BS EN 13346:2000

Characterization of sludges — Determination of trace elements and phosphorus — Aqua regia extraction methods

The European Standard EN 13346:2000 has the status of a British Standard

ICS 13.030.20

National foreword

This British Standard is the official English language version of EN 13346:2000.

The UK participation in its preparation was entrusted to Technical Committee EH/5, Sludge characterization, which has the responsibility to:

- aid enquirers to understand the text;
- present to the responsible European committee any enquiries on the interpretation, or proposals for change, and keep the UK interests informed;
- monitor related international and European developments and promulgate them in the UK.

A list of organizations represented on this committee can be obtained on request to its secretary.

Further information

Users of this standard are informed that the UK submitted some substantial comments at the final voting stage of the draft EN for the following reasons.

1) The scope fails to address the question of whether this method is appropriate for all of the types of sludges in the scope of CEN/TC 308. For example, is it applicable to sludges containing large amounts of lime? Hence, modify the scope to answer the question of applicability to the scope of the TC.

2) The following note should be added to the scope:
"The validation for this standard has only been carried out using materials as described in annex A. For other sludges, the user should validate the method using recovery and reproducibility tests".

3) The final phrase, "and sludge products," in the first sentence of the scope should be removed as it is inappropriate.

4) This is not a single standard since there are 4 alternative methods of extraction and 3 alternative methods of pretreatment. The test report in clause **12** should therefore specify which of the 12 permutations has been used. Therefore, either rewrite c) as "describe which method of pretreatment and which method of digestion was used" or modify the document so that there is only one standard method against which others may be benchmarked.

5) In annex D, the data presented for Method D with reference materials appear to condemn this method as unfit since it is almost invariably outside the 95% confidence of the reference sample. Therefore, suggest deleting Method D.

6) It is recommended that an additional brief section on the use of adequate AQC as per CEN/TC 223 methods be added:
"The analysis described in this standard should be carried out within a quality control system utilizing analytical quality control measures. Where performance data are absent for the sample type, recovery and reproducibility data should be obtained as a minimum".

This British Standard, having been prepared under the direction of the Health and Environment Sector Committee, was published under the authority of the Standards Committee and comes into effect on 15 October 2000

Amendments issued since publication

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Cross-references

The British Standards which implement international or European publications referred to in this document may be found in the BSI Standards Catalogue under the section entitled "International Standards Correspondence Index", or by using the "Find" facility of the BSI Standards Electronic Catalogue.

Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, the EN title page, pages 2 to 29 and a back cover.

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EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM

EN 13346

August 2000

ICS 13.030.20

English version

Characterization of sludges - Determination of trace elements and phosphorus - Aqua regia extraction methods

Caractérisation des boues - Détermination des éléments traces et du phosphore - Méthodes d'extraction à l'eau régale

Charakterisierung von Schlämmen - Bestimmung von Spurenelementen und Phosphor - Extraktionsverfahren mit Königswasser

This European Standard was approved by CEN on 5 August 2000.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Central Secretariat or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Central Secretariat has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and United Kingdom.

EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Central Secretariat: rue de Stassart, 36 B-1050 Brussels

Ref. No. EN 13346:2000 E

Contents

Foreword

This European Standard has been prepared by Technical Committee CEN/TC 308, Characterization of sludges, the Secretariat of which is held by AFNOR.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by February 2001, and conflicting national standards shall be withdrawn at the latest by February 2001.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

The annexes A to D are informative.

Introduction

Elements extractable in aqua regia cannot be described as "total"; conversely they cannot be regarded as the "bio-available" fraction, as the extraction procedure is too vigorous to represent all biological processes.

One extraction method is proposed, using aqua regia. Four heating processes are described, they use the same reagents therefore the same principle of chemical reaction.

Method A is a vigorous digestion procedure allowing larger test portions.

Method B is a fast procedure carried out in a single vessel, smaller test portions are used.

Methods C and D are microwave heating procedures using closed and open systems respectively.

1 Scope

This standard specifies methods for the extraction, with aqua regia, of trace elements and phosphorus from sludges and sludge products. The resulting solution is suitable for the determination of As, Cd, Cr, Cu, Hg, Ni, Pb, Se, Zn and P using spectrometric techniques.

NOTE 1 With high solute concentrations in extract solutions, spectral interferences and background enhancement should be expected.

NOTE 2 This method can be used for other elements except that portion of the elements bonded to silica.

2 Normative references

This European Standard incorporates by dated or undated reference, 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 amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies.

EN 1233, *Water quality - Determination of chromium - Atomic absorption spectrometric methods.*

EN 1483, *Water quality - Determination of mercury.*

EN 12880, *Characterization of sludges - Determination of dry residue and water content.*

EN ISO 3696, *Water for analytical laboratory use - Specification and test methods* (ISO 3696:1987).

EN ISO 5961, *Water quality - Determination of cadmium by atomic absorption spectrometry* (ISO 5961:1994).

EN ISO 11885, *Water quality - Determination of 33 elements by inductively coupled plasma atomic emission spectroscopy* (ISO 11885:1996).

EN ISO 11969, *Water quality - Determination of arsenic - Atomic absorption spectrometric method (hydride technique)* (ISO 11969:1996).

ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results - Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method.*

ISO 8288, *Water quality - Determination of cobalt, nickel, copper, zinc, cadmium and lead - Flame atomic absorption spectrometric methods.*

3 Terms and definitions

For the purposes of this European Standard, the following terms and definitions apply.

3.1
aqua regia
digestion solution obtained by mixing one volume of nitric acid and three volumes of hydrochloric acid

3.2
dry mass (dry matter)
the mass of solids obtained after the specified drying process. It is expressed as grams or kilograms [EN 12880]

4 Principle

The laboratory sample is prepared in order to obtain a representative test portion which is extracted with aqua regia according to one of the following heating procedures:

- boiling for about 2 h with a reflux condenser, followed by filtration and making up to volume in a volumetric flask (method A);
- boiling for about 15 min in a calibrated glass tube, making up to volume in the same tube, allowing to settle and then decanting the supernatant solution for analysis (method B);
- microwave digestion for about 20 min in a closed vessel followed by filtration and making up to volume in a volumetric flask (method C);
- microwave digestion for about 30 min in an open vessel followed by filtration and making up to volume in a volumetric flask (method D).

NOTE Other heating procedures can be used providing they demonstrate equivalent performance.

5 Reagents

5.1 General

The reagents used shall be of sufficient purity so as not to introduce a significant error into the subsequent analysis. A reagent blank comprising the same quantity of acids shall be taken through the entire procedure with each batch of analysis.

5.2 Water

Deionized or distilled water used shall conform to purity grade 2 of EN ISO 3696.

5.3 Hydrochloric acid, solution $c(\mathrm{HCl}) = 12{,}0$ mol/l.

About 37 % (m/m), $\rho \approx 1{,}18$ g/ml.

5.4 Nitric acid, solution, $c(\mathrm{HNO_3}) = 15{,}8$ mol/l.

About 65 % (m/m), $\rho \approx 1{,}42$ g/ml.

5.5 Nitric acid solution, about 1 % (V/V) for cleaning.

Take 10 ml of nitric acid (5.4) and dilute to 1 l in a flask with water. This dilute nitric acid shall be used to clean the glassware.

5.6 n-Dodecane or other suitable antifoaming agents (for addition in method B).

6 Apparatus

6.1 General

All glassware and plasticsware shall be adequately cleaned and stored in order to avoid any contamination.

NOTE It can be necessary to periodically clean the reaction vessel with a suitable surfactant to remove stubborn deposits.

6.2 Reaction vessels

a) glass flask, 250 ml for example (for method A);

b) calibrated borosilicate glass tube 50 ml, for example, with a glass or polypropylene stopper (for method B);

c) plastics vessel (at least 100 ml) made of perfluoroalkoxy polymer (PFA) or tetrafluoromethoxyl polymer (TFM) equipped with a system capable of controlling overpressure in order to avoid explosion of the vessel (for method C);

d) digestion vessel made of borosilicate glass with a volume of at least 50 ml (for method D).

NOTE Quartz vessels can be used instead of glass vessels.

6.3 Reflux condenser

Adaptable to reaction vessels used in methods A or D.

6.4 Heating devices

a) a heating mantle or aluminium block heater (for methods A and B respectively);

b) a microwave oven with programmable power to control fast exothermic reaction and closed microwave vessels equipped with a safety system for method C. A domestic microwave oven is not allowed;

c) a microwave oven with a programmer module (for method D).

NOTE For example an apparatus with microwave frequencies 2,45 GHz, electronic automatic power control which can be pilot-operated from 10 % to 99 % with 5 % increment for maximal power released of 200 W and a pump for reagent.

6.5 Filter papers

Filter paper cellulose based, hardened and resistant to aqua regia.

6.6 Volumetric flasks, capacity 25 ml, 50 ml or 100 ml.

6.7 Analytical balance, with an accuracy of 1 mg or better.

6.8 Boiling aids, anti bumping granules or glass beads, diameter 2 mm to 3 mm, acid washed (for methods A and B).

7 Preparation of the laboratory sample

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.

NOTE Other methods of dried sample preparation are presented in annex A.

8 Procedure

8.1 Extraction procedure under reflux conditions (method A)

Weigh approximately 3 g, to the nearest 0,001 g, of the prepared sample (clause 7) and transfer to the 250 ml reaction vessel [6.2 a)]. Moisten with about 0,5 ml to 1,0 ml of water (5.2) and add, with mixing, (21 ± 0,1) ml of hydrochloric acid (5.3) followed by (7 ± 0,1) ml of nitric acid (5.4) dropwise if necessary to reduce foaming. Connect the condenser (6.3) to the reaction vessel, and stand at room temperature until any effervescence almost ceases to allow for slow oxidation of the organic mass in the sludge.

Transfer to the heating device [6.4 a)] 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 (5.2).

NOTE If the digested sample contains particulates which can clog nebulizers or interfere with injection of the sample, the sample can be centrifuged, allowed to settle, or filtered before transferring into a suitable sized volumetric flask (6.6). For example, the solution should be allowed to pass through the filter paper (6.5), then the insoluble residue washed onto the filter paper with a minimum of water (5.2).

