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When element concentration itself is not sufficient – Quantitative analysis of Arsenic and Chromium species by LC-ICPMS

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Why Species Analysis?

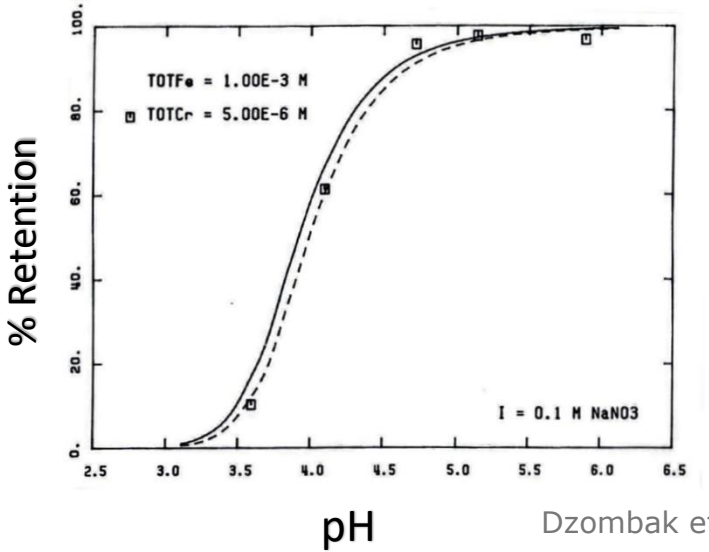
- **Toxicity of "toxic trace elements" depends on not only concentration, but the species which is present!**
  - Chromium: Cr(III) is considered to be essential while Cr(VI) is carcinogenic
  - Tin: Inorganic tin compounds are nutrients for animals but tributyltin (TBT) is an endocrine disruptor
  - Mercury: Methyl mercury can cross the blood/brain barrier, while inorganic mercury can't
  - Arsenic: Inorganic As(III) compounds are carcinogenic while Arsenobetaine is essential non-toxic

Why Species Analysis?

Environmental Mobility - Sorption Properties

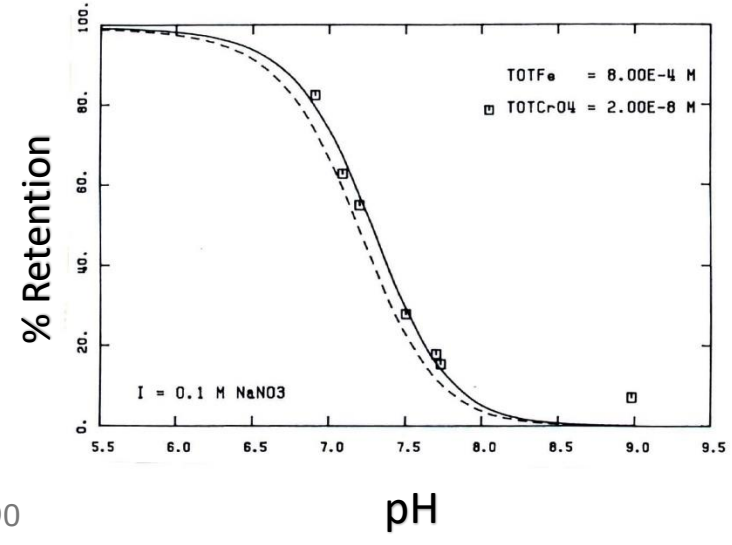
Cr (III)

Rapidly and strongly retained on the surface of different solid phases



Cr (VI)

