqua regia digestion method

All the standards described in the last chapter use similar methods for the digestion of solid samples with aqua regia. But one main difference is obvious at the first look at each standard: While ISO 11466 and EN 13650 describe only one method, EN 13650 contains 4 and EN 13657 3 different methods in one standard. One method of digestion is more or less similar in every standard: Digestion by conventional heating under reflux condition, which is the traditional method used for many years in many laboratories. The experience that many labs have with this method makes this method worth to be chosen as a horizontal standard. As it is a rather time-consuming digestion method (let stand at room temperature for 16 hours, heat for 2 hours, cool down to room temperature) it is not used nowadays in routine labs but mostly replaced by microwave digestion.

Two methods of microwave digestion - in closed system and under reflux conditions – are described in addition to the conventional heating in EN 13346 and EN 13657. In the sludge standard, a quick method for conventional heating in a tube is the fourth method. For sludges, all four methods lead in most cases to comparable results as is indicated by the validation data (EN 13346, 2000). For the tested waste samples in EN 13657 the results indicate comparability for many elements too, as the standard deviations of the different methods overlap (Muntau 2000). But these indications were not proved by statistical calculation, as an additional round robin test with experienced labs that proved to be experienced in digestion of solid samples should have been carried out before a solid data basis could be provided.

The crucial point for drafting a horizontal standard is the decision whether only one or several methods should be mentioned. The advantage of mentioning only the best-known conventional heating method is the comparability of the results for many different matrices. The disadvantage of this approach is the fact that most European labs already work in practice with microwave digestion and they will be cut back in their decision on which method to use. Besides, the microwave method is the more modern one and much faster to apply in routine analyses. To a certain extent, the validation data available in the two standards EN 13346 and EN 13657 indicate comparability, with some additional research need.

Therefore, it is recommended that a horizontal standard be prepared that includes all these three methods for which validation data for several matrices are already available. Further research on robustness and comparability of the three methods are necessary and may result in slight modifications of the draft standard or to the exclusion of one method.

5.2 Nitric acid digestion method

Standards on nitric acid digestion of solid samples are in EU primarily used in the Nordic countries. Here, the only standardized heating method is the autoclave heating method. However microwave heating is used more and more in routine laboratories. Standards on nitric acid digestion are widely used also in the United States (hot plate and microwave oven digestion). Nitric acid digestion is especially superior for samples and elements, where low detection limits are required (ICPMS or GFAAS analysis).

It is considered an advantage to include a high temperature microwave technique in a coming standard on nitric acid digestion to take development into proper consideration. US EPA 3051a is a well-described and validated microwave standard, which is recommended as a basis. This will 1) enable the use of already existing data on comparability with an aqua regia method, 2)

support method comparability internationally and 3) if comparability is demonstrated, provide a very fast digestion method compared to existing methods.

Validation data exist for nitric acid digestion in combination with the subsequent analysis, such as results from interlaboratory comparisons. Examples are given in Annex 3 and 4. Information on the uncertainty component originating from digestion alone has not been identified.

Comparisons exist between the results from using principles equivalent to the draft proposals on aqua regia digestion and on nitric acid digestion, but are usually focussed on other aspects, also. Furthermore, the results, which originate from using methods equivalent to the draft horizontal standards on nitric acid and on aqua regia has not been identified. Thus a comparison based on statistical sufficient data is needed covering the matrices in question.

5.3 Conclusions and recommendations

The comparison of standards for the digestion of solid samples prior to the subsequent analyses demonstrates a potential for preparing horizontal standards for sediment, sludge, soil, and waste. However, some decisions have to be taken. Apart from sludge, soil and biowaste, it is proposed in the final scope of the horizontal standard to include sediment and waste.

One key question is the decision whether to include more heating principles in the standard to take into account the new development (as in the present EN standards on waste and sludge) or to include only the conventional hot plate heating (as in the present ISO standard for soil). The report in hand proposes to include more heating principles, but comparisons are needed that demonstrate that equivalent results are obtained by using the methods on matrices like sediment, soil, municipal sludge and compost.

It is not likely that one partial digestion method alone (nitric acid or aqua regia digestion) will be the most suitable for all elements, solid sample types and subsequent analytical procedures. More data is needed to define the optimum choice of digestion method.

A proposal on investigations to be established prior to validation of methods may be summarised as follows:

- Establishment of requirement on particle size of the laboratory sample (soil, compost, sludge and sediment) for optimisation of reproducibility
- Comparability of hot plate digestion and microwave digestion (open and closed vessel) for digestion of soil, compost, municipal sludge and sediment in relation to aqua regia digestion – covering the elements of interest for monitoring and control purposes in Europe.
- Comparability of the autoclave digestion method and the US EPA method on microwave assisted digestion on selected elements and matrices – covering the elements of interest for monitoring and control purposes in Europe.
- Comparability of nitric acid digestion and aqua regia digestion. It is proposed to investigate comparability between the above aqua regia methods and both autoclave and microwave digestion using nitric acids.

6. DRAFT STANDARDS (SEPARATE CEN TEMPLATES)

The draft standards are attached as separate documents.

REFERENCES

- Ciesielski, H.: unpublished information provided to the authors July 2003
- Ciesielski, H., Proix, N., Sterckeman, T.: 1997, Détermination des incertitudes liées à une méthode de mise en solution des sols et sédiments par étude interlaboratoire, *Analisis*, 25, 188-192
- DHI Institute for Water and Environment – Proficiency test SOLID-5 (2001- 1): Physical parameters, nutrients and metals in soil. 2001
- DIN 38 414 S7 German standard method: Sludge and Sediments (Group S). Digestion using aqua regia for subsequent determination of the acid-soluble portion of metals (S7)(DIN,1983)
- EN 13346 Characterisation of sludge – Determination of trace elements and phosphorus – Aqua regia extraction methods 2000
- EN 13650 Soil improvers and growing media – Extraction of aqua regia soluble elements 2002
- EN 13657 EN 13657: Characterisation of waste – Digestion for subsequent determination of aqua regia soluble portion of elements, 2002
- EN 13656: Characterisation of waste - Microwave assisted digestion with hydrofluoric (HF), nitric (HNO₃) and hydrochloric (HCl) acid mixture for subsequent determination of elements, 2002
- EN ISO 15587-1 Water quality – Digestion for the determination of selected elements in water – Part 1: Aqua regia digestion 2002
- EN ISO 15587-2 Water quality – Digestion for the determination of selected elements in water – Part 1: Nitric acid digestion 2002
- Eurofins – proficiency test. Proficiency test SOLID-5 (2002 - 4): Trace elements, nutrients and physical parameters in sludge. 2002
- Finnish Environment Institute (SYKE), Proficiency test results SYKE 5/2002
- Giove,A.; Politi,M.; Cavallo,G.: Robustness study on standard methods developed by CEN TC 292/WG3, Italy 2000
- Hjelmar, Ole; Holm Peter E.: Determination of total or partial trace element content in soil and inorganic waste material, Nordtest report 446, Finland 1999
- Hofer, Kirchner, A.: State of the art document on microwave digestion für CEN/TC 292/WG 3, University of Leoben, Austria 1997
- ISO 11466 Soil quality – Extraction of trace elements soluble in aqua regia 1995
- ISO 14869-1: Dissolution for the determination of total element content. Part I : Dissolution with hydrofluoric and perchloric acids
- Kåre Helge Karstensen. "Nordic guidelines for Chemical Analysis of Contaminated Soil Samples" NT Techn Report 329, 1996.
- 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
- Nieuwenhuize, J.,Poley-Vos, C.H. van der Akker, A.H. and vanDelft, W " comparison of microwave and conventional extraction techniques for the determination of metals in

soils, sediment and sludge samples by atomic spectrometry" Analyst 116, 347-351 (1991)

van der Sloot, H. A.: Difference between aqua regia destruction and total analysis. Results from the RIVM, ECN Mammoet project 1982, 1998

van der Sloot H.A., R.N.J. Comas, and J.J. Dijkstra: Leaching methods for soil, sludge and treated biowaste. Horizontal Desk study no 23 , August 2003

van der Sloot, H.A.: unpublished information given at CEN TC 292 ad hoc meeting, June 2003, Vienna

US EPA 3051a: Microwave assisted acid digestion of sediments, sludges, soils, and oils – reference to: www.epa.gov/epaoswer/hazwaste/test/pdfs/3051a.pfd. Revised 1998

US EPA 3050b: Acid digestion of sediments, sludges, and soils. Revised 1996.

