Netherlands Food and Consumer
Product Safety Authority
Ministry of Economic Affairs, Agriculture and Innovation

Chemical requirements:

draft standard EN 71-3 migration of certain elements

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Overview

- Directive 2009/48/EC
- *NEW* EN 71-3
- Sample preparation and migration
- General elements
- Chromium speciation
- Organic tin
- Conformity assessment
- Measurement uncertainty
- Time line and future development

Seminar on Testing for Toy Safety

22 October 2012

Netherlands Food and Consumer
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Ministry of Economic Affairs, Agriculture and Innovation

Toy Safety Directive

2009/48/EC

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Toy Safety Directive 88/378/EEC

Bioavailability limits for 8 elements:

- Antimony
- Arsenic
- Barium
- Cadmium
- Chromium
- Lead
- Mercury
- Selenium

EN 71-3: harmonised standard to demonstrate compliance with these requirements

Directive 2009/48/EC

RIVM report (2008): Scientific review of elements in toys and exposure assessment
(http://www.rivm.nl/bibliotheek/rapporten/320003001.pdf)

Basis for requirements for certain elements in new Toy Safety Directive 2009/48/EC

Annex II, III.13 contains:

- Revised limits on certain elements
- Addition of new elements, including Chromium (III) and (VI) and organic tin

Directive 2009/48/EC

Aluminium
Antimony
Arsenic
Barium
Boron
Cadmium
Chromium (III)
Chromium (VI)
Cobalt
Copper
Lead
Manganese
Mercury
Nickel
Selenium
Strontium
Tin
Zinc
Organic Tin

Red colour is new element!

Directive 2009/48/EC

Migration limits based on toxicological data

Differentiation into 3 toy categories, based on assumed consumption:

I. Dry, brittle, powder like or pliable

II. Liquid or sticky

III. Scraped-off

See also Explanatory Guidance Document of the European Commission:

http://ec.europa.eu/enterprise/sectors/toys/files/tsd-guidance/tsd_rev_1-5_explanatory_guidance_document_en.pdf

Category I: Dry, brittle, powder like or pliable

- Solid toy material from which powder-like material is released during play
- The material can be ingested. Contamination of the hands with powder contributes to enhanced oral exposure
- The assumed ingestion is 100 mg per day

Category II: Liquid or Sticky

- Fluid or viscous toy material which can be ingested and/or to which dermal exposure occurs during playing.
- The assumed ingestion is 400 mg per day

Category III: Scraped-off

- Solid toy material with or without a coating which can be ingested as a result of biting, tooth scraping, sucking or licking.
- All materials not classified as category I and II
- The assumed ingestion is 8 mg per day.

Examples toy categories

Category I:

Compressed paint tablets

Chalk

Crayons

Plaster

Modelling compounds

Magic sand

Bouncing putty

Category II:

Bubble solutions

Poster paints

Finger paints

Liquid adhesives

Glue sticks

Slimes

Category III:

Surface coatings

Polymers

Other materials

Wood

Textiles

Glass and ceramics

Metals and alloys

A flow diagram is given to classify a toy

Scope for certain elements

These limit values shall not apply to toys or components of toys which, due to their accessibility, function, volume or mass, clearly exclude any hazard due to sucking, licking, swallowing or prolonged contact with skin.

Both intended and foreseeable use by children must be considered.

NEW EN 71-3

NEW EN 71-3

Requirements and scope are set in Directive 2009/48/EC

EN 71-3 is revised in close analogy with current EN 71-3

prEN71-3 was published in spring 2012

This presentation refers to the formal vote version

Sample preparation

and migration

Sample preparation and migration

Similar to current EN 71-3:

- Based on ingestion (main exposure route)
- Simulates exposure to gastric juices for certain period of time after swallowing
- 100 mg of material in 5 ml of gastric simulant
- 1 hour of dynamic migration at 37°C (shaking bath)
- 1 hour of static migration at 37°C
- Followed by filtration and analysis

Sample preparation and migration

Laboratory sample: one toy

Test portion are taken from this toy

All accessible toy materials must be selected

Sample preparation and migration

< 10 mg: no testing and analysis required

10-100 mg: test if 100 mg of material were available (also for calculation of migration)

100 mg or more: add 50 times its mass of gastric simulant

(Similar to current EN 71-3)

De-waxing step (cat I and II toys)

For toys containing grease, oil, wax or similar material

1. Put sample in high retention filter paper
2. Soxhlet extraction with n-heptane
3. Filter paper including sample material are then macerated with water and subjected to migration test

NOTE!

