



SLOVENSKI STANDARD  
SIST EN 13346:2001

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

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

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

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

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**ICS:**

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EUROPEAN STANDARD

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## 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.

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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.

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

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## 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of an identical text or by endorsement, at the latest by February 2001, and conflicting national standards shall be withdrawn at the latest by February 2001.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.

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## 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.

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

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## 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.

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### 5.2 Water

Deionised or distilled water used shall conform to purity grade 2 of EN ISO 3696:1988.

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

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

### 5.4 Nitric acid, solution, $c(\text{HNO}_3) = 15,8 \text{ mol/l}$ .

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

### 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 method 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,  $(21 \pm 0,1)$  ml of hydrochloric acid (5.3) followed by  $(7 \pm 0,1)$  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 nebulisers 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  $(1,0 \pm 0,1)$  ml of water (5.2) to wet the sample. Add a few boiling aids (6.8). Carefully run  $(6,0 \pm 0,1)$  ml of hydrochloric acid (5.3) down the side of the tube followed by  $(2,0 \pm 0,1)$  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  $(10 \pm 2)$  min, wash down the sides of the tube with about 5 ml of water (5.2). Reflux for a further  $(5 \pm 1)$  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 nebulisers 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  $(2 \pm 0,1)$  ml of nitric acid (5.4) and  $(6 \pm 0,1)$  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 nebulisers 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. [SIST EN 13346:2001](https://standards.iteh.ai/catalog/standards/sist/90dbef0c-3af4-4356-b787-8dadbf447497/sist-en-13346-2001)  
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Table 1 — Steps of a program

Time min	Power watt	HNO <sub>3</sub> 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 reference to this European Standard ;
- complete identification of the sample ;
- information about the pre-treatment and extraction of the sample ;
- any detail not specified in this European Standard, or which are optional ;
- 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.

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**Table 2 — Precision data for As**

Sample	Method	<i>l</i>	<i>n</i>	NAP %	$\bar{x}$ mg/kg	$\sigma_R$ mg/kg	$VC_R$ %	$\sigma_r$ 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 ;

$\sigma_R$  is the standard deviation of reproducibility ;

$VC_R$  is the coefficient of variation of reproducibility ;

$\sigma_r$  is the standard deviation of repeatability ;

$VC_r$  is the coefficient of variation of repeatability.