Transfer the digested sample into a suitable sized volumetric flask (6.6) and dilute to the mark with water (5.2).

8.2 Extraction procedure under boiling in glass tube (method B)

Weigh approximately 0,5 g, to the nearest 0,001 g, of the prepared sample (clause 7) and transfer to the 50 ml glass tube [6.2 b)]. Add (1,0 ± 0,1) ml of water (5.2) to wet the sample. Add a few boiling aids (6.8). Carefully run (6,0 ± 0,1) ml of hydrochloric acid (5.3) down the side of the tube followed by (2,0 ± 0,1) ml of nitric acid (5.4). Place the tube in a rack and allow the initial vigorous reaction to subside. If excessive foaming occurs add two drops of n-dodecane (5.6).

Place the tube in the heating apparatus [6.4 a)] 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 (5.2). Reflux for a further (5 ± 1) min then remove the tube from the block. Allow to cool and make up to volume with water (5.2). Stopper the tube and mix by inversion.

NOTE If the digested sample contains particulates which can clog nebulizers or interfere with injection of the sample, the sample can be centrifuged, allowed to settle, or filtered before transferring into a suitable sized volumetric flask (6.6). For example, the solution should be allowed to pass through the filter paper (6.5), then the insoluble residue washed onto the filter paper with a minimum of water (5.2).

Transfer the digested sample into a suitable sized volumetric flask (6.6) and dilute to the mark with water (5.2).

8.3 Extraction procedure with closed microwave oven (method C)

Weigh approximately 0,3 g to 1 g, to the nearest 0,001 g of the prepared sample (clause 7) and transfer to the vessel (6.2 c)). Add (2 ± 0,1) ml of nitric acid (5.4) and (6 ± 0,1) ml of hydrochloric acid (5.3). Place cover and spring on the top of the vessel according to the manufacturer's instructions. Weigh the reaction vessel to the nearest 0,1 g. Place it in the rotor [6.4 b)]. Place the rotor in the microwave oven [6. 4 b)] and start the digestion programme. Always fill all positions of the rotor.

At the end of the programme, cool the rotor to room temperature to reduce the internal pressure in the vessel. To confirm that no excess loss of digestion solution occurred during the digestion procedure check the mass of the vessel and the condition of the safety membrane or cover, referring to the manufacturer's instructions. Control that the loss of mass shall not exceed 10 % (*m/m*) of the initial mass. Open the vessel slowly under fume extraction.

NOTE 1 If the digested sample contains particulates which can clog nebulizers or interfere with injection of the sample, the sample can be centrifuged, allowed to settle, or filtered before transferring into a suitable sized volumetric flask (6.6). For example, the solution should be allowed to pass through the filter paper (6.5), then the insoluble residue washed onto the filter paper with a minimum of water (5.2).

Transfer the digested sample into a suitable sized volumetric flask (6.6) and dilute to the mark with water (5.2).

NOTE 2 Example of a digestion programme for six samples:

- 2 min at 250 W;
- 2 min at 0 W;
- 5 min at 250 W;
- 5 min at 400 W;
- 5 min at 500 W.

NOTE 3 Calibration of the microwave oven (see B.1).

8.4 Extraction procedure with open microwave oven (method D)

Weigh approximately 0,5 g to 1 g, to the nearest 0,001 g, of the prepared sample (clause 7) and transfer into the vessel [6.2 d)], add the acids according to the programme chosen and to the manufacturer's instructions, cap the vessel with the reflux column and place the vessel in the microwave unit [6.4 c)] and run the programme (see note 2).

At the end of the microwave programme, allow the vessel to cool to room temperature. Complete the preparation of the sample by uncapping and venting under fume extraction.

NOTE 1 If the digested sample contains particulate which can clog nebulizers or interfere with injection of the sample, the sample can be centrifuged, allowed to settle, or filtered before transferring into a suitable sized volumetric flask (6.6). For example, the solution should be allowed to pass through the filter paper (6.5), then the insoluble residue washed onto the filter paper with a minimum of water (5.2).

Transfer the digested sample into a suitable sized volumetric flask (6.6) and dilute to the mark with water (5.2).

NOTE 2 Example of a digestion programme.

Table 1 — Steps of a program

Time min	**Power** watt	**HNO_3** ml	**HCl** ml
15	40	3	9
15	40	3	9

NOTE 3 Calibration of the microwave oven (see B.2).

9 Blank test

A blank test shall be carried out in parallel by the same extraction procedure, using the same quantities of all reagents but omitting the test portion.

10 Measurements

Take into account specific interferences occurring with sludges (see annex C).

Take the extracts (see clause 8) and the blank test (see clause 9) and perform the analysis according to the respective European and International Standards: EN 1233, EN 1483, EN ISO 5961, ISO 8288, EN ISO 11885 and EN ISO 11969. Adjust the acid strengths to match those described in the written procedures.

11 Expression of results

The results shall be expressed in milligrams per kilogram of dry matter or in grams per kilogram for phosphorus (P).

12 Test report

The test report shall be issued separately or in conjunction with the report from the subsequent analytical method. The test report shall contain the following information:

a) a reference to this European Standard;

b) complete identification of the sample;

c) information about the pre-treatment and extraction of the sample;

d) any detail not specified in this European Standard, or which are optional;

e) any other information pertinent to the quality of the analytical data.

