EC End of Life Vehicles Directive and Hexavalent Chromium

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Topics

- Introduction - Cathodic Corrosion Protection
- Content of the End of Life Vehicles (and the Waste of Electrical & Electronic Equipment) Directive and Their Implications on Cr(VI)
- Original Situation - How Much is Present? Analytics
- Technical Options
- Replacement of Chromium(VI) Just Because we Have to?

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Some Facts

- the original drafts for the replacement of chromium(VI) have been much stricter than for hexavalent yellow chromate finishing
- the insight is growing that it obstructs the general introduction of trivalent passivations if simultaneously the demands are strongly raised:
  → intermediately BMW accepts some black layers with 240 h until red rust
  → GM (USA) accepts for existing parts trivalent layers with the values as for yellow chromate
- even with the delay until 2007, the pressure on the market is rather high - simply EVERY layer for the electrical and automotive industry must be free of chromium(VI) until 2006/2007
- a homogeneous quality currently has a higher value than a peak corrosion protection as such: already in July 2002, the German VDA (car manufacturers' association) published an appeal to the market not to stop with the efforts and to improve process security; GGG (Quality Committee Electroplating) was assigned the elaboration of a set of rules
- a wide interlaboratory test was held in Germany to establish the state of the art

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New Guidelines

- **End of Life Vehicles Directive (ELV)**

  steers the recycling of vehicles, components and material (up to 3.5 t) and determines limiting values for the entry of certain substances such as lead, chromium(VI) and others into the shredder

- **Directive on Waste of Electrical and Electronic Equipment (WEEE)**

  steers the recycling, sets collection targets per inhabitant and year and bans certain (about the same as above) hazardous substances

→ **both affect the surface of fasteners** - reason why we should know the two texts more precisely and to repeat why it's about chromium(VI) and not chromium(III) or chromium(0)

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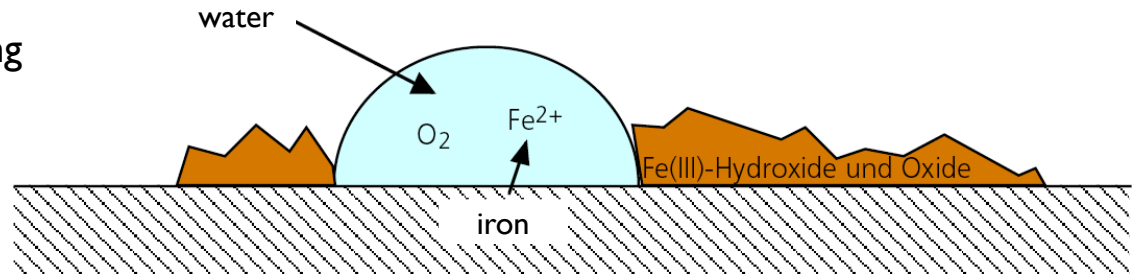
Cathodic Corrosion Protection on Steel

- steel dissolves in salt and air containing water by reducing oxigen resp. forming hydrogen
  it forms iron oxide/hydroxide which precipitates as high volume corrosion product on the surface
  = **Red Rust**

- iron oxide layers are not protecting against further corrosion -
  in contrary to chromium oxide on metallic chromium or aluminium oxide on aluminium



- corrosion protection can be achieved by:

  barrier layers: conversion coatings, lacquers, noble metallic coatings

  redox buffers: less noble coatings (cathodic protection), conversion coatings with different oxidation levels

  duplex layers: a combination of both

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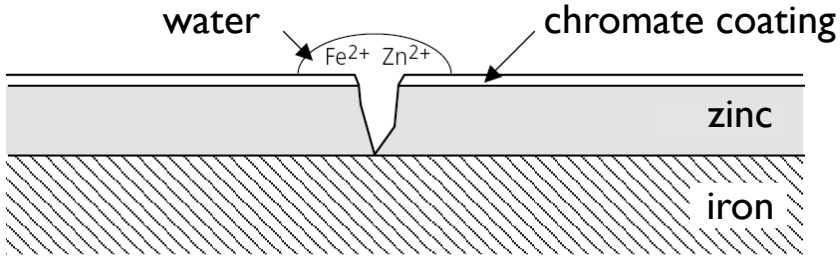
- zinc coatings are the typical protection for steel and iron, because iron is in the electrochemical series more positive than zinc, and thus
- zinc is less noble than iron and represents the anode in the galvanic element (and iron the cathode)
- consequently, iron as the more noble metal is protected until the zinc is consumed by corrosion

mechanism:



