

Trace elements determination AAS

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CONTENTS

LIST OF TABLES	6
SUMMARY	7
1. INTRODUCTION	8
2. EXISTING STANDARDS OR DRAFT STANDARDS	9
2.1 Overview of relevant standards	9
2.2 Determination of trace elements in water, aqua regia and nitric acid digest, and extracts	10
2.2.1 ISO/FDIS 15586	10
2.2.2 ISO 8288	10
2.2.3 ISO 9174, EN 1233, ISO 5961	11
2.2.4 ISO 11047	11
2.2.5 ENV 12506	11
2.3 Determination of mercury in water, aqua regia and nitric acid digest, and extracts	11
2.3.1 EN 1483	11
2.3.2 ISO 5666	12
2.3.3 EN 12338	12
2.3.4 ISO 16590	12
2.3.5 ISO/DIS 16772	12
2.3.6 prEN 13370 (Final Draft)	12
2.4 Determination of arsenic in aqua regia and nitric acid digest	13
2.4.1 EN ISO 11969	13
2.4.2 ENV 12506	13
3. EVALUATION OF DRAFTING A HORIZONTAL STANDARD	14
3.1 Determination of trace elements with graphite furnace atomic absorption spectrometry	14
3.2 Determination of mercury with cold vapour atomic absorption spectrometry	16
3.3 Determination of arsenic with hydride technique	17
4. CRITICAL POINT AND RECOMMENDATIONS	18
4.1 Determination of trace elements	18
4.2 Determination of mercury	18
4.3 Determination of arsenic	19
5. DRAFT STANDARD (CEN TEMPLATE)	20
SCOPE	20
2. NORMATIVE REFERENCES	21
3. PRINCIPLE	21
4. INTERFERENCES	22
5. REAGENTS	22
5.1 Hydrochloric acid, 37 %; $\rho \sim 1,18$ g/ml	22
5.2 Nitric acid, 65 %; $\rho \sim 1,42$ g/ml	22
5.3 Nitric acid, diluted 1 + 3 (V/V)	22
5.4 Sulfuric acid, 98 %; $\rho \sim 1,84$ g/ml	23
5.5 Sulfuric acid, diluted 1 + 9 (V/V)	23
5.6 Lanthanum chloride solution, 37 g/l lanthanum	23
5.7 Blank solution without lanthanum - for calibration	23
5.8 Blank solution with lanthanum - for calibration	23
5.9 Acetone	23
5.10 Stock and standard solutions	23
5.10.1 Cadmium solutions	23
5.10.1.1 Cadmium, stock solution corresponding to 1000 mg/l of cadmium	23

5.10.1.2	Cadmium, standard solution corresponding to 10 mg/l of cadmium	23
5.10.1.3	Cadmium, standard solution corresponding to 0,4 mg/l of cadmium	24
5.10.1.4	Cadmium, standard solution corresponding to 0,02 mg/l of cadmium	24
5.10.2	Chromium solutions	24
5.10.1.1	Chromium, stock solution corresponding to 1000 mg/l of chromium	24
5.10.2.2	Chromium, standard solution corresponding to 10 mg/l of chromium	24
5.10.2.3	Chromium, standard solution corresponding to 0,4 mg/l of chromium	24
5.10.3	Cobalt solutions	24
5.10.3.1	Cobalt, stock solution corresponding to 1000 mg/l of cobalt	24
5.10.3.2	Cobalt, standard solution corresponding to 10 mg/l of cobalt	24
5.10.3.3	Cobalt, standard solution corresponding to 0,4 mg/l of cobalt	24
5.10.4	Copper solutions	25
5.10.4.1	Copper, stock solution corresponding to 1000 mg/l of copper	25
5.10.4.2	Copper, standard solution corresponding to 10 mg/l of copper	25
5.10.3.3	Copper, standard solution corresponding to 0,4 mg/l of copper	25
5.10.5	Lead solutions	25
5.10.5.1	Lead, stock solution corresponding to 1000 mg/l of lead	25
5.10.5.2	Lead, standard solution corresponding to 10 mg/l of lead	25
5.10.5.3	Lead, standard solution corresponding to 0,4 mg/l of lead	25
5.10.6	Manganese solutions	25
5.10.6.1	manganese, stock solution corresponding to 1000 mg/l of manganese	25
5.10.6.2	Manganese, standard solution corresponding to 10 mg/l of manganese	26
5.10.6.3	Manganese, standard solution corresponding to 0,4 mg/l of manganese	26
5.10.7	Nickel solutions	26
5.10.7.1	Nickel, stock solution corresponding to 1000 mg/l of nickel	26
5.10.7.2	Nickel, standard solution corresponding to 10 mg/l of nickel	26
5.10.7.3	Nickel, standard solution corresponding to 0,4 mg/l of nickel	26
5.10.8	Zinc solutions	26
5.10.8.1	Zinc, stock solution corresponding to 1000 mg/l of zinc	26
5.10.8.2	Zinc, standard solution corresponding to 10 mg/l of zinc	27
5.10.8.3	Zinc, standard solution corresponding to 0,4 mg/l of zinc	27
5.10.8.4	Zinc, standard solution corresponding to 0,02 mg/l of zinc	27
6	APPARATUS	27
6.1	Usual laboratory apparatus	27
6.2	Atomic absorption spectrometer	27
6.3	Automated sample introduction system	28
7	PROCEDURE	28
7.1	Test portion	28
7.2	Blank test	28
7.3	Preparation of calibration solutions, aqua regia	28
7.3.1	Blank solution for calibration	28
7.3.2	Blank solution for calibration, diluted 1 + 4	28
7.3.3	Cadmium calibration solution	29
7.3.4	Chromium calibration solution	29
7.3.5	Cobalt calibration solution	29
7.3.6	Copper calibration solution	29
7.3.7	Lead calibration solution	29
7.3.8	Manganese calibration solution	29
7.3.9	Nickel calibration solution	30
7.3.10	Zinc calibration solution	30
7.4	Preparation of calibration solutions, nitric acid	30
7.4.1	Blank solution for calibration	30
7.4.2	Blank solution for calibration, diluted 1 + 4	30
7.4.3	Cadmium calibration solution	30

7.4.4	Chromium calibration solution	30
7.4.5	Cobalt calibration solution	31
7.4.6	Copper calibration solution	31
7.4.7	Lead calibration solution	31
7.4.8	Manganese calibration solution	31
7.4.9	Nickel calibration solution	31
7.4.10	Zinc calibration solution	32
7.5	Calibration and determination	32
7.6	Plotting the graph	33
7.7	Calculation	33
7.8	Expression of results	33
7.9	Precision	33
7.10	Test report	34
1	SCOPE	35
2	PRINCIPLE	35
3	REAGENTS AND GASES	35
3.1	Hydrochloric acid, 37 %; $\rho \sim 1,18$ g/ml	35
3.2	Nitric acid, 65 %; $\rho \sim 1,40$ g/ml	35
3.2.1	Nitric acid, diluted solution	35
3.3	Aqua regia, diluted solution	36
3.4	Tin(II)-chloride solution, 10 % (m/v)	36
3.5	Mercury, stock solution corresponding to 1000 mg/l of mercury	36
3.6	Mercury, standard solution corresponding to 20 mg/l of mercury	36
3.7	Mercury, standard solution corresponding to 0,2 mg/l of mercury	36
4	APPARATUS	36
4.1	Usual laboratory apparatus	36
4.2	Atomic absorption spectrometer (AAS)	36
4.3	Cold-vapour generator, batch system or an automated flow injection analysis system (FIAS)	37
5	PROCEDURE	37
5.1	Test solution	37
5.2	Blank test solution	37
5.3	Preparation of the calibration solutions	37
5.4	Calibration	38
5.5	Plotting the calibration graph	38
5.6	Test portion measurement	38
5.7	Calculation	38
5.7	Expression of results	39
6	PRECISION	39
7	TEST REPORT	39
	REFERENCES	40

LIST OF TABLES

Error! No table of figures entries found. Examples of performance data for the determination of cadmium in different matrices by AAS graphite furnace	12
Error! No table of figures entries found. 2. Examples of performance data for the determination of chromium in different matrices by AAS graphite furnace	12
Table 3. The elements determined with different existing standards	13
Error! No table of figures entries found. 4. Examples of performance data for the determination of mercury in different matrices by cold-vapour AAS	14

SUMMARY

A search for existing standards and draft standards has been made on the home pages of ISO and the Norwegian Standardisation Organisation. The relevant standards for the determination of trace metals with graphite furnace atomic absorption spectrometry are listed and reviewed in chapter 2.1.

An evaluation of the existing standards has been made for potential horizontal standardisation of the determination of trace metals, mercury and arsenic in nitric acid and aqua regia digestion solutions.

Two draft standards have been prepared with annotations to facilitate horizontal standardisation, one for the determination of trace elements in nitric acid digests and aqua regia digests with graphite furnace atomic absorption spectrometry, and one for the determination of mercury in the same digests with cold-vapour atomic absorption spectrometry. Preparation of a horizontal standard for the determination of arsenic in these solutions are not recommended.

A validation of the the two horizontal standards must be performed to compare the determinations in the two acidic media, nitric acid and aqua regia.