ANNEX 1

FIGURES

Figure 3 List of reference materials for which recovery rates were shown in Hofer, 1997

Matrix	Acronym
BCR CRM 38 coal fly ash	CRM 38
BCR CRM 143 amended soil	CRM 143 am. soil, CRM 143
BCR CRM 144 sewage sludge	CRM 144 sew. sludge, CRM 144
BCR CRM 146 industrial origin sewage sludge	CRM 146 ind. sew. sludge, CRM 146
BCR CRM 176 city waste inc. ash	CRM 176 city waste inc. ash, CRM 176
BCR CRM 277 estuarine sediment	CRM 277 est. sed., CRM 277
BCR CRM 320 river sediment	CRM 320 river sed., CRM 320
BCR CRM-144 domestic origin sludge	CRM 144 dom. origin sludge, CRM 144
BCR CRM-145R mixed origin sludge	CRM 145R mixed origin sludge, CRM 145R
BCR-CRM-141 loam soil	CRM 141 loam soil, CRM 141
BCR-CRM-185 river sediment	CRM 185 river sed., CRM 185
MESS-1 sediment	MESS-1 sed.
NBS-SRM 1648 urban particulate	SRM 1648 urb. part., SRM 1648
NIES CRM No.2 pod sediment	CRM No.2 pod sed.
NIST SRM 1632b bituminous coal	SRM 1632b bit. coal, SRM 1632b
NIST SRM 1633a coal fly ash	SRM 1633a coal fly ash, SRM 1633a
NIST SRM 1633b coal fly ash	SRM 1633b coal fly ash, SRM 1633b
NIST SRM 1645 river sediment	SRM 1645 river sed., SRM 1645
NIST SRM 2704 river sediment	SRM 2704 river sed., SRM 2704
NIST SRM 2710 soil	SRM 2710 soil, SRM 2710
NIST SRM 2711 soil	SRM 2711 soil, SRM 2711
NRCC BCSS-1 marine sediment	BCSS-1 mar. sed., BCSS-1
NRCC PACS-1 sediment	PACS-1 sed., PACS-1

Figure 4 Recovery rate of Arsenic in different matrices by digestion with different acid mixtures (Hofer, 1997)

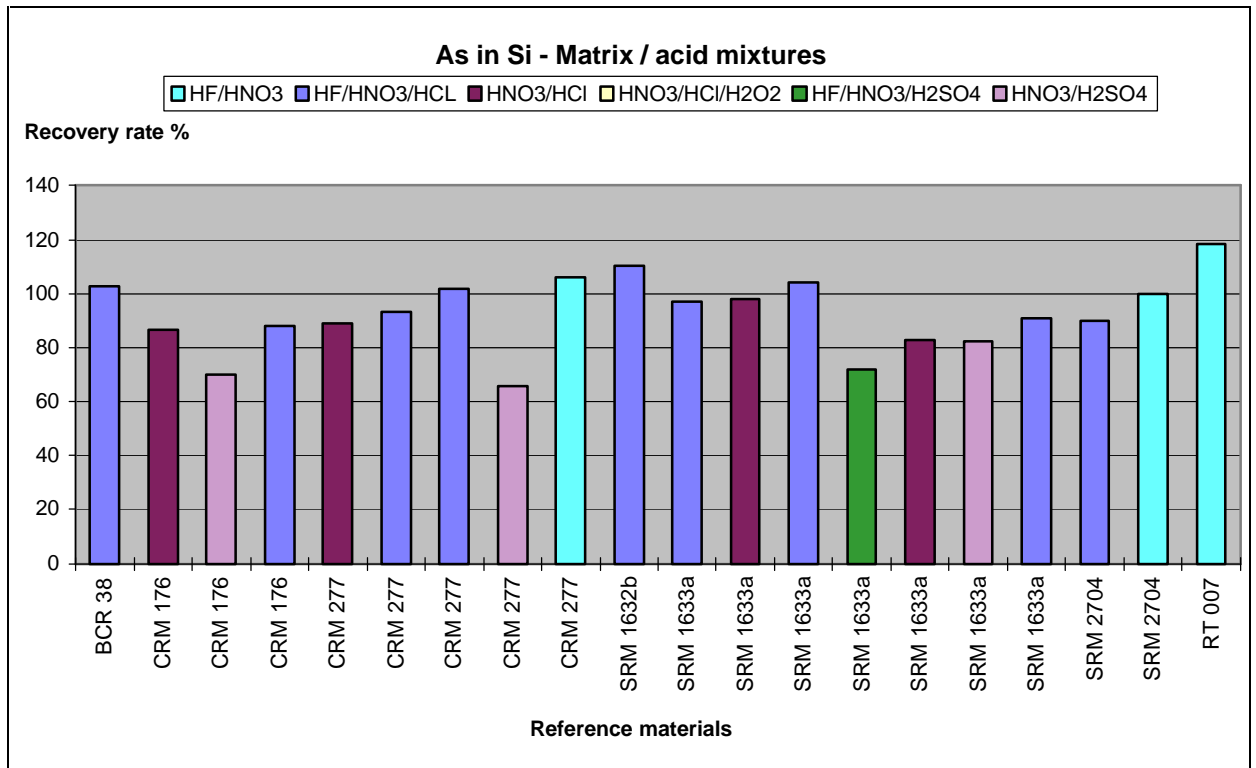


Figure 5 Recovery rate of Lead in different matrices by digestion with different acid mixtures (Hofer, 1997)

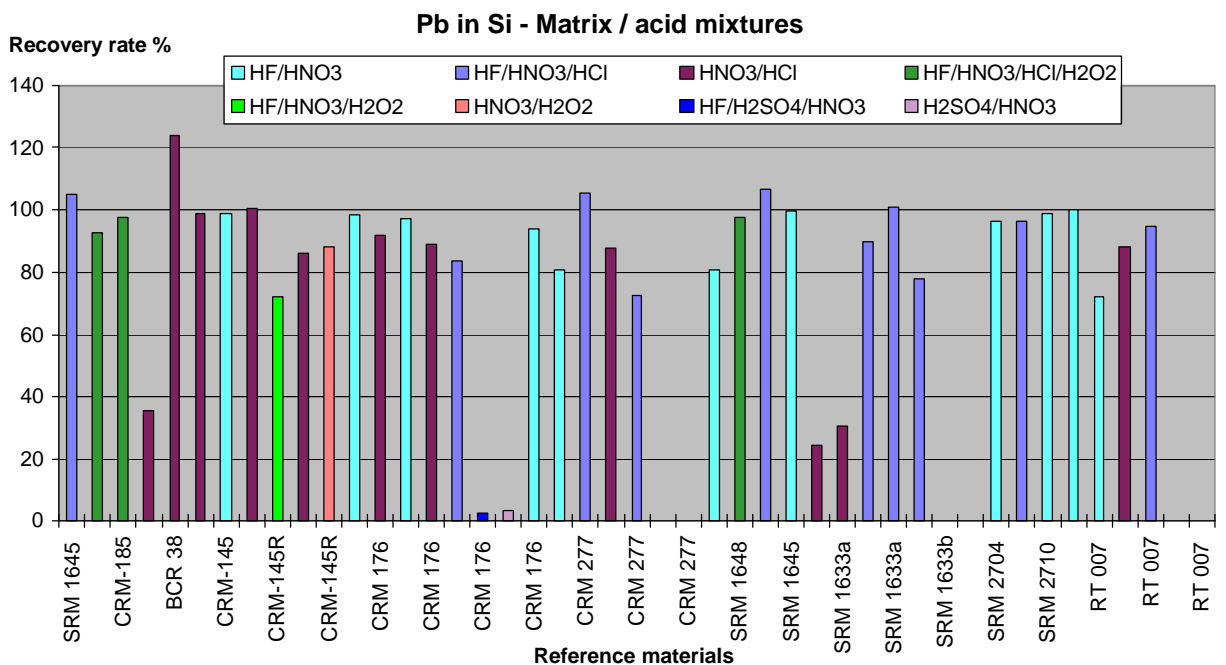


Figure 6 Recovery rate of Chromium in different matrices by digestion with different acid mixtures (Hofer, 1997)

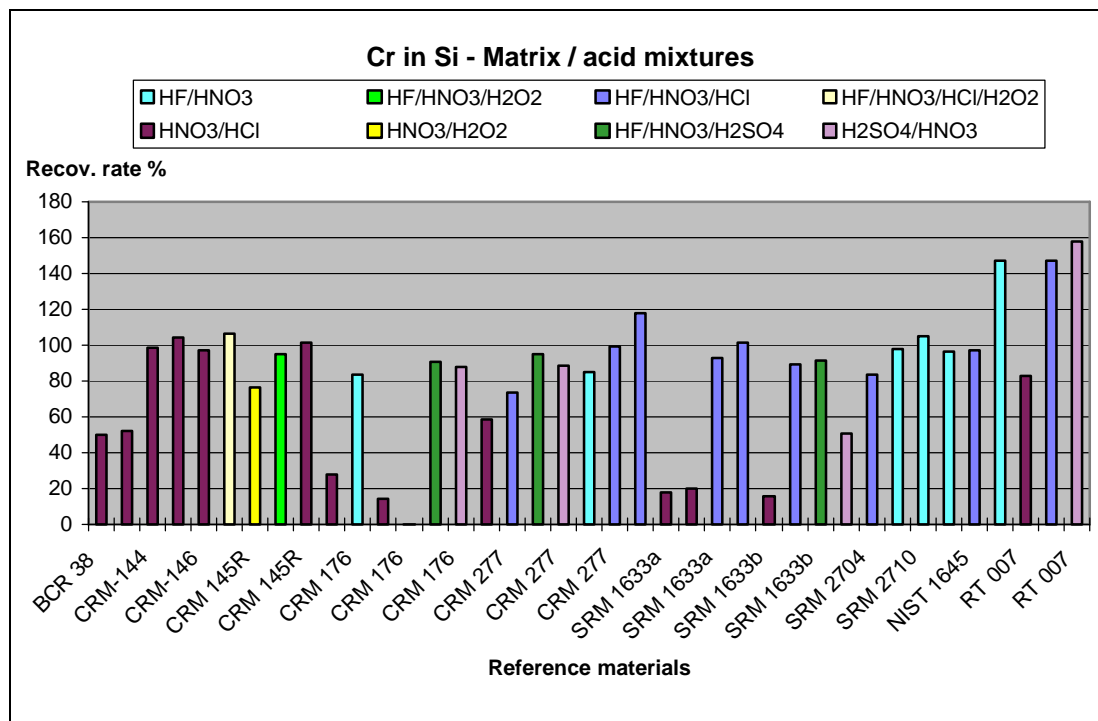


Figure 7 Recovery rate of Cadmium in different matrices by digestion with different acid mixtures (Hofer, 1997)

