

As new and evermore stringent regulations relating to the protection of the environment and consumers have been implemented, manufacturers and the research centres they collaborate with have worked together to put test methods in place that are designed to measure the concentration of the many substances now monitored and controlled.

Weighing up heavy metal standards

Bringing a finished product to market can be a minefield in terms of meeting safety regulations, but anyone responsible for marketing a product must be able to guarantee, through complete traceability, that their products meet all of the standards required. In order to avoid the costly processes involved when a product fails to meet the required standards for controlled substances, French research centre CTC has adopted a proactive approach in this area, participating in standardisation technical committees responsible for the creation or revision of international standards and creating a global network of accredited laboratories to carry out numerous tests for controlled substances in footwear and clothing. In this feature CTC's Dr. Jean-Claude Cannot outlines some of the most important aspects involved in testing for heavy metals.

A testing question

Two criteria must be considered when testing footwear and clothing: the impact on the

Tests have shown that many metals are harmful to humans.
CTC

Test methods

Depending on a specific manufacturer's requirements, CTC's laboratories generally use one of four analysis methods.

Method	Preparation	Processing	Detection	Goals
EN 14602	Shoe fully ground up	Total mineralisation of the sample	ICP OES	Determination of the total concentration of As, Pb, Cd
CTC B method	Textile cut up	Acid sweat extraction (ISO 105 E04)	ICP OES (ISO 11885)	Determination of the concentration of extractable metal according to material and extraction solution.
CTC C method	Leather ground up	Acid sweat extraction (ISO 105 E04)	ICP OES (ISO 11885)	
CTC D method	Sample cut up	Acid extraction (EN 71-3)	ICP OES (ISO 11885)	

environment and the impact on the wearer.

In terms of assessing the impact on the environment, the product or material must be tested in terms of its complete lifecycle from production through usage to its final disposal. This involves analysing the product's total level of heavy metals and therefore requires a complete mineralisation of the sample to determine the total concentration of metals.

When testing for any potential hazards to the human wearer, several heavy metals need to be considered. For example nickel analysis is extremely important as this substance can contain heavy metallic elements that can leach into other materials. The product must therefore be tested with a synthetic sweat solution to extract the heavy metals and determine the concentration of these materials. As a result of tests already carried out, many metals have now been identified as posing a hazard to humans and numerous compulsory and voluntary standards and directives have subsequently been implemented.

Compulsory references

The following are subject to compulsory standards associated with national legislation or European directives and their use is regulated:

Nickel

Uses: Surface treatment to protect metallic items.
Safety: Causes allergies in more than 10% of the population.
Legislation: European Directive 94/27/CE (Decree—July 18 2000).
Test method: NF EN 1811
Limit: Lower than 0.5µg/cm^2/week
Manufacturer's responsibility: To demonstrate compliance with EU Directive.

Cadmium

Uses: Formerly used as a PVC stabiliser.
Safety: Toxic metal.
Legislation: European Directive 91/338/CE (French decree 94-647)
Test method: EN 1122 Synthetic materials, PVC – PVC Cadmium levels
Limit: 0.01% of the polymer mass.
Manufacturer's responsibility: Demonstration of compliance – obligatory for PVC manufacturers.

Various toxic metals in toys

Metals covered: antimony (Sb), arsenic (As), lead (Pb), cadmium (Cd), chrome (Cr), cobalt (Co), copper (Cu), dissolved nickel (Ni), mercury (Hg).
Legislation: European Directive 88/378/CEE (decree n°89-662 dated 12 September 1989)
Toy Directive: Heavy metals. This applies to all types of toys for the following materials: textiles, leathers, polymers. [*Note:* some garments and shoes for children under 36 months are classified as toys by State authorities].
Test method: EN 71-3 (variable acceptance level standard depending on metal).
Responsibility: Demonstration of compliance by person bringing the toy to market.

Voluntary references

The following are voluntary certification systems used to guarantee that the product is harmless.

Footwear Ecolabel: Heavy metals

Uses: All footwear materials (textiles, leathers, furs, polymers, etc.).
Metals covered: cadmium, lead and arsenic.
Application: To guarantee harmlessness and also product life cycle.
Standardisation: EU decision 1999/179/CE (criteria for the attribution of the Ecological Label) revised 2002/231/CE.
Test method: EN 14602 - As Cd and Pb are not detectable (above 100 ppm for each element), the shoe is ground up completely and a sample is fully mineralised and examined.
Responsibility: Demonstration of compliance by the person responsible for bringing the footwear to market if Ecolabel certification is requested.

