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Publication date:
2012

Document Version
Publisher's PDF, also known as Version of record

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Citation (APA):

Sloth, J. J., Trier, X., Loeschner, K., & Larsen, E. H. (2012). ICPMS as an element-specific detector for the analysis of trace element species and nanoparticles [Sound/Visual production (digital)]. Danish Society for Mass Spectrometry Meeting 2012, Svendborg, Denmark, 01/01/2012, <http://www.dsms.dk/>

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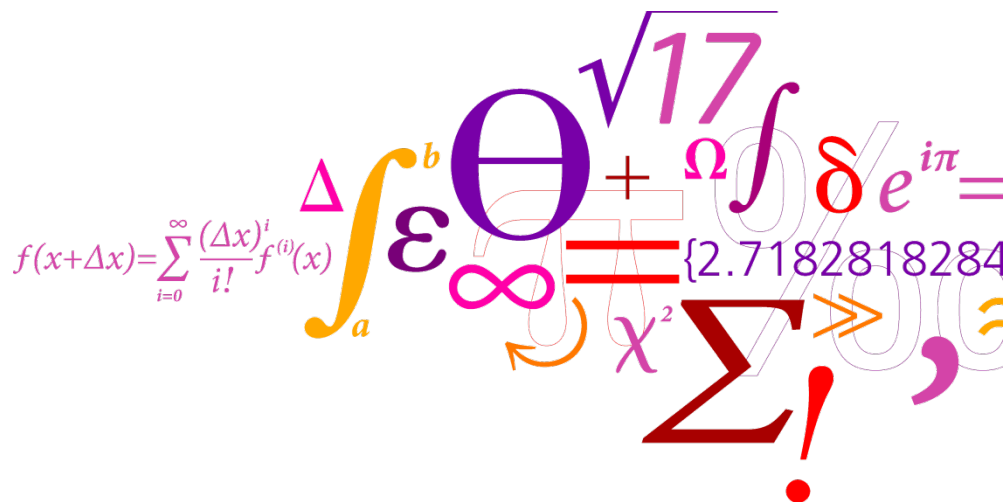
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ICPMS as an element-specific detector for the analysis of trace element species and nanoparticles

Jens J. Sloth

Xenia Trier, Katrin Loeschner and Erik H. Larsen



Inductively Coupled Plasma Mass Spectrometry

ICPMS



ICP-MS (Inductively coupled plasma mass spectrometry) is a type of mass spectrometry that is **highly sensitive** and capable of the determination of **a range of metals and several non-metals** at concentrations below one part in 10^{12} (ppt). It is based on coupling together an inductively coupled plasma as a method of producing ions (ionization) with a mass spectrometer as a method of separating and detecting the ions. ICP-MS is also capable of monitoring **isotopic speciation** for the ions of choice.

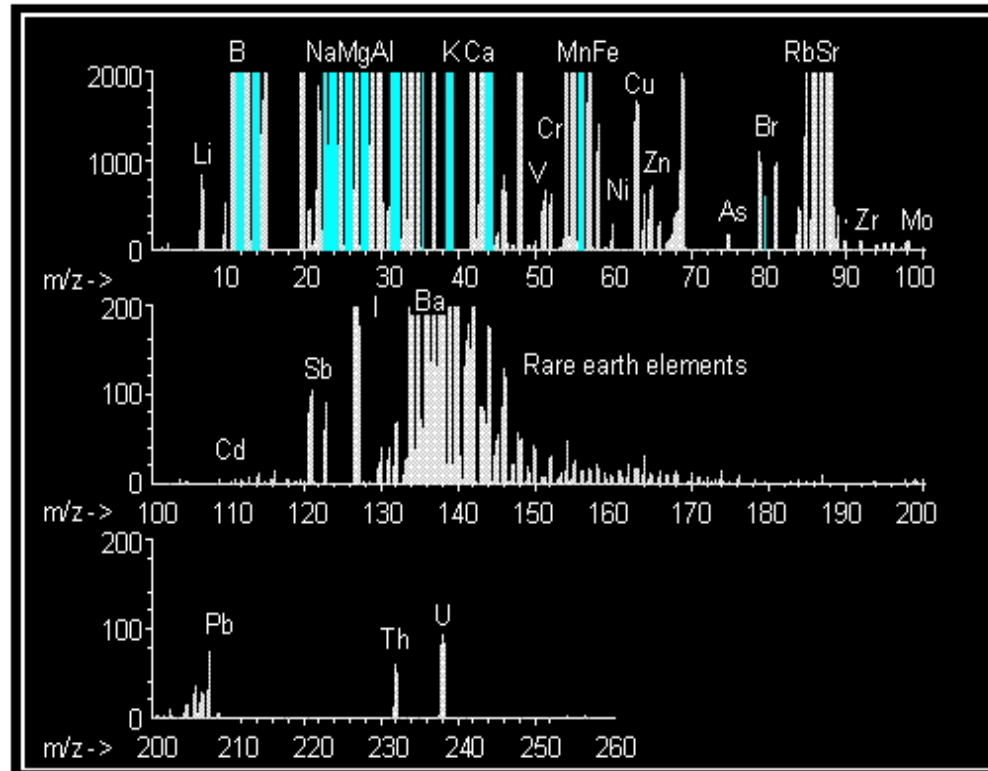
Keywords:

- High sensitivity
- Multielement analysis
- Isotopic speciation



Agilent ICPMS 7500ce

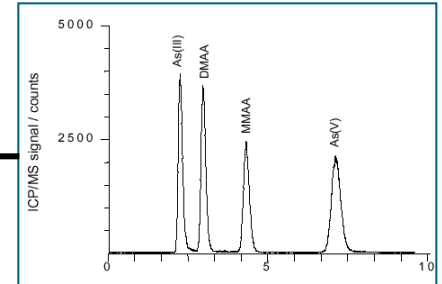
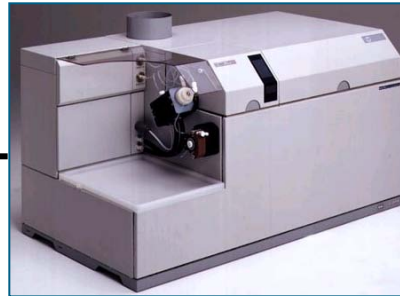
Mass spectrum – isotopic pattern of the elements



ICPMS working range is from 6-250 m/z
From lithium to uranium

Speciation analysis of elements

Workhorse: HPLC-ICPMS (or GC-ICPMS)