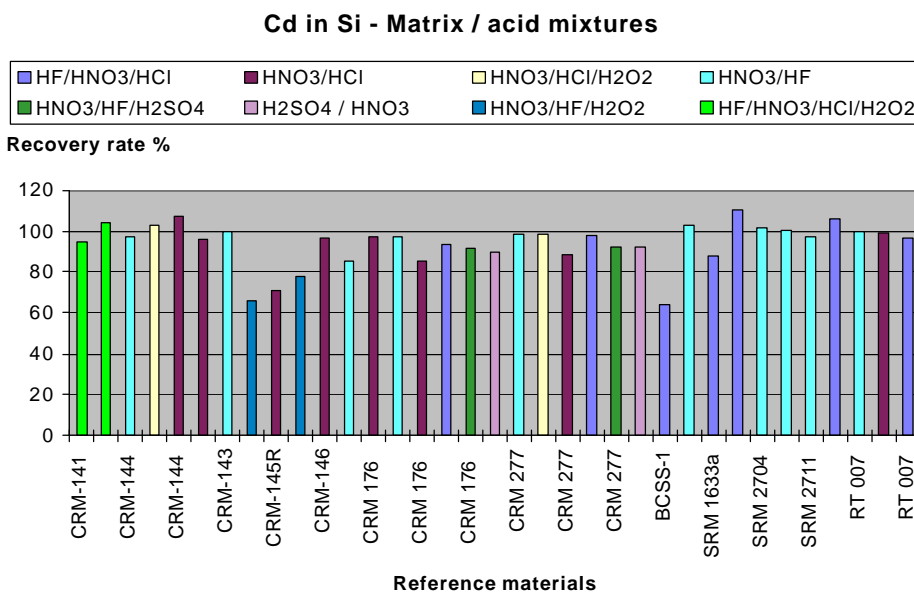


Figure 8 RECOVERY RATE FOR CLOSED DIGESTION WITH HF/HNO₃/HCl (Hofer, 1997)

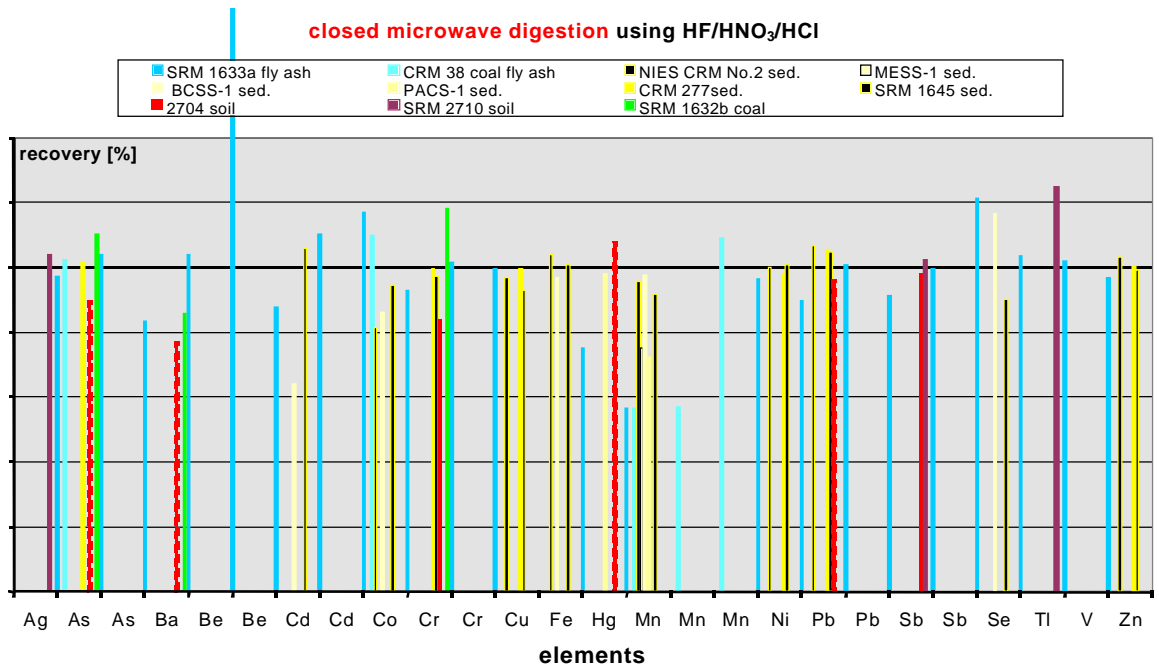
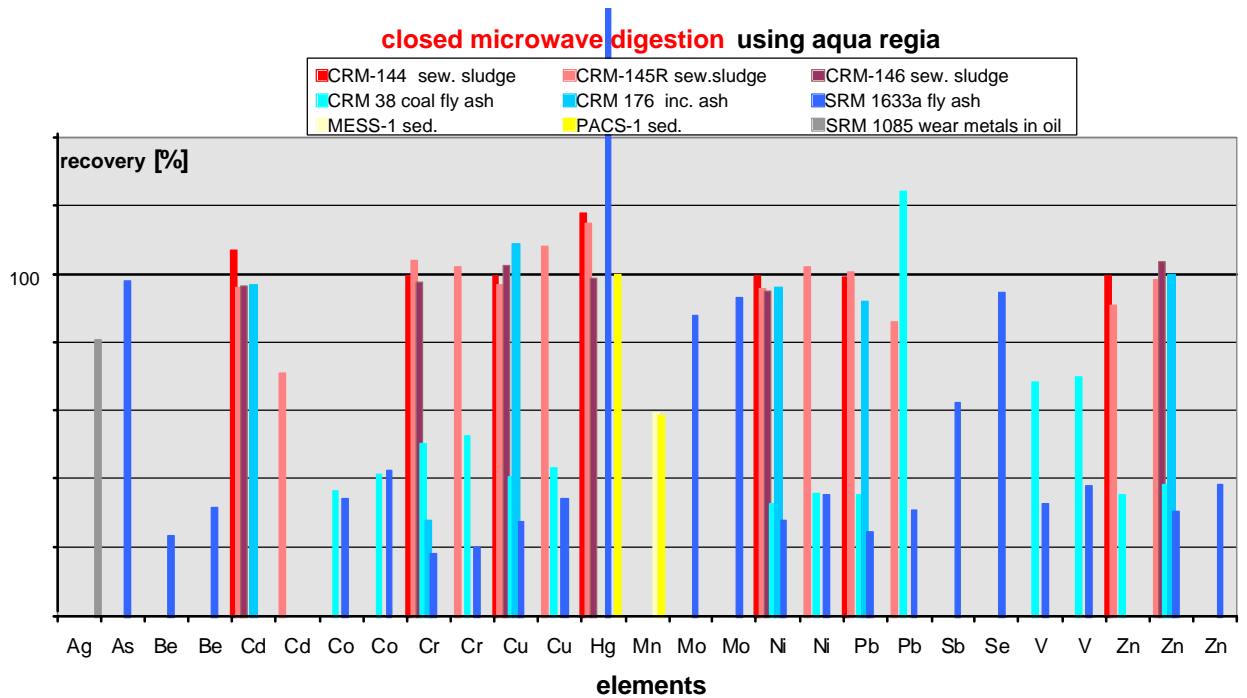


Figure 9 RECOVERY RATE FOR CLOSED DIGESTION WITH AQUA REGIA (Hofer, 1997)



ANNEX 2

A. Comparison of the quantities of trace elements extracted from sludges with aqua regia (EN 13346) and with hydrofluoric and perchloric acids (AFNOR NF X 31-147)

Information provided by Henri Ciesielski, INRA - Laboratoire d'Analyses des Sols, France

This document gives the relationships observed for trace elements extracted from sludges according to a CEN standard and a French standard. The following results (graphs 1 to 6) were presented during a TC 308 WG1/TG1 meeting. Comparisons for nutrients are also available.

Methods

EN 13346: Determination of trace elements and phosphorous – Aqua regia extraction methods (method A)

AFNOR NF X 31-147: Soils, sediments - Total solubilizing by acid attack. This method was subsequently standardised in ISO TC 190 under the reference ISO 14869-1.