- **parameters:** layer thickness, metal distribution, foreign metals (resulting in a more noble zinc layer and thus enhancing corrosion protection)
- the zinc itself is protected by a barrier layer - traditionally a chromate

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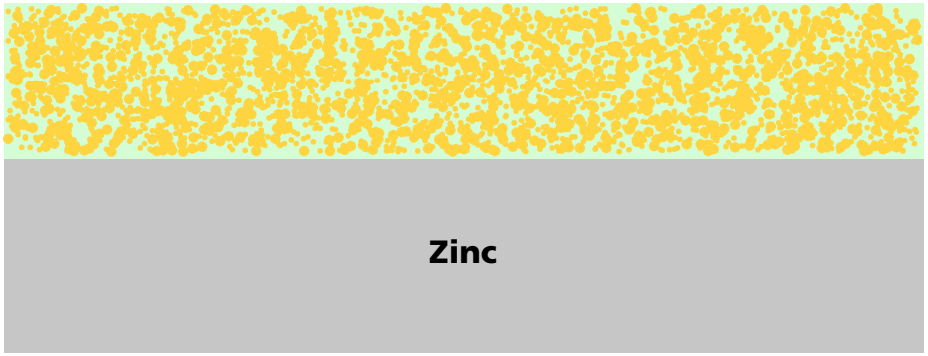
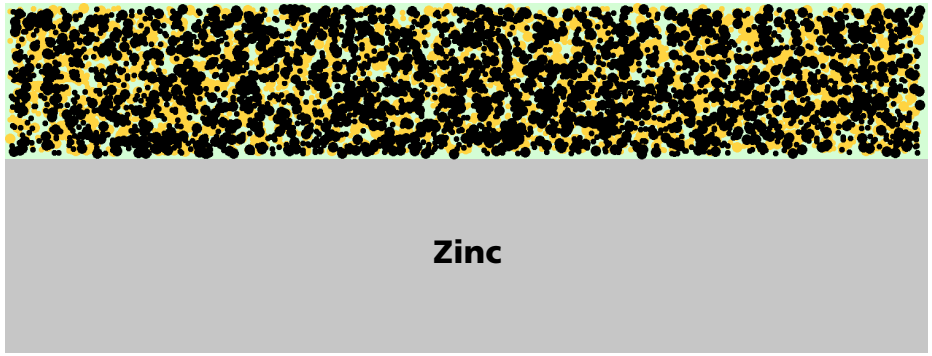
Type of Passivation	Chromium(VI) in mg/m²	Layer Thickness in nm	Salt Spray to White Corrosion [hours]
Yellow Chromate	80-220	250-500	200-300
Olive Chromate	300-400	1000-1500	400-500
Black Chromate	80-400	250-1000	150-300
compare:			
Trivalent Blue Chromate	0	25-80	20-40

hexavalent yellow chromate



hexavalent black chromate



- mechanism: barrier effect, specific effect of hexavalent chromium
- parameters: layer thickness, content of chromium oxide

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Chromium Compounds

Oxidation Level		Examples for Substances and Typical Applications	
	+6 oxoanion	chromic acid (not very stable)	chromium plating electrolytes and yellow chromate
salts	+5	[extremely instable]	
	+4	[extremely instable]	
	+3 cation	chromium nitrate, chloride, sulfate chromite: the ore $FeCr_2O_4$ chromium oxide (extremely stable)	 trivalent electrolytes and passivations natural occurance pigment for painting
	+2	(instable)	
metal	0	metallic chromium	furniture, sanitary fittings, implants, medical instruments

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End of Life Vehicles Directive

- the directive 2000/53/EC was decided on 18.9.2000 - in order to attain legal power, it had to become national law in each European country (in Germany since 1.7.2002)
- the directive was published in 2000 in the EC Official Journal L269 and can be loaded under http://europa.eu.int/eur-lex/pri/en/oj/dat/2000/l_269/l_26920001021en00340042.pdf

✗ **content: basically it is a directive steering the recycling of parts/materials**

→ Article 4 Prevention

→ Chapter 2a

"Member States shall ensure that materials and components of vehicles put on the market after 1 July 2003 do not contain lead, mercury, cadmium or hexavalent chromium other than in cases listed in Annex II under the conditions specified therein."

