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Karakterizacija odpadkov - Dokument stanja tehnike - Analiza izlužkov

Characterization of waste - State-of-the-art document - Analysis of eluates

Charakterisierung von Abfällen - Stand der Technik - Analyse der Eluate

Caractérisation des déchets - Document de l'état de l'art et analyse des éluats

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Characterization of Waste - State-of-the-art document - Analysis of eluates

Caractérisation des déchets - Document de l'état de l'art et analyse des éluats

Charakterisierung von Abfällen - Stand der Technik - Analyse der Eluate

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
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Foreword

This document (FprCEN/TR 16184:2010) has been prepared by Technical Committee CEN/TC 292 “Characterization of waste”, the secretariat of which is held by NEN.

This document is currently submitted to the Technical Committee Approval.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

Introduction

For determining the acceptability of waste at landfills test methods are described in two umbrella European Standards:

— EN 12506, Characterization of waste – Analysis of eluates – Determination of pH, As, Ba, Cd, Cl, Co, Cr, CrVI, Cu, Mo, Ni, NO_2, Pb, total S, SO_4, V and Zn (analysis of inorganic constituents of solid waste and/or its eluate; major, minor and trace elements);

— EN 13370, Characterization of waste – Analysis of eluates – Determination of Ammonium, AOX, conductivity, Hg, phenol index, TOC, easily liberatable CN, F (analysis of inorganic constituents of solid waste and/or its eluate (anions)).

At the moment these standards are under revision and therefore this state-of-the-art document is prepared in order to verify the following items:

— Are all parameters mentioned in the Council Decision of 19 December 2002 included in these two European Standards?

— Should new relevant standards (e.g. EN ISO 17294 series) be included?

— Are the current analytical techniques capable of verifying the prescribed limit values with an acceptable confidence level?

In Clause 4 a proposal is worked out for the revision of the EN 12506 and EN 13370 umbrella standards.

The major changes between the umbrella standard EN 12506:2003 and the proposal for revision are:

— Addition of the parameters Sb and Se together with the related analytical methods;

— Revision of the standards ISO 11885 (ICP-AES) and ISO 10304-1 (IC) (the versions of ISO 10304-1:1992 and ISO 10304-2:1995 have been combined in one standard ISO 10304-1:2007);

— Addition of the ICP-MS method (EN ISO 17294-1:2006 and EN ISO 17294-2:2004);

— Addition of the AAS with graphite furnace technique (EN ISO 15586:2003);

— Addition of the flow analysis techniques for Cl^- (ISO 15682:2000), Cr(VI) (ISO 23913:2006) and SO_4^{2-} (ISO 22743:2006).

The major changes between the umbrella standard EN 13370:2003 and the proposal for revision are:

— Addition of the parameter TDS (total dissolved solids) together with the related analytical method;

— Replacement of the parameter TOC (total organic carbon) by DOC (dissolved organic carbon);

— Revision of the standards EN ISO 11732 (ammonium by flow analyser) and ISO 10304-1 (IC);

— Replacement of EN 1485 (AOX) by EN ISO 9562:2004;

— Revision and addition of new standards for Hg determination – EN 1483, EN ISO 17852 (and EN 12338);

- For the determination of F^- using the ion selective electrode it is recommended to use the buffer as described in DIN 38405-4 instead of the buffer as described in ISO 10359-1, considering the higher efficiency as decomplexing agent for Al, Fe, Mg and Ca-fluoride compounds.

With regard to the revised standards, there is no need for an additional validation round robin test when implementing the revised standards into the umbrella standards EN 12506 and EN 13370.

Regarding the additional standards, all of these have waste water and/or leachates included in their scope, meaning there are strong indications that the method is suitable for the analysis of eluates. Nevertheless an additional validation of these standards for eluate matrices is required when implementing them into the umbrella standard, with the exception of:

- EN 12338:1998 (Hg – enrichment methods by amalgamation): There is no need to incorporate this standard into the umbrella standard EN 13370 because a measurement in this low concentration range is not required;

- EN 15126:2007 (TDS): As this parameter was validated for eluates in the EN 15126:2007, no additional validation is required when implementing this standard into the umbrella standard EN 13370.