Samples and results

100 samples collected in various urban wastewater treatment plants of France. The study was carried out in the Soil Analysis Laboratory of Arras belonging to the French National Institute of Agronomic Research.

For any element considered, results are well correlated ($R^2 > 0.98$).

Except for Cr, differences between the calculated slopes do not exceed $\pm 3\%$.

HF extracts higher quantities of Cr than aqua regia.

Figure 10 Comparison Cd (HCl/HNO₃) and Cd (HF)

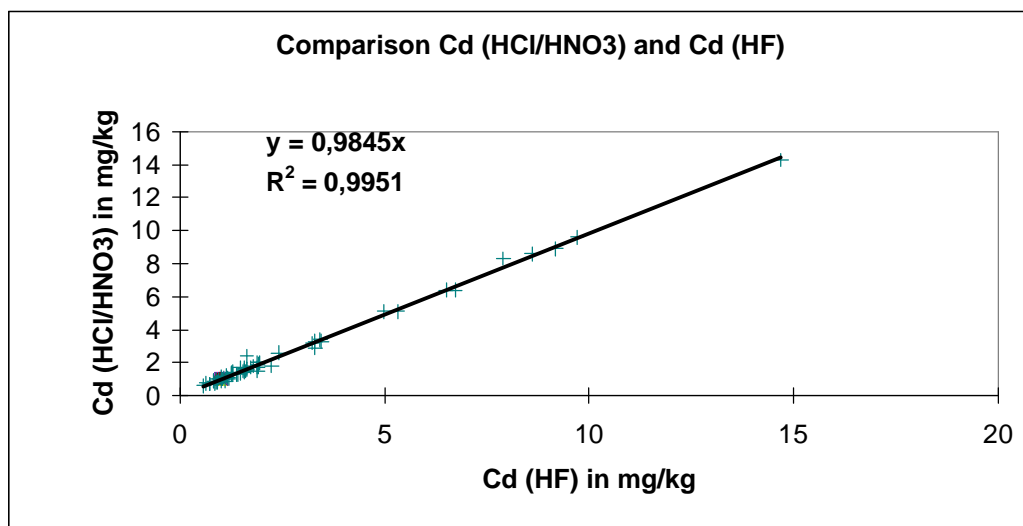


Figure 11 Comparison Cr (HCl/HNO3) and Cr (HF)

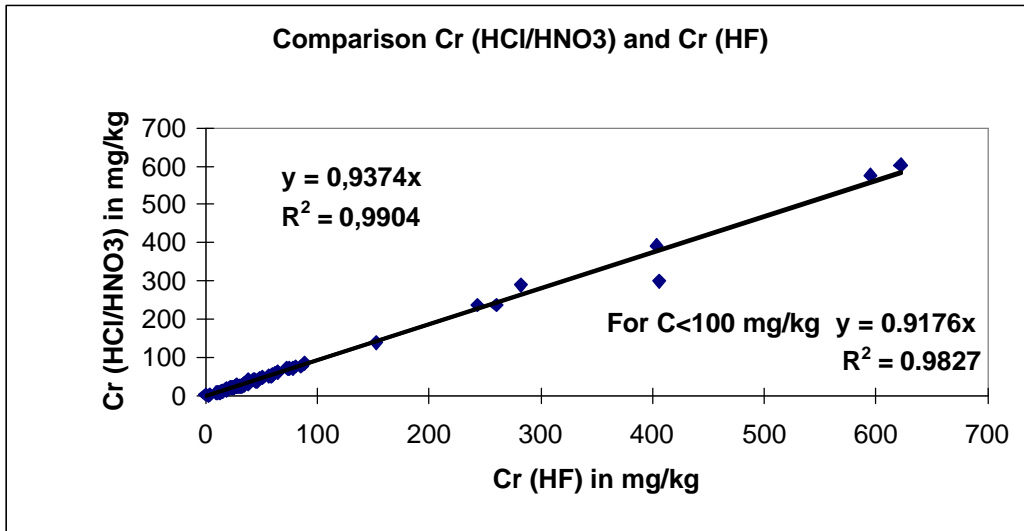


Figure 12 Comparison Cu (HCl/HNO3) and Cu (HF)

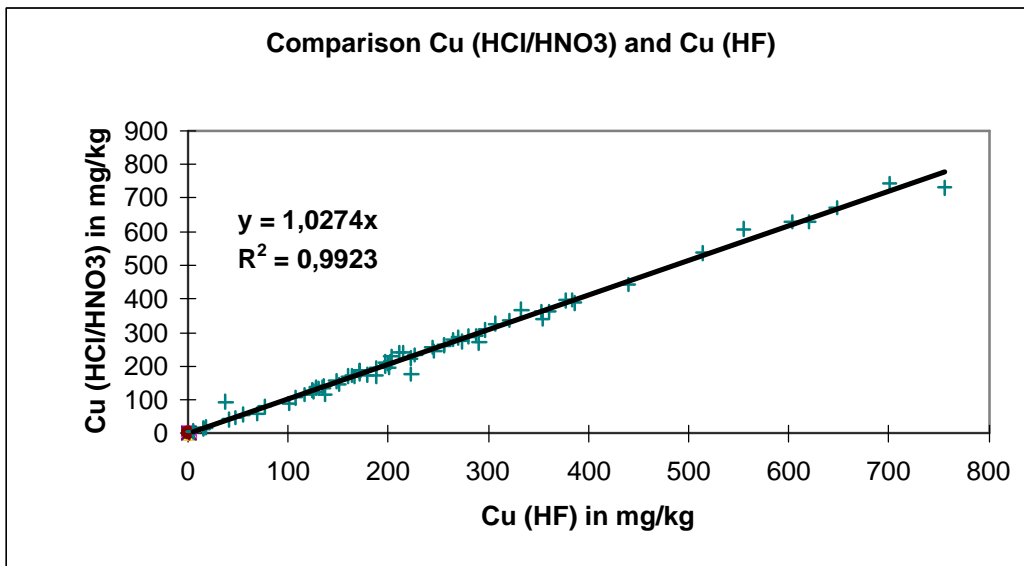


Figure 13 Comparison Ni (HCl/HNO3) and Ni (HF)

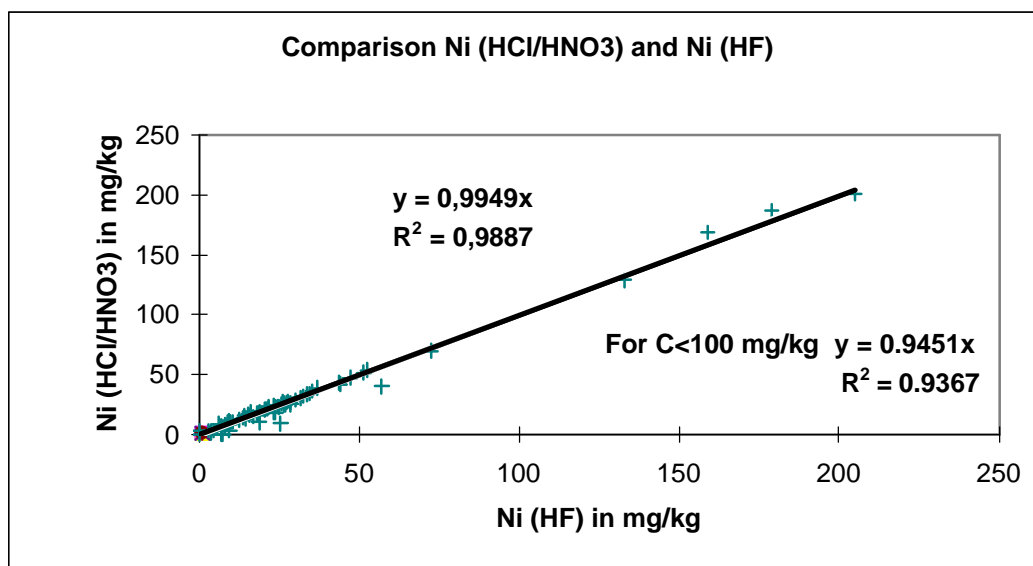


Figure 14 Comparison Pb (HF) and Pb (HCl/HNO3)

