



Cadmium and chromium

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Modern Methods of Pollutant Analysis

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Outline

- Cadmium and chromium in the environment
- Compounds and human exposure
- Toxicity
- Methods
- Legislation
- Summary



Cd and Cr in the environment

- Naturally in Earth's crust
- Natural sources: Volcanic eruptions, erosion
- Anthropogenic sources:
 - mining, industrial wastes, coal combustion, chemical industry, fossil fuels, transportation, fertilisers

Cadmium

- Application:
 - Batteries (Ni-Cd)
 - Electroplating
 - Pigments: Cadmium yellow, cadmium red, cadmium orange



Chromium

- Application:
 - stainless steel
 - Electroplating
 - Dyes and pigments
 - Chrome yellow, green
 - Chromium oxide (green) – main ingredient in infrared reflecting paints
 - Wood preservative
 - Tanning (leather)
 - Catalyst (polyethylene production, water gas shift reaction, hydrogenation)

Compounds and human exposure

Cadmium

Compounds:

Rare in pure state in nature

Mostly in oxidation state II+

Inorganic salts

Organic compound

- microbial formation of monomethyl cadmium (significance not know)

Main sources of human exposure:

- Eating, drinking, smoking, dust breathing

Retains in kidney and liver

Biological half-life: 10 – 30 years

Excretion: urine, hair, nails, breast milk

Chromium

Compounds: oxidation states from –II to +VI.

Cr^{III} and VI+ are relevant.

Cr^{II}, IV+, V+ - short lifetime, CrO₂ nontoxic

Main sources of human exposure:

- Eating, drinking: Higher concentrations in food from stainless steel cans.
- Dust breathing – small amounts, smoking
- Household goods: wood preservatives, cement, textiles, leather products.

Retains mostly in kidneys and lungs.

Cr^{III} unable to cross cell membrane

Cr^{IV} cross cell membranes through phosphate and sulfate anion-exchange carrier pathway.

Biological half-life: varies from 15 days to 5 years (depend on form)

Excretion: urine, breast milk, hair, nails



Toxicity

Cadmium

- renal dysfunction
- Long/high exposure – renal failure
- Bone demineralization - osteoporosis
- Neurotoxic, genotoxic, teratogenic
- IARC carcinogen (Group 1)
 - Lung
 - Endometrium
 - Bladder
 - Breast

Chromium

Cr^{III} essential for mammal's metabolism

Cr^{VI}: Toxic

- irritation of upper respiratory tract and skin
- nose bleeding
- ulceration
- kidney and liver problems
- immunotoxic, neurotoxic
- IARC carcinogen (Group1) only **Cr^{VI}**
 - Lung
 - Upper respiratory tract

- Lack of appropriate data on effect of chromium during lactation.



Methods

Cadmium

Total Cd: ICP-MS, ET-AAS, GF-AAS...

Cd speciation:

1. Separation:

- Gel permeation chromatography,
- Anion-exchange chromatography
- HPLC

2. Detection:

- AAS
- ICP-MS
- Voltametry

Speciation:

Liquid samples – „easy“ to analyze

Solid samples – analytical challenge (for transformation of a solid sample into a liquid state extraction procedure has to be applied -> risk of species conversion)

Chromium

Total Cr: UV/VIS photometry, AAS, ICP-MS

Cr speciation:

1. separation of species: ion pair chromatography
2. Detection: UV/VIS photometry, AAS, ICP-MS, chemiluminescence methods...



Legislation

Cadmium – limits

	limit
Emission	0,05 mg/m ³
Imission (PM10), year average	5 ng/m ³
Water (for babies, surface water, waste water...)	5 ug/l – 0,2 mg/l
Soil (different type)	0,04 – 800 mg/kg (dry mater)
Food (different type) Commission Regulation (EC) No 1881/2006	0,05 – 1,0 mg/kg
Toys Directive 2009/48/EC of the European Parliament	
Many more...	

Chromium

	limit
Emission (suma of metals As, Co, Ni, Se, Tl, Cr)	2 mg/m ³
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Water	0,025 – 0,5 mg/l
Soil	0,29 – 90 mg/kg (dry mater)
Food	0,2 – 4,0 mg/kg
...	

Convention on Long-Range Transboundary Air Pollution (CLRTAP):
Protocol on Heavy Metals (1998) - The protocol addresses the reduction of cadmium, lead and mercury emissions



Summary

- ✓ Presence of Cd and Cr in wide range of matrices – possible sources of human exposure
- ✓ Toxicology data available (gaps – effects in small doses and mixtures)
- ✓ Methods (mostly for total concentrations, speciation of Cd and Cr is hard to perform)
- ✓ Legislation

Future plan:

- Methods for speciation in solid samples (Cr)
- Methods for speciation Cd and Cr in complex matrixes (content of fat and protein e.g. human tissues – milk, blood, muscles...)
- Evaluation of effect during lactation (Cr)
- Evaluation of effect in low doses and mixtures