For the determination of the elements Mo, Ba, Cr, Cd, Sb and Se in eluates validation data are available from a round robin test between 19 recognized laboratories (from Flanders – Belgium and the Netherlands) organized by VITO (see Clause 6). Based on these results it can be concluded that for the various elements using the ICP-AES technique according to ISO 11885 and the ICP-MS technique according to ISO 17294, there are enough validation data available to implement in the umbrella standard. No additional validation of the standard according to EN ISO/IEC 17025 is required. On the other hand, for the determination of Sb and Se using the hydride generation procedure or the graphite furnace technique, additional validation data according to the prescribed standards are required.

For all other parameters determined according to the new standards, additional validation data need to be gathered. Once a year (in March) VITO organizes a round robin test for the analysis of eluates in the framework of the acceptability of waste at landfills (see results of 2005, 2007 and 2008 in Clause 8). For this purpose, round robin samples are yearly prepared. Having these samples available, it may be interesting to distribute the same samples also to other European laboratories in order to validate the various parameters according to the new European Standards.

Additionally, from the laboratories there is an increasing interest to implement the discrete analyser technique in their laboratory to measure parameters such as ammonium, nitrite, chloride, sulfate in water samples. At the moment no International (ISO) or European (EN) Standard method is available. Moreover, the Netherlands Standardization Institute (NEN) has developed and validated a standard method NEN 6604:2007 (Water – Determination of ammonium, nitrate, nitrite, chloride, ortho-phosphate, sulfate and silicate using a discrete analyzer and spectrophotometric detection). This method should also be taken into consideration when revising the standard.

The elements Hg and S are not included in the scope of the ICP-MS standard, however it is advisable to investigate the determination of Hg and S with ICP-MS. Therefore, additional validation is required.

1 Scope

In the Council Decision of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC, the test methods are described for determining the acceptability of waste at landfills. In section 3 of the annex of this decision the following umbrella European Standards are included for the analysis of eluates:

— ENV 12506 Analysis of eluates – Determination of pH, As, Ba, Cd, Cl, Co, Cr, Cr(VI), Cu, Mo, Ni, NO_2, Pb, total S, SO_4, V and Zn (analysis of inorganic constituents of solid waste and/or its eluate; major, minor and trace elements);

— ENV 13370 Analysis of eluates – Determination of ammonium, AOX, conductivity, Hg, phenol index, TOC, easily liberatable CN, F (analysis of inorganic constituents of solid waste and/or its eluate (anions)).

In 2003 both European Standards were approved and became final standards i.e. EN 12506 and EN 13370. At the moment these standards are under revision and therefore a state-of-the-art document is prepared in order to verify the following items:

— Are all parameters mentioned in the decision included in these two European Standards?

— Should new relevant standards (e.g. EN ISO 17294 series) be included?

— Are the current analytical techniques capable of verifying the prescribed limit values with an acceptable confidence level?

2 Normative references

Not applicable.

3 Legislation

In the Council Decision of 19 December 2002 limit values for waste acceptable at the landfills are defined. The limit values differ depending on the type of waste i.e.

— inert waste;

— non-hazardous waste;

— non-hazardous waste (stable, non-reactive);

— hazardous waste.

The limit values taken over from the Council Decision of 19 December 2002 are presented in Table 1.

Table 1 — Leaching limit values for L/S = 10 l/kg

Component	Inert waste	Non-hazardous waste	Non-hazardous waste (stable, non-reactive)	Hazardous waste
	L/S = 10 l/kg mg/kg dm	L/S = 10 l/kg mg/kg dm	L/S = 10 l/kg mg/kg dm	L/S = 10 l/kg mg/kg dm
As	0,5	2	2	25
Ba	20	100	100	300
Cd	0,04	1	1	5
Cr total	0,5	10	10	70
Cu	2	50	50	100
Hg	0,01	0,2	0,2	2
Mo	0,5	10	10	30
Ni	0,4	10	10	40
Pb	0,5	10	10	50
Sb	0,06	0,7	0,7	5
Se	0,1	0,5	0,5	7
Zn	4	50	50	200
Chloride	800	15 000	15 000	25 000
Fluoride	10	150	150	500
Sulphate	1 000[a]	20 000	20 000	50 000
Phenol index	1	-	-	-
DOC	500[b]	800[d]	800[d]	1000[e]
TDS[c]	4 000	60 000	50 000	100 000