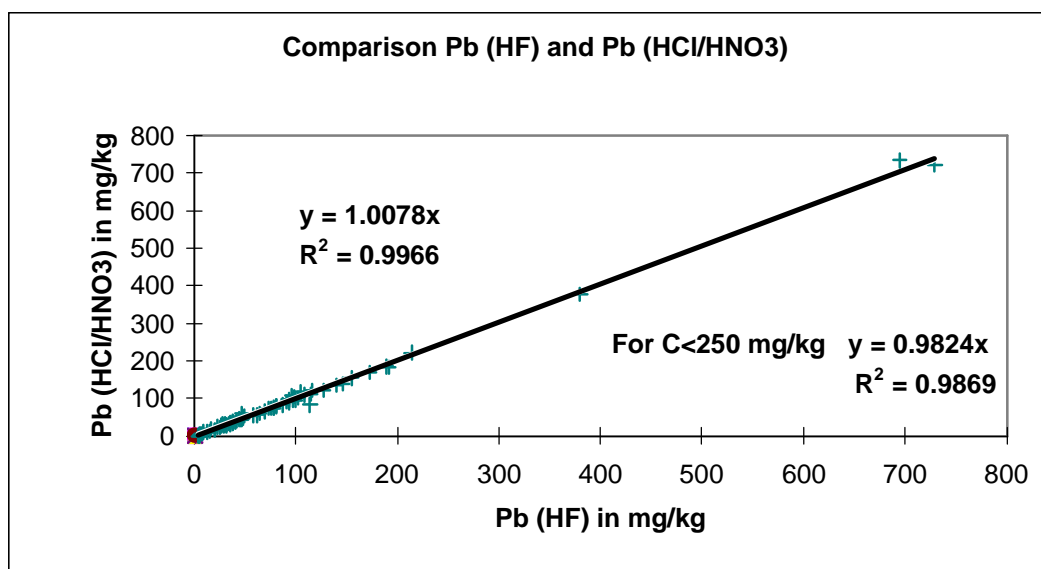
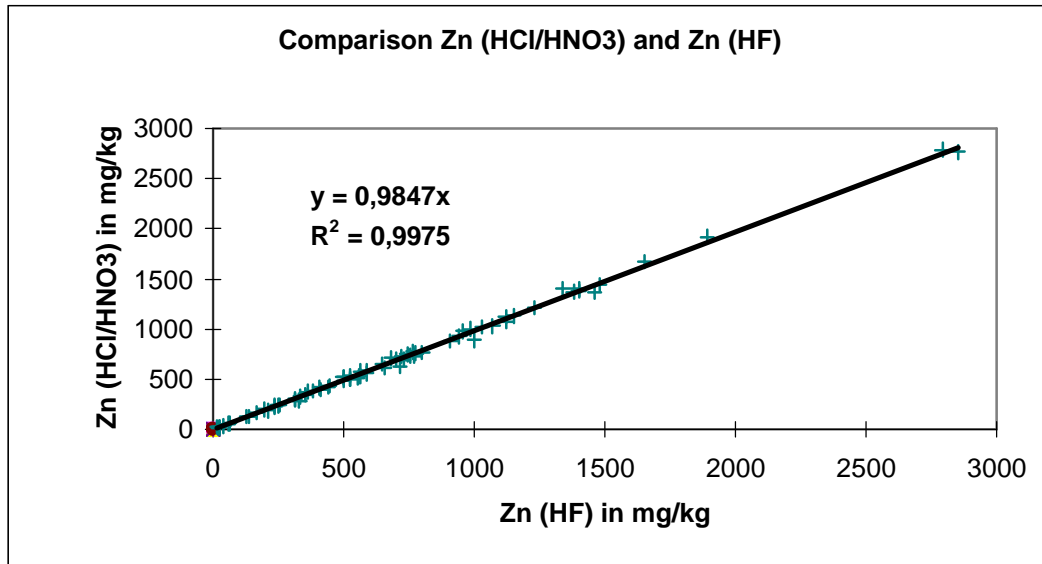


Figure 15 Comparison Zn (HCl/HNO3) and Zn (HF)



B. Comparison of the quantities of trace elements extracted from soils with aqua regia (ISO 11466) and with hydrofluoric and perchloric acids (ISO 14869-1)

Information provided by Henri Ciesielski, INRA - Laboratoire d'Analyses des Sols, France

This document gives some relationships (graphs 1 to 6) observed between the quantities of trace elements extracted from soils according to 2 ISO standards.

Methods

ISO 11466: Extraction of trace elements soluble in aqua regia

ISO 14869-1: Dissolution for the determination of total element content

Part I: Dissolution with hydrofluoric and perchloric acids

Samples and results

20 acid and calcareous soil samples collected in various regions of France. Results were obtained within interlaboratory trials organised by BIPEA (French organisation for the development of analytical methods) involving about 15 laboratories for each method.

Except for Pb the results are well correlated ($R^2 > 0.94$).

HF, compared to aqua regia, extracts more than 30% of Cr. For the other elements, HF always gives higher results but the differences in the calculated slopes do not exceed 11%.

