National Food Institute

Technical University of Denmark DTU

Speciation issues in food control

– are we ready?

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National Food Institute (DTU Food)

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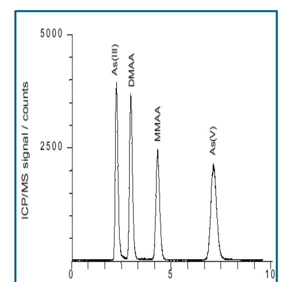


Agenda

- Speciation and food safety – where are we now??
- Haven't we heard about this before??
- Legislation and standardisation issues
- Selected examples

  - Arsenic speciation analysis

  - Organotin speciation analysis
- Are we ready??

…present situation in the food legislation (EU)

COMMISSION REGULATION (EC) No 1881/2006

of 19 December 2006

setting maximum levels for certain contaminants in foodstuffs

+ amendments

3.2	**Cadmium**	
3.2.1	Meat (excluding offal) of bovine animals, sheep, pig and poultry (6)	0,050
3.2.2	Horsemeat, excluding offal (6)	0,20
3.2.3	Liver of bovine animals, sheep, pig, poultry and horse (6)	0,50
3.2.4	Kidney of bovine animals, sheep, pig, poultry and horse (6)	1,0

etc

- only maximum levels for total amounts of Pb, Cd, Hg and Sn
- no regulation on trace element species

Speciation and regulation - some historical viewpoints

1998

ELSEVIER

Spectrochimica Acta Part B 53 (1998) 169–175

SPECTROCHIMICA ACTA PART B

Speciation analysis: where is it going? An attempt at a forecast[1]

Bernhard Welz

Department of Applied Research, Bodenseewerk Perkin-Elmer GmbH, D-

Fresenius J Anal Chem (1999) 363:431–434

CONFERENCE CONTRIBUTION

1999

Torsten Berg · Erik H. Larsen

Speciation and legislation – Where are we today and what do we need for tomorrow?

Handbook of Elemental Speciation II

Species in the Environment, Food, Medicine and Occupational Health

Editor-in-Chief Rita Cornelis

Associate Editors Joe Caruso, Helen Crews, Klaus Heumann

Speciation and the Emerging Legislation

Nicole Proust
THALES Research and Technology France, Orsay, France

Wolfgang Buscher
University of Münster, Münster, Germany

Michael Sperling
University of Münster, Münster, Germany

Wiley 2005

I-SECTION: FORUM

www.rsc.org/analyst | The Analyst

Toxic metal species and food regulations—making a healthy choice

2007

Kevin A. Francesconi

DTU

Vicious circle of progress

Toxicological evaluation
(Risk assessment)

Legislation
(Risk management)