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End of Life Vehicles Directive And Hexavalent Chromium

Annex II *(first version of 2000)*

- Materials and components exempt from article 4(2)(a):
  …
  12. Hexavalent Chromium
  Corrosion preventative coating on numerous key vehicle components
  (maximum 2 g per vehicle)

✗ the limiting value of 2 g Cr(VI) per vehicle was valid for corrosion protection only, besides this (e.g. leather seats) the limiting value was already zero

✗ the limiting values should have been controlled regularly and lowered according the state of the art

✗ it was completely open how the content of hexavalent chromium in a car should be determined (BEFORE shredding!)

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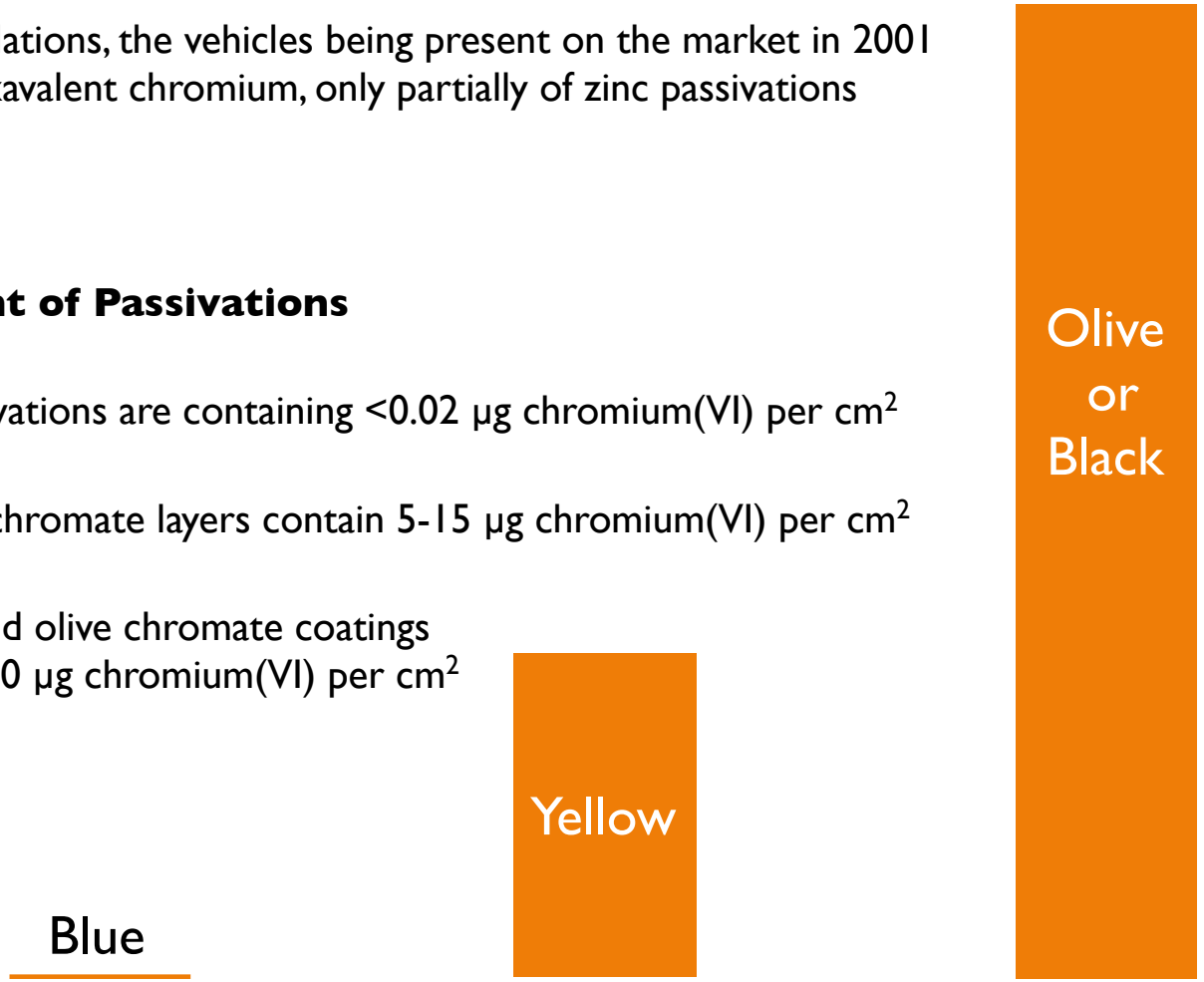
Original Situation: How much is Present?