De-waxing step is not performed for analysis of organic tin!

Category I and II toy materials

100 mg or more in 50 times its mass of gastric simulant

Sample material must be well suspended in the simulant

Category III toy materials

- Paper and paperboard are analysed with coating
- Other coatings are scraped off and sieved (0,5mm)
- Polymers, textiles, paper and paperboard are cut into test pieces of appr. 6 by 6 mm
- Glass and ceramics:
  - If it fits into small parts cylinder: submersed in gastric simulant for 2 hours
  - If it is too big for small parts cylinder: no testing is required

Analysis of certain elements

Resulting migration solution must be analysed for content of certain elements

Requirements for analytical method in normative part:

- Sensitivity of the method
- Linearity of the calibration curves
- Validated method

Validated methods are given in informative Annex E, F and G

Analysis of certain elements

Migration solution is analysed for:

- General elements: Aluminium, Antimony, Barium, Boron, Cadmium, Chromium, Cobalt, Copper, Lead, Manganese, Mercury, Nickel, Selenium, Strontium, Tin and Zinc
- Chromium (III) and Chromium (VI)
- Organic tin

Analysis of certain elements

If all 3 methods are to be performed, more (volume) of migration simulant is needed

- Use 200 or 300 mg of toy material for the migration test
- Or further dilute the obtained migration solution with gastric simulant

  NOTE: this will lower the limit of detection and quantification

General elements (Annex E)

General elements

Migration solution can be analysed directly by ICP-MS or ICP-OES in one run

Examples of working solutions (calibration curves) are given

Examples of ICP-MS and ICP-OES settings are given

Comparable to current EN71-3

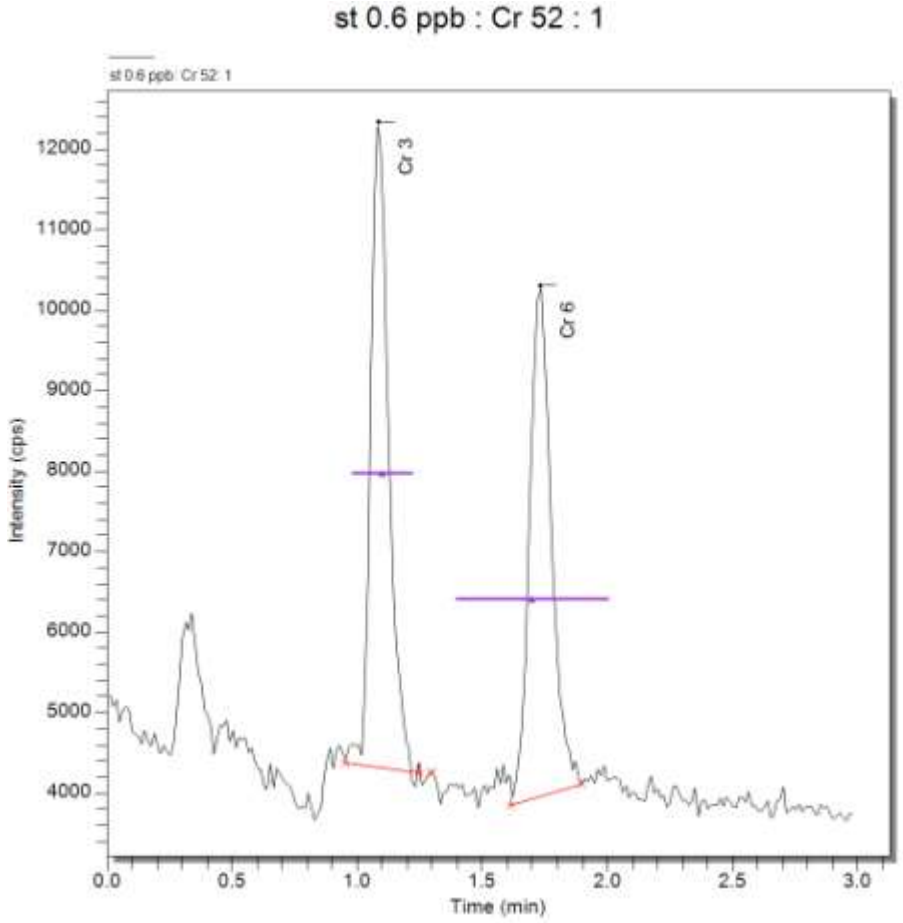
- More elements
- Lower limits (especially category II)