Method development

Analytical data

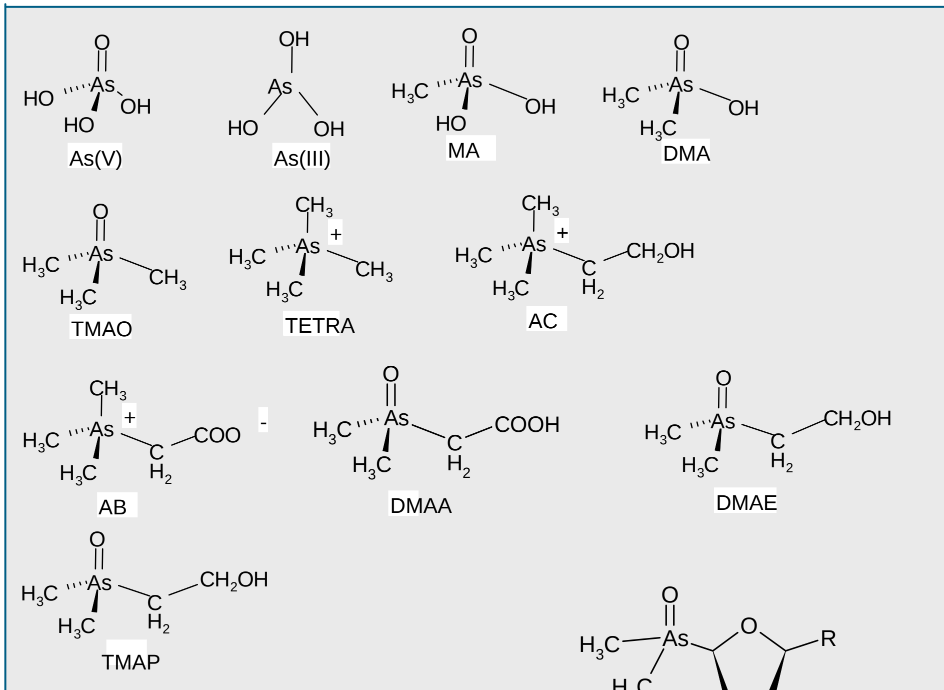
Examples

- Arsenic speciation analysis **HPLC-ICPMS**

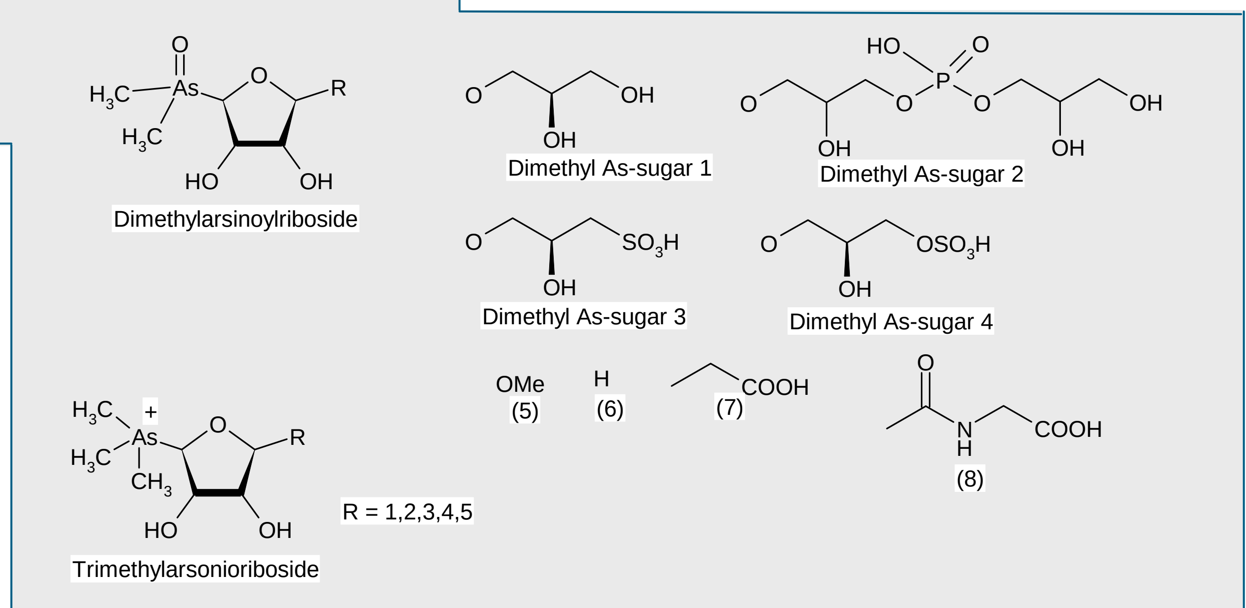
- Organotin speciation analysis **GC-ICPMS**

Food Contact Materials

Arsenic compounds in the marine environment



More than **50** different arsenic species have been found in the marine environment – incl lipid-soluble As compounds.

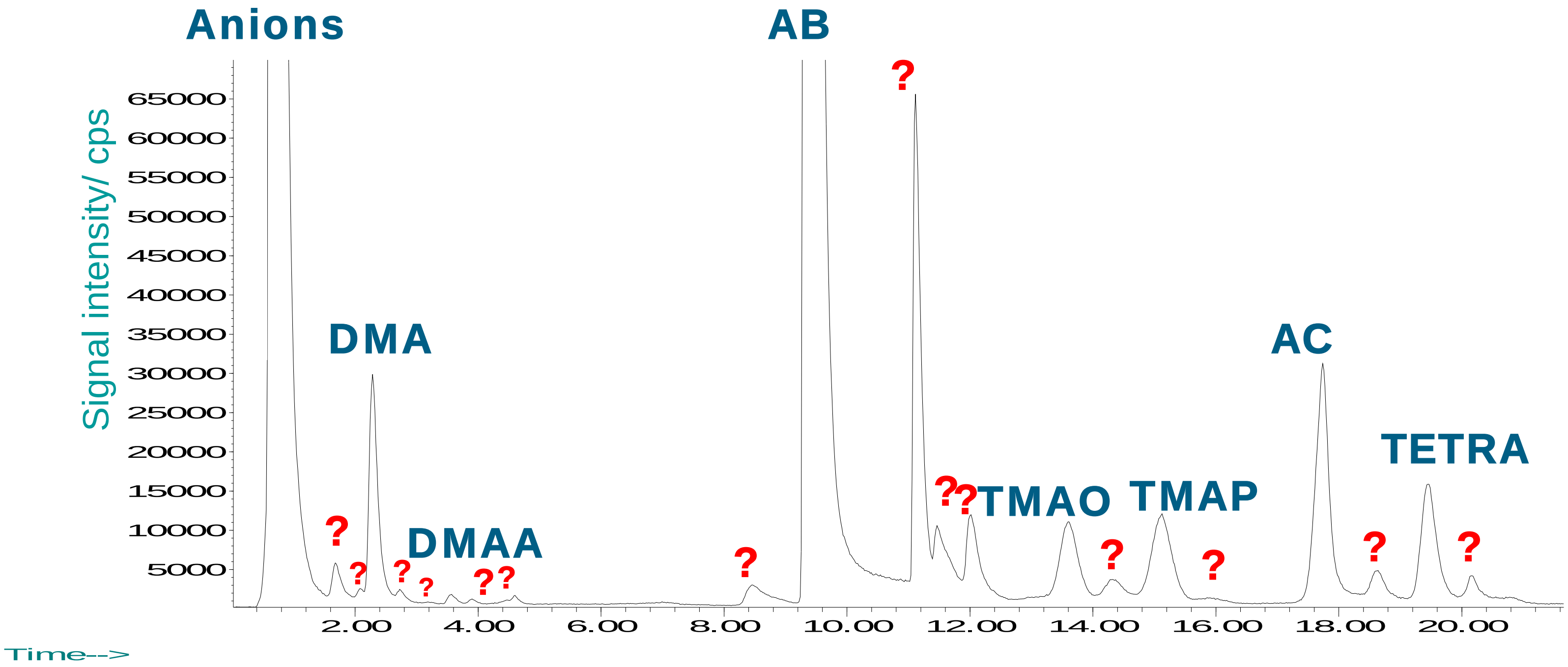


Speciation analysis of arsenic of scallop kidney

Cation-exchange with gradient elution – extraction with aqueous methanol

Column: Chrompack Ionospher 5C; Mobile phase: Pyridine; pH = 2.7

- seven compounds identified by coelution with available standards
- **16** non-identified peaks