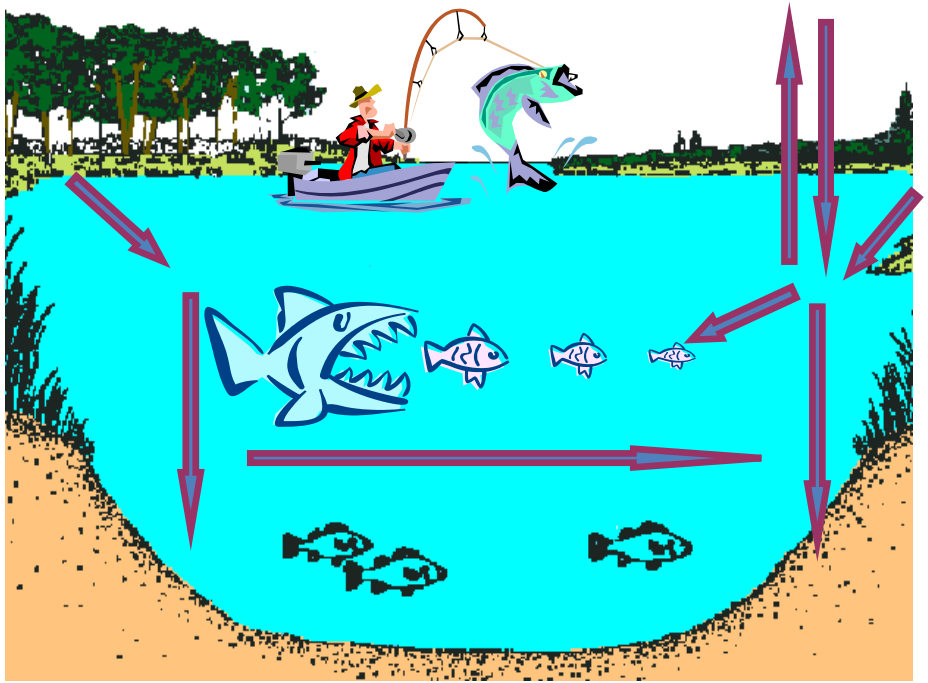
Weakly retained on the surface of different solid phases



Dzombak et Morel, 1990

Why Species Analysis?

Environmental Mobility - answers about:



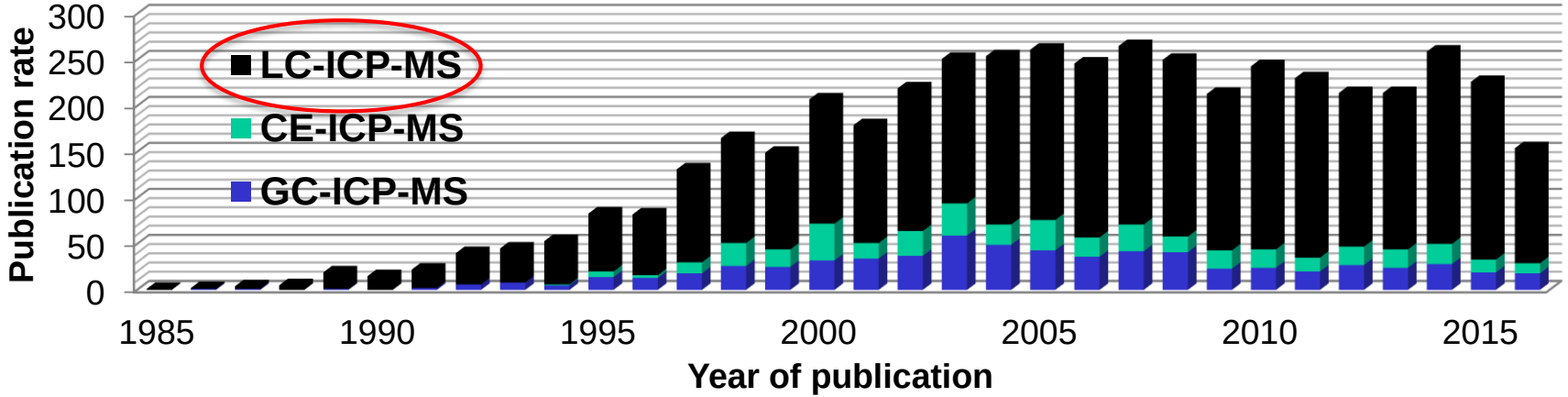
- emission, transport and exchange of matter between different compartments of the environment
- bioaccessibility, bioavailability and toxicity of pollutants towards plants, animals and humans
- chemical and physical effects of pollutants

Why we don‘t do species analysis today?