1. INTRODUCTION

In this desk study, it should be evaluated the potential for horizontal standardisation based on comparison of existing standards, evaluation of needs and material properties, identification of relevant fields for which the standard may be applicable, and where possible including waste. The following three potential draft horizontal standards was discussed:

- determination of trace elements in aqua regia and nitric acids digests - determination with AAS - graphite furnace.
- determination of mercury in aqua regia and nitric acid digests - determination by AAS cold vapour technique.
- determination of arsenic in aqua regia and nitric acid digests - determination by AAS hydride technique.

The latest developments on assessing total elements in sludge, soil, treated biowaste and neighbouring fields have been evaluated. Key points where possible differences exist between methods and use in different fields have been identified, and also evaluated to what extent such differences can be overcome.

2. EXISTING STANDARDS OR DRAFT STANDARDS

2.1 Overview of relevant standards

By searching the home pages of ISO and the Norwegian Standardisation Organisation, the following standards relevant to this project were found. The corresponding norwegian standards are either the ISO or CEN documents with a norwegian front page, or the methods are quite close to corresponding ISO or CEN standards.

Determinations in water:

ISO/FDIS 15586	Water quality - Determination of trace elements by atomic absorption spectrometry with graphite furnace.
ISO 8288	Water quality - Determination of cobalt, nickel, copper, zinc, cadmium and lead - Flame atomic absorption spectrometric methods.
ISO 9174	Water quality - Determination of chromium. - Atomic absorption spectrometric methods.
EN 1233	Water quality - Determination of chromium. - Atomic absorption spectrometric methods.
ISO 5961	Water quality - Determination of cadmium by atomic absorption spectrometry.
NS 4783	Water analysis - Metal content of biological material determined by atomic absorption spectrometry.
ISO 5666	Water quality - Determination of mercury.
ISO 16590	Water quality - Determination of mercury. - Methods involving enrichment by amalgamation.
NS 4768	Water analysis - Determination of mercury by cold vapour atomic absorption spectrometry. Oxidation with nitric acid.
NS-EN 1483	Water quality - Determination of mercury.
NS-EN 12338	Water quality - Determination of mercury. - Methods after enrichment by amalgamation.
ISO 11969	Water quality - Determination of arsenic. - Atomic absorption spectrometric method (hydride technique).
ISO 9965	Water quality - Determination of selenium. - Atomic absorption spectrometric method (hydride technique).

Determinations in soil extracts:

ISO 11047	Soil quality - Determination of cadmium, chromium, cobalt, copper, lead, manganese, nickel and zinc. - Flame and electrothermal atomic absorption spectrometric methods.
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ISO/DIS 16772 Soil quality - Determination of mercury in aqua regia soil extracts with cold-vapour atomic absorption spectrometry or cold-vapour atomic fluorescence spectrometry.

Determinations in waste leachates:

ENV 12506 Characterisation of waste. Analysis of eluates. Determination of pH, As, Cd, Cr(VI), Cu, Ni, Pb, Zn, Cl^- , NO_2^- , SO_4^- .

prEN 12457 Characterization of waste - Leaching - Compliance test for leaching of granular waste materials - Determination of the leaching of constituents from granular waste materials and sludge.

2.2 Determination of trace elements in water, aqua regia and nitric acid digest, and extracts

2.2.1 ISO/FDIS 15586

This standard describes the determination of trace levels of Ag, Al, As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Tl, V, Zn in surface water, ground water, drinking water, waste water and sediments, using atomic absorption spectrometry with electrothermal atomization in graphite furnace.

The method detection limit for each element depends on the sample matrix as well as the instrument used. For water samples with a simple matrix, the detection limits of the method will be close to the instrument detection limit. Table ?

Water samples are preserved with nitric acid, or filtered and acid preserved and digested, sediment samples are always digested. Some sample solutions, especially waste waters and digestions of sediments, may contain large amounts of substances that may affect the results. High concentrations of chloride may cause low results, because the volatility of many elements are increased and analyte loss may occur during the pyrolysis step! Matrix effects may be overcome in different ways, different modifiers are suggested to reduce the interference effects.

Digestion of water samples with aqua regia and nitric acid is described in ISO/FDIS 15587-1, 1991, and ISO/FDIS 15587-2, 1991, respectively. Since chloride may cause severe interference problems in the graphite furnace technique, digestion with nitric acid is recommended. For some elements, for instance Sb, nitric acid is not suitable and aqua regia should be used. Digestion of sediments is referred to.

2.2.2 ISO 8288

ISO 8288 describes the determination of cobalt, nickel, copper, zinc, cadmium and lead in water samples using flame atomic absorption methods. In addition to the direct determination method, two extraction methods are also described where the determination is performed in the organic phase. One of them is extraction with MIBK after chelation with APDC, and the other one uses chelation with HMA-HMDC and extraction with DIPK-xylene. These two

extraction techniques are used for low concentration samples, and for samples containing disturbing amounts of other compounds. If the total heavy metal concentration is exceeding 20 mg/l, a diluted sample should be extracted.

2.2.3 ISO 9174, EN 1233, ISO 5961

These standards describe the determination of single elements with atomic absorption spectrometry, and are in principles formed in the same way as the standards ISO/FDIS 15586 and ISO 8288.

2.2.4 ISO 11047

This standard deals with the determination of Cd, Cr, Co, Cu, Pb, Mn, Ni, and Zn in aqua regia extracts of soil with atomic absorption spectrometry. The choice of determination method (flame or graphite furnace) is dependent on the amount of the specific element in the sample. The extraction is performed according to ISO 11466, 1995. The efficiency of the extraction of chromium from soils by aqua regia depends strongly on the nature of chromium compounds present, and the analytical signal is strongly affected by matrix elements in the extracts.

2.2.5 ENV 12506

This standard describes the determination of pH, As, Cd, Cr(VI), Cu, Ni, Pb, Zn, chloride, nitrite and sulfate which has been extracted by leaching of waste samples with water solution. The eluate is analysed for its total content, thus the eluate is acidified for the determination of metals.

Several types of interference effects can contribute to inaccuracies in the determination of the various parameters, especially the trace elements. These potential interferences are listed in the individual standards, and the interferences is considered separately for each analytical technique.

2.3 Determination of mercury in water, aqua regia and nitric acid digest, and extracts

2.3.1 EN 1483

In natural water sources, mercury compounds generally occur in very small concentrations of less than 0,1 µg/l. Higher concentrations may be found, for example in waste water. Both inorganic and organic compounds of mercury may be present, and mercury can accumulate in sediment and sludge.

Digestion procedure is necessary to fully decompose the mercury compounds, and can only be omitted if it is certain that the mercury concentration can be measured without this

pretreatment. For measurements in the low concentration range, highest purity reagents, clean reaction vessels, and mercury free air are essential.

The standard describes two methods. 1) reduction with tin(II)chloride, and 2) reduction with sodium tetrahydroborate. The choice of method depends on the matrix and the equipment available. Fewer interferences from heavy metals arise if tin(II) chloride is used rather than sodium tetrahydroborate. Using flow systems, interference effects due to heavy metals can be further reduced. Both methods are suitable for the determination of mercury in ground, surface and waste water, in the concentration range 0,1 - 10 µg/l. Higher concentrations can be determined after dilution of the samples.

Three digestion methods are described, of which the ultrasonic digestion method with permanganate is of no interest in connection to the horizontal project. The autoclave digestion with nitric acid, and the microwave digestion with aqua regia, may both be used here.

2.3.2 ISO 5666

This standard is essentially the same as EN 1483.

2.3.3 EN 12338

This standard describes determination of mercury after enrichment by amalgamation, and is used for the concentration range 0,01 - 1 µg/l mercury in ground, surface and waste water. The method is in principle the same as the method described above, except for the amalgamation step.

2.3.4 ISO 16590

This standard is essentially the same as EN 12338.

2.3.5 ISO/DIS 16772

This International standard specifies a method for the determination of mercury in aqua regia extracts of soil, obtained in accordance with the ISO 11466, 1995. Tin(II)chloride as reduction agent is preferred in this standard because sodium tetrahydroborate reduces many elements common in soil extract solutions to the elemental state, which may cause matrix problems under particular circumstances. The determination step is in principle the same as described above.

2.3.6 prEN 13370 (Final Draft)

This European Standard specifies, among others, a method for the determination of mercury in aqueous eluates for the characterization of waste. The extraction by leaching is described in EN 12457, and the determination step is referred to EN 1483.

2.4 Determination of arsenic in aqua regia and nitric acid digest

2.4.1 EN ISO 11969

This International Standard specifies a method for the determination of arsenic including organically bound arsenic in drinking waters, ground waters and surface waters, in the concentration range 1 - 10 µg/l. The method is based on the atomic absorption measurement of arsenic generated by the thermal decomposition of arsenic(III)hydride. Other oxidation states need to be converted to As(III) prior to the determination. As(III) is reduced to arsenic(III)hydride, AsH₃, by reaction with sodium tetrahydroborate in hydrochloric acid medium.

Most organic materials interfere with the arsenic determination, and must be removed prior to the analysis by a digestion procedure. This is based on boiling the sample with sulfuric acid and hydrogen peroxide, and the condensate is collected in a condensate reservoir. The As(V) is transferred to As(III) by heating the digested sample with potassium iodide / ascorbic acid solution in presence of hydrochloric acid.

2.4.2 ENV 12506

In this standard the determination of arsenic in water leachate of waste is referred to the standard described above.