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Sloth et al, JAAS, 2003, 18, 452-459

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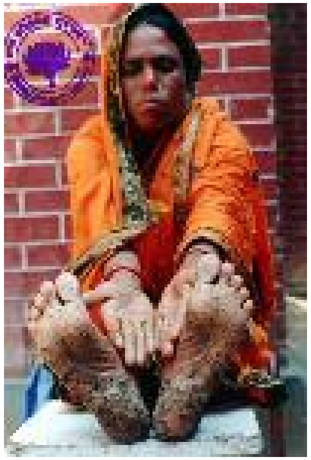
Arsenic – chronic toxicity



Long term exposure => skin diseases

- Keratosis, gangrene, melatosis
- Skin cancer

… and also

- lung, kidney, liver, bladder cancers
- Cancer slope factor: 1.5 (mg kg^{-1} day^{-1})$^{-1}$ (for inorganic As)
  (US EPA 2005)

WHO PTWI for inorganic arsenic: 15 µg/kg bw/week

(**P**rovisional **T**olerable **W**eekly **I**ntake)

For a 70 kg person => 150 µg / day

Analysis of inorganic arsenic in seafood samples

Microwave assisted alkaline hydrolysis

Subsample + extractant

⇩

Microwave treatment 20 min, 90°C

I: Solubilisation of sample matrix
II: Conversion of As(III) to As(V)

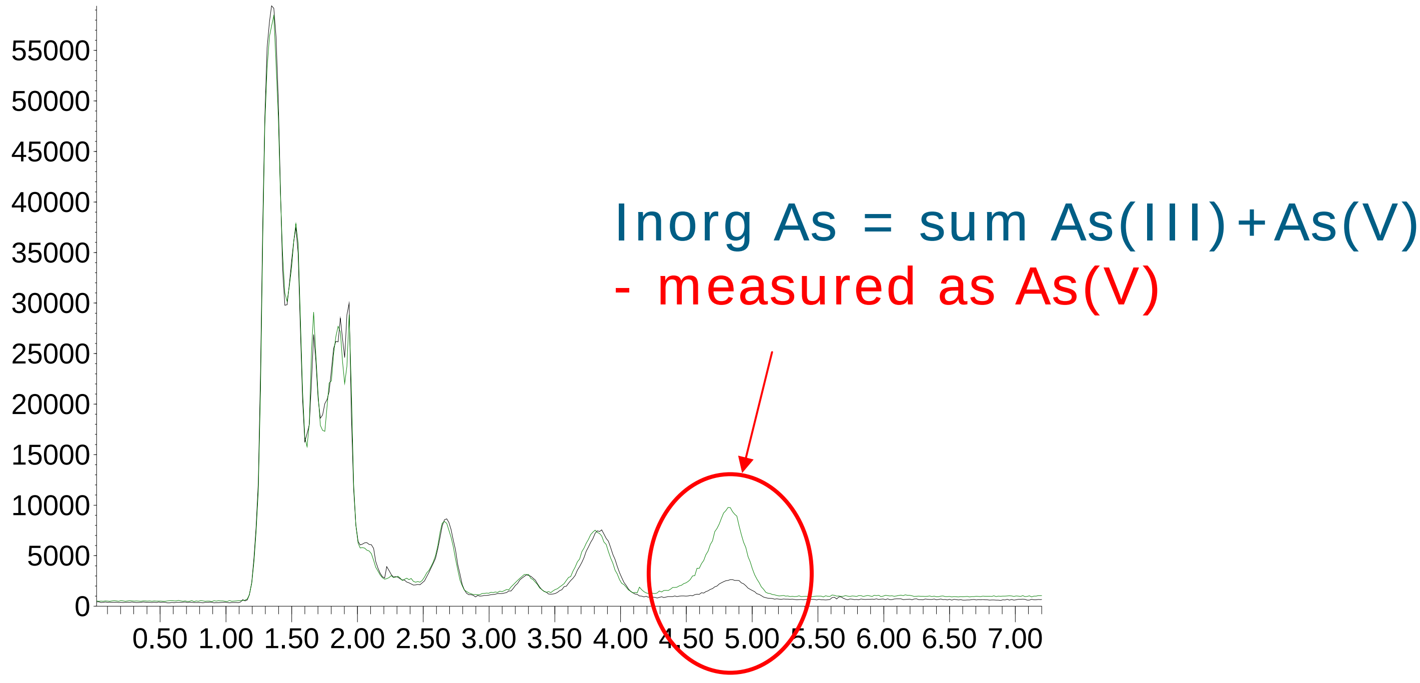
⇩

Determination of total inorganic arsenic as As(V) by anion-exchange HPLC-ICP-MS

- **No conversion of other arsenic compounds to inorganic arsenic**

Sloth et al, J. Agric. Food Chem., 2005, 53, 6011-6018

Analysis of inorganic arsenic by anion exchange HPLC-ICPMS



Blue mussel sample BCR278R

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Sloth et al, J.Agric.Food Chem., 2005, 53, 6011-6018

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Sloth et al, J.Agric.Food Chem., 2005, 53, 6011-6018