- From history, it was most easy to determine element concentrations
- Lack of species-related legislation:
  - **Most existing rules and legislation still forces analytical laboratories to only report total element concentrations**
- The European Water Framework Directive (2000/60/EC) specifies that the species of **Cd, Pb, Hg, Ni** as well as **tributyltin** have to be controlled in water,
  - **there are very few national rules and standards implemented, that regulate species related measurements**

Publications related to

- Most common ICP-MS hyphenated techniques



- The number of publication increases
- Esp. **LC-ICPMS** is getting more and more common technique
- It takes long time to implement new legislative rules, but a few arise…

Speciation in Legislations?

- **In progress**

Hexavalent Chromium, Cr(VI)	Waste water; cement; leather; automobile & metal parts; electronic devices (RoHS, WEEE); personal safety equipment; toys
Tributyltin, TBT	antifoaling paint; natural water
Bromate, BrO_3^-	drinking water
Tetraethyllead, TEL	gasoline
Inorganic arsenic, As_i	rice

- **On hold/under discussion**

Hexavalent Chromium, Cr(VI)	drinking water and food
Methylmercury, MM	seafood

Cr Species in Toys (I)

- **Health properties of hexavalent chromium (Cr(VI))**
  - Toxic
  - Irritating properties
  - Can induce allergic reactions
  - Known to cause cancer (inhalation)
  - **Expected to case cancer (oral intake)**

www.speciation.net/News/EU-notifies-WTO-of-change-to-chromium-VI-limit-in-toys-;~/2017/09/14/8517.html

Cr Species in Toys (II)

- **DIN EN 71-3 requires to determine the migration of chromium (III) and chromium (VI) from toy materials**

  - Specified maximum migration limits for these species give a direct connection to the toxicity,

  - 9.4 mg/kg for Cr(III)
  - 0.005 mg/kg for Cr(VI)

http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:02009L0048-20140721
www.speciation.net/News/EU-notifies-WTO-of-change-to-chromium-VI-limit-in-toys-;~/2017/09/14/8517.html

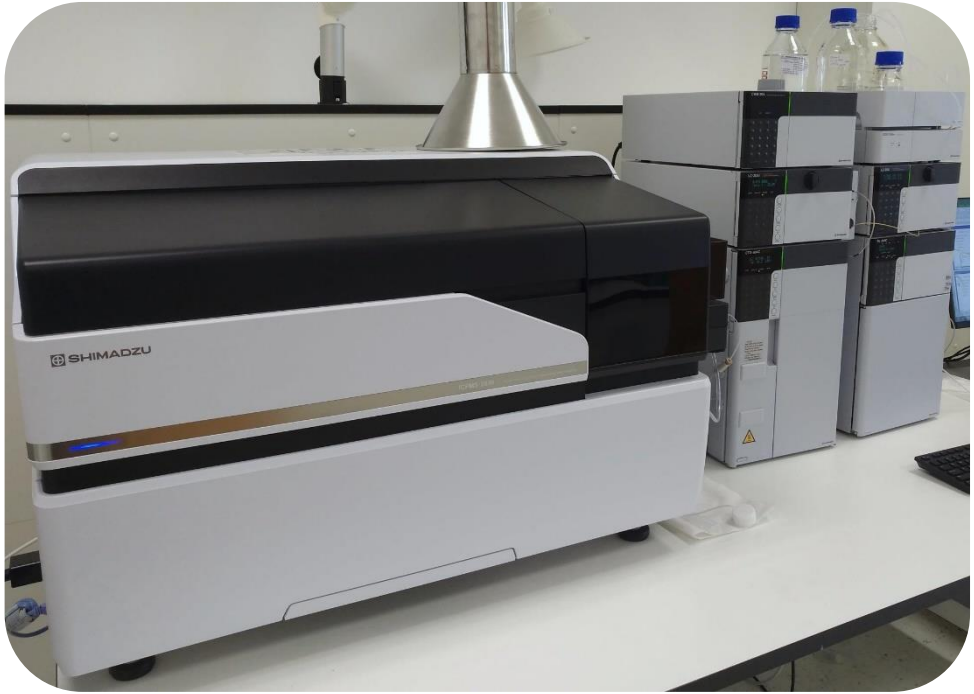
Cr Species in Toys (III)

- What is the standard analysis workflow?