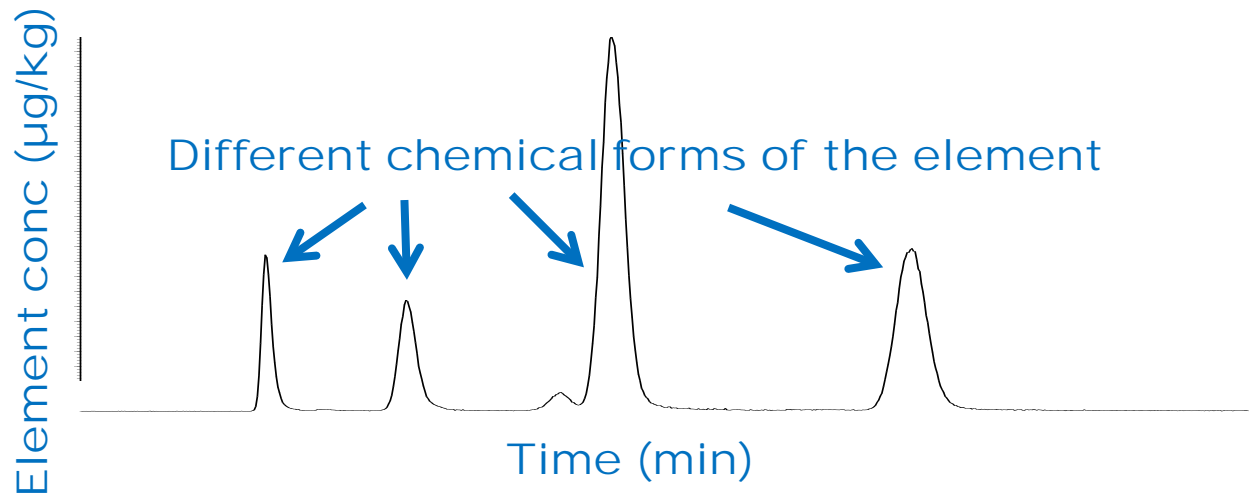
HPLC/GC
Sample introduction

Column
Separation

ICPMS
Element specific detection

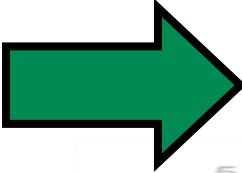
Result
Chromatogram

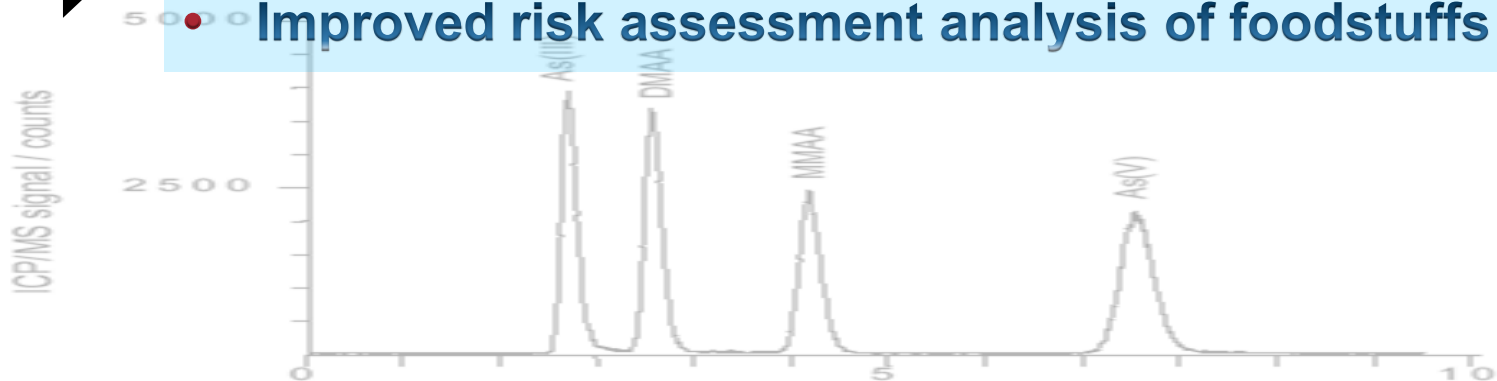
Output:
Element-specific
chromatogram



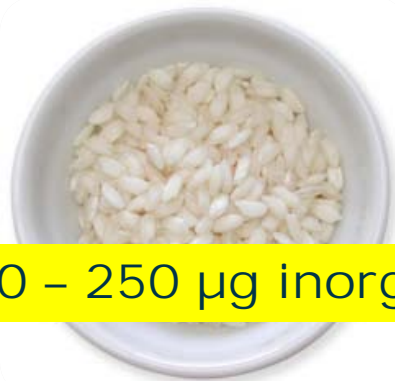
EXAMPLES

- Arsenic speciation analysis by HPLC-ICPMS
- Organotin speciation analysis by GC-ICPMS
- Nanoparticle determination by FFF-MALS-ICPMS

- 
- Beyond total element determination
 - Species-specific information
 - Improved risk assessment analysis of foodstuffs



Example – arsenic speciation analysis Important for correct risk assessment



~ 40 – 250 μg inorg As

1 kg rice => 50-300 μg As



<10 μg inorg As

1 kg fish => 3000-10000 μg As

There is most focus on rice from a food safety point of view – why???



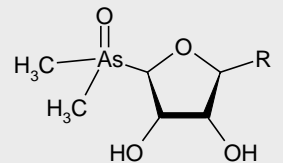
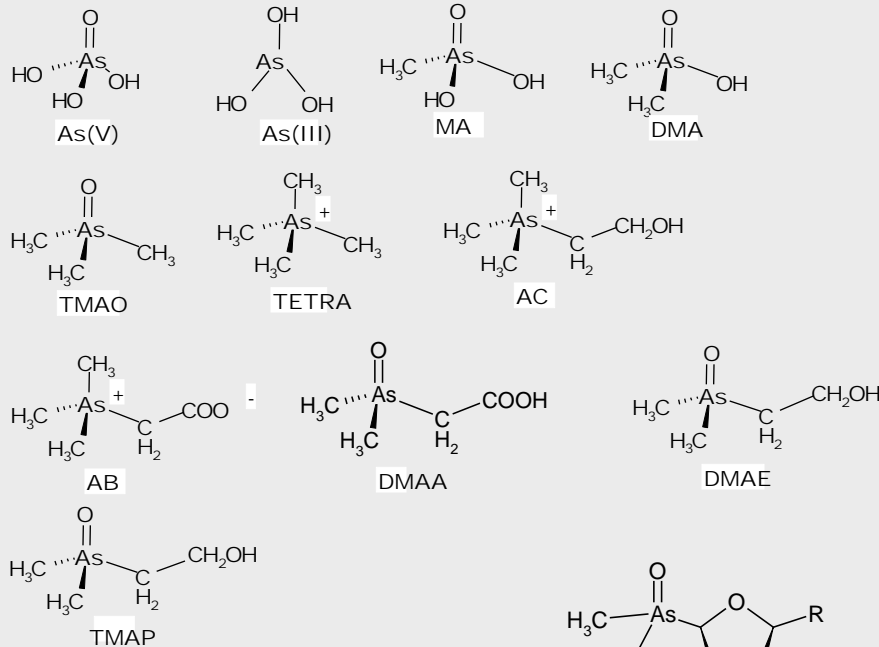
The chemical form of arsenic is important
=> Arsenic speciation



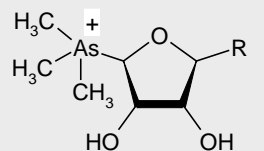
Focus
on
Food
Safety

Arsenic compounds in the marine environment

More than **50** different arsenic species have been found in the marine environment

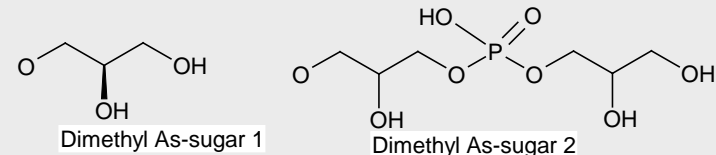


Dimethylarsinoylribose



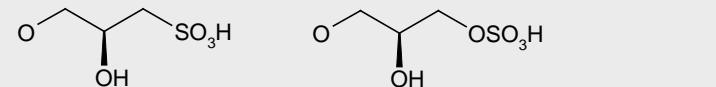
R = 1,2,3,4,5

Trimethylarsonioriboside



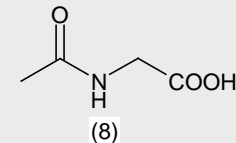
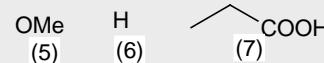
Dimethyl As-sugar 1