13 Precision data

One interlaboratory test carried out in July 1997 in Europe (12 countries and 55 laboratories) has given the values indicated in the Tables 2 to 11 and the evaluation was made using ISO 5725-2.

Table 2 — Precision data for As

Sample	Method	l	n	NAP %	$\bar{x}$ mg/kg	σ_R mg/kg	VC_R %	σ_r mg/kg	VC_r %
Sludge 1	A	31	124	6,4	1,94	1,29	66,7	0,29	15,0
	B	8	32	0	1,83	0,81	44,2	0,26	14,2
	C	20	80	5	1,71	0,69	40,1	0,23	13,7
	D	5	20	0	2,63	1,55	58,9	0,39	14,7
Sludge 2	A	31	124	6,4	2,45	1,32	53,2	0,16	6,4
	B	9	36	0	2,43	0,62	25,4	0,53	21,7
	C	20	80	5	2,28	0,77	33,6	0,32	13,9
	D	5	20	0	2,29	0,59	25,7	0,17	7,3

Sludge 1	Mixture of drinking water sludge and sewage sludge.
Sludge 2	Mixture of industrial sludge and drinking water sludge.
l	is the number of laboratories;
n	is the number of values;
NAP	is the percentage of outliers;
$\bar{x}$	is the overall mean;
σ_R	is the standard deviation of reproducibility;
VC_R	is the coefficient of variation of reproducibility;
σ_r	is the standard deviation of repeatability;
VC_r	is the coefficient of variation of repeatability.

Table 3 — Precision data for Cd

Sample	**Method**	l	N	**NAP** %	$\bar{x}$ mg/kg	σ_R mg/kg	VC_R %	σ_r mg/kg	VC_r %
Sludge 1	A	33	132	3	0,9	0,22	24,6	0,05	5,9
	B	12	48	8,3	1,09	0,65	59,2	0,05	4,8
	C	22	88	4,5	1,06	0,53	49,6	0,1	9,5
	D	7	28	0	0,91	0,2	21,5	0,06	6,7
Sludge 2	A	32	128	3,1	1,19	0,68	57,1	0,1	8,3
	B	13	52	7,7	1,86	2,16	116	0,44	23,6
	C	23	92	4,3	1,9	2,18	114	0,46	24,4
	D	7	28	14,3	1,07	0,48	44,3	0,09	8,3

Sludge 1	Mixture of drinking water sludge and sewage sludge.
Sludge 2	Mixture of industrial sludge and drinking water sludge.
l	is the number of laboratories;
n	is the number of values;
NAP	is the percentage of outliers;
$\bar{x}$	is the overall mean;
σ_R	is the standard deviation of reproducibility;
VC_R	is the coefficient of variation of reproducibility;
σ_r	is the standard deviation of repeatability;
VC_r	is the coefficient of variation of repeatability.

Table 4 — Precision data for Cr

Sample	Method	l	n	NAP %	$\bar{x}$ mg/kg	σ_R mg/kg	VC_R %	σ_r mg/kg	VC_r %
Sludge 1	A	35	140	2,8	18,96	2,90	15,3	2,34	12,3
	B	9	36	0	18,76	2,98	15,9	1,41	7,5
	C	24	96	0	20,67	3,23	15,6	1,10	5,3
	D	8	32	0	17,73	2,06	11,6	1,18	6,7
Sludge 2	A	35	140	2,8	40,79	6,15	15,1	1,55	3,8
	B	10	40	0	40,63	7,08	17,4	1,34	3,3
	C	25	100	0	43,90	5,61	12,8	2,51	5,7
	D	8	32	0	39,26	6,58	16,8	1,35	3,5

Sludge 1	Mixture of drinking water sludge and sewage sludge.
Sludge 2	Mixture of industrial sludge and drinking water sludge.
l	is the number of laboratories;
n	is the number of values;
NAP	is the percentage of outliers;
$\bar{x}$	is the overall mean;
σ_R	is the standard deviation of reproducibility;
VC_R	is the coefficient of variation of reproducibility;
σ_r	is the standard deviation of repeatability;
VC_r	is the coefficient of variation of repeatability.

Table 5 — Precision data for Cu

Sample	**Method**	l	n	**NAP** %	$\bar{x}$ mg/kg	σ_R mg/kg	VC_R %	σ_r mg/kg	VC_r %
Sludge 1	A	35	140	2,8	92,34	4,99	5,4	1,59	1,7
	B	13	52	7,7	91,08	17,02	18,7	4,15	4,6
	C	27	108	3,7	92,84	6,89	7,4	2,88	3,1
	D	9	36	11,1	93,48	6,98	7,5	2,94	3,1
Sludge 2	A	35	140	2,8	234,20	14,07	6,0	8,94	3,8
	B	14	56	7,1	231,40	26,23	11,3	4,94	2,1
	C	28	112	3,6	233,00	16,32	7,0	10,46	4,5
	D	9	36	11,1	236,70	17,44	7,4	8,28	3,5

Sludge 1	Mixture of drinking water sludge and sewage sludge.
Sludge 2	Mixture of industrial sludge and drinking water sludge.
l	is the number of laboratories;
n	is the number of values;
NAP	is the percentage of outliers;
$\bar{x}$	is the overall mean;
σ_R	is the standard deviation of reproducibility;
VC_R	is the coefficient of variation of reproducibility;
σ_r	is the standard deviation of repeatability;
VC_r	is the coefficient of variation of repeatability.