- according to own calculations, the vehicles being present on the market in 2001 contained 3-30 g of hexavalent chromium, only partially of zinc passivations

Chromium(VI) Content of Passivations

- trivalent blue passivations are containing <0.02 µg chromium(VI) per cm^2
- hexavalent yellow chromate layers contain 5-15 µg chromium(VI) per cm^2
- hexavalent black and olive chromate coatings are containing 10-50 µg chromium(VI) per cm^2



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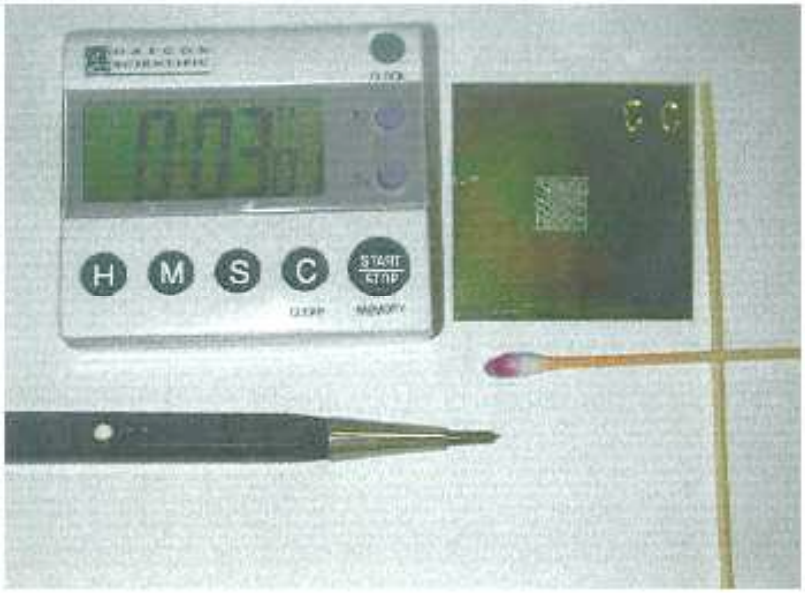
Analytical Determination of Chromium(VI) Traces

- a working group (automotive industry and suppliers of chemicals) has been founded
- a qualitative test (spot test) and a quantitative (photometrical) method were developed, both based on ISO methods
- these methods have been validated in an interlaboratory test with 16 participating laboratories
- the qualitative spot test was finally rejected



both methods are available on our homepage:
http://Chromiting.SurTec.com ➞ Technical Information ➞ Chromium(VI)-Analysis

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New Annex II

- annex II was modified with the decision 2002/525/EC on 27.6.2002:
  http://europa.eu.int/eur-lex/pri/en/oj/dat/2002/l_170/l_17020020629en00810084.pdf

- Article 1:
  Annex II to Directive 2000/53/EC is replaced by the text set out in the Annex to this Decision.

Annex II, Version 2002

Materials and components exempt from Article 4(2)(a):

Materials and components	Scope and expiry date of the exemption	To be labelled or made identifiable in accordance with Article 4(2)(b)(iv)
...		
Hexavalent Chromium		
17. Corrosion Preventive Coatings	1 July 2007	
18. Absorption refrigerators in motorcaravans		X

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Most Important Changes in the New Annex II

- ✗ the 2 g per vehicle are no longer valid = **each** part must be free of chromium(VI)
- ✗ there are **interesting remarks** at the end of the new Annex II:

"a maximum concentration value up to 0,1 % by weight and per homogeneous material, for lead, hexavalent chromium and mercury and up to 0,01 % by weight per homogeneous material for cadmium shall be tolerated, provided these substances are not intentionally introduced (1)."

…

"(1) Intentionally introduced shall mean deliberately utilised in the formulation of a material or component where its continued presence is desired in the final product to provide a specific characteristic, appearance or quality. The use of recycled materials as feedstock for the manufacture of new products, where some portion of the recycled materials may contain amounts of regulated metals, is not to be considered as intentionally introduced."