Figure 16 Comparison Cd

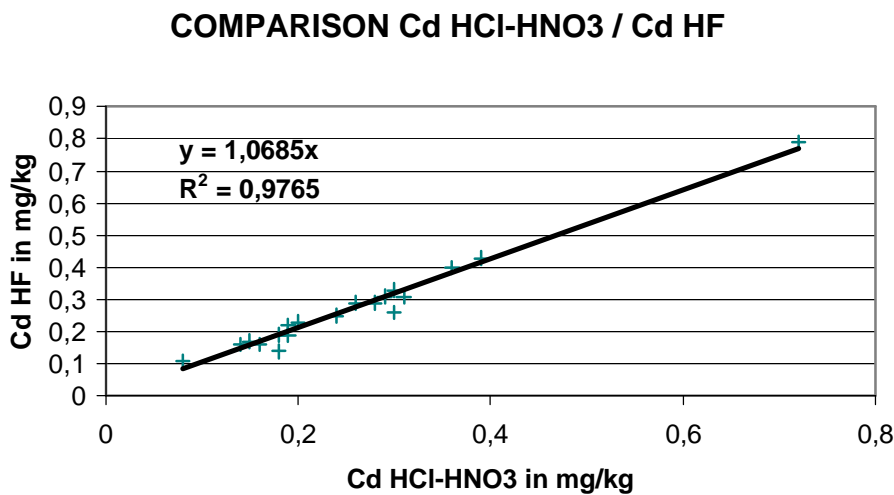


Figure 17 Comparison Cr

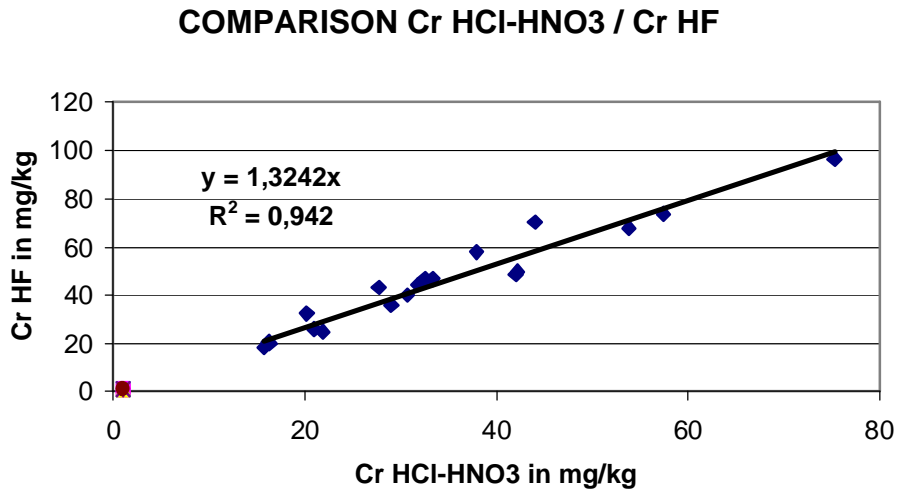


Figure 18 Comparison Cu

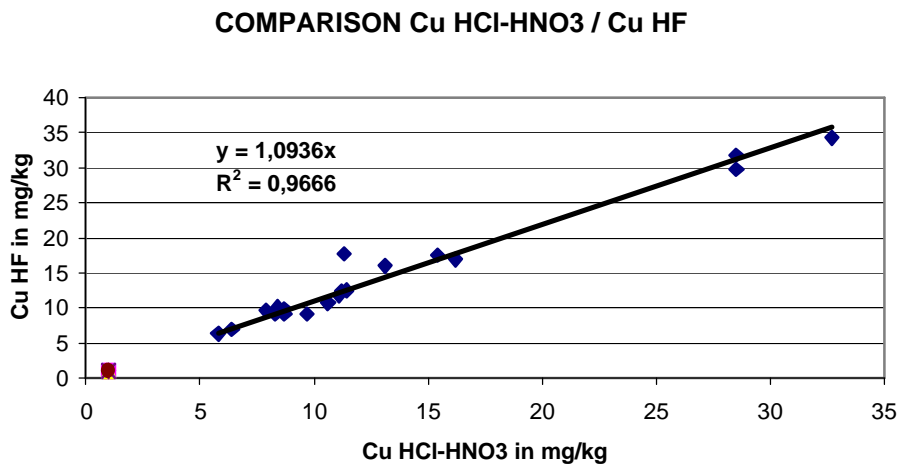


Figure 19 Comparison Ni

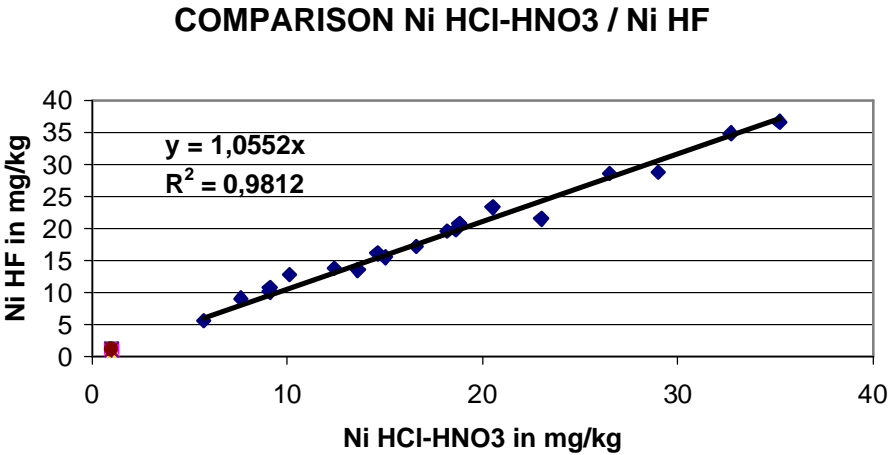


Figure 20 Comparison Pb

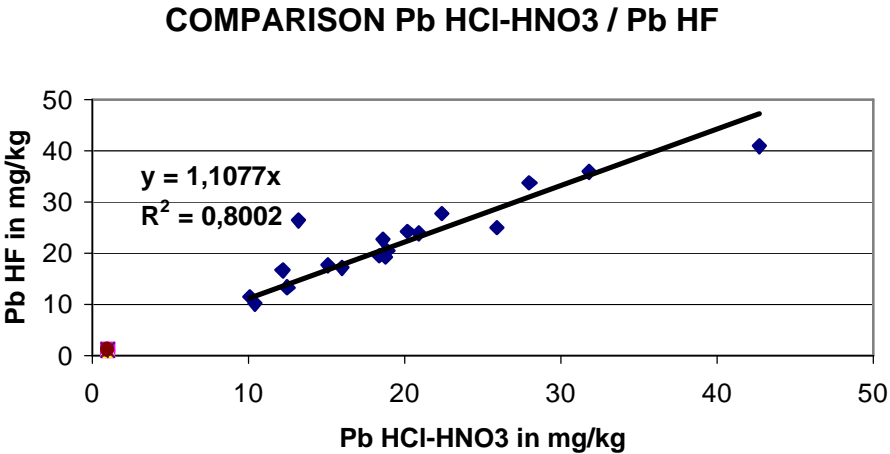
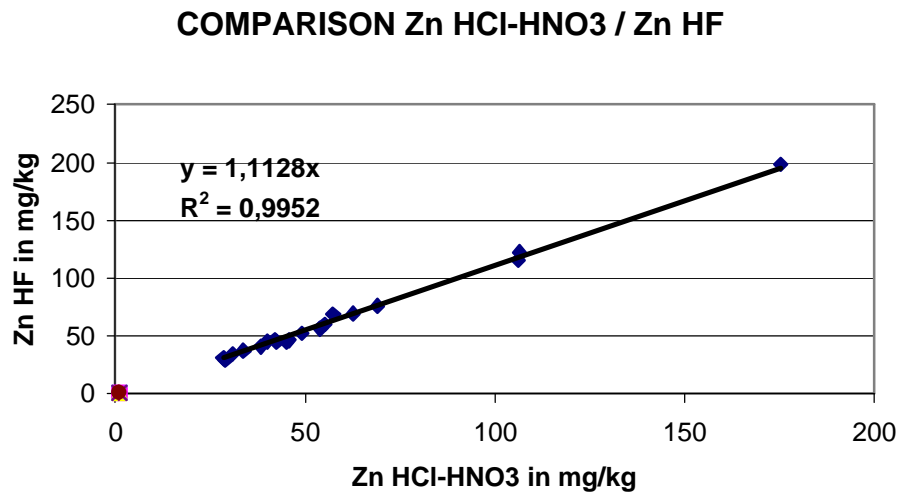


Figure 21 Comparison Zn



C. Influence of sample particle size on aqua regia digestion method

Results of the robustness study for EN 13656 and EN 13657

Table 18 Influence of sample particle size on aqua regia digestion method (Giove 2000)

Matrix: coal bottom ash, analytical results in mg/kg

	mg	µm	Al	StdDev	Ba	StdDev	Be	StdDev	Mg	StdDev
Aqua regia	100	90	108614	7001	1400	89	6.7	0.4	615.5	34.0
	300	90	100263	4301	1162	22	5.7	0.2	560.0	18.6
	500	90	100365	4642	1137	65	5.6	0.2	545.8	21.7
	300	560	81163	8667	949	77	4.5	0.4	420.1	42.9
Total	100	90	162888	3983	2088	101	8.9	0.3	876.2	43.0
	300	90	152504	3781	1798	109	8.4	0.2	734.1	44.6
	400	90	160125	4122	1875	69	8.2	0.1	799.3	32.6
	500	90	159060	11191	1817	17	7.9	0.4	755.2	15.9
	300	560	119963	18421	1577	153	9.0	0.2	600.7	127.2

	mg	µm	Co	StdDev	Cr	StdDev	Cu	StdDev	Fe	StdDev
Aqua regia	100	90	30.9	2.2	40.7	2.1	26.5	0.9	24873	1946
	300	90	25.2	1.0	34.5	1.3	22.6	1.0	22021	690
	500	90	24.3	0.8	34.3	1.4	22.9	0.5	20751	745
	300	560	18.3	2.3	24.7	3.5	18.3	1.4	15725	1948
Total	100	90	47.5	2.3	131.1	5.8	40.3	1.1	35766	2572
	300	90	43.9	1.0	122.1	1.4	38.1	0.8	34535	1311
	400	90	42.2	0.6	116.1	2.2	37.4	0.7	30883	1397
	500	90	41.2	2.0	112.8	6.7	36.9	2.4	31749	2446
	300	560	44.9	0.8	122.6	1.8	38.2	1.0	34025	1308

	mg	µm	Mn	StdDev	Mo	StdDev	Ni	StdDev	Pb	StdDev
Aqua regia	100	90	339	13	2.6	0.4	122	5	22.5	1.2
	300	90	287	13	2.3	0.2	108	7	20.4	0.8
	500	90	279	13	2.0	0.1	116	8	18.2	0.6
	300	560	224	24	1.9	0.5	91	9	15.3	2.8
Total	100	90	431	16	3.0	0.8	152	17	28.6	2.6
	300	90	413	6	2.5	0.4	148	5	29.4	4.6
	400	90	404	8	2.1	0.2	135	8	29.4	1.2
	500	90	389	18	2.2	0.3	133	9	25.9	1.8
	300	560	426	7	2.1	0.3	151	8	25.4	1.7

	mg	µm	Sn	StdDev	Ti	StdDev	V	StdDev	Zn	StdDev
Aqua regia	100	90	5.5	1.8	5020	423	249	6	38.7	1.6
	300	90	3.7	1.1	3749	116	223	6	25.7	1.1
	500	90	3.6	1.0	3481	74	226	9	24.8	1.5
	300	560	3.4	2.6	2689	437	196	15	28.7	4.1
Total	100	90	13.7	1.5	8459	230	293	14	47.7	3.7
	300	90	8.9	1.1	8299	268	279	3	41.7	4.0
	400	90	7.5	0.3	8237	184	277	7	35.6	0.4
	500	90	6.6	0.8	8346	505	267	13	34.5	2.5
	300	560	9.1	1.6	8589	219	281	8	44.0	3.4

Most selected elements (Al, Ba, Be, Co, Cr, Cu, Fe, Mg, Mn, Mo, Pb, Ni, Ti, V) show almost the same behavior: as the particle size of sample increases, recovery gets lower.