Making the grade

CTC applies the requirements set out by legislation relating to metallic nickel, toys and cadmium and the criteria recommended are described in the table below.

CTC acceptance crtteria for heavy metals in finished materials or products, textile, leather, footwear, leather good

Unit of metal in mg per kg of footwear	Method	SB Antimony	AS Arsenic	PB Lead	CD Cadmium	CR Chromium	CO Cobalt	CU Copper	NI Nickel	HG Mercury
Footwear: priority parameters In mg of total metal per kg of footwear	A	X	Lower than 100	Lower than 100	Lower than 100	X	X	X	X	X
Footwear: secondary parameters In mg of extracted metal per kg of footwear	B	Lower than 2				X	Lower than 1	Lower than 25	Lower than 1	Lower than 0.02
Textile Clothing – Leather goods: In mg of extracted metal per kg of product	B	Lower than 2	Lower than 0.2	Lower than 0.2	Lower than 0.1	X	Lower than 1	Lower than 25	Lower than 1	Lower than 0.02
Leather – Raw material: In mg of extracted metal per kg of leather	C	Lower than 2	Lower than 0.2	Lower than 0.2	Lower than 0.1	X	Lower than 1	Lower than 25	Lower than 1	Lower than 0.02
Raw materials – Other than leather In mg of extracted metal per kg of material	B	Lower than 2	Lower than 0.2	Lower than 0.2	Lower than 0.1	Lower than 1	Lower than 1	Lower than 25	Lower than 1	Lower than 0.02

Textile Ecolabel: Heavy metals

Uses: All types of textile.
Metals covered: None. This reference forbids the presence of certain heavy metals in colourings or pigments.
Application: Lifecycle.
Standardisation: EU decision 1999/178/CE (criteria for the attribution of the Ecological Label).
Responsibility: Demonstration of compliance by the colouring substance supplier to the person responsible for bringing the textile to market if Ecolabel certification is requested.

Oekotex: Heavy metals

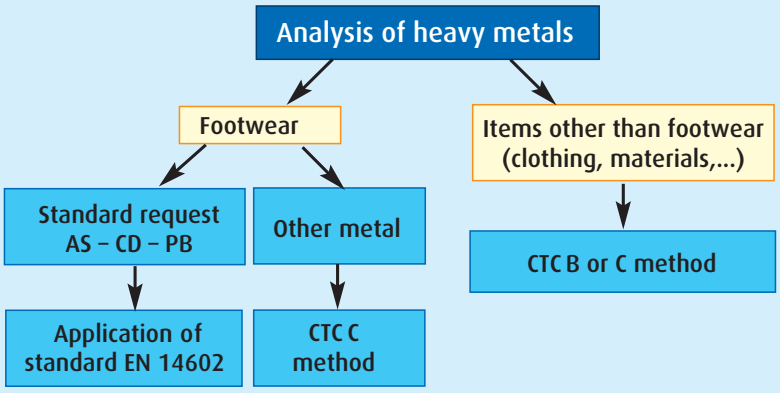
Uses: All types of textile.
Metals covered: antimony (Sb), arsenic (As), lead (Pb), cadmium (Cd), chrome (Cr), cobalt (Co), copper (Cu), dissolved nickel (Ni), mercury (Hg).
Application: Toxic metals.
Standardisation: Voluntary German reference.
Test method: CTC B method.
Responsibility: Demonstration of compliance by the person responsible for bringing the finished product to market if Oekotex certification is requested.

SG: Heavy metals

Uses: All footwear materials (textiles, leathers, furs, polymers, etc.).

Defining moments

As it is not always clear which tests for heavy metals need to be carried out, CTC laboratories use a specific set of criteria to define the analyses required for different samples.



Safety: Toxic metals.
Metals covered: antimony (Sb), arsenic (As), lead (Pb), cadmium (Cd), chrome (Cr), cobalt (Co), copper (Cu), dissolved nickel (Ni), mercury (Hg).
Standardisation: Voluntary German reference.
Test method: CTC B or C method.
Responsibility: Demonstration of compliance by the person responsible for bringing the finished product to market if SG certification is requested.