Digestion and extraction methods are excluded as they are studied by others.

3. EVALUATION OF DRAFTING A HORIZONTAL STANDARD

3.1 Determination of trace elements with graphite furnace atomic absorption spectrometry

The existing standards for water quality describes methods for the determination of a lot of trace elements in water samples with rather low concentrations of dissolved salts, and contain some additional informations about determinations in waste water samples and solutions from digestion of solid samples like sludges and sediments, and to a smaller degree digested biological materials. A Standard for soil quality describes the determination of trace elements in aqua regia extracts from soil. The standard for characterisation of waste does not contain any performance characteristics of the method.

Table 1. Examples of performance data for the determination of cadmium in different matrices by AAS graphite furnace.

Sample (µg/l)	No	Excl.	True	Mean	Recovery	CVr %	CVR %
ISO 15586							
Synthetic low	33	1	0,3	0,303	101	3,5	17,0
Synth.high	34	2	2,7	2,81	104	1,9	10,7
Fresh w. low	31	2		0,572		2,9	14,9
Fresh w. high	31	3		3,07		2,1	10,4
Waste water	27	2		1,00		3,1	27,5
Dig. sed. HNO3	29	2		48,7		2,2	14,8
EN-ISO 5961							
Waste water	22		0,91	1,148	126	4,2	23,5
Waste water	22		2,70	2,78	103	7,2	22,8
Spiked dist. w.	23		16,2	17,14	106	4,4	13,0
ISO 11047							
Soil 1 (mg/kg)	15			1,85		15,1	21,6
Soil 2 (mg/kg)	16			2,36		13,1	27,5
Soil 3 (mg/kg)	12			0,048		20,8	62,5

Table 2. Examples of performance data for the determination of chromium in different matrices by AAS graphite furnace.

Sample (µg/l)	No	Excl.	True	Mean	Recovery	CVr %	CVR %
ISO 15586							
Synthetic low	21	3	1,9	1,91	101	7,5	12,4
Synth.high	24	1	17,1	17,5	102	2,0	7,9
Fresh w. low	23	1		1,95		7,7	24,7
Fresh w. high	23	2		14,0		2,0	7,3
Waste water	17	4		3,91		4,2	40,5
Dig. sed. HNO3	19			246		3,7	8,7
EN 1233							
Std. solution	18		25	23,99	96	2,96	14,9
Water + addn.	18		10	10,94	109	6,2	37,0
ISO 11047							
Soil 1 (mg/kg)	13			51,2		4,4	21,6
Soil 2 (mg/kg)	11			88,5		5,8	27,9
Soil 3 (mg/kg)	11			61,0		2,8	28,6

The informations given about the performance characteristics given in the different standards are varying a lot, and are not easily compared. The two tables above contain performance data for different matrices for the determination of cadmium and chromium, respectively: acidified water samples, waste water samples digested with nitric acid, sediment digested with nitric acid, and soil samples digested with aqua regia. Cadmium is an element which is rather easily extracted quantitatively from different samples with acids. Even for this element there is very varying precision data for different fields, indicating that there is a need for the evaluation of validation of an harmonized method. For elements like chromium, where the analytical results are strongly depending on the chemical environment during digestion, we have to expect that there will be marked differences in the results obtained between the different acid media used for extraction.

The digestion of sludges and soils with aqua regia is described in the Standard ISO 11466, Soil quality - Extraction of trace elements soluble in aqua regia. In the description of the desk study it is pointed out that the latest developments on assessing total elements in sludge, soil, treated biowaste and neighbouring fields should be evaluated. The aqua regia does not digest all inorganic compounds in the samples, however, normally the aqua regia extract contains the trace elements very close to the total for most metals, with some few exceptions, e.g. chromium and aluminium. For the determination of the total content of heavy metals in sediments and soils hydrofluoric acid has to be used, this technique is described in the Standard ISO 14869-1. So far there is no decision taken that digests performed by this method shall be used, therefore such solutions are omitted in the further work.

For the characterisation of waste the water leaching of the sample is described in the Standard prEN 12457, Characterization of waste - Leaching - Compliance test for leaching of granular waste materials - Determination of the leaching of constituents from granular waste materials and sludge. The determinations may be performed according to the existing Standards.

The existing standards are describing the determination of a limited number of elements in different matrices, see table 3.

Table 3. The elements determined with different existing standards.

Standard	Elements determined
ISO/DIS 15586	Ag, Al, As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Tl, V, Zn
ISO 8288	Cd, Co, Cu, Ni, Pb, Zn
ISO/FDIS 9174	Cr
= EN1233	Cr
EN ISO 5961	Cd
ISO 11047	Cd, Co, Cr, Cu, Pb, Mn, Ni, Zn
ENV 12506	As, Cd, Cu, Ni, Pb, Zn

The problem with the high concentrations may easily be overcome by diluting the samples before determination with graphite furnace.

Some sample solutions, especially waste waters and digestions of sediments and soils, often contain large amounts of substances that may affect the results. High concentrations of chloride may cause low results, because the volatility of many elements is increased and

analyte loss may occur during the pyrolysis step. Matrix effects may be overcome, partially or completely, by optimization of the temperature programme, the use of pyrolytically coated tubes or platforms, the use of chemical modifiers, the standard addition technique and the use of background correction.

It is necessary to evaluate possible interferences in nitric acid digests and aqua regia digests. Especially for wastes there is only information given for solutions prepared by extractions, there is no information about digested wastes. This is simply done by the determination of possible interfering substances by the analysis of samples to which the element in question and various concentrations of the potential interfering substances have been added. Some ions, even present in low concentrations, can cause interferences. Combinations of ions can also lead to depression or enhancement of the measured signal, even present in lower concentrations than when the element alone does not lead to any problems. The method of standard addition should therefore be given preference to the normal calibration.

No standards were found, that describes digestion of solid samples with nitric acid as thoroughly as with aqua regia in ISO 11047. In the proposed draft horizontal standard, therefore, information about nitric acid extracts have been taken from the water quality standards. Some details in this draft have to be adjusted according to the horizontal standards for digestion of solid samples with nitric acid and with aqua regia. As a basis for the preparation of a draft horizontal standard for the determination of trace elements in solid samples, therefore, ISO 11047 and water quality standards have been used.

3.2 Determination of mercury with cold vapour atomic absorption spectrometry

Table 4. Examples of performance data for the determination of mercury in different matrices by cold vapour atomic absorption spectrometry.

Sample (µg/l)	No	Excl.	True	Mean	Recovery	CVr %	CVR %
EN 1483							
Drinking water	13	14 %	0,819	0,737	90	9,9	29,4
Surface water	13	14 %	1,474	1,335	91	14,6	28,5
Waste water	13	14 %	5,732	5,588	98	4,2	15,0
EN 12338							
Potable water	21	5 %	0,060	0,0705	118	17,2	38,8
Potable water	21	5 %	0,088	0,0854	97	15,0	28,9
Surface water	21	5 %	0,283	0,260	92	8,8	18,9
Waste water	21	0 %	0,800	0,756	56	8,4	28,6
ISO/DIS 16772							
Soil 1	11			0,430		5,4	22,06
Soil 2	11			12,49		2,56	8,84
prEN 13370							
Synth. eluate	12	1		6,25		2,1	21,8

The performance data summarized for the determination of mercury in table 4 is indicating that the precision is strongly dependent on the matrix of the samples. Here is presented the results for different kinds of water samples, only one set of samples is available for digests of soil. It is obviously necessary to establish precision performance data for several sample types and for both nitric acid digests and aqua regia digests.

Iodide in concentrations $> 0,1$ mg/l causes interferences in the determination due to formation of mercury complexes. In this case the method with sodium tetrahydroborate is necessary, even when fewer interferences from heavy metals arise if tin(II)chloride is used rather than sodium tetrahydroborate. Because the redox potential of the tin(II)chloride solution, various mercury compounds, such as mercury sulfide and organic mercury compounds, cannot be reduced fully without digestion.

It is possible to prepare a draft horizontal standard for the determination of mercury in aqua regia and nitric acid digest, based on ISO/DIS 16772, and excluding the part describing determination with atomic fluorescence. Informations about nitric acid digests had to be taken from the water quality standards so far. Evaluation of possible differences in the validation data when using nitric acid digest and aqua regia digest must be performed.

3.3 Determination of arsenic with hydride technique

For arsenic there may be greater problems than for the other metals to prepare a horizontal standard, because the reduction of As(V) to As(III) is taking place in hydrochloric acid medium, and we have aqua regia and nitric acid digests of soil and sludge. High concentrations of nitrate (as nitric acid) may lead to interferences in the determination of arsenic by the hydride technique. If a horizontal standard for the determination of arsenic shall be prepared, a digestion method excluding the use of nitric acid, more or less, has to be used.

Inorganic arsenic normally occurs in two oxidation states, As(V) and As(III). It is essential to convert all arsenic species to the As(III) state prior to generating the hydrides. Arsenic(V) gives a significantly lower response than arsenic(III). Naturally occurring organoarsenic compounds do not react with sodium tetrahydroborate. These compounds require vigorous digestion (e.g. $\text{HNO}_3/\text{HClO}_4$ - UV digestion). A number of methods are available for breaking down organoarsenic compounds (Anal. Chim. Acta 1985).