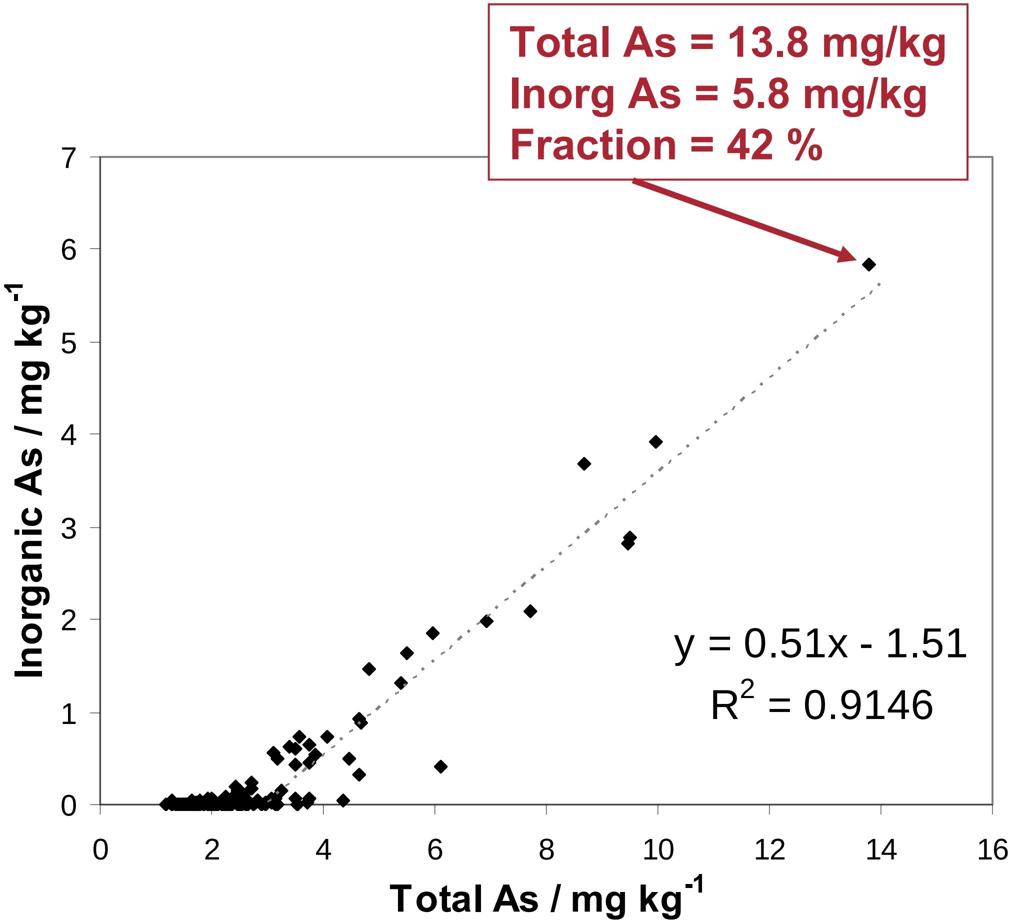
Sample identification	Inorganic arsenic	Total arsenic
Salmon (*Salmo salar*)	< 0.0006	1.9 ± 0.2
Cod (*Gadus morhua*)	< 0.0006	17 ± 2
Cod (*Gadus morhua*)	< 0.0006	15 ± 2
Wolffish (*Anarhichas lupus*)	< 0.0006	4.1 ± 0.5
Wolffish (*Anarhichas lupus*)	< 0.0006	31 ± 4
Anglerfish (*Lophius piscatorius*)	< 0.0006	15 ± 2
Anglerfish (*Lophius piscatorius*)	< 0.0006	44 ± 6
Atlantic halibut (*Hippoglossus hippoglossus*)	< 0.0006	12 ± 1
Mackerel (*Scomber scombrus*)	< 0.0006	1.7 ± 0.2
Mackerel (*Scomber scombrus*)	< 0.0006	2.8 ± 0.4
Herring (*Clupea harengus*)	< 0.0006	1.5 ± 0.2
Herring (*Clupea harengus*)	< 0.0006	1.7 ± 0.2
Herring (*Clupea harengus*)	< 0.0006	1.7 ± 0.2
Tuna fish (Thunnus alalunga)	0.008 ± 0.001	0.9 ± 0.1
Lobster, tail meat (*Homarus gammarus*)	< 0.0006	14 ± 2
Lobster, head and thorax meat (*Homarus gammarus*)	0.037 ± 0.005	22 ± 3
Crab, white meat (*Cancer pagurus*)	0.016 ± 0.002	32 ± 4
Crab, head and thorax meat (*Cancer pagurus*)	0.060 ± 0.009	26 ± 3
King crab, white meat (*Paralithodes camschaticus*)	0.005 ± 0.001	26 ± 3
Norway lobster (*Nephrops norvegicus*)	0.020 ± 0.003	21 ± 3
Shrimp (*Pandalus borealis*)	< 0.0006	3.8 ± 0.5
Shrimp (*Pandalus borealis*)	< 0.0006	60 ± 8
Shrimp (*Pandalus borealis*)	< 0.0006	[illegible]
Horse mussel (*Modilous modiolus*)	0.0012 ± 0.002	3.4 ± 0.4
Scallop muscle (*Pecten maximus*)	0.008 ± 0.001	3.1 ± 0.3
Oyster (*Ostrea edulis*)	0.014 ± 0.002	1.8 ± 0.2
Mink whale (*Balaenoptera Acutorostrata*)	< 0.0006	0.61 ± 0.08
Harp seal (*Pagophilus groenlandicus*)		0.9 ± 0.1
Hooded seal (*Cystophora cristata*)		0.22 ±0.03

Fish muscle

Crustaceans & bivalves

Marine mammals

For all samples inorganic arsenic constitutes less than 1% of total arsenic



Data from 175 blue mussel (*Mytilus edulis*) samples collected along the Norwegian Coastline.

Sloth and Julshamn 2008, J. Agri.Food Chem., 56, 1269-1273

Arsenic in rice – an emerging health issue?