Chromium speciation (Annex F)

Chromium speciation by LC-ICP-MS

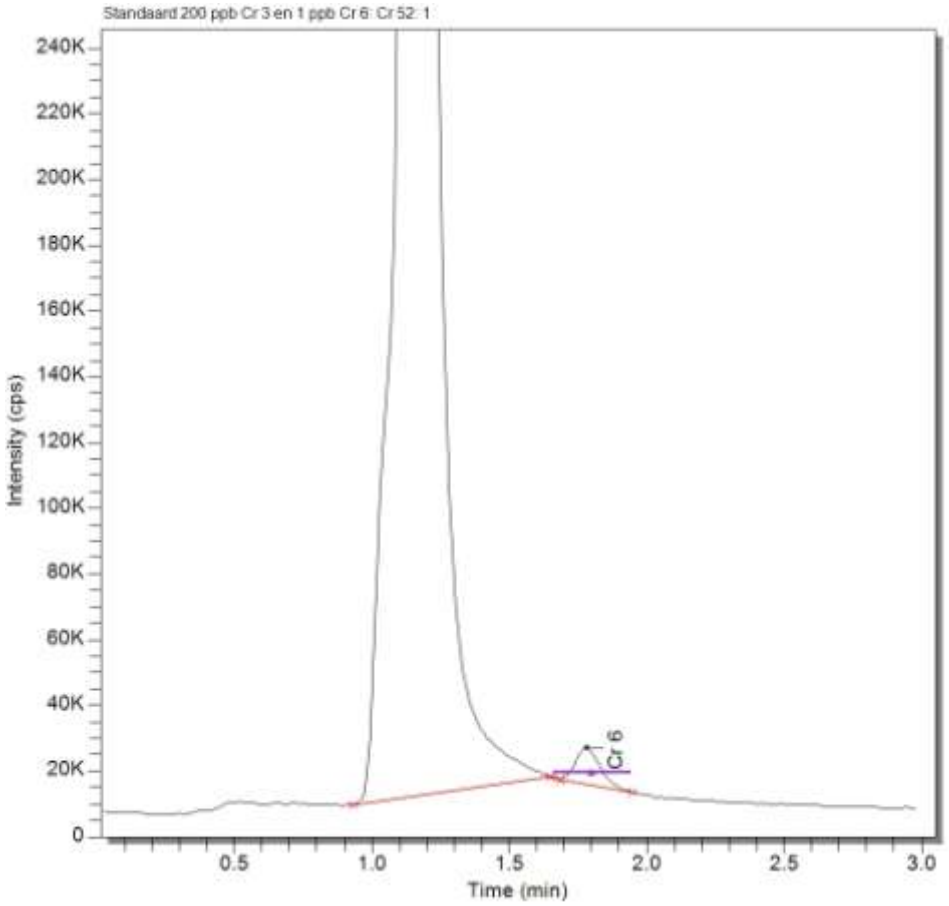
- Interconversion of Chromium (III) and (VI) can take place, therefore immediately after migration step the migration solution is stabilised at pH 7.1
- Complexation of Chromium (III) with EDTA
- Separation of Chromium (III) and Chromium (VI) using liquid chromatography (LC)
- Confirmation and quantification by ICP-MS

Example of chromatogram



Standards at 0.6 ppb of Chromium (III) and (VI)

High Chromium (III) and low Chromium (VI)



Chromium (III) 200 ppb
Chromium (VI) 1 ppb

Solution:
Skip complexation step, only Cr VI peak appears

Chromium III:
a) Cr (combined) – Cr(VI)
b) analyse migration solution also after complexation step

Analytical difficulties Chromium (VI)

Interconversion Chromium III and VI, influenced by pH, presence of oxidizing agents (for example Manganese)

Interference by matrix components (high level of noise)

Analytical difficulties Chromium (VI)

Chromium VI:

LOD: 0.026 mg/kg

LOQ: 0.053 mg/kg

Migration limits:

Cat I: 0.02 mg/kg

Cat II: 0.005 mg/kg

Cat III: 0.2 mg/kg

LOD and LOQ only suitable for category III!