[a] If the waste does not meet these values for sulphate, it may still be considered as complying with the acceptance criteria if the leaching does not exceed either of the following values: 1500 mg/l as C_0 at L/S = 0,1 l/kg and 6 000 mg/kg at L/S = 10 l/kg. It will be necessary to use a percolation test to determine the limit value at L/S = 0,1 l/kg under initial equilibrium conditions, whereas the value at L/S = 10 l/g may be determined either by a batch leaching test or by a percolation test under conditions approaching local equilibrium.

[b] If the waste does not meet these values for DOC at its own pH value, it may alternatively be tested at L/S = 10 l/kg and a pH between 7,5 and 8,0. The waste may be considered as complying with the acceptance criteria for DOC, if the results of this determination does not exceed 500 mg/kg. (A draft method based on EN 14429 is available).

[c] The values for total dissolved solids (TDS) can be used alternatively to the values for sulphate and chloride.

[d] If the waste does not meet these values for DOC at its own pH value, it may alternatively be tested at L/S = 10 l/kg and a pH between 7,5 and 8,0. The waste may be considered as complying with the acceptance criteria for DOC, if the results of this determination does not exceed 800 mg/kg. (A draft method based on EN 14429 is available).

[e] If the waste does not meet these values for DOC at its own pH value, it may alternatively be tested at L/S = 10 l/kg and a pH between 7,5 and 8,0. The waste may be considered as complying with the acceptance criteria for DOC, if the results of this determination does not exceed 1 000 mg/kg. (A draft method based on EN 14429 is available).

4 EN 12506:2003 and EN 13370:2003 - Current status

The reference methods included in the current version of the umbrella standard EN 12506:2003 are described in Table 2. The following text is included in the EN standard:

"*It is pointed out that the standardized test methods listed in Table 2 have primarily been developed for the analysis of water samples. They were validated in a new interlaboratory trial for a limited number of waste eluate matrices performed by CEN/TC 292. Their suitability for other waste eluates has to be checked in the laboratory performing the analysis.*

If the test methods referred to in Table 2 are found to be inappropriate by reason of, for example, detection limits, repeatability or interference, other methods validated for water analysis such as GF-AAS, ICP-MS can be used. Their suitability for waste eluates has to be checked in the laboratory performing the analysis. The reason for the deviation shall be stated in the test report."

Table 2 — Parameters and test methods EN 12506:2003

Parameter	Test method
pH[a]	ISO 10523
As	EN ISO 11885 EN ISO 11969
Ba	EN ISO 11885
Cd	ISO 8288 EN ISO 11885
Cl^-	ISO 9297 EN ISO 10304-1 EN ISO 10304-2
Co	EN ISO 11885
Cr	EN ISO 11885
Cr VI	ISO 11083
Cu	ISO 8288 EN ISO 11885
Mo	EN ISO 11885
Ni	ISO 8288 EN ISO 11885
NO_2^-	EN 26777 EN ISO 10304-1 EN ISO 10304-2 EN ISO 13395
Pb	ISO 8288 EN ISO 11885
Total S	EN ISO 11885
SO_4^{2-}	EN ISO 10304-1 EN ISO 10304-2
V	EN ISO 11885
Zn	ISO 8288 EN ISO 11885

[a] at pH < 3 or pH > 10 use the same method but be aware that inaccuracy can increase.

NOTE The references towards the European or International Standards are those published at the moment the EN 12506:2003 standard was approved.

The reference methods included in the current version of the umbrella standard EN 13370:2003 are described in Table 3. The following text is included in the EN standard:

> "*It is pointed out that the standardized test methods listed in Table 3 have primarily been developed for the analysis of water samples. They were validated in a new interlaboratory trial for a limited number of waste eluate matrices performed by CEN/TC 292. Their suitability for other waste eluates has to be checked in the laboratory performing the analysis.*
>
> *If the test methods referred to in Table 3 are found to be inappropriate by reason of, for example, detection limits, repeatability or interference, other methods validated for water analysis such as AFS, ICP-MS can be used. Their suitability for waste eluates has to be checked in the laboratory performing the analysis. The reason for the deviation shall be stated in the test report*."