D. Validation data for Sewage Sludge of EN 13657

Table 19 Results of the round robin test for validation of EN 13567

SAMPLE CEN9/99 "SEWAGE SLUDGE SL11 POWDER"																								
	<i>Method A: Microwave assisted with aqua regia in closed vessel</i>								<i>Method - B: Microwave assisted, with aqua regia in semi-open vessel</i>								<i>Method C: Thermal heating, with aqua regia in reflux systems</i>							
	N	L	NA	XREF	Mean	% Recov	% Reprod	% Repeat	N	L	NA	XREF	Mean	% Recov	% Reprod	% Repeat	N	L	NA	XREF	Mean	% Recov	% Reprod	% Repeat
Al	67	16	5		81847.8		6.7	2.5	21	6	1		77367.8		16.7	1.7	29	7	0		79678.5		24.6	6.4
Sb	44	11	0		9.77		151.1	30.8	8	3	0		3.24		56.5	1.8	22	5	0		2.99		64.1	10.6
As	39	10	4		4.67		78.3	14.6	10	3	0		4.42		32.1	8.3	28	7	0		2.41		73.4	20.1
B	33	8	2		279.94		15.6	3.4	12	3	1		282.57		14.1	0.9	19	4	0		328.05		28.4	16.6
Ba	51	12	8		76.52		8.6	2.7	22	6	4		75.52		4.5	1.2	27	6	0		61.8		18.9	7.9
Be	26	6	6		0.45		48.9	11.3	6	2	0		3		74.5	0	14	3	0		1.13		55.5	13.7
Cd	78	19	11		0.68		99.6	12	23	6	0		1.02		112.4	20.8	30	7	9		0.26		67.6	36.3
Ca	60	14	0		57231.7		11	5.9	19	5	5		58796.6		4	5.8	21	5	0		58521		17.2	2.6
Cr	97	24	5		78.02		10.9	4	27	7	0		73.22		10.8	3.1	44	10	0		80.18		19.6	5.4
Co	57	15	0		3.99		57.3	8.6	12	4	0		5.43		48.1	52.5	30	7	0		3.41		49.5	10.7
Cu	100	24	1		96479.8		12.9	3.5	31	8	0		93526.1		6.3	1.4	40	10	5		94191.3		9.5	2
Fe	85	21	3		4449.03		10.8	3.5	26	7	0		4437.73		4.2	2.3	47	11	0		4125.21		13.8	6.9
Pb	100	24	3		9339.37		10.9	2.8	31	8	0		9323.84		3.5	1.2	42	10	5		9739.83		10.2	3.3
Mg	60	14	0		2309.07		14.2	4.2	21	6	4		2177.29		5	2.9	21	5	0		1992.14		19	5.6
Mn	96	24	1		591.06		12	3.2	31	8	0		583.76		3.6	1.4	50	12	1		590.52		8.8	3
Hg	43	11	0		0.33		121.4	27	16	4	0		0.36		32.9	6.2	23	5	0		0.15		66	11.3
Mo	26	7	6		4.31		10.2	6.4	20	5	0		4.91		49.9	9.5	15	4	0		3.65		12	6.9
Ni	104	26	1		1727.32		10.4	3.2	26	7	5		1719.96		5.5	1.7	49	11	0		1710.41		25.1	5.8
P	18	4	10		4724.51		3.8	6.3	22	5	0		5834.64		33.9	5.6	13	3	0		4012.85		24.7	6.7
K	48	12	4		629.48		39.1	6.8	11	3	0		436.27		31.7	5.5	21	5	0		467.76		58.6	3.8
Se	26	6	0		5.52		99	16.5	2	1	0		10		0	0	9	2	0		2.78		81	0
Ag	28	7	0		10.53		14.7	13.1	18	4	0		7.73		20.5	11.8	18	4	0		9.68		21	7
S	26	6	0		61982.3		8.8	1.7	7	2	0		60495.7		2.6	2.5	10	2	0		59697.9		12.8	1.8
Na	64	15	0		11040.6		22.7	6	7	2	0		12595.7		7.7	1.3	28	6	1		11805.5		10.8	4.3
Sr	41	10	10		200.79		5.6	2.4	15	4	0		197.3		3.3	2.2	18	4	0		195.16		9.5	2.2
Sn	35	8	5		19154.7		5.2	6.6	15	4	0		16768.4		15.1	5.1	14	3	0		17840		18.2	1.8
Te	9	2	0		7.78		36.2	0	9	2	0		1.44		38.9	0	10	2	0		7.5		35.1	0
Tl	11	3	7		1.81		9.8	11.1	11	3	0		3		173.2	0	9	2	0		7.22		38.9	0
Ti	21	5	3		29.78		28.2	8.9	8	3	9		26.34		10.1	0.5	12	3	0		24.64		35.7	3
V	31	8	23		5.75		12.3	2.2	22	6	0		6.09		89.4	31.7	22	5	5		8.32		70.4	24.1
Zn	103	25	0		230.12		34.2	5.5	31	8	0		323.33		44.6	7	52	12	1		209.32		34.1	22.2

N = Number of results, L = Number of laboratories, NA = Number of outliers, XREF = Conventional true value (where applicable)

SAMPLE CEN10/99 "SEWAGE SLUDGE" (BCR 146R)

	<i>Method A: Microwave assisted with aqua regia in closed vessel</i>								<i>Method - B: Microwave assisted, with aqua regia in semi-open vessel</i>								<i>Method C: Thermal heating, with aqua regia in reflux systems</i>							
	N	L	NA	XREF	Mean	% Recov	% Reprod	% Repeat	N	L	NA	XREF	Mean	% Recov	% Reprod	% Repeat	N	L	NA	XREF	Mean	% Recov	% Reprod	% Repeat
Al	79	20	0	25130	20690.2	82.3	19.1	6	20	6	1	25130	18942.7	75.4	13.7	2.1	37	9	0	25130	21230.3	84.5	25.4	5.4
Sb	32	8	4	16.25	9.23	56.8	21.1	7.4	17	5	0	16.25	9.1	56	57.4	5.6	19	5	0	16.25	7.24	44.6	55.8	4.8
As	56	14	0	6.3	6.33	100.4	50.9	15.8	15	4	0	6.3	8.61	136.6	33.4	11.6	33	8	0	6.3	6.32	100.2	49.9	37.9
B	23	6	0		38.18		36.8	15.4	11	3	0		30.87		33.8	6	15	4	0		21.9		15	16.8
Ba	63	15	0	735	572.84	77.9	20	4.6	19	5	1	735	391.83	53.3	16.9	7.7	23	5	0	735	479.31	65.2	13.9	13.7
Be	31	7	2		0.79		10.5	5.5	18	4	0		1.1		53.3	4.2	18	4	0		1.05		31.4	7.2
Cd	86	21	14	18.76	17.16	91.5	8.6	4.5	22	6	4	18.76	15.75	84	13	2.3	49	12	0	18.76	16.51	88	14.9	9.1
Ca	60	14	0	154600	140455	90.9	8.7	3.7	18	5	5	154600	145312	94	7.3	1.4	27	6	1	154600	154356	99.8	17	4.4
Cr	107	26	0	196	164.91	84.1	13.4	3.4	27	8	4	196	157.48	80.3	12.3	4.4	49	11	4	196	165.94	84.7	14	3.3
Co	66	17	0	7.39	6.05	81.8	19.2	5.7	22	7	0	7.39	7.59	102.8	37.4	22.5	41	10	0	7.39	6.13	82.9	33.7	7.7
Cu	116	28	0	837.9	804.93	96.1	13.1	7.2	35	10	5	837.9	798.91	95.3	9.4	2.3	34	8	9	837.9	771.47	92.1	3.7	2.8
Fe	93	23	0	16100	13906.8	86.4	11.4	3.6	21	6	5	16100	13922.4	86.5	6.8	1.9	38	9	5	16100	13508.3	83.9	11.6	4.8
Pb	102	25	0	608.7	534.3	87.8	13.4	3.4	31	8	0	608.7	562.93	92.5	7.6	1.7	46	11	5	608.7	541.77	89	10.8	3.8
Mg	64	15	0	10460	9031.16	86.3	9.3	3.3	21	6	5	10460	8449.24	80.8	8.1	1.9	30	7	1	10460	9446.1	90.3	17.8	8.5
Mn	96	24	0	323.5	274.45	84.8	10.6	2.8	37	9	0	323.5	281.41	87	8.6	1.6	47	11	0	323.5	265.87	82.2	14.1	3.1
Hg	45	11	0	8.62	7.44	86.3	23.9	10.3	18	5	0	8.62	8.73	101.3	16.8	6.9	35	8	0	8.62	7.21	83.6	26	11.4
Mo	32	8	4		7.95		8.1	5.2	17	5	0		8.09		29.6	5.7	16	4	0		8.67		13.2	2.9
Ni	105	26	4	69.7	61.25	87.9	18.7	4.6	31	8	0	69.7	59.17	84.9	15.3	2.7	53	12	0	69.7	58.4	83.8	17.3	5.4
P	31	7	1	25600	27626	107.9	2.4	2.9	24	6	0	25600	30286.2	118.3	17.5	5	18	4	0		6068.72		8.1	4.3
K	56	14	0	5240	2025.58	38.7	34.7	17.3	16	5	1	5240	1306.19	24.9	24.8	9.4	30	7	5	5240	1313.79	25.1	33.7	5.3
Se	26	6	0		5.46		62.4	10.3	11	3	0		3.48		141.7	4.6	6	2	0		4.22		41.1	0
Ag	38	9	0		190.91		23.1	1.9	24	6	0		205.89		6.6	5.2	18	4	1		198.75		4.4	1.1
S	26	6	0	10620	9188.44	86.5	17.7	2.4	2	1	0		9180		0	0	10	2	0	10620	9021.6	84.9	15.4	8.7
Na	44	11	6	1804	777	43.1	28.1	4.3	6	2	0		481.82		5.9	10.1	41	9	0	1804	701.27	38.9	55.2	18.3
Sr	46	11	5	1179	1027.18	87.1	4.9	2	11	3	1	1179	975.11	82.7	4.4	2.4	19	4	0	1179	1019.59	86.5	10.6	1.3
Sn	30	7	3	95.8	59.79	62.4	32.5	6.3	15	4	0	95.8	61.15	63.8	33	3.8	14	3	0	95.8	63.94	66.7	28.6	4.6
Te	9	2	0		7.78		36.2	0	9	2	0		1.44		38.9	0	9	2	0		7.78		36.2	0
Tl	29	7	0	2771	302.74	10.9	58	21.7	21	6	0	2771	182.77	6.6	59.4	19	14	3	0	2771	183.56	6.6	34.1	7.2
Ti	22	5	0		3.54		44.6	4.3	15	4	0		1.68		127.5	2	9	2	0		3		84.5	0.8
V	50	12	8	42.7	34.08	79.8	8.4	3.5	14	4	8	42.7	27.76	65	3.4	2.8	31	7	0	42.7	41.21	96.5	56.3	4.9
Zn	105	26	7	3061	2858.47	93.4	8.9	4.1	31	8	0	3061	2761.77	90.2	7.1	3.1	47	11	6	3061	2819.79	92.1	11.6	6.4

