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Leaching, eluate analysis and content measurement

Udo Wiens, CEN/TC 351/WG 1 convenor
Hans van der Sloot, CEN/TC 351/WG 5 convenor

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Slide 2

Leaching to soil, ground water and surface water (WG1)

• Two test principles:
  – Dynamic surface leaching test (monolithic and sheet-like products)
  – Up-flow percolation test (granular products)

• Both methods are expected to be suitable for assessing release from both inorganic and organic substances.

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Key points to be considered for the test methods (WG 1):

• Release mechanisms in intended use (e.g. surface related diffusion or percolation with equilibrium like conditions)
• General/specific properties of the product (e.g. shape, dimensions, grain size distribution, …)
• Product testing „as it is"
• Regulatory requirements (DE, NL ➔ e.g. size reduction)

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Release scenarios – Soil and groundwater (WG 1)

Release scenario		Test method to be developed related to scenario	Products (examples)
I.	Non permeable product. Water is flowing over the surface of the product	Dynamic surface leaching test (DSLT)	Coatings, ceramic tiles, glass, bituminous products…
II.	Low permeable product. Water is transported into the matrix by capillary forces; contribution of core to surface	Dynamic surface leaching test (DSLT) (including procedure for compacted granular products)	Structural concrete, bricks, treated wood, cement mortar, coatings, road materials, …
III.	Permeable product. Water may infiltrate into the matrix driven by gravity	Percolation (column) test	Unbound aggregate, drain concrete, …

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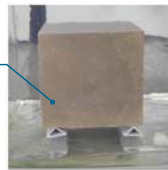
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Published standards on release of Regulated Dangerous substances (WG 1)

Reference	Title: Construction products: Assessment of release of dangerous substances –	TG/WG	Remark
CEN/TS 16637-1:2018	Guidance for the determination of leaching tests and additional testing steps	WG 1	Criteria for the selection of test method (TT or PT) for the relevant product
CEN/TS 16637-2:2014	Horizontal dynamic surface leaching test	WG 1	Release of substances from monolithic or plate-like or sheet-like construction products
CEN/TS 16637-3:2016	Horizontal up-flow percolation test	WG 1	Release of substances from granular construction products
CEN/TR 17105:2017	Guidance on the use of ecotoxicity tests applied to construction products	WG 1	Assessment of ecotoxicological properties of eluates of construction products received from TS2 or TS3

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Tank test (TS-2) / Percolation test (TS-3) – Set ups

| Tank test (TS-2) | Percolation test (TS-3) |

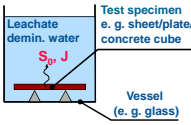e.g. concrete with fly ash conforming to EN 450-1

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Dynamic Surface Leaching Test (Tank test)

Monolithic construction products

Leachate demin. water S_0, J

Test specimen e. g. sheet/plate/ concrete cube

Vessel (e. g. glass)

Test principle (standard conditions)

- Tank leaching test
- Samples collection and preparation (moulding, cutting)
- Size: > 40 mm, > 100 cm² (plates, sheets)
- Curing (exclude contamination!)
- Water volume / specimen surface = 80 l/m² (20 l/m²: sheets/plates)
- Water renewal scheme: 6 hrs, 1d, 2,25d, 9d, 16d, 28d, 36d, 64d ➔ E_{64d}
- Temperature: 22 ± 3 ºC
- Analysis of eluates (sulphate, chloride, fluoride, bromide, Ca, Mg, Si, Na, K, Al, P, Fe, Mn, As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Se, Sn, Sr, V, Zn,..)