The hydride generation technique is prone to interferences by transition metals. For the majority of natural water samples, this type of interference should not be significant. However, in digests of soil and waste the situation is quite different, and the user should carry out recovery tests, and also determine the maximum concentrations of transition metals. Increasing the hydrochloric acid in the final sample solution, and reducing the sodium tetrahydroborate concentration minimises the interference effect on arsenic.

4. CRITICAL POINT AND RECOMMENDATIONS

4.1 Determination of trace elements

There is no specification in the project description which elements should be included in the horizontal standard. The existing standards are quite different with respect to which elements are included. Before starting the preparation of a horizontal standard it is necessary to decide which elements should be included. It is not possible to include all elements in the same method, the determination of elements like Hg, As, and Se, for instance, must be described in separate standards.

In digestion solutions of sediments, soils and sludges, some elements will be present in higher concentrations. Thus flame atomic absorption may be a more suitable technique for the determination of these elements in such samples, and it must be decided whether or not the flame method shall be included in this project.

Graphite furnace atomic absorption spectrometry is used for determination of several trace metals, both in nitric acid digestion solutions and aqua regia digestion solutions. However, the presence of chloride in the aqua regia solutions may introduce some limitations in the application of this analytical technique. High concentrations of chloride is known to cause low results, because the volatility of many elements is increased and analyte loss may occur during the pyrolysis step. This matrix effect may be reduced by optimization of the temperature programme in combination with the use of chemical modifiers. We have to expect that this may introduce some differences between the methods used for nitric acid and aqua regia digestion solutions, and the effect of these differences must be evaluated through a validation of the harmonized method. The validation must also include the application of the standard addition technique.

For the determinations of trace metals in acid extracts from sediments and soils, and acid extracts of waste, the existing standards have been used with only minor changes to prepare a draft horizontal standard. As a basis for the preparation of a draft horizontal standard for the determination of trace elements in solid samples, therefore, ISO 11047 have been used. In addition there have been used informations given in the water quality standards where necessary, even when the standards describing digestion of water samples with nitric acid or aqua regia are limited to sample solutions with a suspended solids mass concentration less than 20 g/l and total organic carbon less than 5 g/l. The validation process, therefore, has to include digestion solutions of sediments, soils, inorganic waste and biological waste which contain large amounts of substances that may affect the results.

4.2 Determination of mercury

For mercury it is recommended that tin(II)-chloride is used as reduction agent in the horizontal standard, because there arise fewer interferences from heavy metals when tin(II)chloride is used instead of sodium tetrahydroborate. So far the gold trap technique have not been included in the evaluation of potential horizontal standard, probably there is no need for the low detection limit obtained with this technique. If, in the future, there arise a need for

a lower detection limit than is obtainable with the direct method, it is rather easy to include it into the draft standard.

A draft horizontal standard for the determination of mercury in aqua regia and nitric acid digest was based on ISO/DIS 16772, excluding the part describing determination with atomic fluorescence. Some informations about nitric acid digests had to be taken from the water quality standards so far. Therefore the performance data for a standard combining the determination of mercury in both nitric acid digest and aqua regia digestion solutions is insufficient, and evaluation of possible differences in the validation data must be performed.

4.3 Determination of arsenic

The reduction of As(V) to As(III) has to take place in hydrochloric acid medium, however, we have aqua regia and nitric acid digestion solutions of soil, sludge and waste as matrix. High concentrations of nitrate (as nitric acid) is known to lead to interferences in the determination of arsenic by the hydride technique. Therefore, it is suggested that a horizontal standard for the determination of arsenic using the hydride technique is omitted. Instead it is recommended that other determination techniques than the hydride method for the determination of arsenic are used, for instance ICP or ICP-MS methods.

5. DRAFT STANDARD (CEN TEMPLATE)

5.1 Determination of trace elements in aqua regia and nitric acid digests by atomic absorption spectrometry - graphite furnace

SCOPE

This Horizontal Standard includes principles and procedures for the determination of trace levels of trace metals in aqua regia and nitric acid digests of sludge, soil and treated biowaste and neighbouring samples, using atomic absorption spectrometry with electrothermal atomization in a graphite furnace. The method is applicable for determination of low concentrations of elements.

The method detection limit for each element depends on the sample matrix as well as of the instrument, the type of atomizer and the use of chemical modifiers. For water samples with a simple matrix (i.e. low concentration of dissolved solids and particles), the method detection limits will be close to instrument detection limits. In digests containing higher concentrations of dissolved solids, interference effects may lead to an increase in the method detection limit. The values of Table 1 should at least be obtainable, using a 20 µl sample volume.

Table 1 - Approximate characteristic masses, instrument detection limits and optimum working ranges for water samples using a 20 µl sample volume.

Element	Characteristic mass (m ₀) ^a , pg	Detection limit ^b , µg/l	Optimum working range ^c , µg/l
Ag	1,5	0,2	1 - 10
Al	10	1	6 - 60
Cd	0,7	0,1	0,4 - 4
Co	10	1	6 - 60
Cr	3	0,5	2 - 20
Cu	5 ^d	0,5	3 - 30
Fe	5	1	3 - 30
Mn	2,5	0,5	1,5 - 15
Mo	10	1	6 - 60
Ni	13	1	7 - 70
Pb	15	1	10 - 100
Sb	20	1	10 - 100
Tl	10 ^d	1	6 - 60
V	35	2	20 - 200
Zn	0,8	0,5	0,5 - 5

^a The characteristic mass (m₀) of an element is the mass in picograms, corresponding to a signal of 0,0044 seconds (s), using the integrated absorbance (peak area) for evaluation.

- ^b The detection limits are calculated as 3 times the standard deviation of repeated measurements of a blank solution.
- ^c The optimum working range is defined as the concentration range that corresponds to integrated absorbance readings between 0,05 and 0,5 s.
- ^d If Zeeman effect background correction is used, the m_0 value will be higher.

2 NORMATIVE REFERENCES

This Horizontal Standard incorporates by dated or undated references, provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendment to or revisions of these publications apply to this Horizontal Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies.

ISO/FDIS 15586: 2001	Water quality - Determination of trace elements by atomic absorption spectrometry with graphite furnace.
ISO 8288: 1988	Water quality - Determination of cobalt, nickel, copper, zinc, cadmium and lead - Flame atomic absorption spectrometric methods.
ISO 9174: 1999	Water quality - Determination of chromium. - Atomic absorption spectrometric methods.
EN 1233: 1996	Water quality - Determination of chromium. - Atomic absorption spectrometric methods.
ISO 5961: 1995	Water quality - Determination of cadmium by atomic absorption spectrometry.
NS 4783: 1988	Water analysis - Metal content of biological material determined by atomic absorption spectrometry.

3 PRINCIPLE

In electrothermal atomization atomic absorption spectrometry, discrete sample aliquots are dispensed into a graphite tube (of which there are several types), which can be heated to over 2800 °C very rapidly and in a controlled manner. By increasing the temperature stepwise, the processes of drying, thermal decomposition of the matrix and thermal dissociation into free atoms occur. Atomic absorption spectrometry is based on the ability of free atoms to absorb light. A light source emits light specific for a certain element (or elements). When the light beam passes through the atom cloud in the heated graphite furnace, the light is selectively absorbed by atoms of the chosen element(s). The decrease in light intensity is measured with a detector at a specific wavelength. The concentration of an element in the sample is determined by comparing the absorbance of the sample with the absorbance of calibration solutions. The signal-peak produced is, under optimum conditions, sharp and symmetrical, and of narrow half-width. The height of the peak is, for most elements, proportional to the concentration of the element in solution, although for certain elements it is preferable to work from peak area. The measurements are made at the wavelengths given in Table 2.

If necessary, interferences may be overcome by adding a matrix modifier to the samples before analysis, or by performing the calibration with standard addition technique.

The results are given as the mass of analyte (micrograms μg of milligrams mg) per litre of water, or per kilogram of dried materials in sediments and soils.

Table 2. General conditions for electrothermal atomic absorption spectrometry

Element	Wavelength	Atomization conditions	Recommended background correction technique
Cadmium	228,8	Platform recommended	Zeeman, deuterium
Chromium	357,9	No platform	Zeeman or Smith-Hieftje
Cobalt	240,7	No platform	Zeeman, deuterium
Copper	324,8	Platform recommended	Zeeman or Smith-Hieftje is better
Lead	217,0	Platform recommended	Zeeman, deuterium
Manganese	279,5	Platform recommended	Zeeman or Smith-Hieftje is better
Nickel	232,0	No platform	Zeeman, deuterium
Zinc	213,9	Platform recommended	Zeeman, deuterium

4 INTERFERENCES

Some sample solutions, especially waste waters and digestions of sediments and soils, may contain large amounts of substances that may affect the results. High concentrations of chloride may cause low results, because the volatility of many elements is increased and analyte loss may occur during the pyrolysis step. Matrix effects may be overcome, partially or completely, by optimization of the temperature programme, the use of pyrolytically coated tubes or platforms, the use of chemical modifiers, the standard addition technique and the use of background correction.

5 REAGENTS

All reagents shall be of recognized analytical grade. Use deionized water or water distilled from all-glass apparatus, conforming to grade 1 of ISO 3696 ($\leq 0,01$ mS/m, or better).

The water used for blank determinations and for preparing reagents and standard solutions shall have a concentration of the element to be determined that is negligible compared with the lowest concentration of that element in the sample solutions.