Dimethyl As-sugar 2



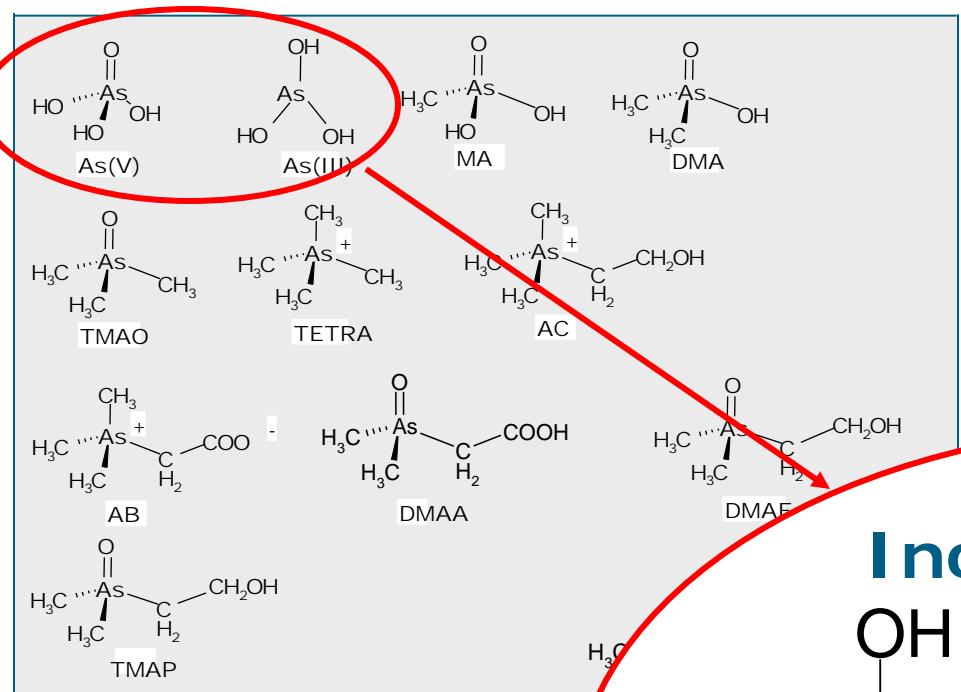
Dimethyl As-sugar 3

Dimethyl As-sugar 4

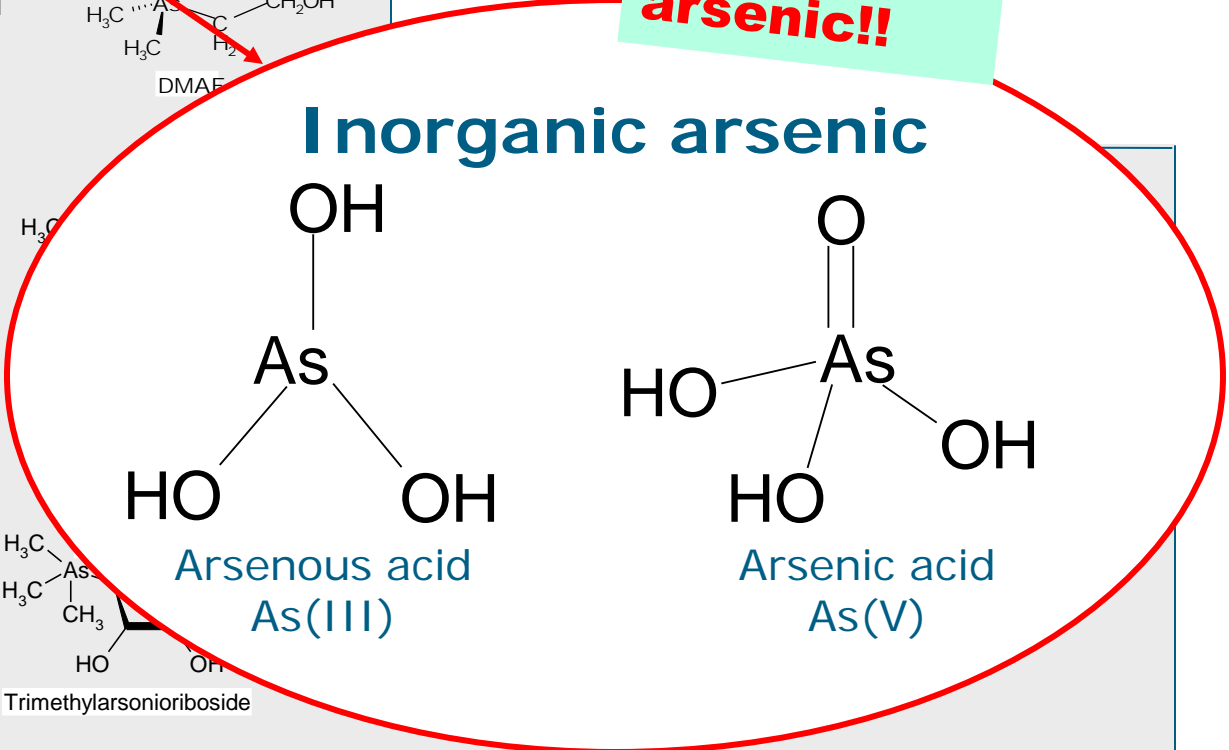


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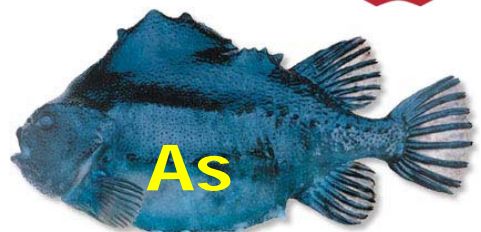
Arsenic compounds in the marine environment



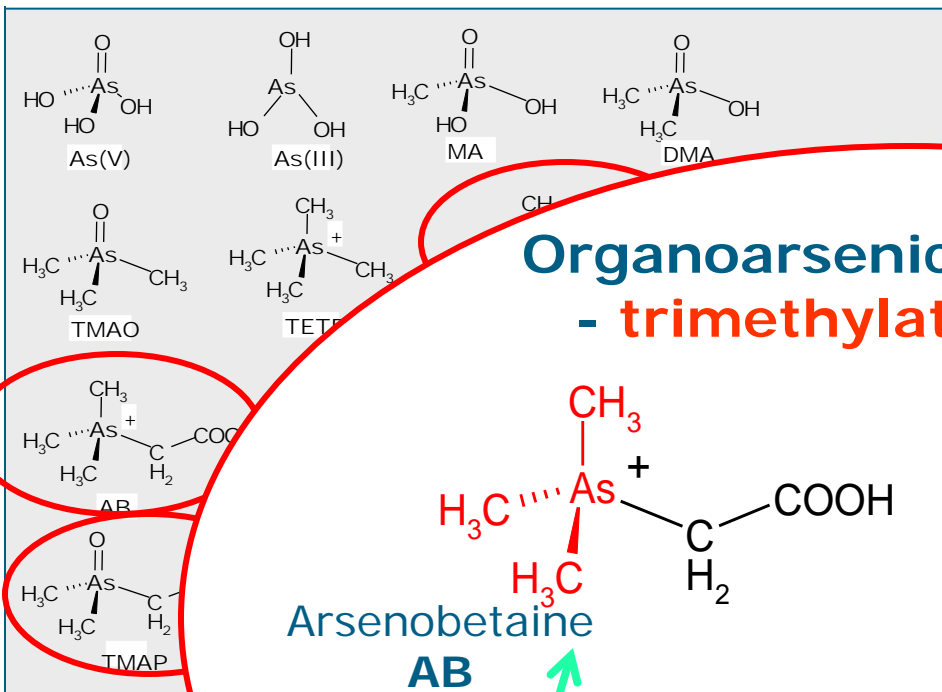
Most toxic form of arsenic!!



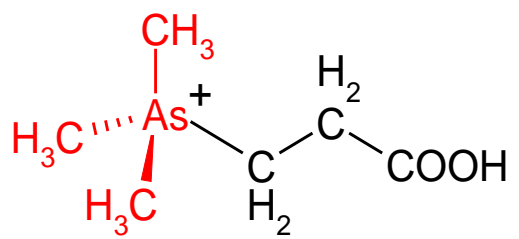
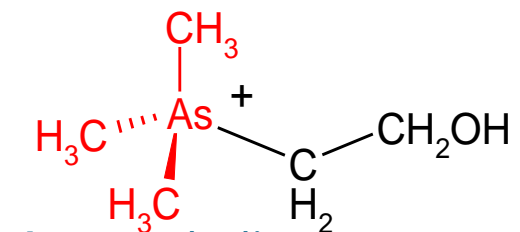
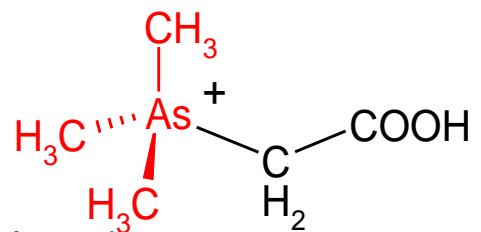
Arsenic compounds in the marine environment



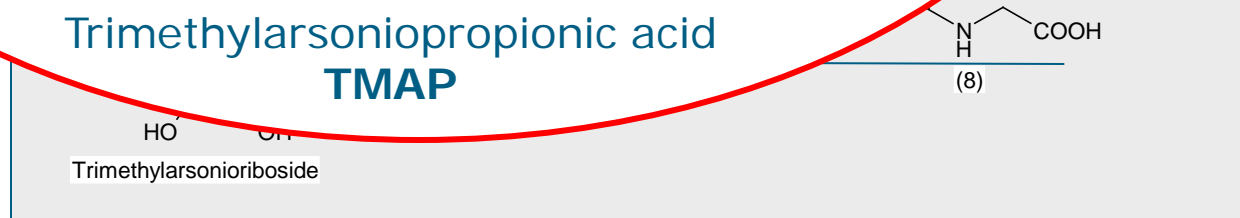
AB="fish arsenic"