Commentary Environmental Pollution 154 (2008) 169–171

Exposure to inorganic arsenic from rice: A global health issue?☆

Yong-Guan Zhu[a,b,*], Paul N Williams[a,c], Andrew A Meharg[c,**]

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FOOD SAFETY

Arsenic and Paddy Rice: A Neglected Cancer Risk?

11 JULY 2008 VOL 321 SCIENCE www.sciencemag.org

–RICHARD STONE

Arsenic in rice – an emerging health issue?

ER

Environmental Pollution 152 (2008) 746–749

Rapid communication

Inorganic arsenic levels in baby rice are of concern

Andrew A. Meharg [a,*], Guoxin Sun [b], Paul N. Williams [a,b], Eureka Adomako [a], Claire Deacon [a], Yong-Guan Zhu [b], Joerg Feldmann [c], Andrea Raab [c]

[a] School of Biological Sciences, University of Aberdeen, Cruickshank Building, St. Machar Drive, Aberdeen AB24 3UU, UK
[b] Research Centre for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

Median consumption of organic arsenic levels for UK babies from baby rice is above threshold considered safe.

- 17 samples from supermarkets in Aberdeen
- Total arsenic levels: 0.12 – 0.47 mg/kg
- Inorganic
- 35% abo

COMMUNICATION www.rsc.org/jem | Journal of Environmental Monitoring

Inorganic arsenic levels in rice milk exceed EU and US drinking water standards

Andrew A. Meharg,[a] Claire Deacon,[a] Robert C. J. Campbell,[a] Anne-Marie Carey,[a] Paul N. Williams,[a] Joerg Feldmann[b] and Andrea Raab[ab]

- 19 rice milk samples from supermarkets
- EU drinking water ML: 10 µg/L total As (100% of samples exceeded)
- US drinking water ML: 10 µg/L iAs (80% of samples exceeded)

Commission Directive 2003/100/EC on animal feed

Undesirable substances	Products intended for animal feed	Maximum content in mg/kg (ppm) relative to a feedingstuff with a moisture content of 12 %
(1)	(2)	(3)
'1. Arsenic ([8])	Feed materials with the exception of:	2
	— meal made from grass, from dried lucerne and from dried clover, and dried sugar beet pulp and dried molasses sugar beet pulp	4
	— palm kernel expeller	4 ([9])
	— phosphates and calcareous marine algae	10
	— calcium carbonate	15
	— magnesium oxide	20
	— feedingstuffs obtained from the processing of fish or other marine animals	15 ([9])
	— seaweed meal and feed materials derived from seaweed	40 ([9])
	Complete feedingstuffs with the exception of:	2
	— complete feedingstuffs for fish and complete feedingstuffs for fur animals	6 ([9])
	Complementary feedingstuffs with the exception of:	4
	— mineral feedingstuffs	12

Max levels for total arsenic

([9]) Upon req… inorganic … ıonstrate that the content of … es *Hizikia fusiforme*.'

Footnote in the Commission directive

Total arsenic in fish feed products

33% > ML

Product	N	Median	Mean	SD	Range
Complete feedingstuffs		5.87	5.80	1.17	3.40 - 8.34
Fish meal	10	7.93	7.70	4.00	3.62 - 18.2
Fish oils	6	11.30	11.17	1.81	

10% > ML

Results in mg kg^{-1}

ML = 15 mg As / kg
Marine feed ingredients

ML = 6 mg As / kg
Complete feedingstuffs

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Sloth et al, Aquaculture Nutr., 2005, 11, 61-66

Inorganic arsenic in fish feed products

Product	N	Range	% of total As
Complete Feedingstuffs	13	10 - 61	0.18 - 1.20
Fish meal	10	All < 7	-