➔ CEN/TSs 17195, 17197 and 17200 (2018)
➔ WG 5

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Upflow Percolation Test (PT)

Granular construction products

Test principle (standard conditions)

- Upflow percolation for granular products
- Sample preparation for the column: „Test as it is" (moderate crushing)
- Pre-equilibrium time: 48 h
- Flow rate: (300 ± 40) mm/day
- Temperature: 22 ± 3 ºC
- Analysis of eluates at different cumulative L/S-ratios (sulphate, chloride, fluoride, bromide, Ca, Mg, Si, Na, K, Al, P, Fe, Mn, As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Se, Sn, Sr, V, Zn,..)
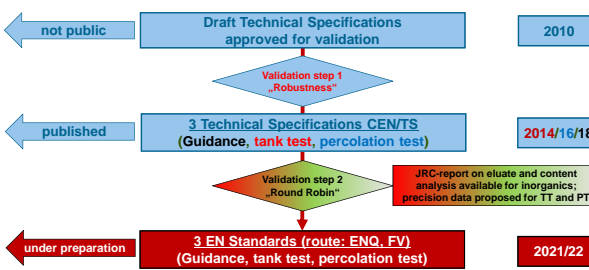
➔ WG 5
➔ CEN/TSs 17195, 17197 and 17200 (2018)

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CEN/TC 351/WG 1 – Time schedule for test standards/specifications (October 2019)

not public ← **Draft Technical Specifications approved for validation** — 2010

Validation step 1 „Robustness"

published ← **3 Technical Specifications CEN/TS (Guidance, tank test, percolation test)** — 2014/16/18

Validation step 2 „Round Robin" — JRC-report on eluate and content analysis available for inorganics; precision data proposed for TT and PT

under preparation ← **3 EN Standards (route: ENQ, FV) (Guidance, tank test, percolation test)** — 2021/22

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Performance characteristics

1 Performance characteristics

The performance characteristics of the method as determined in the inter-comparison validation of TS16637-3 are reported in [JRC report]. Table X gives the resulting typical values for repeatability and reproducibility standard deviations as their observed ranges. The typical value is derived from the intercomparison validation data by taking the median value and rounding the numbers after eliminating substances with measurements too close to the detection limit (between DTL and MQL).

Table X — Typical values and observed ranges of the repeatability and reproducibility limits

Results of the validation of the release of substances as a function of liquid to solid ratio in a percolation test on construction products	Typical range %
Repeatability standard deviation, s_r	18 - 25
Reproducibility standard deviation, s_R	40 - 50

The reproducibility standard deviation provides a determination of the differences (positive and negative) that can be found (with a 68 % statistical confidence) between a single test result obtained by a laboratory using its own facilities and another test result obtained by another laboratory using its own facilities, both test results being obtained under the following conditions : The tests are performed in accordance with all the requirements of the present standard and the two laboratory samples are obtained from the same primary field sample and prepared under identical procedures. The repeatability standard deviation refers to measurements obtained from the same laboratory, all other conditions being identical. The reproducibility limit and the repeatability standard deviation do not cover sampling but cover all activities carried out on the laboratory sample including its preparation from the primary field sample.

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Standards on release of Regulated Dangerous substances (WG 1) – next steps

Reference	Title: Construction products: Assessment of release of dangerous substances –	TG/WG	Next steps
CEN/TS 16637-1:2018	Guidance for the determination of leaching tests and additional testing steps	WG 1	Prepare draft for CEN-ENQ ➔ FV ➔ EN
CEN/TS 16637-2:2014	Horizontal dynamic surface leaching test	WG 1	Prepare draft for CEN-ENQ ➔ FV ➔ EN
CEN/TS 16637-3:2016	Horizontal up-flow percolation test	WG 1	Prepare draft for CEN-ENQ ➔ FV ➔ EN
CEN/TR 17105:2017	Guidance on the use of ecotoxicity tests applied to construction products	WG 1	Conversion TR to TS; vote on FprCEN/TS 17459 until end of Jan. 2020 ➔ CEN/TS

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Status on content and eluate analysis methods (WG 5) covering Inorganic Regulated Dangerous substances