Organoarsenic compounds - trimethylated species



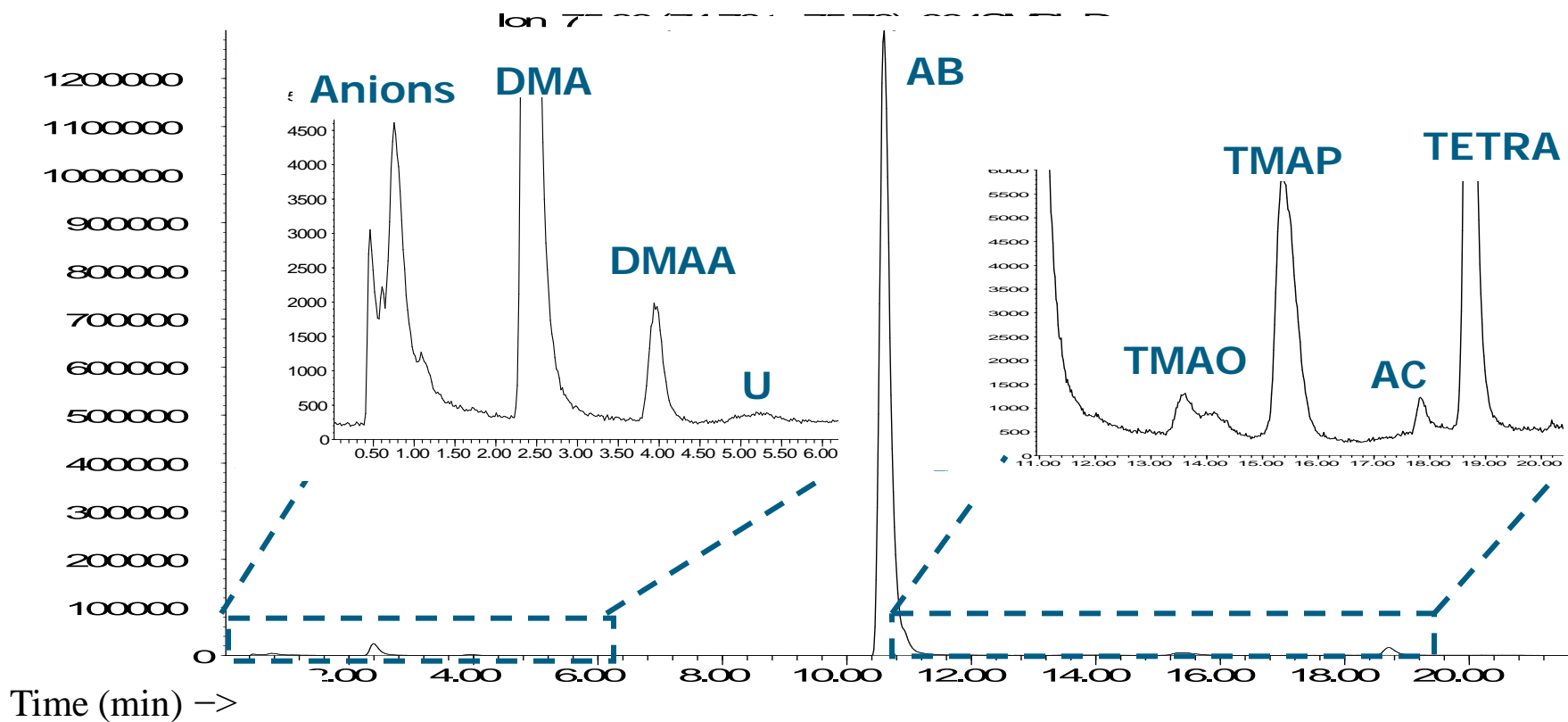
Predominant form of arsenic in most seafood!!



Arsenic speciation in fish muscle by HPLC-ICPMS

Cation-exchange chromatogram of a MeOH/H₂O extract of CRM DORM-2

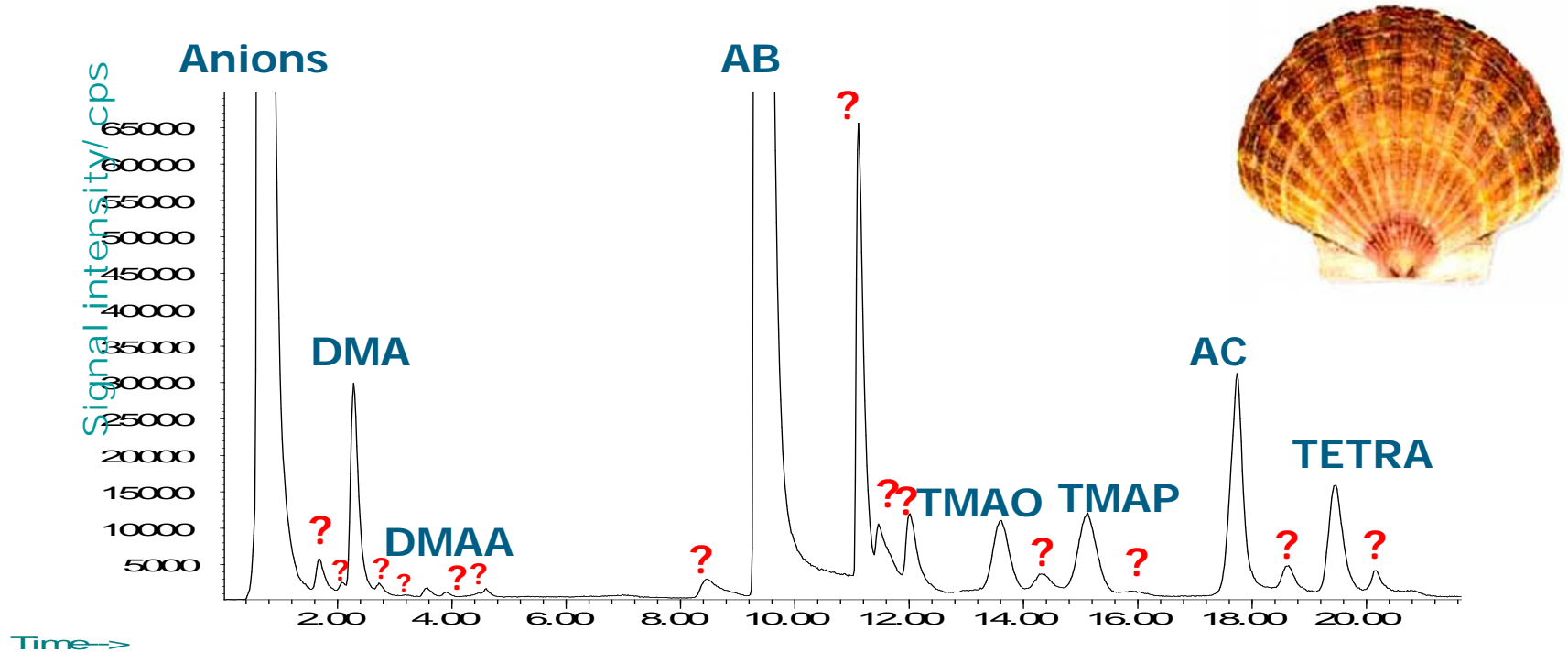
Column: Chrompack Ionospher 5C; Mobile phase: Pyridine; pH = 2.7



Speciation analysis of arsenic of scallop kidney

Cation-exchange with gradient elution – extraction with aqueous methanol (50%)
 Column: Chrompack Ionospher 5C; Mobile phase: Pyridine; pH = 2.7

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



? = unknowns (limitation of ICPMS detection)

EFSA (2009) and JECFA (2010) opinions on arsenic in food

=> Risk assessments of dietary arsenic exposure

FOCUS ON INORGANIC ARSENIC



- **NEW!** $\text{BMDL}_{1.0} = \underline{0.3 - 8 \mu\text{g/kg bw per day}}$ for **inorganic arsenic**
- => *EU dietary exposures within this range for average and high level consumers*
- => *Risk to some consumers cannot be excluded*



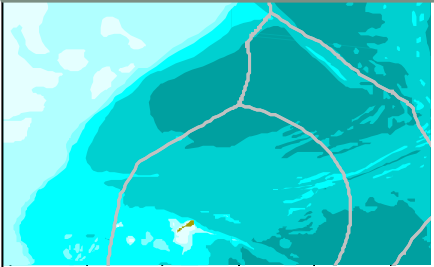



- **NEW!** $\text{BMDL}_{0.5} = \underline{3 \mu\text{g/kg bw per day}}$ for **inorganic arsenic**
- => *0.5% increased incidence of lung cancer for 12 y exposure*

“...there is a need to produce **speciation data** for different food commodities to support dietary exposure assessment...”