Conformity assessment Chromium VI

1. Determine migration combined Chromium. If this is below Cr (VI) limit, compliance with both Cr (III) and (VI) is demonstrated

2. Safety assessment by the producer, demonstrating the absence of Chromium

3. Determination of content of chromium. Maximum migration of Chromium (VI) can be calculated.

Alternative methods Chromium VI

Alternative methods may also be used, such as

- IC-UV-Vis
- IC-ICP-MS

The method must be validated and meet requirements of the standard (clause 8 and 9)

Organic tin
(Annex G)

Organic tin

- Requirement for organic tin (group limit)
- Organic tin compound contains an organic moiety in its structure
- Most organic tin compounds are too polar to be analysed directly
- Derivatisation to non-polar aklyltin compounds using tetraethylborate
- Extraction with hexane
- Analysis by GC-MS

Organic tin

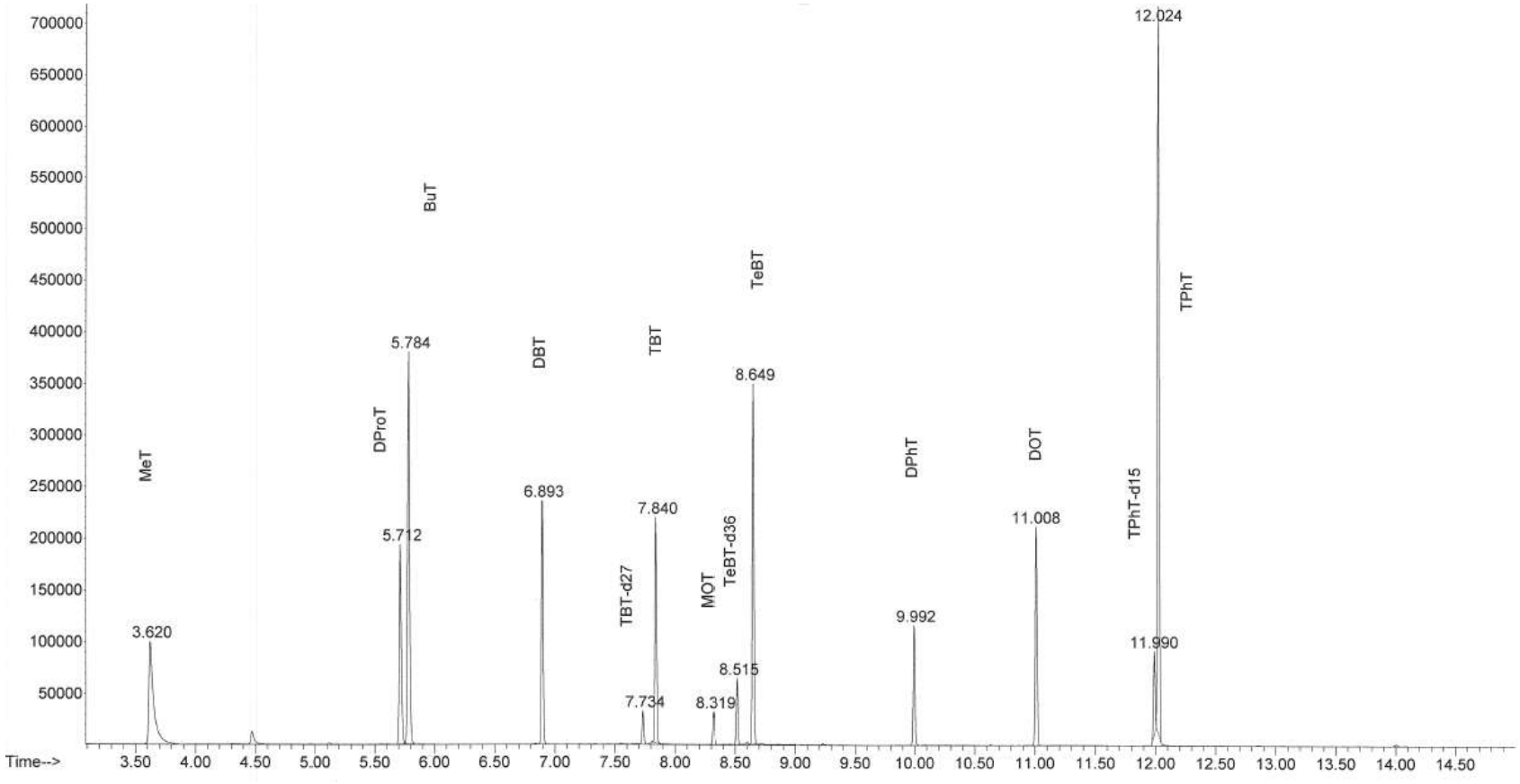
- The requirement for organic tin is a group limit for all organic tin compounds
- This selection is not a limited list of organic tin compounds
- The method was validated for these specific compounds
- Other organic tin compounds may also be present, see informative Annex J
- Then the method needs to be validated for this organic tin compound as well