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Chromates on Zinc and Zinc Alloys

- use of blue passivations instead of yellow chromate, accepting a drop in corrosion protection
- replacement by trivalent Thick Layer Passivation (Chromiting) or by blue passivation + sealer
- replacement of olive chromate on zinc by Thick Layer Passivation on zinc alloy or TLP on zinc + sealer
- the first trivalent black Thick Layer Passivations on zinc/iron are in use

Zinc/Aluminium Flake Coatings

- chromium-free versions are on the market and have been successfully tested

Chromates on Aluminium

- chromium-free conversion coating for lacquer adhesion
- green phosphate as a corrosion protection coating in unlacquered systems

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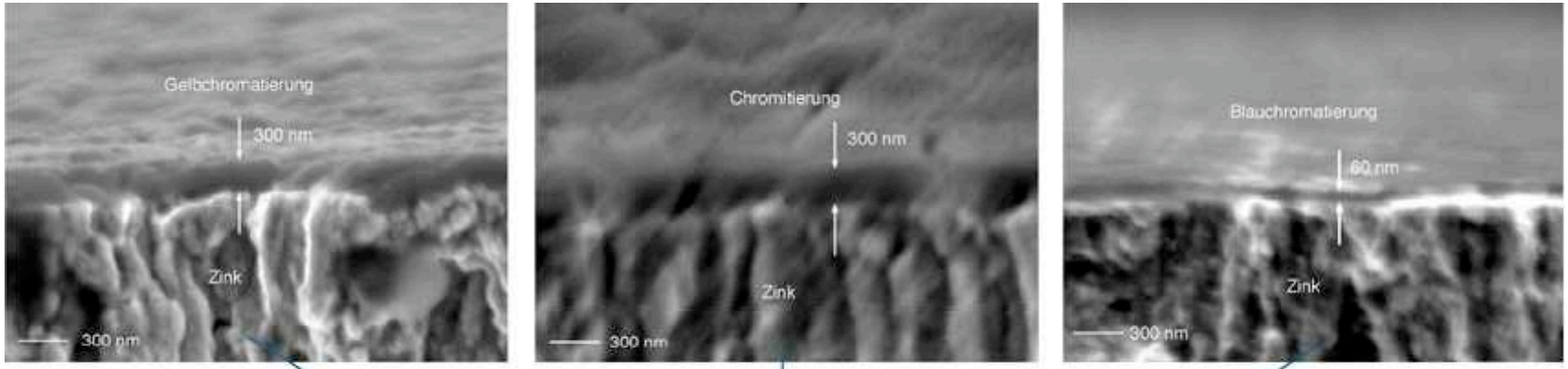
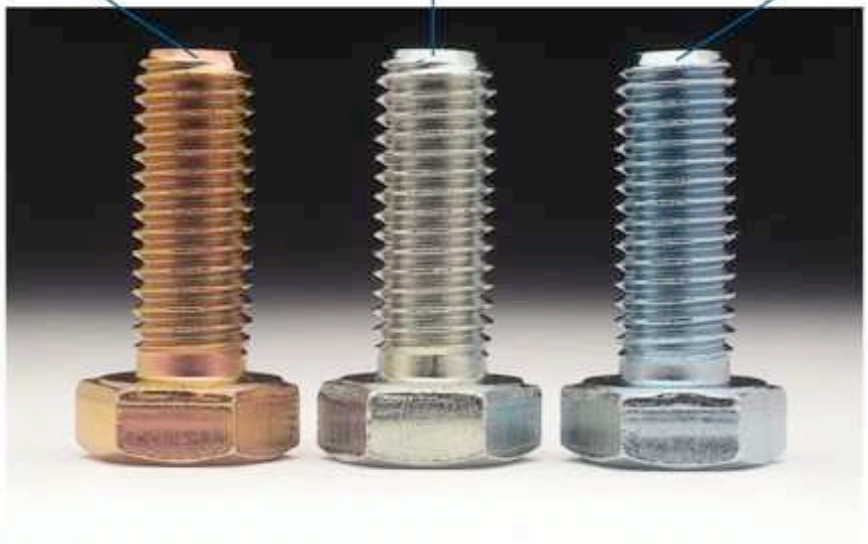
Cr(VI) Replacement on Zinc



Thick Layer Passivation



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Process Solution

- contains chromium(VI), phosphoric acid and fluorides

Conversion Coating

- consists of chromium(III)phosphate and Al/Cr oxide
- transparent, greenish-iridescent appearance

Corrosion Protection (Without Lacquer)

- as a yellow chromate on aluminium

Chromium(VI) Content of the Layer

- can be stabilised at 0.01 µg/cm^2 by an appropriate post rinse

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Why Chromium(III) as a 1:1 Replacement?