- For all inorganic substances methods are available and suitable to assess release with sufficient precision
- From the available tools more sensitive methods may have to be selected in specific cases (e.g. hydride generation for oxyanions such as antimony and selenium)
- Cyanide appears in the indicative list but no methods have been developed so far, as we have no indication of any construction product containing or generating this substance as a result of exposure conditions
- Chromate analysis not yet addressed – method available in CEN/TC 444

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Published standards on content and eluate analysis for Inorganic Regulated Dangerous substances

Reference	Title: Construction products: Assessment of release of dangerous substances –	TG/WG	WI
CEN/TS 17195:2018	Analysis of inorganic substances in eluates	WG 5	00351016
CEN/TS 17196:2018	Digestion by aqua regia for subsequent analysis of inorganic substances	WG 5	00351017
CEN/TS 17197:2018	Analysis of inorganic substances in digests and eluates – Analysis by Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES)	WG 5	00351018
CEN/TS 17200:2018	Analysis of inorganic substances in digests and eluates – Analysis by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS)	WG 5	00351019
CEN/TS 17201:2018	Content of inorganic substances – Methods for analysis of aqua regia digests	WG 5	00351021

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Full ENs for content and eluate analysis

Following the intercomparison validation performance data for the inorganic substances are in preparation for final discussion in the next joint WG 1/WG 5 meeting in November 2019. Subsequently, full ENs will be prepared for submission for formal vote.

Methods cover: aluminium, antimony, arsenic, barium, beryllium, bismuth, boron, bromide, cadmium, calcium, cerium, chloride, chromium, cobalt, copper, fluoride, iron, lanthanum, lead, lithium, magnesium, manganese, mercury, molybdenum, neodymium, nickel, phosphorus, potassium, praseodymium, samarium, scandium, selenium, silicon, silver, sodium, strontium, sulphate, sulphur, tellurium, thallium, thorium, tin, titanium, tungsten, uranium, vanadium, zinc and zirconium.

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Further work on content methods

- Preparation for a standard on asbestos has started – first step is to evaluate available method(s) in the next WG 5 meeting to be held on 19 and 20 November 2019 in Berlin in conjunction with WG 1.
- The definition of 'similar' or 'other' fibres is not clear. According to the indicative list, Germany and Denmark have regulations for the content of these fibres. The topic was discussed during last SGDS meeting in May 2019. If there is no method nor a need to declare these fibres, WG 5 will recommend CEN/TC 351 to skip the issue from the work programme and focus on asbestos fibres only.

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Status on content and eluate analysis methods covering Organic Regulated Dangerous substances

Reference	Title: Construction products: Assessment of release of dangerous substances –	TG/WG	WI
CEN/TS 17331: 2019	Content of organic substances — Methods for extraction and analysis	WG 5	00351024
CEN/TS 17332: 2019	Analysis of organic substances in eluates	WG 5	00351026
EN17087: 2019	Preparation of test portions from the laboratory sample for testing of release and analysis of content	WG 5	00351027

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Organic substances covered by CEN/TS 17331 and CEN/TS 17332

- **PAH:**
Anthracene
Benzo(a)pyrene
Dibenz(a,h)anthracene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benz(g,h,i)perylene
Indeno(1,2,3-cd)pyrene
Fluoranthene
Naphthalene
Acenaphthene
Acenaphthylene
Phenanthrene
Benzo(a)anthracene
Fluorene
Pyrene
Chrysene

- **PCB:**
Sum of PCB-28, PCB-52, PCB-101, PCB-118, PCB-138, PCB-153, PCB-180

- **Hydrocarbons:**
Sum of Hydrocarbons (C10 – C40)

- Alkylated Benzenes (**BTEX**):
Sum of Benzene, Toluene, Ethylbenzene, Xylene

- **Nonylphenols:**
4-Nonylphenole and Isomers

- **Organotin compounds***

- **Phthalates**

- **PBDE**

* Organotin compounds not validated for construction products

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Further development on content and eluate analysis methods following the robustness validation

For the following substances NWI are developed based on existing documents and recommendations in the Robustness validation report (VITO)

Title	WI	Circulation of 1st Working Draft in TC	Dispatch to CMC for vote	DAV	State of progress
		Target dates			
Determination of the content of PAHs and BTEX – Gas chromatographic method with mass spectrometric detection	00351034	2018-12	ENQ: 2019-04 FV: 2020-06	2021-02	Registered in August 2018 (Decision 280).
Determination of biocide residues using LC-MS/MS	00351035	2018-12	ENQ: 2019-04 FV: 2020-06	2021-02	Registered in August 2018 (Decision 281).