Table 6 — Precision data for Hg

Sample	Method	l	n	NAP %	$\bar{x}$ mg/kg	σ_R mg/kg	VC_R %	σ_r mg/kg	VC_r %
Sludge 1	A	28	112	0	0,49	0,07	14,5	0,04	8,8
	B	9	36	22,2	0,50	0,09	18,7	0,05	9,3
	C	20	80	5	0,51	0,12	23,6	0,08	16,1
	D	5	20	0	0,55	0,10	17,4	0,05	8,8
Sludge 2	A	28	112	0	1,05	0,15	14,2	0,06	6,0
	B	10	40	20	1,05	0,16	14,9	0,07	6,8
	C	21	84	0	1,08	0,18	16,9	0,08	7,4
	D	5	20	0	1,14	0,20	17,6	0,12	10,5

Sludge 1	Mixture of drinking water sludge and sewage sludge.
Sludge 2	Mixture of industrial sludge and drinking water sludge.
l	is the number of laboratories;
n	is the number of values;
NAP	is the percentage of outliers;
$\bar{x}$	is the overall mean;
σ_R	is the standard deviation of reproducibility;
VC_R	is the coefficient of variation of reproducibility;
σ_r	is the standard deviation of repeatability;
VC_r	is the coefficient of variation of repeatability.

Table 7 — Precision data for Ni

Sample	**Method**	l	N	**NAP** %	$\bar{x}$ mg/kg	σ_R mg/kg	VC_R %	σ_r mg/kg	VC_r %
Sludge 1	A	34	136	13,11	13,28	2,90	22,2	1,53	11,7
	B	11	44	0	13,28	2,53	19,1	0,76	5,7
	C	26	104	3,8	12,74	2,73	21,4	0,92	7,2
	D	9	36	0	13,09	1,79	13,7	0,78	6,0
Sludge 2	A	35	140	0	21,99	4,41	20,0	1,27	5,8
	B	12	48	0	22,01	4,18	19,0	0,79	3,6
	C	24	96	0	22,33	5,30	23,7	1,80	8,1
	D	9	36	0	22,90	2,50	10,9	0,91	4,0

Sludge 1	Mixture of drinking water sludge and sewage sludge.
Sludge 2	Mixture of industrial sludge and drinking water sludge.
l	is the number of laboratories;
n	is the number of values;
NAP	is the percentage of outliers;
$\bar{x}$	is the overall mean;
σ_R	is the standard deviation of reproducibility;
VC_R	is the coefficient of variation of reproducibility;
σ_r	is the standard deviation of repeatability;
VC_r	is the coefficient of variation of repeatability.

Table 8 — Precision data for Pb

Sample	**Method**	l	n	**NAP** %	$\bar{x}$ mg/kg	σ_R mg/kg	VC_R %	σ_r mg/kg	VC_r %
Sludge 1	A	33	132	0	13,17	4,26	32,3	1,52	11,5
	B	11	44	0	12,59	5,07	40,2	0,92	7,3
	C	24	96	4,2	13,04	4,04	31,0	1,28	9,8
	D	10	40	0	13,16	10,05	76,3	0,76	5,8
Sludge 2	A	34	136	0	31,48	5,46	17,4	1,26	4,0
	B	13	52	0	29,15	12,38	42,5	1,92	6,6
	C	25	100	0	33,94	10,05	29,6	3,12	9,2
	D	10	40	0	29,63	15,24	51,4	1,77	6,0

Sludge 1	Mixture of drinking water sludge and sewage sludge.
Sludge 2	Mixture of industrial sludge and drinking water sludge.
l	is the number of laboratories;
n	is the number of values;
NAP	is the percentage of outliers;
$\bar{x}$	is the overall mean;
σ_R	is the standard deviation of reproducibility;
VC_R	is the coefficient of variation of reproducibility;
σ_r	is the standard deviation of repeatability;
VC_r	is the coefficient of variation of repeatability.

Table 9 — Precision data for Se

Sample	Method	l	N	NAP %	$\bar{x}$ mg/kg	σ_R mg/kg	VC_R %	σ_r mg/kg	VC_r %
Sludge 1	A	19	76	5,3	0,66	0,47	70,8	0,11	16,0
	B	6	24	16,7	0,51	0,16	32,4	0,02	3,0
	C	13	52	0	0,90	0,84	93,6	0,17	18,5
	D	3	12	0	0,47	0,26	54,8	0,05	11,0
Sludge 2	A	19	76	5,3	1,27	0,74	58,3	0,18	14,0
	B	7	28	0	1,25	0,42	33,3	0,03	2,6
	C	13	52	0	1,23	0,62	50,5	0,17	13,5
	D	3	12	0	0,96	0,53	54,8	0,05	5,7

Sludge 1	Mixture of drinking water sludge and sewage sludge.
Sludge 2	Mixture of industrial sludge and drinking water sludge.
l	is the number of laboratories;
n	is the number of values;
NAP	is the percentage of outliers;
$\bar{x}$	is the overall mean;
σ_R	is the standard deviation of reproducibility;
VC_R	is the coefficient of variation of reproducibility;
σ_r	is the standard deviation of repeatability;
VC_r	is the coefficient of variation of repeatability.