Results in µg kg^{-1}

Sloth et al, Aquaculture Nutr., 2005, 11, 61-66

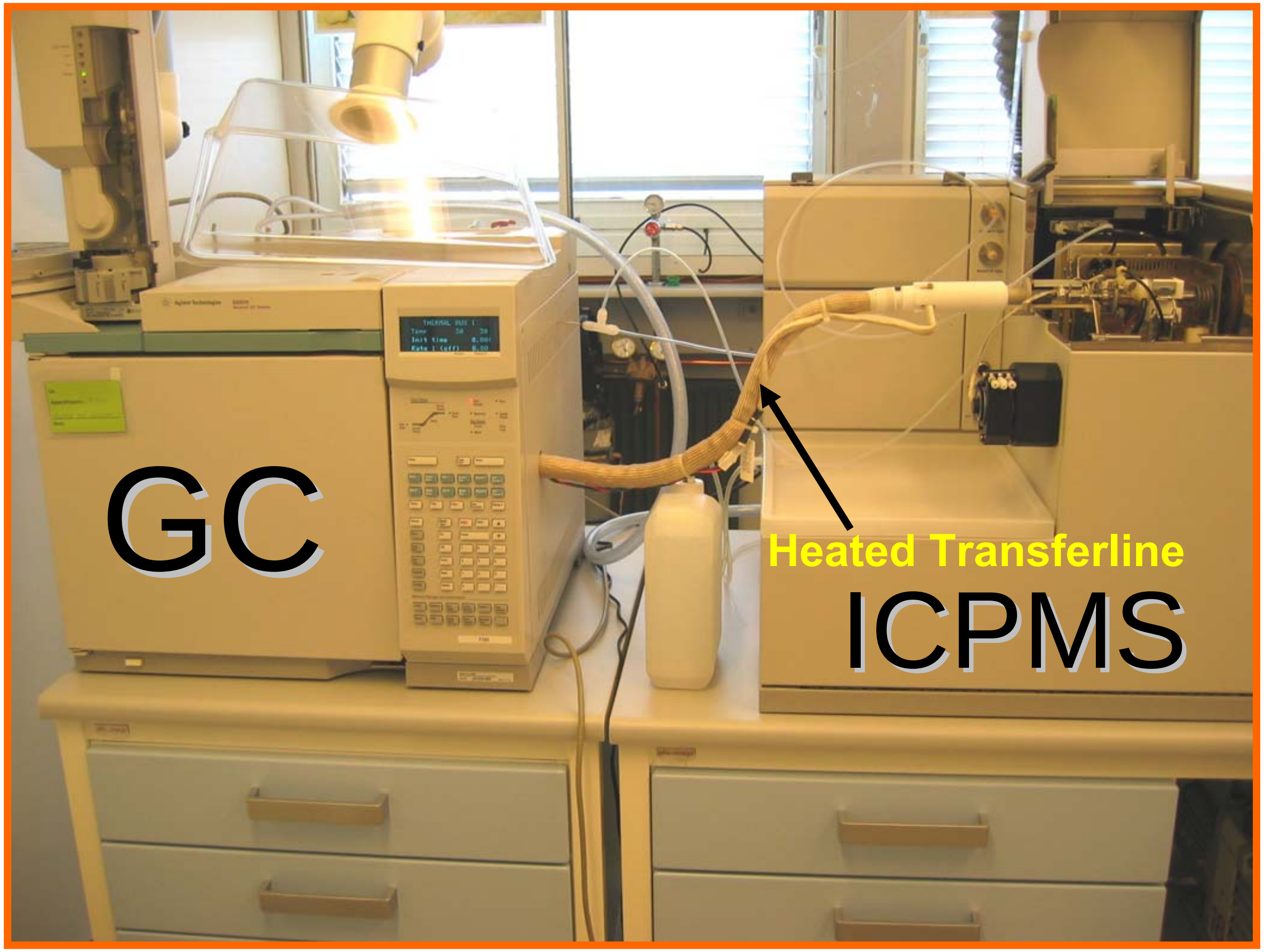
Arsenic and food/feed control – present status

- Food – no maximum levels etablished
- Feed – maximum levels for total arsenic

- EFSA opinion on arsenic in food – expected in 2009

- CEN (European Standardisation Organisation)
  - TC327 WG4 Feedingstuffs (Heavy metals and minerals)
  - TC275 WG10 Foodstuffs (Trace elements)