Organic tin

- In order to develop, test and validate the method a selection of organic tin compounds was made
- Based on toxicity and occurrence in toys
- Mono-, di-, tri, tetra-alkyl tins and aryl tin compound

Methyltin	N-octyltin
Di-n-propyltin	Di-n-octyltin
Butyltin	Tetrabutyltin
Dibutyltin	Ddiphenyltin
Tributyltin	Triphenyltin

Organic tin: GC-MS chromatogram



Organic tin – calculation

- Based on an EFSA opinion, organic tin compounds shall be expressed as tributyltin
- Table is given with Mw (molecular weight) of the selection of organic tin compounds
- Migration of single organic tin compounds must be calculated, expressed as tributyltin
- If more than 1 organic tin compound is present, the migration values must be added to calculate total organic tin

http://www.efsa.europa.eu/fr/efsajournal/doc/102.pdf

Conformity Assessment (Annex I)

Conformity assessment

- Testing according to EN 71-3
- Assessment by the manufacturer (see explanatory guidance document)
  - Some elements are only present in certain materials
  - The scope of testing can be limited based on assessment which elements could be present
  - This assessment must be maintained within the technical documentation

Conformity assessment

- Migration of total Tin can be used as a screening tool. If total tin is below the limit of organic tin, then compliance is also demonstrated

- Content of an element can be used to calculate maximum migration and in this way compliance can be demonstrated

Measurement uncertainty (Annex B)

Measurement uncertainty

- In current EN 71-3 correction factors were introduced
- In new EN 71-3 they are replaced by measurement uncertainty
- Laboratories must determine their method performance including measurement uncertainty
  - Routine samples can be used to establish reproducibility
  - Bias must be determined
  - Measurement uncertainty can be determined by:
    1. Certified reference materials (not yet available)
    2. Blank toy material (spike the migration simulant)

Measurement uncertainty

Measurement uncertainty must be used to interpret the analytical result for compliance assessment

Eurachem/CITAC guide (www.eurachem.com)

Principle: Decision rules

- Prescription for the acceptance or rejection of a product based on measurement result, its uncertainty and the limit
- Application of decision rules depends on the role of the laboratory: enforcement lab or (commercial) test lab

Measurement uncertainty

One decision rule: non-compliance if the result exceeds the limit expanded by uncertainty

(Normally applied by enforcement laboratories)

Other decision rule:

- non-compliance if the result is equal or above the limit
- compliant if the result is below the limit, deduced by the uncertainty

(Normally applied by (industrial) test laboratories)

Time line

And future developments

EN 71-3

- prEN71-3 was published in spring 2012:
  - 21 positive votes
  - 5 negative votes
  - 4 abstentions
  - 2 non-votes
- Formal vote version is being prepared
- Probably published in beginning 2013
- EN 71-3 should be published in July 2013

Migration limits

Limits for lead and barium are being re- evaluated

This may result in new migration limits

Thank you for your attention!