Table 10 — Precision data for Zn

Sample	Method	l	n	NAP %	$\bar{x}$ mg/kg	σ_R mg/kg	VC_R %	σ_r mg/kg	VC_r %
Sludge 1	A	37	148	5,4	606,7	45,3	7,5	14,5	2,4
	B	11	44	18,2	637,2	42,3	6,6	20,7	3,3
	C	27	108	3,7	617,8	54,2	8,8	18,8	3,0
	D	8	32	0	596,7	44,9	7,5	11,2	1,9
Sludge 2	A	37	148	2,7	338,4	29,7	8,8	10,6	3,1
	B	12	48	0	343,3	52,0	15,1	13,6	4,0
	C	27	108	3,7	348,2	36,7	10,5	18,4	5,3
	D	8	32	0	340,6	42,0	12,3	17,2	5,1

Sludge 1	Mixture of drinking water sludge and sewage sludge.
Sludge 2	Mixture of industrial sludge and drinking water sludge.
l	is the number of laboratories;
n	is the number of values;
NAP	is the percentage of outliers;
$\bar{x}$	is the overall mean;
σ_R	is the standard deviation of reproducibility;
VC_R	is the coefficient of variation of reproducibility;
σ_r	is the standard deviation of repeatability;
VC_r	is the coefficient of variation of repeatability.

Table 11 — Precision data for P

Sample	**Method**	l	n	**NAP**	$\bar{x}$	σ_R	VC_R	σ_r	VC_r
				%	mg/kg	mg/kg	%	mg/kg	%
Sludge 1	A	23	92	8,7	10,49	0,78	7,5	0,33	3,2
	B	7	28	0	10,82	1,30	12,0	0,22	2,0
	C	19	76	0	10,63	0,75	7,0	0,36	3,4
	D	7	28	0	11,41	1,63	14,3	0,51	4,4
	H_2SO_4/HNO_3	6	24	0	10,10	0,66	6,5	0,31	3,0
Sludge 2	A	23	92	4,3	17,27	1,35	7,8	0,36	2,1
	B	8	32	0	16,21	2,29	14,1	0,58	3,6
	C	19	76	5,3	18,04	1,32	7,3	0,56	3,1
	D	7	28	14,3	16,99	1,41	8,3	0,61	3,6
	H_2SO_4/HNO_3	6	24	0	17,39	0,81	4,7	0,57	3,3

Sludge 1	Mixture of drinking water sludge and sewage sludge.
Sludge 2	Mixture of industrial sludge and drinking water sludge.
l	is the number of laboratories;
n	is the number of values;
NAP	is the percentage of outliers;
$\bar{x}$	is the overall mean;
σ_R	is the standard deviation of reproducibility;
VC_R	is the coefficient of variation of reproducibility;
σ_r	is the standard deviation of repeatability;
VC_r	is the coefficient of variation of repeatability.

Annex A
(informative)

Pretreatment of the sample

A.1 General

Three methods are given concerning the pretreatment of samples received by the laboratory in order to use test portions taken from:

- wet sludge;
- freeze-dried sludge;
- partially air-dried sludge or a partially freeze-dried sludge.

A.2 Wet sludge

The dry residue has to be known in order to take a test portion in accordance with 8.1, 8.2, 8.3 and 8.4. Measure the dry residue in percent (q_1) according to EN 12880. Calculate the required amount (m) expressed in grams of wet sludge according to the following equation:

$$m = \frac{m_0 \times 100}{q_1}$$

where

m_0 is the amount of dry matter given in 8.1, 8.2, 8.3 or 8.4 in grams;

q_1 is the percentage of dry mass (dry residue).

Shake the sample bottle vigorously so that a representative sample can be taken.

A.3 Freezed-dried sludge

Weigh approximately 200 g of the wet sample and put it into a suitable glass dish with a cover fitted with a hole.

Put the samples in a freeze drier at a temperature of –25 °C for 16 h. Start the condenser of the freeze drier and wait till the temperature is –45 °C.

Put the frozen samples on the heating plates of the freeze drier, close the vacuum tap and start the pump. When there is a vacuum of 13 Pa, start the heating at a temperature of approximately +10 °C. Dry until the water content is less than 1 ml.

NOTE As a reference, a bottle approximately 150 ml water should be dried. When there is more than 1 ml water left after the drying stage there is a need to dry the samples another day.

Take the dried sample off the heater and put it in a mortar. Homogenize the sample with a pestle, put the sample in flask and close it.

A.4 Partially air-dried or freeze-dried sludges

Partially dried sludges are defined here as sludges containing a remaining water content low enough to enable the partially dried sample to be ground and homogenized. Generally a residual water content of (5 ± 3) % is suitable.

The dry residue in percent in the partially dried sample is determined according to EN 12880.