“...more accurate information on **the inorganic arsenic content** of foods is needed to improve assessments of dietary exposures to inorganic arsenic”

Inorganic arsenic in wild caught fish => no concern

iAs analysed by HPLC-ICPMS

Norwegian survey

900 individual fish samples

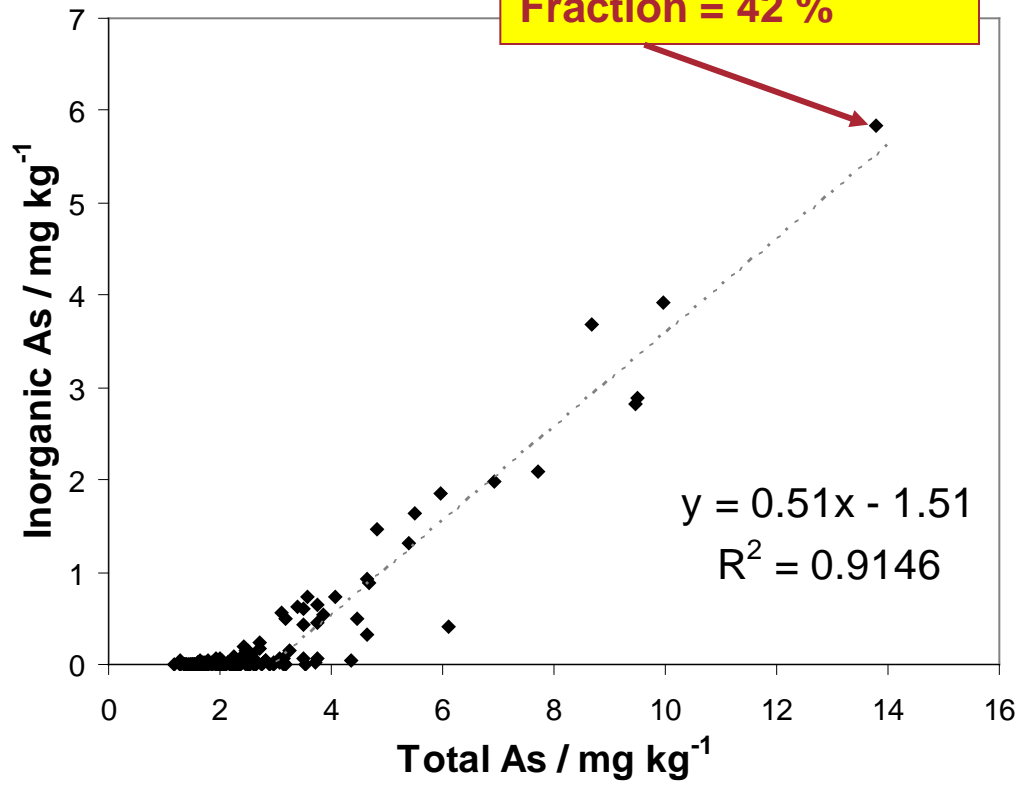
- Atlantic halibut
- Cod
- Greenland halibut
- Mackerel
- Herring
- Tusk

Results
 Total arsenic.....0.3-110 mg/kg
 Inorganic arsenic.... < 0.01 mg/kg
(only 37 samples > LOQ)

...but in bivalves high contents in some samples...

iAs analysed by HPLC-ICPMS

**Total As = 13.8 mg/kg
Inorg As = 5.8 mg/kg
Fraction = 42 %**



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



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

COMMUNICATION

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

- Inorganic arsenic levels in rice milk exceed EU and US drinking water standards
- 35%

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}

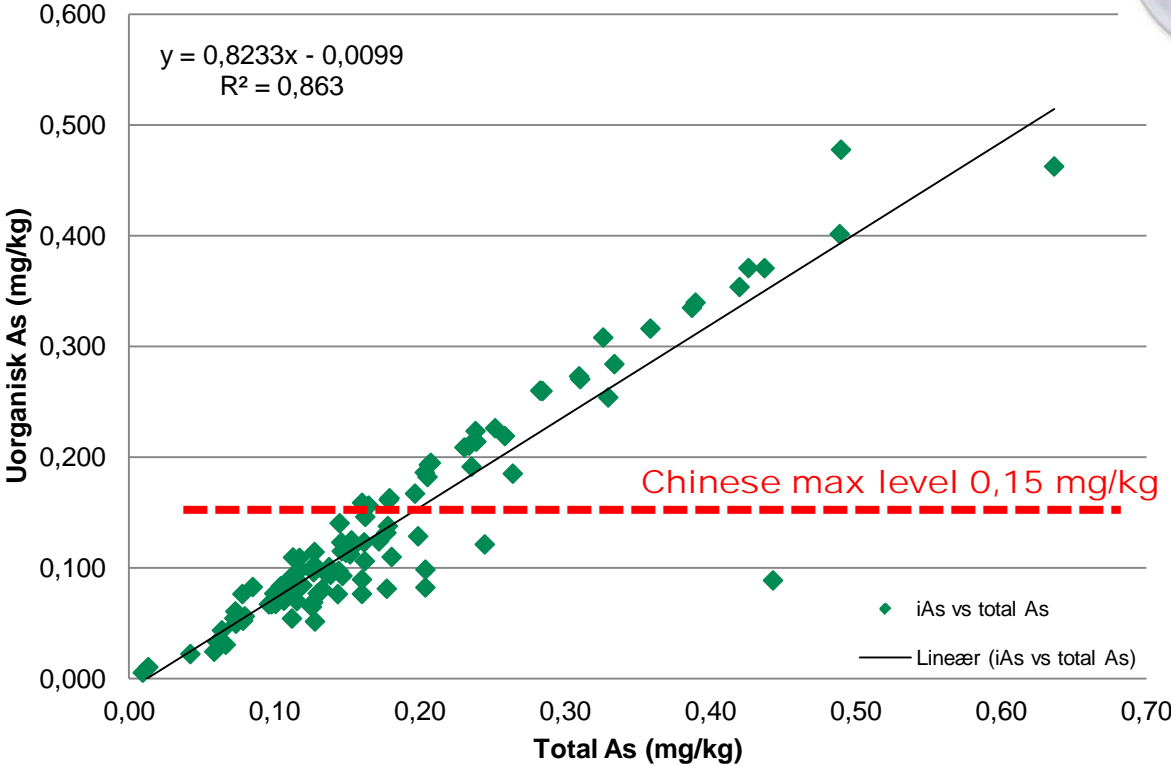
- 19 rice milk samples from supermarkets
- EU drinking water ML: 10 µg/L total As (100% of samples exceeded)
- US drinking water ML: 10 µg/L iAs (80% of samples exceeded)



Arsenic in rice products DK - survey



iAs vs total As



iAs analysed by HPLC-ICPMS

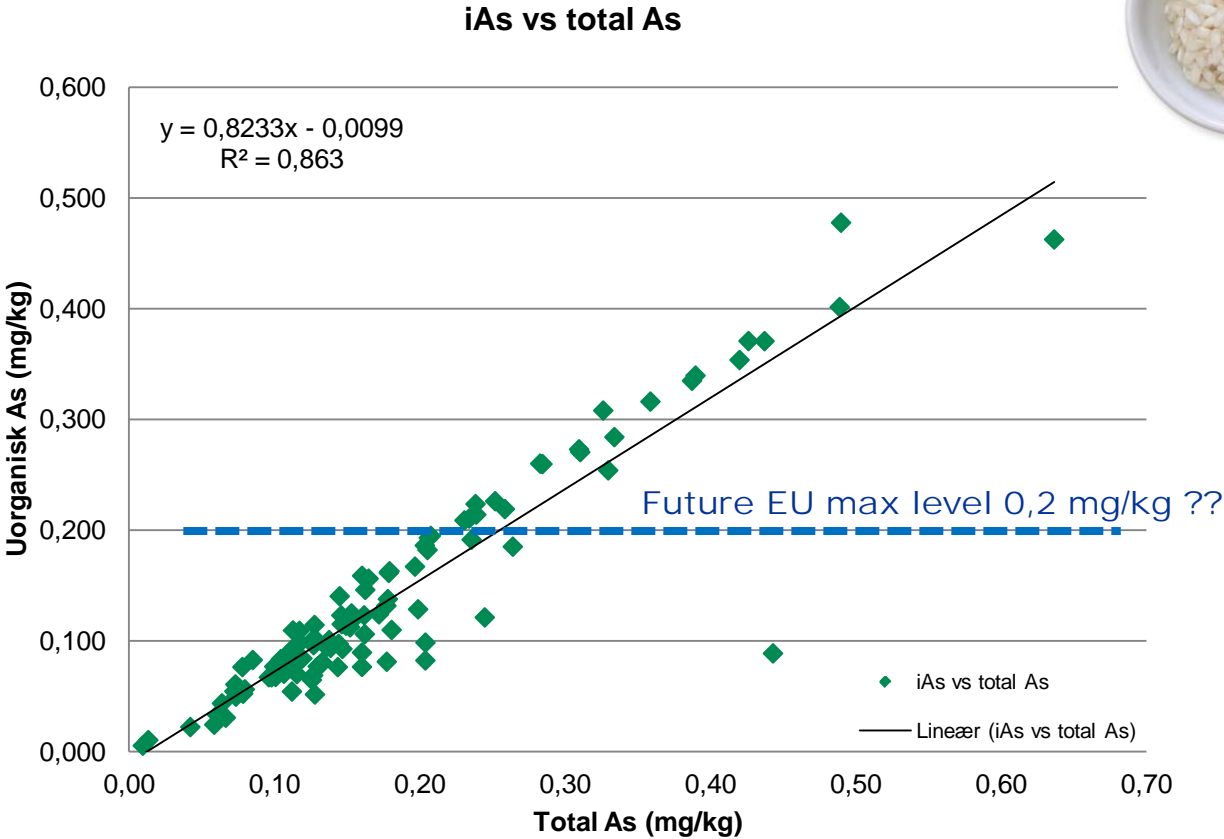
105 samples

- white rice
- brown rice
- red rice
- black rice
- rice crackers

33 samples > 0,15 mg/kg

- 2 parboiled (20%)
- 4 brown (50%)
- 4 red (50%)
- 5 black (71%)
- 1 Basmati (10%)
- 1 Pudding rice (9%)
- 1 wild rice (20%)
- 15 rice crackers (100%)