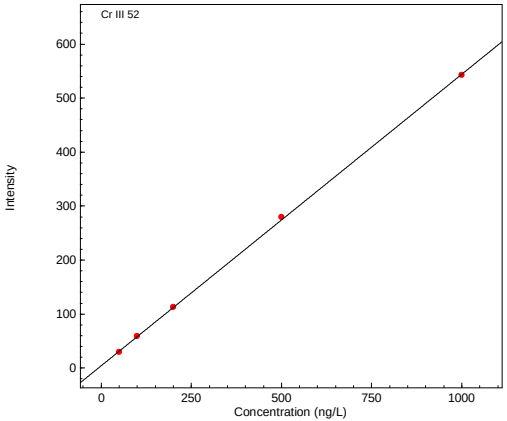
1. **Determine total Cr together with the other elements (almost no additional efforts)**
2. **Ensure total Cr is below toxic Cr(VI) limit, and the toy can enter the EU market**
3. **But if the content is above this trace level, speciation is necessary!**
   Otherwise the product cannot be approved.

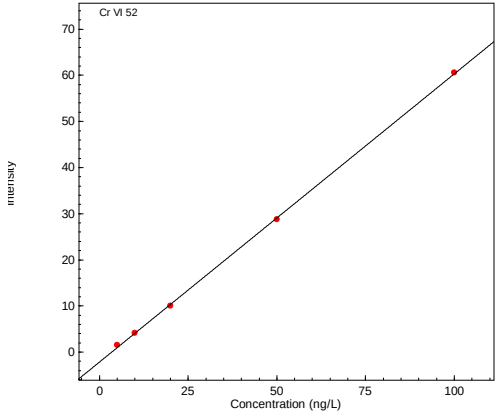
LC-ICPMS

- **Prominence Inert LC**
  - gradient or isocratic
- **ICPMS-2030**
- **LabSolutions ICPMS TRM Software**
  - Time resoled measurement
  - It controls both, LC and ICPMS including method parameters
  - Communication in both direction



Cr Speciation in Toys





Parameter	Setting
Mobile phase	30Mm Ammonium Nitrate(V) pH=7,1
Column	Hamilton PRP-X100, 250x4,1mm, 10µm

Parameter	Setting
RF generator power	1.2 kW
Plasma gas	8 l/min
Auxilliary gas	1,1 l/min
Carrier gas	0.75 l/min
Nebulizer	coaxial
Sampling depth	4.5 mm
Spray Chamber temperature	4 °C
Helium flow (collision)	4.4 ml/min
Cell Voltage	-10 V
Energy Filter	5.5 V

Arsenic Speciation in Rice

- **Over the past 10 yrs the global rice consumption increases**
- **Compared to other leading food crops, global rice production accounted 78% for human consumption**
  - whereat the rate is much lower for wheat (64%) or maize (14%)
- **COMMISSION REGULATION**
  - (EU) 2015/1006 of 25 June 2015 amending Regulation (EC) No 1881/2006 as regards maximum levels of inorganic arsenic in foodstuffs:

Rice type / intention of use	As_i [mk/kg]
Non-parboiled milled rice (polished or white rice)	0,20
Parboiled rice and husked rice	0,25
Rice waffles, rice wafers, rice crackers and rice cakes	0,30
Rice destined for the production of food for infants and young children ([3])	0,10’

Arsenic Species Toxicity

CHEMICAL SPECIES	DL50 (mg/kg)
Arsenite (As(III))	14
Arsenate (As(V))	20
Arsine (AsH3)	3
Monomethylarsonic Acid (MMA)	700 - 1800
Dimethylarsinic Acid (DMA)	700 - 2600
Arsenocholine	> 10000
Arsenobetaine	> 10000