Table 3 — Parameters and test methods EN 13370:2003

Parameter	Test method – current status
Ammonium	EN ISO 11732 ISO 7150-1
AOX	EN 1485
Conductivity	EN 27888
Hg	EN 1483
Phenol index	ISO 6439 EN ISO 14402[a]
TOC	EN 1484
CN^- easily liberatable	ISO 6703-2 EN ISO 14403[b]
F^-	EN ISO 10304-1[c] ISO 10359-1

[a] after distillation.

[b] free cyanide is equivalent to easily liberatable cyanide.

[c] for eluates with low organic contamination.

5 EN 12506 and EN 13370 – Proposal revision

After the final approval in 2003 of both umbrella EN standards some of the cited standards were revised or new standards were developed within CEN/TC 230 'Water analysis' or ISO/TC 147 'Water Quality'. Additional, some parameters which are included in the Council Decision of 19 December 2002 are not included in the current umbrella standards.

In Table 4, a proposal is worked out for the new EN 12506 umbrella standard, including all the cited parameters in the Directive, related test methods and also the indication whether these standards are validated for waste water by ISO/TC 147 or within the development of the EN 12506:2003 standard. Parameters to be added (Sb and Se) and parameters which are not cited in the Directive (Co, Cr(VI), NO_2^-, total S, V), but are currently included in EN 12506:2003 are indicated in bold.

Table 4 — Parameters and test methods EN 12506 – proposal revision

Parameter	Test methods – 2003 version[b]	Test methods – Proposal revision	Validated by ISO on waste water [d]	Validated by EN 12506 in 2003 [a]
pH[c]	ISO 10523 (1994)	ISO 10523:1994		X
As	EN ISO 11885 (1997) EN ISO 11969 (1996)	EN ISO 11885:2009 EN ISO 11969:1996 EN ISO 17294-1:2006 EN ISO 17294-2:2004 EN ISO 15586:2003	X X X	X 1 matrix
Ba	EN ISO 11885 (1997)	EN ISO 11885:2009 EN ISO 17294-1:2006 EN ISO 17294-2:2004	X X	X
Cd	ISO 8288 (1986) EN ISO 11885 (1997)	ISO 8288:1996 EN ISO 11885:2009 EN ISO 17294-1:2006 EN ISO 17294-2:2004 EN ISO 15586:2003	 X . X X	X X
Cl^-	ISO 9297 (1989) EN ISO 10304-1 (1995) EN ISO 10304-2 (1996)	ISO 9297:1989 ISO 15682:2000 EN ISO 10304-1:2009	X X X	X X
Co	EN ISO 11885 (1997)	EN ISO 11885:2009 EN ISO 17294-1:2006 EN ISO 17294-2:2004 EN ISO 15586:2003	X X X	X
Cr	EN ISO 11885 (1997)	EN ISO 11885:2009 EN ISO 17294-1:2006 EN ISO 17294-2:2004 EN ISO 15586:2003	X X X	X
Cr(VI)	ISO 11083 (1994)	ISO 11083:1994 EN ISO 10304-3:1997 EN ISO 23913:2009	X X	X
Cu	ISO 8288 (1986) EN ISO 11885 (1997)	ISO 8288:1986 EN ISO 11885:2009 EN ISO 17294-1:2006 EN ISO 17294-2:2004 EN ISO 15586:2003	 X X X	X X
Mo	EN ISO 11885 (1997)	EN ISO 11885:2009 EN ISO 17294-1:2006 EN ISO 17294-2:2004 EN ISO 15586:2003	 X X	X
Ni	ISO 8288 (1986) EN ISO 11885 (1997)	ISO 8288:1986 EN ISO 11885:2009 EN ISO 17294-1:2006 EN ISO 17294-2:2004 EN ISO 15586:2003	 X X X	X X