Organotin speciation by GC-ICPMS



Routes of exposure to organotin compounds

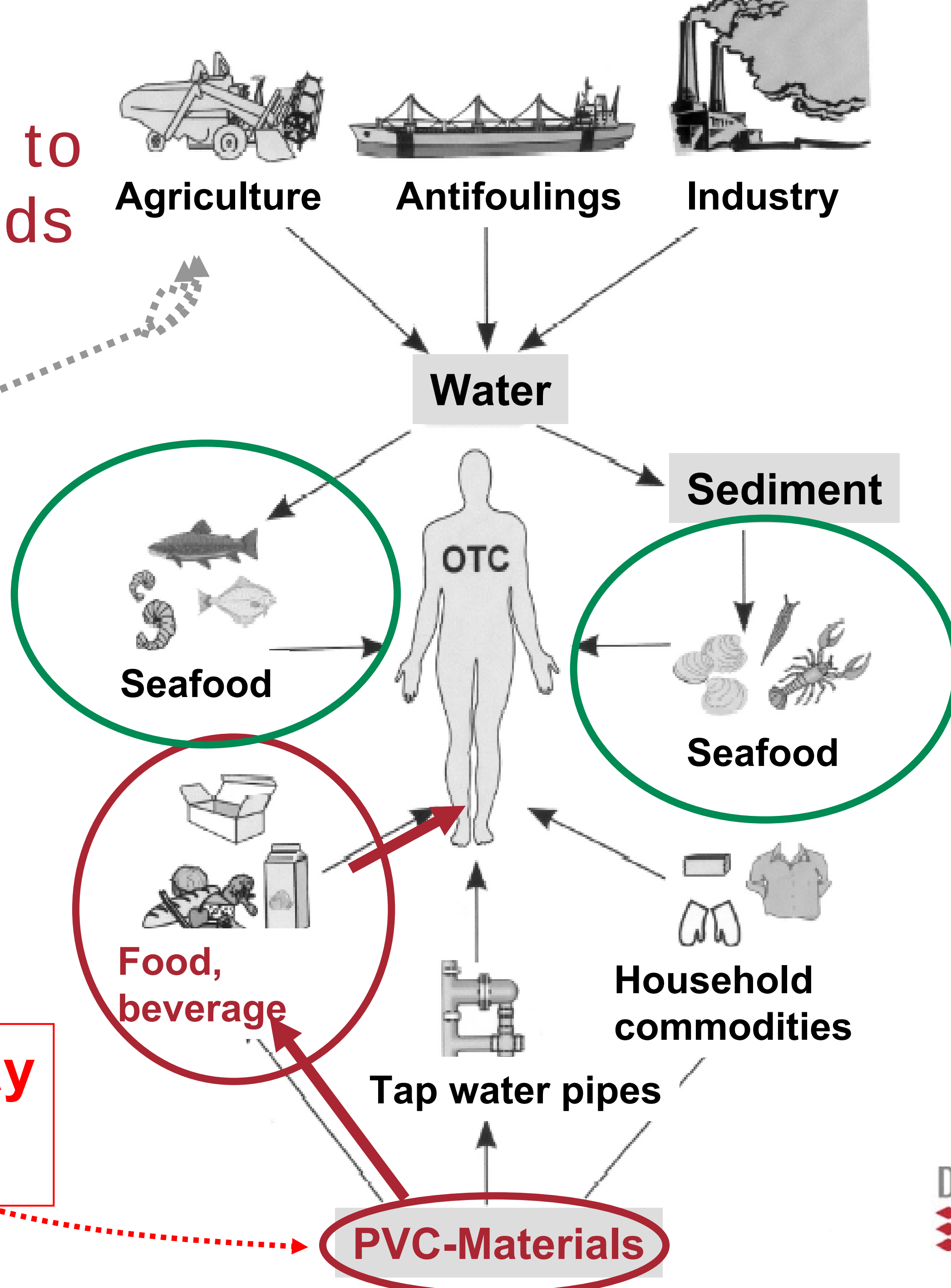
Used in

- **Agriculture**
- **Antifoulings**
- **Industry**

- **PVC-Materials**

TDI: 0.25 µg/kg bw/day

∑TBT, DBT, TPhT and DOT



Hoch, Appl. Geochem., 2001, 719-43

Legislation on OTCs in Food Contact Materials

Compounds	Maximum level (µg Sn/kg foodstuff)
$\sum$DBT, TBT, TPhT and DOT	40 (6)
$\sum$MMT, DMT	180
MOT	1200
MDDT	12000 (50)
DDDT	24000 (50)

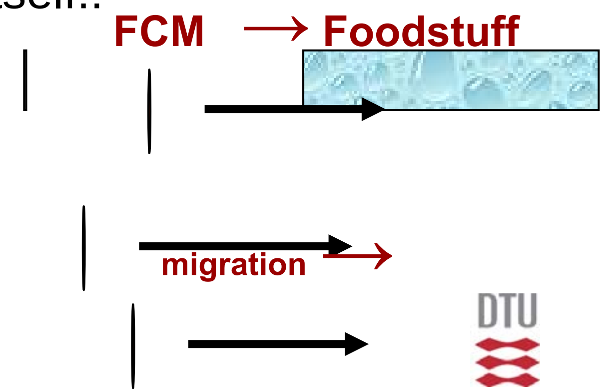
Ref: EFSA (2005); proposed EFSA values in parenthesis

Assumptions:

- 1 kg food per 6 dm^2

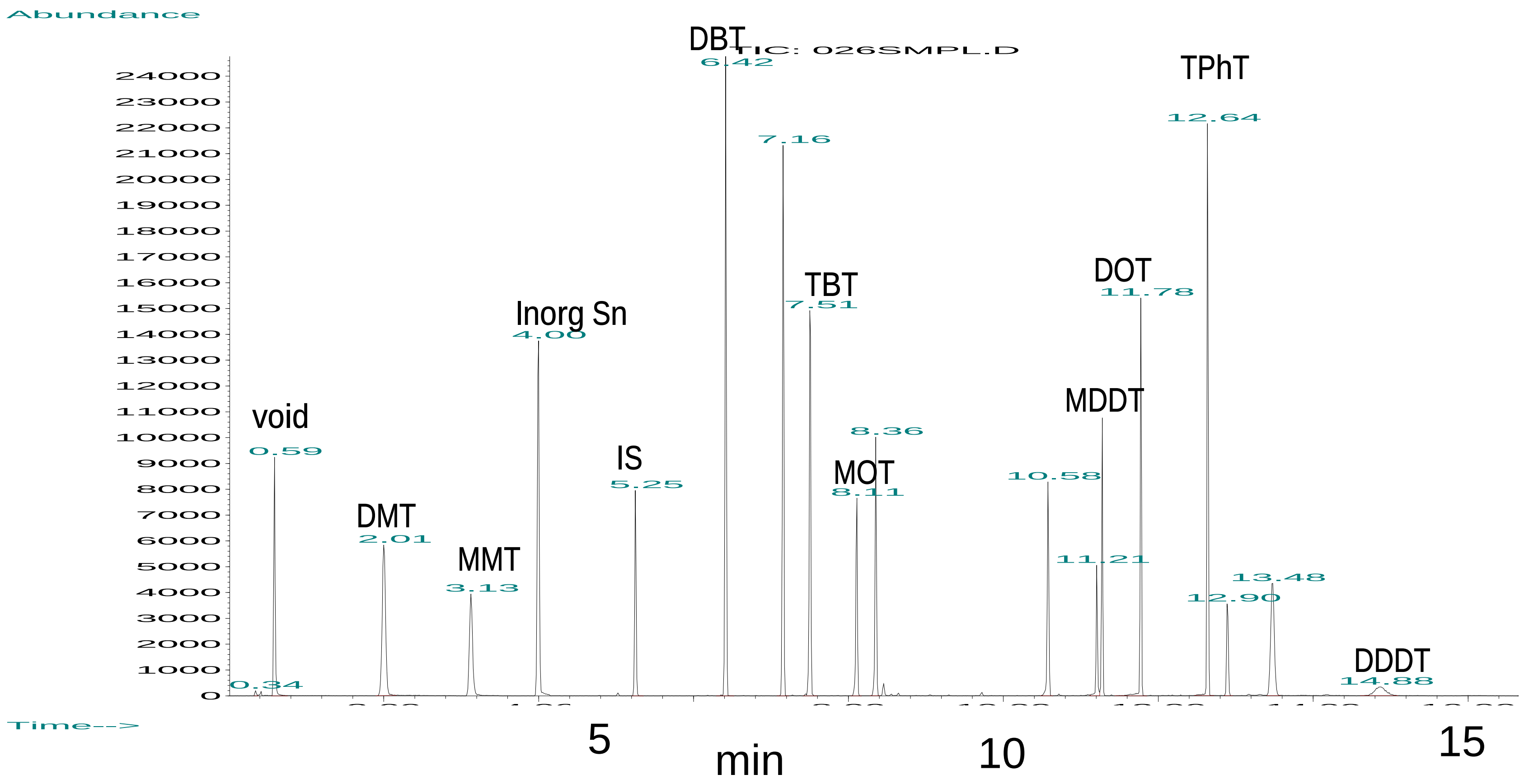
- 100 mL in contact with 0.6 dm^2

- Max levels on organotin migrating from the packaging material
- Testing by the use of food simulators (water, acid, oil, alcohol etc)
- BUT no maximum levels on organotins in the foodstuff itself!!