DL50 rat: concentration leading to the death of 50 % of a rat population

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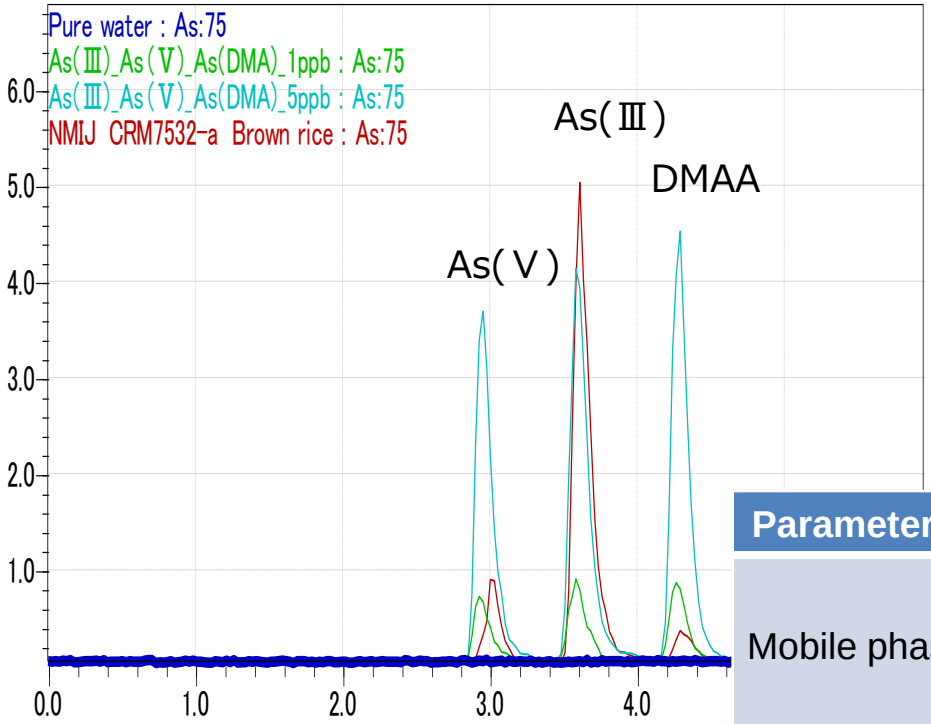
Arsenic Speciation in Rice



Parameter	Setting
RF generator power	1.2 kW
Plasma gas	8 l/min
Auxilliary gas	1,1 l/min
Carrier gas	0.6 l/min
Nebulizer	coaxial
Sampling depth	5.0 mm
Spray Chamber temperature	5 °C
Collision Cell Gas flow (Helium)	6.0 ml/min
Cell Voltage	-21 V
Energy Filter	7.0 V

Parameter	Setting
Mobile phase	10mM Sodium 1-butanesulfonate 4mM Tetramethylammonium hydroxide 4mM Malonic acid (pH=3) 0.05% Methanol
Column	Shiseido Capcell Pak C18 MG S5
Sample injection volume	20 µL

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Arsenic Speciation in Rice

- Recovery Rate within 100 +/- 2 %

Results in [mg/kg]		As(Ⅲ)	As(v)	DMAA
White Rice	Measurement Result (n=3)	0.0649	0.0203	0.0138
	Total Inorganic Arsenic	0.0852		-
	NMIJ Certified Value	0.0841		0.0133
	Recovery rate	**98.7 %**		**96.3 %**
Brown Rice	Measurement Result (n=3)	0.251	0.0511	0.0186
	Total Inorganic Arsenic	0.302		-
	NMIJ Certified Value	0.298		0.0186
	Recovery rate	**98.6 %**		**100%**
	RSD(%) (n=6)	1.1		2.6

Summary & Outlook

- If you want to learn more about your sample whether it is an industrial product, from environmental or any other source,

  → **speciation analysis will give additional answers e.g. on toxicity or mobility of the elements (species!) which are present.**

- As the scientiffic world spends a lot of time (publications) to this topic,

  → **speciation analysis will become more and more important in the future.**