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Evaluation of needs on content and eluate analysis methods covering Organic Regulated Dangerous substances

- The following organic substances are listed but due to lack of an appropriate standard at the time have not been taken on board in the standardisation process:
  - Organophosphorus compounds
  - Perfluoro-alkylated substances: PFOA, PFOS and PFOSA
- Position of the WG is to wait for a decision by the Commission/EGDS on further needs for standardisation

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Overall Performance of release of DS

- The overall performance of the release of dangerous substances from construction products is strongly controlled by the precision in the test performance and the analytical precision
- Further improvement of experience in test performance and analysis is crucial in this respect, as reduced uncertainty leads to clearer decisions (Presentation by Daan Smulders tomorrow)

- However, there are uncontrolled aspects related to variation of product quality, changes in product behaviour due to ageing, exposure to the atmosphere (CO_2 and O_2), and remineralization

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Recommended generic performance data for percolation (expressed in mg/kg at L/S=2 and L/S=10) and monolith leach test (expressed as mg/m² at 64 days)

Test method	s_r %	s_R %
CEN/TS 16637-2 Monolith leaching	20 - 25	30 - 40
CEN/TS 16637-3 Column leaching	18 - 25	40 - 50

- Monolith leaching of copper slag results in large within and between standard deviation due to sample heterogeneity (about 2 × the values in the table)
- Measurements close to detection limit excluded
- More experience and proficiency testing should improve these performance data

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Recommended generic performance data for content (mg/kg) and eluate analysis (mg/L)

Test method	s_r %	s_R %
CEN/TS 17201 Content analysis	2 - 4	12 - 24
CEN/TS 17195 Eluate analysis	2 - 4	10 - 20

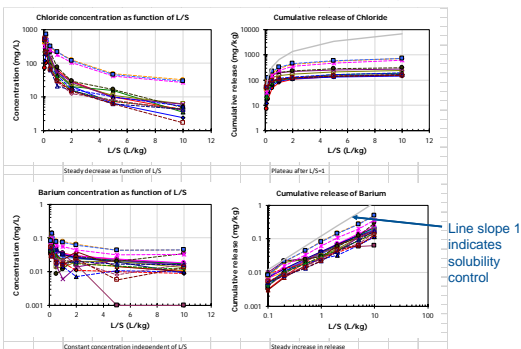Within lab variability is OK, but between lab variability should be better; normally 2 – 3 times s_r

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Illustration of washout and solubility control

In case of solubility control, good repeatability and reproducibility are easier achieved.

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Guidance on test use and evaluation

- As part of the discussion around the validation data, it was concluded that further guidance on test use and interpretation would be helpful for end users
- In an annex to the standard 16637-1 (TS-1), information is foreseen on handling specific materials that may cause problems in testing without additional measures, such as alkaline materials setting upon contact with water in the percolation test and other guidance on recognizing causes for unexpected behaviour in testing or test outcome
- Further information in the next presentation

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Intercomparison validation for organic substances

- Following the issuing of the robustness validation report the plan for validation of organic substances was formulated
- Given the experiences with obtaining materials for testing in the Robustness work, the ambition for the organic substances intercomparison validation work was adjusted
- Two products (render and a sealant) were selected for 16637-2 testing (dynamic surface leaching test) and two products (asphalt aggregate and recycled mixed aggregate) were selected for 16637-3 testing (percolation test)
- Details of this work will be presented tomorrow by Silvia Garcia-Ruiz from JRC

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