Arsenic in rice products DK - survey



iAs analysed by HPLC-ICPMS

105 samples

- white rice
- brown rice
- red rice
- black rice
- rice crackers

22 samples > 0,2 mg/kg

- 1 parboiled (10%)
- 1 brown (12%)
- 3 red (37%)
- 2 black (28%)
- 0 Basmati (0%)
- 0 Pudding rice (0%)
- 0 wild rice (0%)
- 15 rice crackers

Rice cracker mean: 0.31 mg/kg - intake 50 g/dag => 15 µg iAs (~1 µg/kg bw/dag)

> EFSA BMDL₀₁ 0.3-8 µg/kg bw/dag



Inorganic arsenic in chinese food supplements

Name of Food supplement	Total Arsenic ($\mu\text{g/g}$)	Inorganic arsenic ($\mu\text{g/g}$)
Xiao Yao Wan	0.82	0.85
Bu Zhong Yi Qi Wan	0.62	0.50
Da Bu Yin Wan	0.59	0.55
Six Flavor teapills	0.72	N.D.
Golden Book Teapills	0.58	0.57
Xiang Sha Liu Jun Zi Wan	0.94	0.80
Gan Mao Ling	1.24	1.01
Chuan Xin Lian	5.00	3.17
Bi Yan Pian	0.70	0.58
Arouse power	1.12	1.02
Bio Chlorella	0.62	0.21
Unik Spirulina Kapsler	2.59	0.13
Chlorella	0.58	0.03
Ez-Biloba	0.63	0.67
Qvinde Dong Quai	0.68	0.48



Gan Mao Ling
(against flu and common cold)

Rec dose: 18 pills per day
 \Rightarrow iAs \sim 13 $\mu\text{g/day}$
 \Rightarrow 0.22 $\mu\text{g/kg bw/day}$ (@60 kg)
 Close to EFSA BMDL_{01} !!

iAs analysed by HPLC-ICPMS

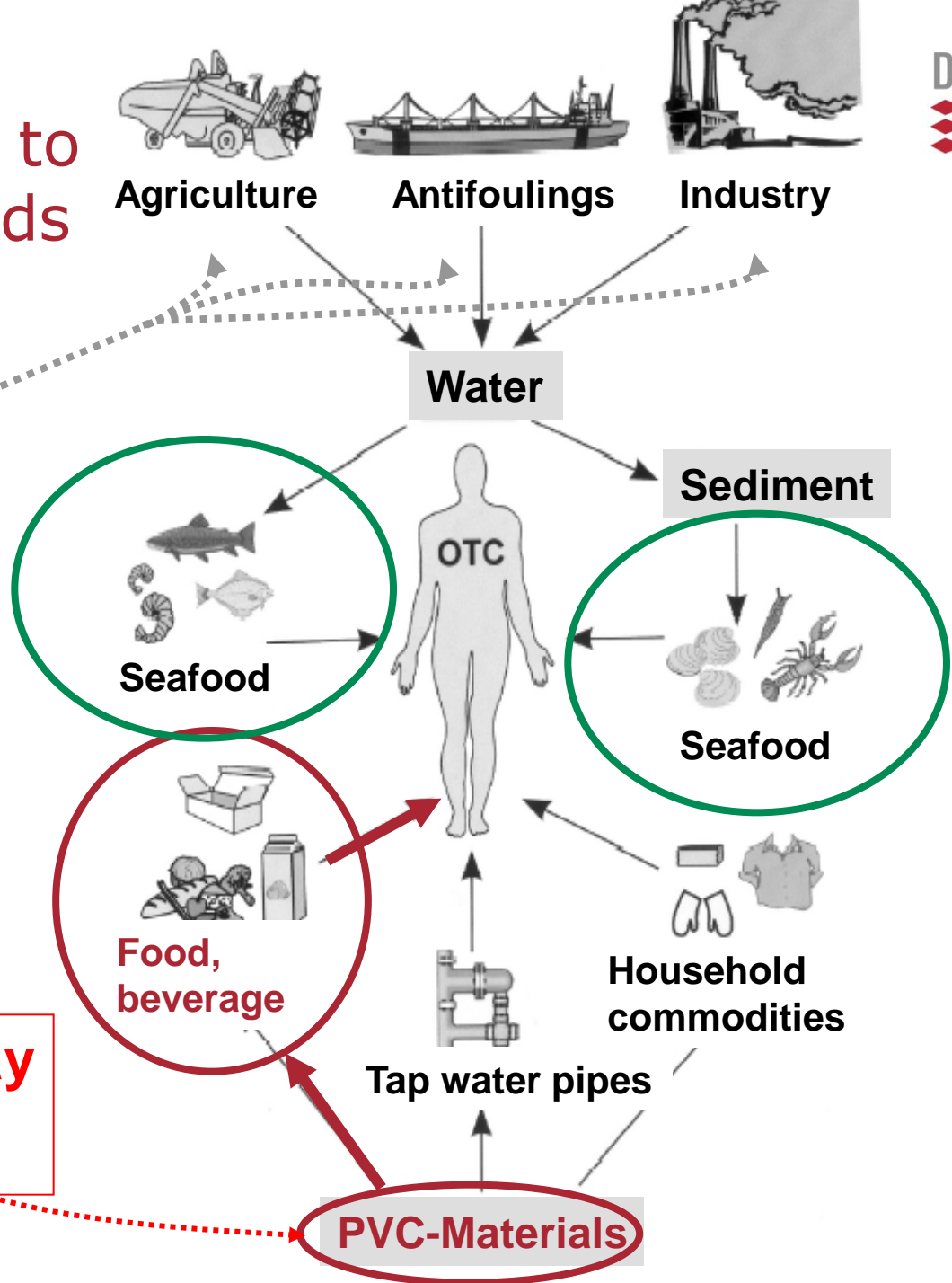
Routes of exposure to organotin compounds

Used in

- Agriculture
- Antifoulings
- Industry

- PVC-Materials

TDI: 0.25 $\mu\text{g}/\text{kg bw}/\text{day}$
 \sum TBT, DBT, TPhT and DOT



Legislation on OTCs in Food Contact Materials



Compounds	Maximum level ($\mu\text{g Sn/kg}$ foodstuff)
Σ DBT, TBT, TPhT and DOT	40 (6)
Σ MMT, DMT	180
MOT	1200
MDDT	12000 (50)
DDDT	24000 (50)

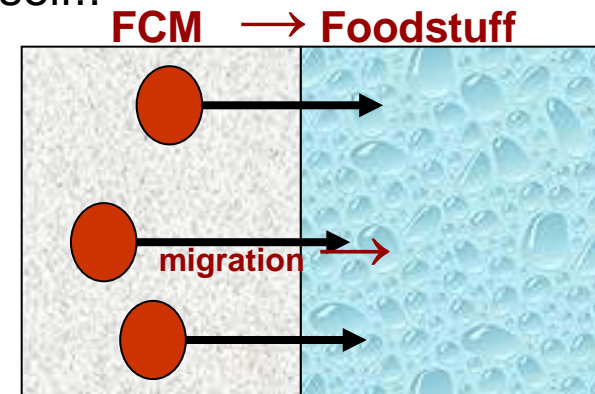
Ref: EFSA (2005); proposed EFSA values in parenthesis

Assumptions:

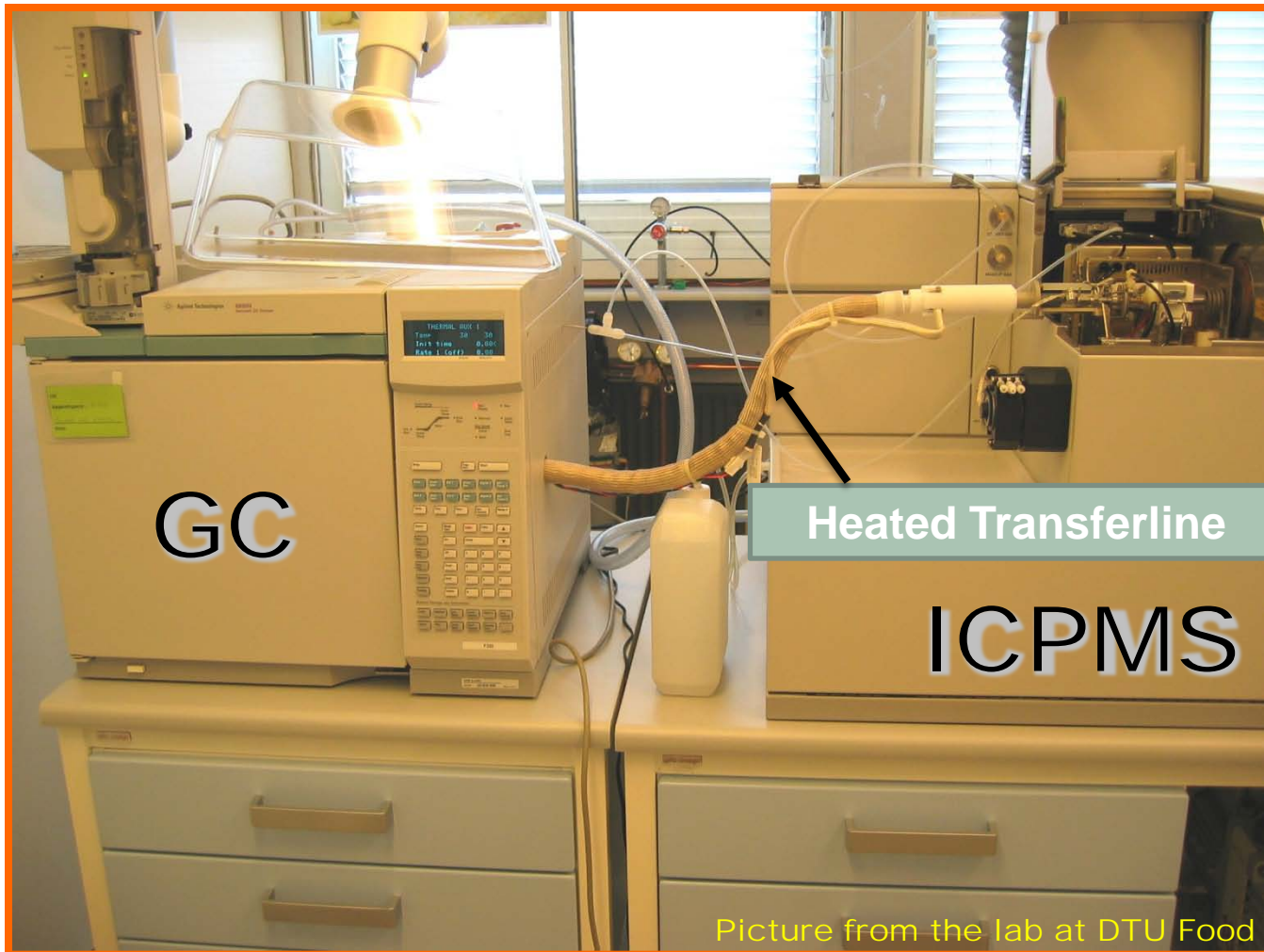
- 1 kg food per 6 dm²

- 100 mL in contact with 0.6 dm²

- 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!!



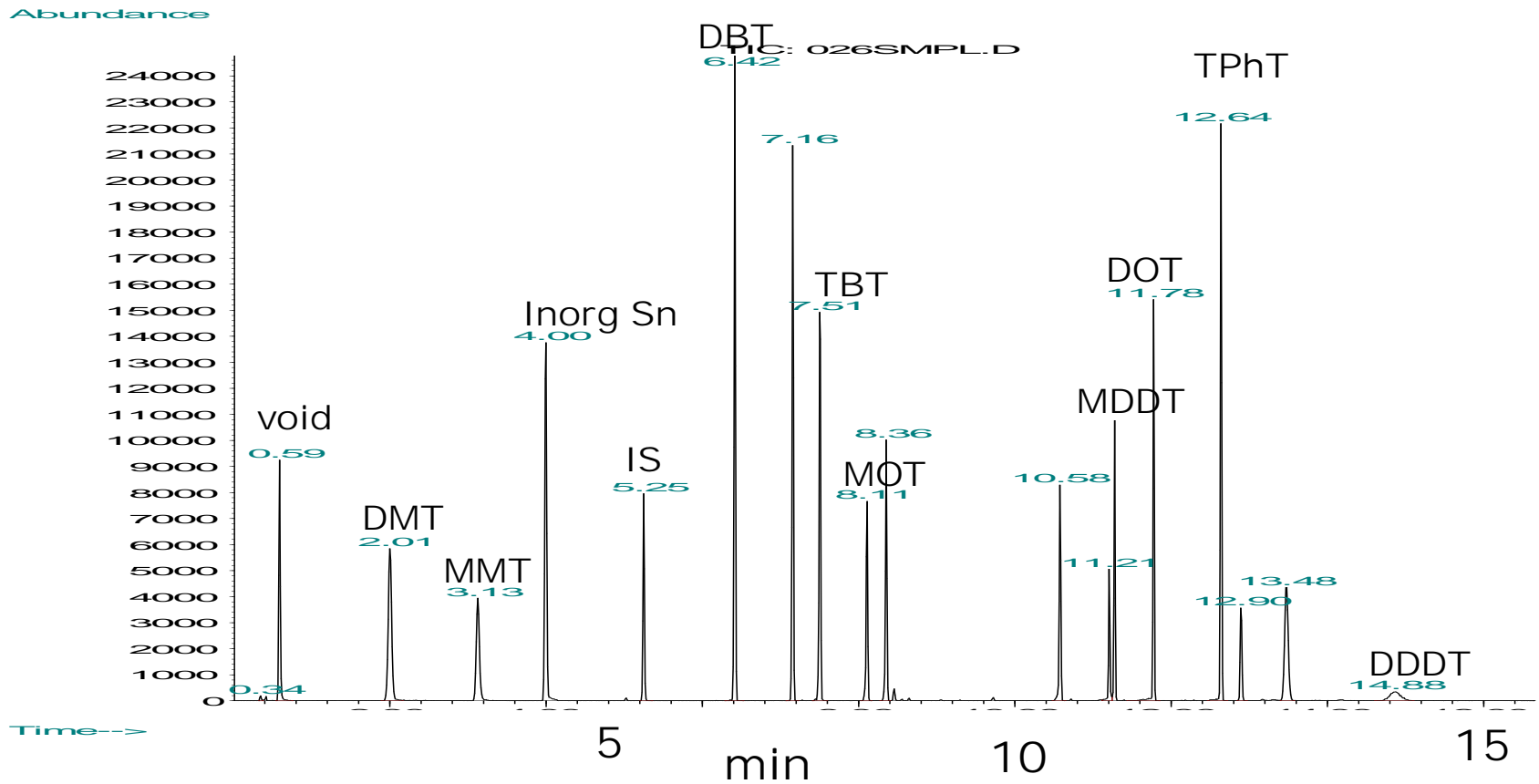
GC coupled to ICPMS



...can be used to determine organotin compounds

Organotin speciation by GC-ICPMS

- Chromatogram of 9 standards + IS



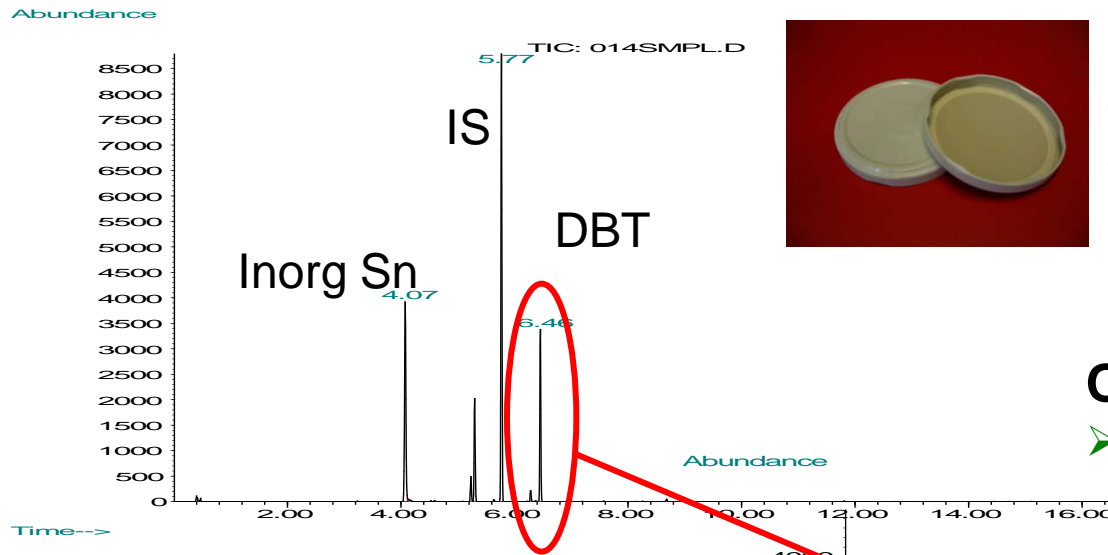
Derivatisation (ethylation) with NaBEt_4