Chemical Properties

- good water and acid solubility
  (a conversion coating always requires a first pickling attack)
- formation of oxides, extremely insoluble in water, acid and alkalinity

General Properties

- availability (mass production)
- recyclability (compatible with steel production)
- costs (request of overall low raw material costs)
- known toxicity of all possible oxidation levels

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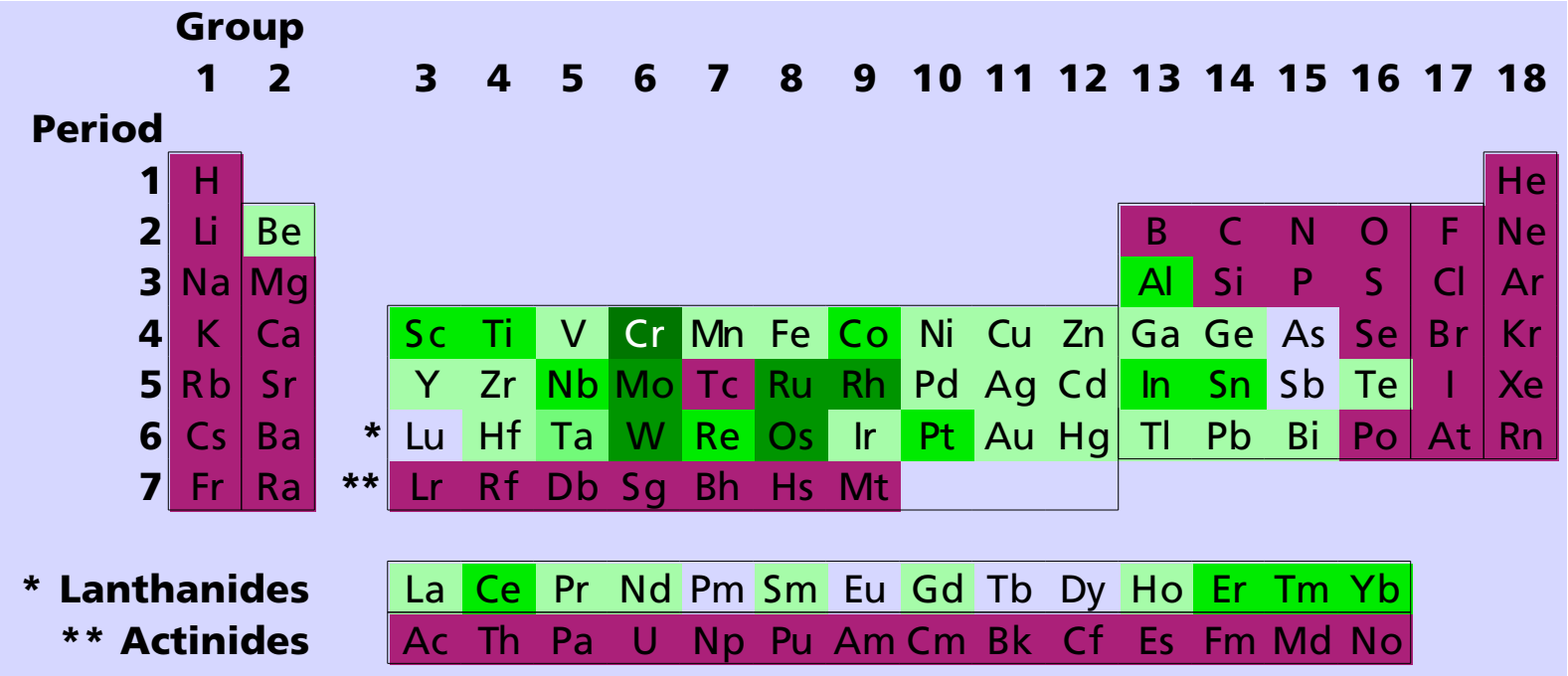
Periodic Table of Elements

- **solubilities of oxides** light green (insoluble in water)
  green (insoluble in acids or lyes)
  dark green (insoluble in acids and lyes)



- 6 element oxides are possible, of those chromium(III) is the least soluble

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Replacement of Hexavalent Chromium Just Because of a Law?

- hexavalent chromium compounds are acutely poisonous, sensitising and carcinogenic
- hexavalent chromium is significantly present in yellow, black and olive chromates
- coated surfaces (e.g. on screws) come into contact with the hands of general public
- these persons don't know about the properties of the surfaces and are handling them without precaution

- the professional work with hexavalent chromium (e.g. electroplating) is not critical - if it is done in controlled environment and only metallic chromium(0) is given to the public
- consequently, a general ban of chromium(VI) is not necessary - it must be handled by professionals - however, Cr(VI) must not be given to people who don't know about their risks

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"An initiative for stability and process security for chromium(VI)-free processes is necessary, and you should not forget that the materials and parts of the models of 2007 are being developed in this very moment!"

VDA, July 2002

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