The test portion is taken in the ground and homogenized partially dried sample.

Air-drying can be carried out at a temperature between 35 °C and 50 °C. It is advisable to mix the sample roughly several times during this operation to improve the drying.

There is no need to control the freeze-drying as accurately as explained in A.3. The drying time depends on the quantities, the types of sludges and the kind of apparatus used for that operation. Some experience is then necessary to appreciate the time needed to obtain partially dried samples.

Annex B
(informative)

Calibration of the microwave oven

B.1 Calibration of the microwave oven for method C

The calibration of the microwave oven is an essential step before using it. By means of calibration, indications of the power adjustment scale can be correlated with the actually supplied (effective power) in order to adjust the power applied whatever the microwave oven in use. This annex describes the calibration procedure of a microwave oven used for digestion of sludge samples.

A microwave oven should be calibrated periodically. In practice, biannual calibration usually turns out to be sufficient.

Depending on the relationship between the supplied power in the microwave oven and the scale of its electronic system (generally in percents of total power), a choice should be made between a two-point or a multi-point calibration. For the first calibration or when the relationship is not linear oven the whole used range, a multi-point calibration is required. For example, a calibration is carried out at 80 %, 70 %, 60 %, 50 % and 40 % power and the results plotted in a graph. Use of the non-linear part can be excluded or limited. In case of linear relationship, calibration can be done at two positions (for example 40 % and 100 % power).

Effective power is determined by measuring the power dissipated by the oven in a given sample, for example by heating 1 kg water for a fixed time period of 2 min.

For that purpose the following procedure should be used: transfer the water in a plastics beaker (or a beaker of any microwave energy non-absorbent material) and stir. Glass beakers absorb microwave energy and should not be used. Measure the temperature of the water, its value should be near the room temperature value at the beginning of the experiment.

Place the plastics beaker in the microwave oven. Do always select the same position and preferably in the middle of the turntable. Apply the selected power for 2 min. Remove the beaker, stir, and measure the final temperature. Repeat this procedure with the other selected power settings.

The measurements should be accurate to 0,1 °C and be carried out within 30 s after heating. When several measurements are done, do not use the same water, unless this has been cooled to room temperature.

The absorbed power is determined with the following equation:

$$P = \frac{C_p \times m \times \Delta T}{t} \tag{B.1}$$

where

P is the power absorbed by the water, in watts;

C_p is the specific heat for water, in J/kg·K (= 4184 J/kg·K);

m is the mass of water used for the calibration in kilograms;

ΔT is the difference between initial and final temperature, in Kelvin;

t is the time period, in seconds.

If in the above described procedure 2 min and 1 kg water are used, the equation (B.1) can be simplified to:

$$P = \Delta T \times 34{,}87$$

In this way the relationship between the actually supplied (effective) power and the graduation of the scale can be determined.

B.2 Calibration of the microwave oven for method D

Calibration is initially achieved and periodically verified by the manufacturer.

Annex C
(informative)

Guidelines for measurement techniques

C.1 Kind of sludge

Mostly from wastewater treatment plants. The sludge can have been treated with lime, kept in a digestion tank or not treated at all. The wastewaters, from which the sludge originates from, have often been treated with reagents containing Al– or Fe salts and calcium oxide.

The dry residue can vary from less than 1 % up to about 80 % by mass.

The loss on ignition varies approximately from to 15 % up to 75 % (as percent of dry mass) (most commonly 50 % to 70 %).

C.2 Atomic absorption spectrometry (AAS)

Atomic absorption spectrometry has historically been the most widely used technique for elemental analysis in sludges. The detection limits achievable using flame AAS are satisfactory for most applications, with flameless AAS limited to very low level determinations of less abundant elements such as cadmium. Because of the wide variety of configurations no guidance is given here with regard to instrument set-up, however it is relevant to discuss some of the common interferences associated with the technique.

a) Physical interferences

Physical interferences are defined as depression or enhancement of the analyte signal in the sample relative to the calibration standard that are due to differences in physical properties such as viscosity, surface tension and vapour pressure. They are more important in flame AAS than flameless AAS due to the greater complexity of the sample introduction system. Such interferences can be overcome by matrix matching the calibration standards, diluting the sample, or very much as a last resort, using the method of standard additions.

b) Chemical interferences

Chemical interferences in flame AAS are due to incomplete atomization of the analyte or chemical reaction of analyte atoms to form stable compounds. These interferences are overcome either by using a hotter flame (nitrous oxide-acetylene) or by adding a chemical releasing/shielding agent to the sample. In flameless AAS, chemical interferences are due either to volatile compound formation in which the analyte is lost prior to atomization, or stable compound formation. These interferences are overcome by the use of matrix modifiers and careful selection of the cuvette type and atomization conditions.

c) Ionization interferences

If the analyte is ionized in the flame, atomic absorption does not occur and a depressed response is observed. This type of interference is a problem in the analysis of easily ionized elements such as the alkali and alkaline earth metals. It is overcome by "buffering" the calibration standards and sample with a large excess of a more easily ionized element such as caesium.

d) Spectral interferences

Spectral interferences in atomic absorption spectrometry are relatively uncommon and are due mainly to molecular absorption. Such broad band or continuum type absorption can often be eliminated by background correction.