N = Number of results, L = Number of laboratories, NA = Number of outliers, XREF = Conventional true value (where applicable)

E. Reproducibility % values of "cleaned data sets" Inter-laboratory validation of EN 13656 and EN 13657

Table 20 Comparison of reproducibility for all the samples used in the round robin test for validation of EN 13567

	Clean metals solution (analysis only)	Pre-digested fly ash (CW6) (analysis only)	Powder fly ash (CW6) (digestion + analysis)	Pre-digested ash (CW4) (analysis only)	Powder ash (CW4) (digestion + analysis)	Pre-digested ink sludge (CW12) (analysis only)	Powder ink sludge (CW12) (digestion + analysis)	Pre-digested sludge (SL11) (analysis only)	Powder sludge (SL11) (digestion + analysis)
Al	9.3	10.5	25.4	13.9	17.7	18.1	22.4	10.4	6.7
Sb	11.4	25.1	24.4	22.6	20	62.1	89.8	21.5	103.9
As	13.2	29.8	30.6	28.8	27.6	25.5	52.5	25.9	78.1
B	36.2	9.1	16.2	8.8	9.4	72.5	68.7	13.1	15.6
Ba	6.5	41.1	36.8	31.7	108.8	9.8	18.9	65.9	8.6
Be	11.3	50.8	11.7	19.9	17.4	109.5	116.9	22.6	147.8
Cd	10.1	11.3	14.1	11.8	12.7	13.5	112	20.5	32.1
Ca	9.5	11.8	14.2	13.3	12.9	10.2	7.9	6	11
Cr	6.3	14.7	12.1	13.7	17.6	13.8	11.4	15	10.2
Co	9.3	28.6	27.9	18.9	22.6	29.9	22.5	18.7	24.9
Cu	9.5	10	20.3	7.5	13	7.8	10.3	12.4	13.2
Fe	9.1	14.2	12.6	9.8	11	9.5	11.8	15.1	11
Pb	7.9	13.3	11.5	8.7	10.8	7.7	8.6	25	11.2
Mg	9.3	7.7	8.8	8.6	12.6	12.1	25.9	5.2	14.2
Mn	7.8	13.9	12.7	13.2	12	11.7	11.9	20.5	12.2
Hg	11.7	28.4	37.4	15.8	17.2	11.1	48.9	45.2	52.7
Mo	4.5	19.3	9.6	14.7	9.8	17.2	70.4	31.6	11.1
Ni	7.3	16.2	13	13.3	19.2	19	31.8	10	10.6
P	16.9	20.4	5.8	6	2.3	10	3.2	24.5	3.8
K	63.6	13.2	9.5	23.3	12.2	18.9	47.9	44.9	39.1
Se	10.7	10.8	8.9	15.1	12.1	37.2	206.7	19.9	110.2
Ag	99.4	27.8	17.3	42.8	24.9	22.3	73.6	24.2	14.7
S	9.5	11.7	10.3	6.9	24.2	9.6	9.4	2.9	8.8
Na	29.9	12	12.5	14.4	20.1	14.7	22.4	16.8	22.7
Sr	7	13.9	11.5	14.2	13.5	15	14.5	11.1	5.6
Sn	10.2	54.9	7.9	11.7	10.6	40.1	147	63.3	5.2
Te	61.9	77.5		8.4		0		4.3	
Tl	9.7	109	82.8	104.5	103.8	36.1	75.8	23.2	203
Ti	5.9	35.7	14.2	22.9	23.8	34.5	4.2	50.2	28.2
V	13	38.9	14.9	21.3	13.1	30.6	34.2	21.7	17.6
Zn	12	12.1	9.9	13.4	12.1	9.9	11.5	23.7	34.9
Average	17.4	25.6	18.2	18.7	21.5	23.9	46.4	23.1	35.6

ANNEX 3

Results from interlaboratory comparison on sludge – digestion method: Nitric acid/autoclave digestion /Proficiency test SOLID-5 (2002-5) Eurofins 2002

Table 21 Data from interlaboratory comparison on two municipal sludge samples. Particle size < 4 mm. No of participants: 17.

Parameter	Unit	Median* A	Median* B	S _{R(A)}	S _{R(B)}	CV (%) A	CV (%) B
Arsenic	mg/kg	3.9	7.9	2.3	1.9	59	24
Cadmium	mg/kg	1.4	1.3	0.13	0.14	9	11
Chromium	mg/kg	21.2	34.3	2.9	5.8	14	17
Copper	mg/kg	582	293	33.6	15.7	6	5
Mercury	mg/kg	2.0	1.3	0.246	0.136	12	10
Nickel	mg/kg	14.6	16.0	2.19	1.95	15	12
Lead	mg/kg	81	73	7.5	9.7	9	14
Zinc	mg/kg	923	724	66	64	7	14
Selenium	mg/kg	1.6	2.3	0.44	0.75	28	29
Molybdenum	mg/kg	5.4	5.6	0.97	1.3	17	23

* Excluding outliers

Results from interlaboratory comparison on soil samples – digestion method: Nitric acid/autoclave digestion /Proficiency test SOLID-5 (2001-4)DHI Water & Environment 2001

Table 22 Data from interlaboratory comparison on two municipal sludge samples. Particle size < 2 mm. No of participants: 19 (Denmark, Norway and Sweden)

Parameter	Unit	Median* A	Median* B	SR(A)	SR(B)	CV (%) A	CV (%) B
Arsenic	mg/kg	770	498	44	30	6	6
Cadmium	mg/kg	0.089	0.068	0.013	0.014	15*	20*
Chromium	mg/kg	20.9	89.8	1.7	7.1	8	8
Copper	mg/kg	253	1332	19	98	7	7
Mercury	mg/kg	0.130	0.025	0.025	0.005	18	21
Nickel	mg/kg	3.16	7.26	0.35	0.89	11	13
Lead	mg/kg	22.2	10.7	1.6	1.8	7	16
Zinc	mg/kg	33.7	32.9	3.2	4.2	9	13
Selenium	mg/kg	0.997	0.171	0.32	0.09	32	56
Molybdenum	mg/kg	0.120	0.297	0.021	0.061	18	20
Iron	g/kg	3.80	8.28	1.07	1.52	1	2

* Excluding outliers

** Results from ICP-OES determinations included, all though contents were below method detection limit

The data analysis was performed in accordance with ISO 5725: “Accuracy (trueness and precision) of measurement methods and results” (1994) and as described in detail in Spliid (1992)

ANNEX 4

Results in the Finnish PTs for analysis of metals in solid samples

Table 23 Results in the Finnish PTs
SYKE 5/2002 sludge (mg/kg)

L1	Al	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn	Number of labs
X all	13.71	0.821	7.63	104.8	410.6	104.8	0.34	77.07	21.94	18.76	588.7	28 (EDXRF excl)
S(R) %	16	12	22	16	7	9	9	18	14	18	9	
lab _{HF}	19.38	0.99	7.96	120.3	469.8	127.8	0.52	77.03	26.43	27.28	608.9	1
lab _{EDXRF}	16.77	-	37.45	101.4	394.7	99.57	0.377	75.3	21.07	28.9	603.3	1
lab _{HCl}	15.3		9.7	120.5	439.4	112.8	0.372	81.7	35.5	19.17	656.8	1
lab _{HNO3}	13.19	0.818	7.51	104.2	409.1	103.1	0.337	79.28	21.92	18.84	587.8	22
lab _{H2O2}	13.55	0.803	7.4	102.1	396.1	107	0.345	70.78	22.06	18.68	543.3	4

SYKE 7/2000 sludges L1 & L2, soils M1 & M2

L1	Al	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	24 lab: HNO3
X all	31.15	1.64	63.55	288	5.59	179.5	34.4	96.55	886.5	7 lab: HNO3+H2O2
labEDX RF	32.1		95.3	245	6.27	204	32.5	97.7	758	2 lab: HNO3+HCl
labHF	37.2	1.99	94.7	296	6.42	195	43	99.8	899	1 lab: HNO3+HF 1 lab: EDXRF
L2	Al	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	
X all	5.335	0.47	11.4	193	148.5	497	16.3	11.35	523	
labEDX RF	5.73			165	149	525		9.85	427	
labHF	8.36	0.563	16.1	203	159	533	16.1	14.8	553	
M1	Al	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	
X all	9.645	0.46	19.4	92.45	11.95	157.5	30.1	11.15	48.85	
labEDX RF	36.6		35.6	87.5	16.3	315	24.1	19.1	53.3	
labHF	46.2	0.514	32.8	97.7	16.2	282	33.3	18.4	61.1	
M2	Al	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	
X all	11.1	4.355	230	338	13.2	254	178.5	73.3	408.5	
labEDX RF	43.4		266	312	18.3	437	172	81.7	385	
labHF	47.6	5.07	222	350	17.9	371	184	80.8	413	