Organotin migration from Food Contact Materials

Small scale survey on 33 Food Contact Materials

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: 9.9 µg/kg

TIC: 005SMPL.D
TIC: 014SMPL.D

DBT

> EFSA guideline value of 6 µg/kg

Output of DK survey:

- 33 samples
- 11 contained OT (mainly DBT)
- 3 exceeded EFSA guideline limit

Silver nanoparticles in products related to food and beverages



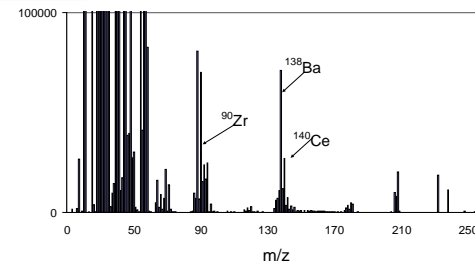
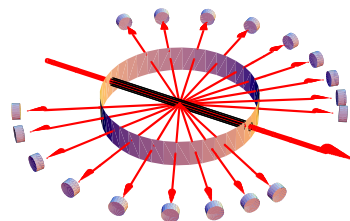
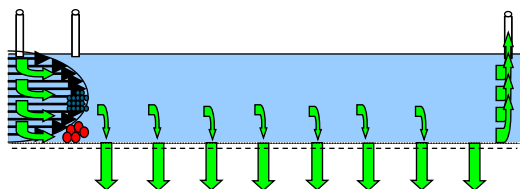
- Ergonomic**: Ergonomic fit is best fit baby's physical nature and it is developed to assure good blending of saliva in mouth thus reduces gastric trouble and vomit symptom.
- Medical**: Through silver nano poly system 99.9% of germs are prevented and it maintains anti-bacteria, deodorizing function as well as freshness.
- Scientific**: It has air hole so it is possible to adjust amount of air at the time of feeding thus prevents stomach trouble and typhants.



American Biotech Lab
ASAP
NanoSil
 SOLUTION
 Protect Your Family and Loved Ones

The analytical platform

AF⁴ – MALS - ICPMS



**Asymmetric flow
field flow
fractionation**

Optical detection
(multi angle and
dynamic light
scattering, UV and
fluorescence)

**Inductively
coupled plasma
mass spectrometry
(ICP-MS)**

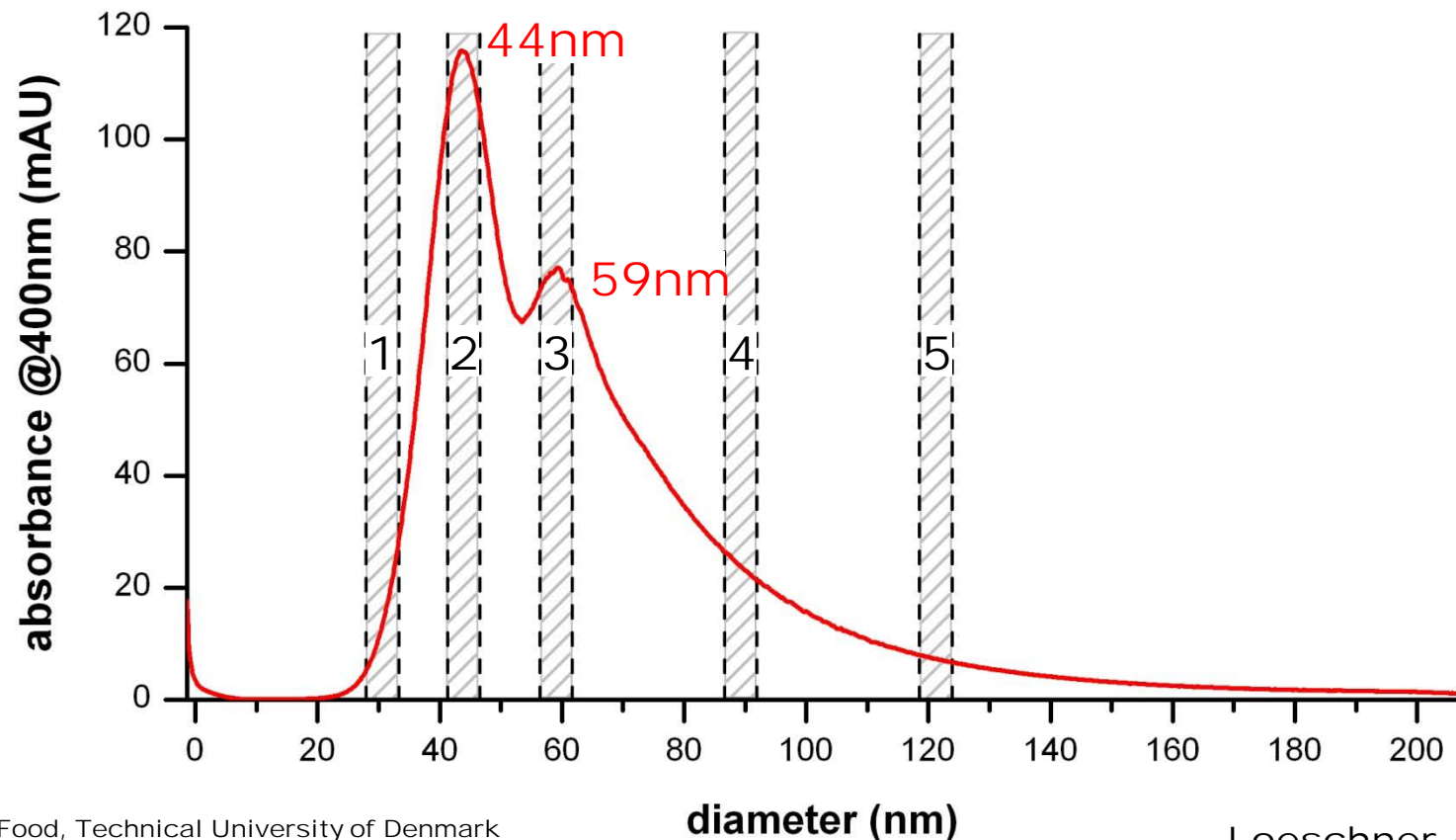
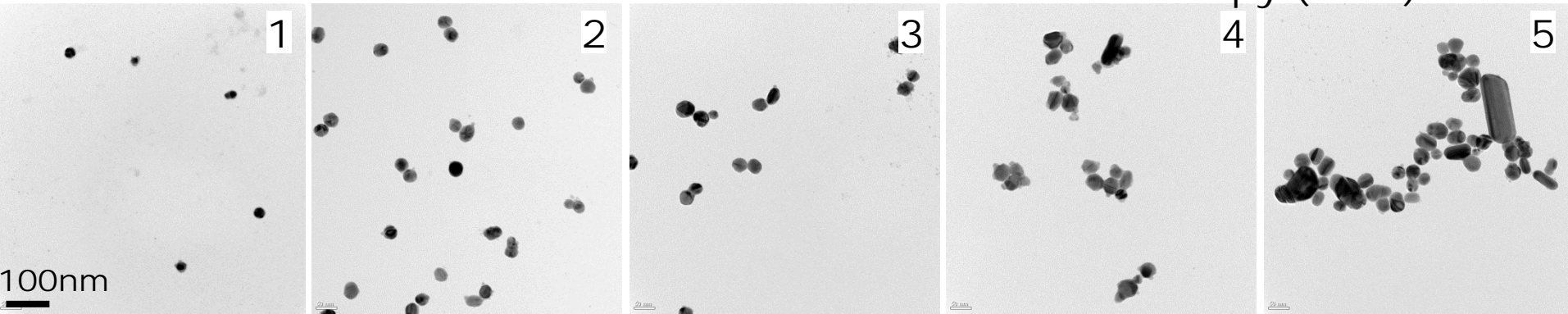
Particle separation
according to their size
(small NPs elute first)

Particle detection
(fractogram)
Size determination

Elemental detection
for ID of the particles
Quantification

Determination of Ag-nanoparticle size distribution

Fraction collection for transmission electron microscopy (TEM)



NanoLyse Project

"Nanoparticles in Food: Analytical methods for detection and characterisation"

Validated methods for the determination of inorganic ENP in food extracts, based on size separation, size determination and specific detection

silver nanoparticles in lean meat



silica nanoparticles in tomato soup



Acknowledgements and funding sources

Coworkers:

Rie R. Rasmussen, Rikke V. Hedegaard, Bjørn Schmidt,
Xenia T. Trier, Katrin Löschner and Erik H. Larsen

Inge Rokkjær, Gudrun Hilbert and Dorthe L. Cederberg

Kåre Julshamn



Funding sources:

European Community's Seventh Framework Programme

Danish Food Administration (DFVA)

Norwegian Food Authority



Thanks for your attention! 🙌😊