C.3 Inductively coupled plasma optical emission spectrometry (ICP-OES)

For those laboratories with high sample throughput, ICP-OES spectrometry is increasingly becoming the primary technique for sludge analysis. The multi-element capabilities, wide linear dynamic range and relative freedom from interferences of ICP-OES give it significant advantages over AAS. Once again there are too many different instrument configurations to discuss the technique in detail. Common interferences are summarized below.

a) Physical interferences

Because of the similarity in sample introduction systems, the physical interferences, and the procedures for overcoming them, are much the same as for AAS. However, because ICP-OES is a multi-element technique it is possible to use internal standardization in preference to the method of standard additions.

b) Chemical and ionization interferences

These interferences are much less common in ICP-OES than in AAS, however in the latest generation of axial ICP instruments where the plasma is viewed "end on" to improve detection limits, chemical and ionization interferences can be more of a problem because it is not possible to be as selective about which zone of the plasma is viewed by the optics.

c) Spectral interferences

Spectral interferences are by far the most important potential source of error in ICP-OES. Emission spectra are extremely complex and in a matrix such as a sludge digest there are many elements present at high concentration. Spectral interferences can be due to background shift caused by continuum emission from high concentrations of elements such as aluminium and calcium or line overlap from another element in the sample. Continuum emission can usually be background corrected. In cases of line overlap, if there is no other available emission line, it is usually necessary to calculate and apply an inter-element correction factor though there are some instruments coming on to the market that use powerful mathematical modelling techniques to correct for line overlap.

C.4 Inductively coupled plasma mass spectrometry (ICP-MS)

In terms of detectability and range of elements covered, ICP-MS is the most powerful technique available for elemental analysis. However, it has a number of limitations that make it less suitable for sludge analysis than ICP-OES. ICP-MS instruments cannot cope with dissolved solids above about 0,2 %. Finally, interferences due to ions with the same mass/charge ratio (isobaric interferences) are a particular problem for monoisotopic elements (e.g. arsenic). Nevertheless there are some laboratories that use ICP-MS, with sample dilution, for the analysis of sludges.

Annex D
(informative)

Precision data for methods C and D with reference materials

The following table presents the means and 95 % confidence intervals obtained for six experiments using methods C and D, and the certified values.

CRM 143 R:	Sewage sludge amended soil - Aqua regia certified value
CRM 144:	Sewage sludge from domestic origin
CRM 145 R:	Sewage sludge from mixed origin - Aqua regia certified value
CRM 146:	Sewage sludge from industrial origin

Table D.1 — Metals recovery from reference materials - Method C

	Cr µg/g	Cu µg/g	Ni µg/g	Zn µg/g	Pb µg/g	Cd µg/g	Hg µg/g
CRM 144							
mean	▨ 481	▨ 707	▨ 935	▨ 3 125	▨ 490	▨ 3,66	▨ 1,76
95 % confidence interval	14	22	36	42	33	0,75	0,61
Total content certified value	485	713	942	3 143	495	3,41	1,49
95 % confidence interval	20	26	22	103	19	0,25	0,22
CRM 145 R							
mean	▨ 320	685	▨ 240	▨ 2 102	▨ 287	▨ 3,37	▨ 2,31
95 % confidence interval	14	28	58	116	17	0,33	0,42
Aqua regia certified value	307	707	251	2 137	282	3,50 [a]	2,01
95 % confidence interval	13	9	6	50	9	0,15	0,22
CRM 146							
mean	▨ 765	▨ 956	▨ 266	▨ 4 196			▨ 9,38
95 % confidence interval	50	72	25	292			1,36
Total content certified value	784	934	280	4 059			9,49
95 % confidence interval	31	24	18	90			0,76

[a] Total content value.

In grey: result not significantly different from the certified value.

Table D.2 — Metals recovery from reference materials - Method D

	Cr µg/g	Cu µg/g	Ni µg/g	Zn µg/g	Pb µg/g	Cd µg/g
CRM 144						
mean	523	675	938	3 007	492	3,43
95 % confidence interval	44	27	55	104	13	0,15
Total content certified value	485	713	942	3 143	495	3,41
95 % confidence interval	20	26	22	103	19	0,25
CRM 145 R						
mean	331	680	257	2 095	285	3,38
95 % confidence interval	6	19	6	57	5	0,1
Aqua regia certified value	307	707	251	2 137	282	3,50 [a]
95 % confidence interval	13	9	6	50	9	0,15
CRM 143 R						
mean	422	124	297	1 027	182	70
95 % confidence interval	16	7,5	12,8	27	4	1,8
Aqua regia soluble	426	130,6 [a]	296	1 063	174	72
95 % confidence interval	12	1,4	4	16	5	1,8

[a] Total content value.

In grey: result not significantly different from the certified value.

NOTE Other studies on Cd, Cr, Cu, Ni, P, Pb and Zn have shown good agreement between the total digestion ($HF/HClO_4$) solution and aqua regia digestion. The comparison between the methods gives a coefficient of the slope between 0,95 and 1,05 leading to the conclusion that both digestion techniques can be used for the determination of total content.

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