Organotin migration from Food Contact Materials I

- Chromatogram of 9 standards + IS

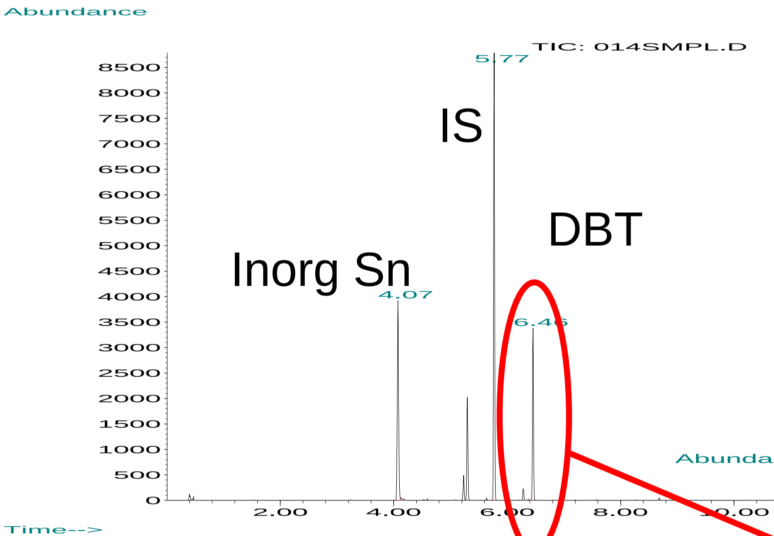


Organotin migration from Food Contact Materials II

Small scale survey on 33 FCMs

Baking paper, PVC cling films, silicone baking forms, lids with PVC gaskets

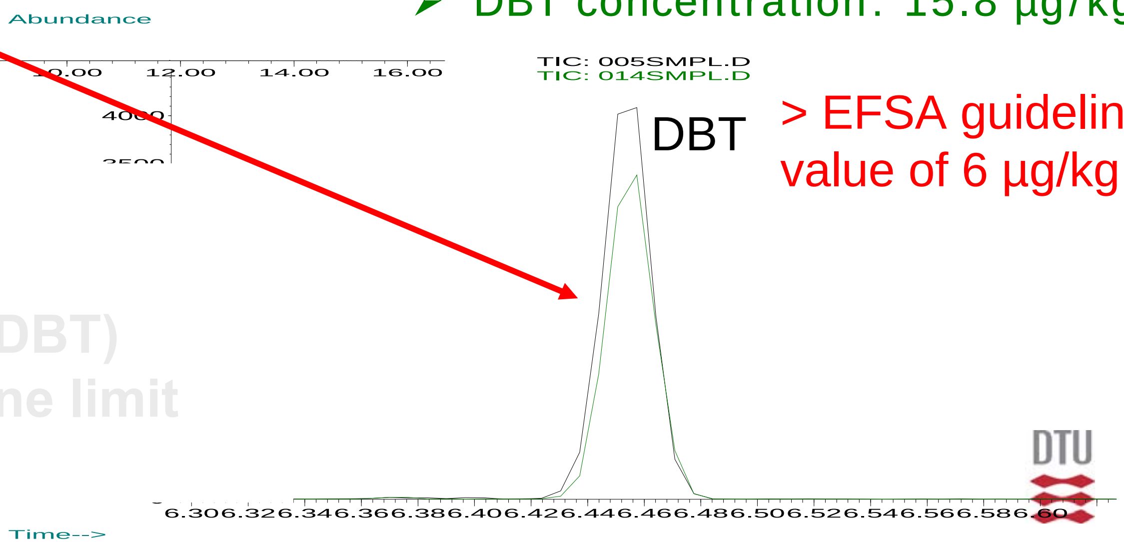
PUR-agglomerated cork wine stoppers



- PVC lid
- 3% acetic acid

Overlaid standard and sample

- ➢ DBT concentration: 15.8 µg/kg



> EFSA guideline value of 6 µg/kg

Output of DK survey:

-33 samples

-11 contained OT (mainly DBT)

-3 exceeded EFSA guideline limit

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…so are we ready or what??

- ✓ speciation methods are more and more commonly used
- ✓ instrumentation is widely available
- ✓ legislation on species has started
- ✓ …and more is expected in the future!

- ✓ standardised methods are not ready!
- ✓ …but the need is known by authorities
- ✓ legislation is still behind!
- ✓ Lack of CRMs (e.g. for iAs)

...so are we ready or what?

Toxicological evaluation
(Risk assessment)

Legislation
(Risk management)

Method development

Analytical data

...has the circle been broken??

Acknowledgements

Coworkers:

Rikke V. Hedegaard, Birgitte Koch Herbst, Marianne Hansen

Xenia T. Trier and Erik H. Larsen

Kåre Julshamn, Heidi Amlund

Siri Bargaard and A.K. Lundebye

Funding:

EU FP7 CONffIDENCE

CEN TC327

Danish Food Administration

Norwegian Research Council

THANKS FOR YOUR ATTENTION !!