5.1 Hydrochloric acid, 37 %; $\rho \sim 1,18$ g/ml

The same batch of hydrochloric acid shall be used throughout the procedure.

5.2 Nitric acid, 65 %; $\rho \sim 1,42$ g/ml

The same batch of nitric acid shall be used throughout the procedure.

5.3 Nitric acid, diluted 1 + 3 (V/V)

Add 250 ml of nitric acid (5.3) to 500 ml of water in a 1000 ml volumetric flask and fill to the mark with water.

5.4 Sulfuric acid, 98 %; $\rho \sim 1,84$ g/ml

The same batch of sulfuric acid shall be used throughout the procedure.

5.5 Sulfuric acid, diluted 1 + 9 (V/V)

Add slowly with swirling or stirring (magnetic stirrer bar) 100 ml of sulfuric acid (5.4) to 700 ml water in a 1000 ml volumetric flask, mix, cool and fill to the mark with water.

5.6 Lanthanum chloride solution, 37 g/l lanthanum

Dissolve 100 g lanthanum(III) chloride, $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$, in 700 ml water. Then quantitatively transfer it to a 1000 ml volumetric flask and fill to the mark with water.

5.7 Blank solution without lanthanum - for calibration

Dilute 210 ml of hydrochloric acid (5.1) and 70 ml of nitric acid (5.2) with 500 ml water in a 1000 ml volumetric flask and fill to the mark with water.

5.8 Blank solution with lanthanum - for calibration

Dilute 210 ml of hydrochloric acid (5.1) and 70 ml of nitric acid (5.2) with 500 ml water in a 1000 ml volumetric flask. Add 100 ml lanthanum chloride solution (5.6) and fill to the mark with water.

5.9 Acetone

5.10 Stock and standard solutions

Stock solutions shall be replaced after one year as a maximum, and standard solutions with concentrations of 10 mg/l (first dilution step) shall be renewed monthly as a minimum.

5.10.1 Cadmium solutions

Warning - Cadmium is highly toxic. Safety measures shall be taken to avoid ingestion.

5.10.1.1 Cadmium, stock solution corresponding to 1000 mg/l of cadmium

Weigh, to the nearest $\pm 0,0002$ g, approximately 1,0000 g cadmium metal (minimum purity 99,5 %) and dilute it in a covered 250 ml glass beaker with 40 ml nitric acid (5.3). Then add 100 ml of water. Boil to expel nitrous fumes, cool, transfer to a 1000 ml volumetric flask and fill to the mark with water.

5.10.1.2 Cadmium, standard solution corresponding to 10 mg/l of cadmium

Pipette 10,00 ml of the cadmium stock solution (5.10.1.1) into a 1000 ml volumetric flask. Add 20 ml of nitric acid (5.3), fill to the mark with water and mix well.

5.10.1.3 Cadmium, standard solution corresponding to 0,4 mg/l of cadmium

Pipette 20,00 ml of the cadmium standard solution (5.10.1.2) into a 500 ml volumetric flask. Add 10 ml of nitric acid (5.3), fill to the mark with water and mix well. Prepare this solution on the day of use.

5.10.1.4 Cadmium, standard solution corresponding to 0,02 mg/l of cadmium

Pipette 5,00 ml of the cadmium standard solution (5.10.1.3) into a 100 ml volumetric flask. Add 2 ml of nitric acid (5.3), fill to the mark with water and mix well. Prepare this solution on the day of use.

5.10.2 Chromium solutions

5.10.2.1 Chromium, stock solution corresponding to 1000 mg/l of chromium

Dissolve 2,8290 g \pm 0,0002 g potassium dichromate, $K_2Cr_2O_7$, dried at 130 °C for 24 hours, in a covered 400 ml glass beaker with 40 ml of water. Add 5 ml of sulfuric acid (5.4), cool, transfer to a 1000 ml volumetric flask and fill to the mark with water.

5.10.2.2 Chromium, standard solution corresponding to 10 mg/l of chromium

Pipette 10,00 ml of the chromium stock solution (5.10.2.1) into a 1000 ml volumetric flask. Add 20 ml of nitric acid (5.3), fill to the mark with water and mix well.

5.10.2.3 Chromium, standard solution corresponding to 0,4 mg/l of chromium

Pipette 20,00 ml of the chromium standard solution (5.10.2.2) into a 500 ml volumetric flask. Add 10 ml of nitric acid (5.3), fill to the mark with water and mix well. Prepare this solution on the day of use.

5.10.3 Cobalt solutions

5.10.3.1 Cobalt, stock solution corresponding to 1000 mg/l of cobalt

Weigh, to the nearest \pm 0,0002 g, approximately 1,0000 g cobalt metal (minimum purity 99,5 %) and dilute it in a covered 250 ml glass beaker with 10 ml nitric acid (5.3) and 10 ml hydrochloric acid (5.1). Then add 100 ml of water. Boil to expel nitrous fumes, cool, transfer to a 1000 ml volumetric flask and fill to the mark with water.

5.10.3.2 Cobalt, standard solution corresponding to 10 mg/l of cobalt

Pipette 10,00 ml of the cobalt stock solution (5.10.3.1) into a 1000 ml volumetric flask. Add 20 ml of nitric acid (5.3), fill to the mark with water and mix well.

5.10.3.3 Cobalt, standard solution corresponding to 0,4 mg/l of cobalt

Pipette 20,00 ml of the cobalt standard solution (5.10.3.2) into a 500 ml volumetric flask. Add 10 ml of nitric acid (5.3), fill to the mark with water and mix well. Prepare this solution on the day of use.

5.10.4 Copper solutions

5.10.4.1 Copper, stock solution corresponding to 1000 mg/l of copper

Weigh, to the nearest $\pm 0,0002$ g, approximately 1,0000 g copper metal (minimum purity 99,5 %) and dilute it in a covered 250 ml glass beaker with 10 ml nitric acid (5.3). Then add 100 ml of water. Boil to expel nitrous fumes, cool, transfer to a 1000 ml volumetric flask and fill to the mark with water.

5.10.4.2 Copper, standard solution corresponding to 10 mg/l of copper

Pipette 10,00 ml of the copper stock solution (5.10.4.1) into a 1000 ml volumetric flask. Add 20 ml of nitric acid (5.3), fill to the mark with water and mix well.

5.10.3.3 Copper, standard solution corresponding to 0,4 mg/l of copper

Pipette 20,00 ml of the copper standard solution (5.10.4.2) into a 500 ml volumetric flask. Add 10 ml of nitric acid (5.3), fill to the mark with water and mix well. Prepare this solution on the day of use.

5.10.5 Lead solutions

5.10.5.1 Lead, stock solution corresponding to 1000 mg/l of lead

Weigh, to the nearest $\pm 0,0002$ g, approximately 1,0000 g lead metal (minimum purity 99,5 %) and dilute it in a covered 250 ml glass beaker with 10 ml nitric acid (5.3). Then add 100 ml of water. Boil to expel nitrous fumes, cool, transfer to a 1000 ml volumetric flask and fill to the mark with water.

5.10.5.2 Lead, standard solution corresponding to 10 mg/l of lead

Pipette 10,00 ml of the lead stock solution (5.10.5.1) into a 1000 ml volumetric flask. Add 20 ml of nitric acid (5.3), fill to the mark with water and mix well.

5.10.5.3 Lead, standard solution corresponding to 0,4 mg/l of lead

Pipette 20,00 ml of the lead standard solution (5.10.5.2) into a 500 ml volumetric flask. Add 10 ml of nitric acid (5.3), fill to the mark with water and mix well. Prepare this solution on the day of use.

5.10.6 Manganese solutions

5.10.6.1 manganese, stock solution corresponding to 1000 mg/l of manganese

Clean manganese metal by transferring several grams of electrolytic manganese (minimum purity 99,5 %) and dissolve it in a covered 250 glass beaker containing about 150 ml dilute sulfuric acid (5.5). Stir and allow the manganese to settle for several minutes. Decant, wash several times with water and finally with acetone (5.9). Decant the surplus acetone, dry the metal for 2 minutes at 105 °C and cool in a desiccator.

Weigh, to the nearest $\pm 0,0002$ g, approximately 1,0000 g of such cleaned manganese metal and dissolve it in a covered 250 ml glass beaker with 20 ml hydrochloric acid (5.1) and 20 ml nitric acid (5.3). Then add 100 ml of water. Boil to expel nitrous fumes, cool, transfer to a 1000 ml volumetric flask and fill to the mark with water.

5.10.6.2 Manganese, standard solution corresponding to 10 mg/l of manganese

Pipette 10,00 ml of the manganese stock solution (5.10.5.1) into a 1000 ml volumetric flask. Add 20 ml of nitric acid (5.3), fill to the mark with water and mix well.

5.10.6.3 Manganese, standard solution corresponding to 0,4 mg/l of manganese

Pipette 20,00 ml of the manganese standard solution (5.10.5.2) into a 500 ml volumetric flask. Add 10 ml of nitric acid (5.3), fill to the mark with water and mix well. Prepare this solution on the day of use.

5.10.7 Nickel solutions

5.10.7.1 Nickel, stock solution corresponding to 1000 mg/l of nickel

Weigh, to the nearest $\pm 0,0002$ g, approximately 1,0000 g nickel metal (minimum purity 99,5 %) and dilute it in a covered 250 ml glass beaker with 10 ml hydrochloric acid (5.1) and 10 ml nitric acid (5.3). Then add 100 ml of water. Boil to expel nitrous fumes, cool, transfer to a 1000 ml volumetric flask and fill to the mark with water.

5.10.7.2 Nickel, standard solution corresponding to 10 mg/l of nickel

Pipette 10,00 ml of the nickel stock solution (5.10.7.1) into a 1000 ml volumetric flask. Add 20 ml of nitric acid (5.3), fill to the mark with water and mix well.

5.10.7.3 Nickel, standard solution corresponding to 0,4 mg/l of nickel

Pipette 20,00 ml of the nickel standard solution (5.10.7.2) into a 500 ml volumetric flask. Add 10 ml of nitric acid (5.3), fill to the mark with water and mix well. Prepare this solution on the day of use.

5.10.8 Zinc solutions

5.10.8.1 Zinc, stock solution corresponding to 1000 mg/l of zinc

Weigh, to the nearest $\pm 0,0002$ g, approximately 1,0000 g zinc metal (minimum purity 99,5 %) and dilute it in a covered 250 ml glass beaker with 40 ml nitric acid (5.3). Then add 100 ml of water. Boil to expel nitrous fumes, cool, transfer to a 1000 ml volumetric flask and fill to the mark with water.

5.10.8.2 Zinc, standard solution corresponding to 10 mg/l of zinc

Pipette 10,00 ml of the zinc stock solution (5.10.8.1) into a 1000 ml volumetric flask. Add 20 ml of nitric acid (5.3), fill to the mark with water and mix well.

5.10.8.3 Zinc, standard solution corresponding to 0,4 mg/l of zinc

Pipette 20,00 ml of the zinc standard solution (5.10.8.2) into a 500 ml volumetric flask. Add 10 ml of nitric acid (5.3), fill to the mark with water and mix well. Prepare this solution on the day of use.

5.10.8.4 Zinc, standard solution corresponding to 0,02 mg/l of zinc

Pipette 5,00 ml of the zinc standard solution (5.10.8.3) into a 500 ml volumetric flask. Add 10 ml of nitric acid (5.3), fill to the mark with water and mix well. Prepare this solution on the day of use.

6 APPARATUS

6.1 Usual laboratory apparatus

All glass or plastic ware shall be cleaned carefully before trace element determinations, e.g. by immersion in warm 5 % (V/V) aqueous nitric acid solution for a minimum of 6 hours, followed by rinsing with water before use. The nitric acid shall be replaced each week.

NOTE It has been found convenient to to keep separate sets of glass or plastic ware for the determinations given in this Horizontal Standard, in order to reduce the possibility of within-laboratory contamination. Similarly, it can be convenient to carry out the acid cleaning step overnight. Certain kinds of plastic are effected by nitric acid, so care should be taken in the choice of plastic. Because of the high sensitivity of electrothermal atomic absorption spectrometry, stringent precautions should be taken to clean all glass or plastic ware and avoid contamination of sample, standard and calibration solutions from foreign material and dust from the laboratory atmosphere.

6.2 Atomic absorption spectrometer

This shall be equipped with an electrothermal atomizer, a hollow cathod lamp or electrodeless discard lamp appropriate to the element of interest and operated at a current recommended for the lamp by the instrument manufacturer, an automatic background correction device, and a computerized read-out or a high speed chart recorder. Background correction shall be used with electrothermal atomic absorption spectrometry, the minimum acceptable technical specification (below 350 nm wavelength>) of which is that based on deuterium.

NOTE Deuterium background correction is appropriate for cadmium, zinc and lead, if the limited application of deuterium background correction for som instruments to about 0,6 to 0,8 absorbance is not exceeded. Smith-Hieftje or Zeeman background correction is required for all elements if the backgroud signal is high. To increase the analyte-to-background-signal ratio, application of a graphite tube with a pyrolytic platform together with matrix modifiers such as diammonium hydrogen phosphat ($(\text{NH}_4)_2\text{HPO}_4$, reduced palladium or other, plus peak

integration read-out, are recommended for samples with high acid and matrix load. Pyrolytic graphite has the additional advantage that carry-over from sample to sample is likely to be greatly reduced for most elements, in comparison with non-pyrolytic graphite. Users of this Horizontal Standard should not assume that the routine instrumental settings recommended by the manufacturers will necessarily give the best results with complex matrices such as those dealt with in this Horizontal Standard. Careful development of temperature programmes is essential.

6.3 Automated sample introduction system

This system shall be capable of delivering fixed volumes up to 70 µl.

7 PROCEDURE

7.1 Test portion

The solid samples shall be extracted with aqua regia or nitric acid in accordance with ISO, respectively. To cover the calibration range of the very sensitive electrothermal absorption method and to protect the graphite tubes from high acid concentrations, it is recommended to dilute the sample solutions 1 + 4 with water, as follows. Pipette 20,00 ml of each sample solution into a 100 ml volumetric flask and fill to the mark with water.

7.2 Blank test

Carry out a blank test at the same time as the extraction with aqua regia or nitric acid using cleaned quartz sand instead of the soil sample and following the same procedure, using the same quantities of all reagents for the determination.

To prepare the blank test solutions diluted 1 + 4, pipette 20,00 ml of the above solution into a volumetric flask and fill to the mark with water.

7.3 Preparation of calibration solutions, aqua regia

Before each batch of determinations, prepare, from the standard solutions of each element (5.10), at least four calibration solutions covering the range of concentrations to be determined, as below. Calibration solutions shall be prepared on the day of use.

7.3.1 Blank solution for calibration

Dilute 210 ml of hydrochloric acid (5.1) and 70 ml of nitric acid (5.2) with 500 ml of water in a 1000 ml volumetric flask and fill to the mark with water.

7.3.2 Blank solution for calibration, diluted 1 + 4

Dilute 20,00 ml of blank solution (7.3.1) with water in a 100 ml volumetric flask and fill to the mark with water.

7.3.3 Cadmium calibration solution

Pipette 2,00 ml, 5,00 ml, 10,00 ml, 20,00 ml and 30,00 ml of cadmium standard solution (5.10.1.4) into a series of 100 ml volumetric flasks. Add 20 ml of the blank solution (7.3.1) and fill to the mark with water and mix well.

These solutions correspond to cadmium concentrations of 0,0004 mg/l, 0,001 mg/l, 0,002 mg/l, 0,004 mg/l and 0,006 mg/l, respectively.

7.3.4 Chromium calibration solution

Pipette 5,00 ml, 10,00 ml, 15,00 ml and 20,00 ml chromium standard solution (5.10.2.3) into a series of 100 ml volumetric flasks. Add 20 ml of the blank solution (7.3.1) and fill to the mark with water and mix well.

These solutions correspond to chromium concentrations of 0,02 mg/l, 0,04 mg/l, 0,06 mg/l and 0,08 mg/l, respectively.

7.3.5 Cobalt calibration solution

Pipette 5,00 ml, 10,00 ml, 20,00 ml and 30,00 ml cobalt standard solution (5.10.3.3) into a series of 100 ml volumetric flasks. Add 20 ml of the blank solution (7.3.1) and fill to the mark with water and mix well.

These solutions correspond to cobalt concentrations of 0,02 mg/l, 0,04 mg/l, 0,08 mg/l and 0,12 mg/l, respectively.

7.3.6 Copper calibration solution

Pipette 5,00 ml, 10,00 ml, 15,00 ml and 20,00 ml copper standard solution (5.10.4.3) into a series of 100 ml volumetric flasks. Add 20 ml of the blank solution (7.3.1) and fill to the mark with water and mix well.

These solutions correspond to copper concentrations of 0,02 mg/l, 0,04 mg/l, 0,06 mg/l and 0,08 mg/l, respectively.

7.3.7 Lead calibration solution

Pipette 5,00 ml, 10,00 ml, 15,00 ml and 20,00 ml lead standard solution (5.10.5.3) into a series of 100 ml volumetric flasks. Add 20 ml of the blank solution (7.3.1) and fill to the mark with water and mix well.

These solutions correspond to lead concentrations of 0,02 mg/l, 0,04 mg/l, 0,06 mg/l and 0,08 mg/l, respectively.

7.3.8 Manganese calibration solution

Pipette 1,00 ml, 2,00 ml, 5,00 ml and 7,50 ml manganese standard solution (5.10.6.3) into a series of 100 ml volumetric flasks. Add 20 ml of the blank solution (7.3.1) and fill to the mark with water and mix well.

These solutions correspond to manganese concentrations of 0,004 mg/l, 0,008 mg/l, 0,02 mg/l and 0,03 mg/l, respectively.

7.3.9 Nickel calibration solution

Pipette 5,00 ml, 10,00 ml, 15,00 ml and 20,00 ml nickel standard solution (5.10.7.3) into a series of 100 ml volumetric flasks. Add 20 ml of the blank solution (7.3.1) and fill to the mark with water and mix well.

These solutions correspond to nickel concentrations of 0,02 mg/l, 0,04 mg/l, 0,06 mg/l and 0,08 mg/l, respectively.

7.3.10 Zinc calibration solution

Pipette 5,00 ml, 10,00 ml, 15,00 ml and 20,00 ml zinc standard solution (5.10.8.4) into a series of 100 ml volumetric flasks. Add 20 ml of the blank solution (7.3.1) and fill to the mark with water and mix well.

These solutions correspond to zinc concentrations of 0,001 mg/l, 0,002 mg/l, 0,004 mg/l and 0,006 mg/l, respectively.

7.4 Preparation of calibration solutions, nitric acid

Before each batch of determinations, prepare, from the standard solutions of each element (5.10), at least four calibration solutions covering the range of concentrations to be determined, as below. Calibration solutions shall be prepared on the day of use.

7.4.1 Blank solution for calibration

Dilute 70 ml of nitric acid (5.2) with 500 ml of water in a 1000 ml volumetric flask and fill to the mark with water.

7.4.2 Blank solution for calibration, diluted 1 + 4

Dilute 20,00 ml of blank solution (7.4.1) with water in a 100 ml volumetric flask and fill to the mark with water.

7.4.3 Cadmium calibration solution

Pipette 2,00 ml, 5,00 ml, 10,00 ml, 20,00 ml and 30,00 ml of cadmium standard solution (5.10.1.4) into a series of 100 ml volumetric flasks. Add 20 ml of the blank solution (7.4.1) and fill to the mark with water and mix well.

These solutions correspond to cadmium concentrations of 0,0004 mg/l, 0,001 mg/l, 0,002 mg/l, 0,004 mg/l and 0,006 mg/l, respectively.

7.4.4 Chromium calibration solution

Pipette 5,00 ml, 10,00 ml, 15,00 ml and 20,00 ml chromium standard solution (5.10.2.3) into a series of 100 ml volumetric flasks. Add 20 ml of the blank solution (7.4.1) and fill to the mark with water and mix well.

These solutions correspond to chromium concentrations of 0,02 mg/l, 0,04 mg/l, 0,06 mg/l and 0,08 mg/l, respectively.

7.4.5 Cobalt calibration solution

Pipette 5,00 ml, 10,00 ml, 20,00 ml and 30,00 ml cobalt standard solution (5.10.3.3) into a series of 100 ml volumetric flasks. Add 20 ml of the blank solution (7.4.1) and fill to the mark with water and mix well.

These solutions correspond to cobalt concentrations of 0,02 mg/l, 0,04 mg/l, 0,08 mg/l and 0,12 mg/l, respectively.

7.4.6 Copper calibration solution

Pipette 5,00 ml, 10,00 ml, 15,00 ml and 20,00 ml copper standard solution (5.10.4.3) into a series of 100 ml volumetric flasks. Add 20 ml of the blank solution (7.4.1) and fill to the mark with water and mix well.

These solutions correspond to copper concentrations of 0,02 mg/l, 0,04 mg/l, 0,06 mg/l and 0,08 mg/l, respectively.

7.4.7 Lead calibration solution

Pipette 5,00 ml, 10,00 ml, 15,00 ml and 20,00 ml lead standard solution (5.10.5.3) into a series of 100 ml volumetric flasks. Add 20 ml of the blank solution (7.4.1) and fill to the mark with water and mix well.

These solutions correspond to lead concentrations of 0,02 mg/l, 0,04 mg/l, 0,06 mg/l and 0,08 mg/l, respectively.

7.4.8 Manganese calibration solution

Pipette 1,00 ml, 2,00 ml, 5,00 ml and 7,50 ml manganese standard solution (5.10.6.3) into a series of 100 ml volumetric flasks. Add 20 ml of the blank solution (7.4.1) and fill to the mark with water and mix well.

These solutions correspond to manganese concentrations of 0,004 mg/l, 0,008 mg/l, 0,02 mg/l and 0,03 mg/l, respectively.

7.4.9 Nickel calibration solution

Pipette 5,00 ml, 10,00 ml, 15,00 ml and 20,00 ml nickel standard solution (5.10.7.3) into a series of 100 ml volumetric flasks. Add 20 ml of the blank solution (7.4.1) and fill to the mark with water and mix well.

These solutions correspond to nickel concentrations of 0,02 mg/l, 0,04 mg/l, 0,06 mg/l and 0,08 mg/l, respectively.

7.4.10 Zinc calibration solution

Pipette 5,00 ml, 10,00 ml, 15,00 ml and 20,00 ml zinc standard solution (5.10.8.4) into a series of 100 ml volumetric flasks. Add 20 ml of the blank solution (7.4.1) and fill to the mark with water and mix well.

These solutions correspond to zinc concentrations of 0,001 mg/l, 0,002 mg/l, 0,004 mg/l and 0,006 mg/l, respectively.

7.5 Calibration and determination

7.5.1 Set up the instrument parameters and align the electrothermal atomizer according to the manufacturer's instructions to take full advantage of the background correction system. Set up the sampler similarly. Determine the optimum electrothermal atomizer parameters for the particular type of atomizer and sample volume (up to 70 μ l) as recommended by the instrument manufacturer to cover the optimal working range. Set the instrument baseline to zero. Check the zero stability within the atomization system by running the pre-set heating programme for blank firing of the graphite atomizer. Check the lack of spectral interferences by running real sample solutions with standard additions. Repeat the blank firing to ensure baseline stability.

7.5.2 Using the autosampler, inject into the atomiser the predetermined volume (up to 70 μ l) of each of the diluted test solutions. Add a fixed volume of modifier solution, atomize and note the instrument response. If possible, sort the test solutions into groups of three or four with similar concentrations of the analyte, starting with the lowest. Be careful to note any memory effects caused by particular samples, especially at high analyte levels.

7.5.3 Using an autosampler, inject a fixed volume of solution. Add a fixed volume of modifier solution and atomize the diluted blank calibration solution (7.3.2 or 7.4.2), the calibration solutions (7.3 or 7.4), the diluted blank test solution (7.2) and the diluted test solutions (7.1) in order of increasing instrument response. If the peak height (or peak area) of the test portion exceeds the value of the highest calibration solution, a smaller volume of the test portion shall be used.

Atomize each solution at least twice and, if the reproducibility is acceptable according to the quality control system in use in the laboratory, average the readings. Check the instrument again for absence of memory effects, especially at high analyte levels, by running the blank firing programme after high readings. Reset the baseline to zero if necessary.

If an unknown type of sample is to be handled, each element concentration shall be determined by means of the standard addition method. If the analytical results according to the standard addition method and calibration curve are equal, the calibration curve method can be applied.

NOTE The reproducibility of the instrument readings expressed as an absolute difference, coefficient of variation, or a standard deviation, will vary depending on the concentration of the element in the extracts.

7.6 Plotting the graph

plot a graph having the element concentration of the calibration solutions (from which has been subtracted the blank calibration reading), in milligrams per litre, as abscissa, and the corresponding values of peak height (or area) as ordinate.

7.7 Calculation

By reference to the calibration graph obtained, determine the concentration of the element corresponding to the absorbance of the test portion (7.1) and of the diluted blank test solution (7.2). Calculate the content (w) of the element in the sample using the following equation:

$$w_{(M)} = (\rho_1 - \rho_0).f.V/m$$

where

$w_{(M)}$ is the mass fraction of the element M in the sample, in milligrams per kilogram;

ρ_1 is the concentration of the element, in milligrams per litre, corresponding to the absorbance of the diluted test portion (7.1);

ρ_0 is the concentration of the element, in milligrams per liter, corresponding to the absorbance of the diluted blank test solution (7.2);

f is the dilution factor (= 5) of the diluted test portion (7.1);

V is the volume, in litres, of the test portion taken for the analysis, e.g. 0,1 litre in accordance with ISO 11466;

m is the mass of the sample, in kilograms, corrected for water content in accordance with ISO 11465, and treated in accordance with ISO 11466.

7.8 Expression of results

The measurement uncertainty reported for the results should reflect the results from the quality control measures and incorporate the deviation between the individual readings for the sample in question. In general, values shall not be expressed to a greater degree of accuracy than two significant figures. The rounding of values will depend on the statistics of the quality control procedures mentioned earlier, and the requirements of the analysis. For results below 1 mg/kg, experience shows that greater accuracy than one significant figure is rarely achieved.

Example: $w(\text{Co}) = 2,5 \text{ mg/kg}$
 $w(\text{Co}) = 0,3 \text{ mg/kg}$

7.9 Precision

An interlaboratory test has to be performed to yield precision data. Repeatability and reproducibility shall be calculated according to ISO 5725.1.

7.10 Test report

The test report shall contain the following information:

- a) a reference to this horizontal standard;
- b) a reference to the method used;
- c) complete identification of the sample;
- d) the results of the determination;
- e) any detail not specified in this horizontal standard or which are optional, as well as any factor which may have affected the results.

5.2 Determination of mercury in aqua regia and nitric acid digests with cold-vapour atomic absorption spectrometry

1 SCOPE

This horizontal standard specifies a method for the determination of mercury in nitric acid digest or aqua regia extract of soil, obtained in accordance with ISO 11466 with cold-vapour atomic absorption spectrometry method.

2 PRINCIPLE

Mercury is reduced to the elemental state by tin(II)-chloride solution and liberated from solution in a closed system. The mercury vapour passes through a cell positioned in the light path of an atomic absorption spectrometer. Its absorbance at a wavelength of 253,7 nm is measured. The absorbance signal is a function of mercury concentration.

NOTE Tin(II)-chloride as a reduction substance is preferred in this standard because sodium borohydride reduces many elements common in soil extract solutions to the elemental state, which cause matrix problems under particular circumstances.

3 REAGENTS AND GASES

All reagents shall be of recognised analytical grade. Use deionized water or water distilled from an all-glass apparatus, complying with grade 2 as defined in ISO 3696. The water used for blank determinations, and for preparing reagents and standard solutions shall have a mercury concentration that is negligible compared with the lowest concentration to be determined in the sample solutions.

Purity of argon or nitrogen should be $\geq 99,99$ %.

3.1 Hydrochloric acid, 37 %; $\rho \sim 1,18$ g/ml

The same batch of hydrochloric acid shall be used throughout the procedure.

3.2 Nitric acid, 65 %; $\rho \sim 1,40$ g/ml

The same batch of nitric acid shall be used throughout the procedure.

3.2.1 Nitric acid, diluted solution

Pour 500 ml of water into a 1000 ml volumetric flask. Add 250 ml of nitric acid (3.2) with caution, mix and fill to the mark with water.

3.3 Aqua regia, diluted solution

Add 21 ml hydrochloric acid (3.1) and 7 ml nitric acid (3.2) to 500 ml of water in a 1000 ml volumetric flask, mix and fill to the mark with water.

3.4 Tin(II)-chloride solution, 10 % (m/v)

Dissolve 10 g of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 30 ml of hydrochloric acid (3.1), transfer to a 100 ml volumetric flask and fill to the mark with water. The blank concentration of mercury can be reduced by bubbling a stream of nitrogen through the solution for 30 minutes, if necessary. Prepare this solution on the day of use.

3.5 Mercury, stock solution corresponding to 1000 mg/l of mercury

Two sources of stock solutions can be used:

- commercially available stock solutions.
- stock solutions prepared in the laboratory from pure elements or stoichiometrically defined and dried salts or oxides.

Dissolve $100 \text{ mg} \pm 0,4 \text{ mg}$ of mercury metal (minimum purity 99,99 %) in a 100 ml volumetric flask with 17 ml nitric acid (3.2) and fill to the mark with water.

NOTE Commercially available stock solutions have the advantage that they remove the need to handle toxic mercury. However, special care needs to be taken that these solutions are supplied with a certified composition from a reputable source and are checked on a regular basis.

3.6 Mercury, standard solution corresponding to 20 mg/l of mercury

Pipette 2 ml of the stock mercury solution (3.5) into a 100 ml volumetric flask, add 10 ml nitric acid (3.2.1), mix and fill to the mark with water.

3.7 Mercury, standard solution corresponding to 0,2 mg/l of mercury

Pipette 1 ml of the standard mercury solution (3.6) into a 100 ml volumetric flask, add 10 ml nitric acid (3.2.1), mix and fill to the mark with water.

4 APPARATUS

4.1 Usual laboratory apparatus

All glassware shall be carefully cleaned for low trace element determinations, e.g. by immersion in 5 % (V/V) aqueous nitric acid solution for a minimum of six hours, followed by rinsing with water before use. The nitric acid shall be replaced each week. Grade A volumetric glassware shall be used throughout.

4.2 Atomic absorption spectrometer (AAS)

Equipped with an element hollow cathode or, preferably, an electrodeless discharge lamp (which give a greater and more stable light intensity) operated at a current recommended by the lamp and instrument manufacturer, an automatic background correction device and a computerised read out.

4.3 Cold-vapour generator, batch system or an automated flow injection analysis system (FIAS)

Which should be adaptable to the atomic absorption spectrometer (4.2). A flow-controlled nitrogen (3) or argon stream (3) is used as an inert carrier to transport mercury vapour into the cell. Time-controlled addition of tin(II)-chloride reducing solution (3.4) in combination with automatic start of the read signal of the spectrometer is required. Systems with a 10 cm quartz cell with quartz windows adapted for atomic absorption spectrometry (4.2) are commercially available. In this case, the quartz cell is electrically heated to a temperature of 100 °C to avoid condensation of water.

NOTE If an automated system is used, where the reaction occurred continuously (FIA-System), the concentration of stannous chloride solution, reaction time and the gas-liquid separator configuration must be optimised due to the slow reaction kinetics of the reducing system.

Warning - It is essential that the manufacturer's safety recommendations are strictly observed.

5 PROCEDURE

5.1 Test solution

Transfer 10 ml nitric acid or aqua regia soil extracts according to ISO 15587-2 or ISO 11466, respectively, into a 100 ml volumetric flask and fill to the mark with water.

5.2 Blank test solution

Carry out a blank test at the same time as the extraction with nitric acid or aqua regia using cleaned quartz sand instead of the soil sample and following the sample procedure, using the same quantities of all reagents for the determination, but omit the test portion. Transfer 10 ml of the blank test solution to a 100 ml volumetric flask and fill to the mark with water.

5.3 Preparation of the calibration solutions

Before each batch of determinations, prepare a blank calibration solution and from the 0,2 mg/l mercury standard solution (3.7) at least five calibration solutions covering the range of concentrations to be determined.

Pipette 1 ml, 2 ml, 3 ml, 5 ml and 8 ml of mercury standard solution (3.7) into a series of 100 ml volumetric flasks. Fill to the mark with diluted nitric acid solution (3.2.1) or diluted aqua regia solution (3.3) and mix well. These solutions correspond to mercury concentrations of 2 µg/l, 4 µg/l, 6 µg/l, 10 µg/l and 16 µg/l, respectively. Using 10 ml of each solution for the cold-vapour generator these solutions correspond to 20 ng, 40 ng, 60 ng, 100 ng and 150 ng of mercury, respectively.

5.4 Calibration

Set up the atomic absorption spectrometer (4.2) and the cold-vapour generator (4.4) according to the manufacturer's instructions, select a wavelength of 253,7 nm and adjust the quartz cell, the gas flow and the reaction time and flow rate of tin(II)-chloride solution (3.4) to get acceptable sensitivity. Transfer 10 ml of blank calibration solution (5.3) into the cold-vapour generation bottle, connect the bottle to the system and start the time-controlled programme. The signal of the blank calibration solution should be negligible compared to with the lowest standard solution. Adjust the response of the instrument to zero signal. Repeat the measurement with each standard calibration solution (5.3) at least twice and record the signal and, if the two values fall within an accepted range, average the values.

5.5 Plotting the calibration graph

Plot a graph having the mercury concentrations of the calibration solutions (5.3), from which the blank calibration solution reading has been subtracted, as abscissa, and the corresponding signal values as ordinate.

5.6 Test portion measurement

Transfer 10 ml of blank test solution (5.2) into the cold-vapour generator bottle, connect the bottle to the system and start the time-controlled programme and record the signal. Repeat the measurement with each test solution (5.1) at least twice, record the signal and, if the two values fall within an accepted range, average the values.

If the mercury concentration of the test solution exceeds the range of calibration, the test solution shall be diluted with diluted nitric acid solution (3.2.1) or diluted aqua regia solution (3.3) accordingly.

NOTE The standard addition method can be used to check the absence of matrix effects. If the analytical results according to the standard addition method and the calibration curve method are equal, the calibration curve method can be applied.

5.7 Calculation

By reference to the calibration graph obtained, determine the concentration of the element corresponding to the signal of the test solution (5.1) and of the blank test solution (5.2). Calculate the mercury content (w) of the sample, expressed as mg/kg per dried matter using the equation:

$$w(\text{Hg}) = (p_1 - p_0) \cdot f \cdot V \cdot C / m \cdot 1000$$

where

w is the mass fraction of mercury in the sample, in mg/kg dry matter;

p_1 is the mercury concentration, in $\mu\text{g/l}$, corresponding to the signal of the test portion (5.1);

- p_0 is the mercury concentration, in $\mu\text{g/l}$, corresponding to the signal of the same blank (5.2);
- f $f = 10$ is the dilution factor of the test solution (5.1) used in this standard;
- V is the volume, in l, of the test portion taken for the analysis (0,1 l);
- m is the mass of the sample in kg, treated according to ISO 11466 or...;
- C is the correction factor for the dry soil sample, $C = 100/\text{wdm}$;
- wdm is the dry matter content of the soil expressed as a percentage according to ISO 11465.

5.7 Expression of results

Values shall be rounded to 0,01 mg/kg, but only significant figures should be expressed.

Example: $w(\text{Hg}) = 0,45 \text{ mg/kg}$
 $w(\text{Hg}) = 12,5 \text{ mg/kg}$

6 PRECISION

For aqua regia the informations given in ISO/DIS 16772 can be used, for nitric acid an interlaboratory comparison should be carried throug for the current sample types.

7 TEST REPORT

The test report shall contain the following information:

- a) a reference to this horizontal standard;
- b) a reference to the method used (nitric acid or aqua regia);
- c) complete identification of the sample;
- d) the results of the determination;
- e) any details not specified in this standard or which are optional, as well as any factor which may have affected the results.

REFERENCES

- ISO/FDIS 15587-1, 1991: Water quality - Digestion for the determination of selected elements in water - Part 1: Aqua regia digestion
- ISO/FDIS 15587-2, 1991: Water quality - Digestion for the determination of selected elements in water - Part 1: Nitric acid digestion
- ISO 11466, 1995: Soil quality - Extraction of trace elements soluble in aqua regia
- Anal. Chim. Acta 1985, 171, 285: N.G. Van der Veen, H.J. Keukens and G. Vos: Comparison of ten digestion procedures for the determination of arsenic in soils by hydride generation AAS