ARSENIC SPECIES IN URINE, - a way to tell what you ate for dinner?

Barbro Kollander

The 16:th Nordic user meeting on AAS, ICP-AES and ICP-MS,
Nova Park, March 2018

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Flashback!

Topics presented at previous user meetings

SP, Sigtuna 2012
ICP-MS at National Food Agency - Lead in game meat

Kemistutbildarna, Nova Park 2013
Speciation of Arsenic by IC-ICP-MS
- A candidate CEN standard method a on baby food samples

EU standard EN16802:2016

SP, Friiberghs herrgård 2014
Determination of Inorganic Arsenic in Foodstuffs by IC-ICP-MS
- Validation of a new method

Kemistutbildarna, Nova Park 2015
The Big Four - the 4 metals on the Top-10 list of priority chemicals of public health concern and the monitoring of their levels in food

SP, Sigtuna 2016
The Big Four becoming the Big Five? - Nickel and the 4 metals on the Top-10 list of priority chemicals of public health concern and their monitoring of their levels in food

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Outline

Background – why of any interest?

Method for water soluble arsenic species

Consequences of eating Sushi

On-going project

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Vision of the National Food Agency

The food is good
for the consumers'
health and well-being.

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Arsenic is of public health concern

efsa
European Food Safety Authority

Food and Agriculture Organization of the United Nations

JECFA Joint FAO/WHO Expert Committee on Food Additives

- **New values** for toxicity of arsenic, specified for ***inorganic arsenic***, JECFA 2011 and Efsa 2014 .
- **The dietary exposures of arsenic** for average and high level consumers in Europe are within a range where risk cannot be excluded, Efsa 2014.

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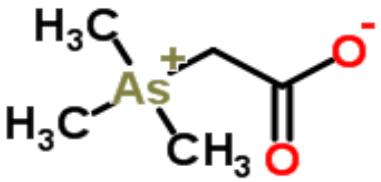
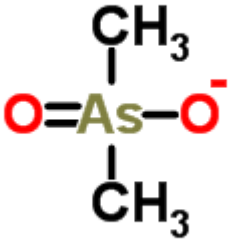
Examples of arsenic species in food

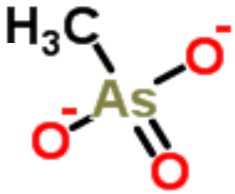
Organic arsenic



Arsenobetaine (AB)

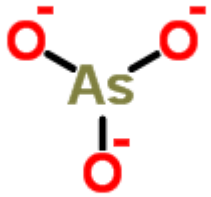


Dimethyl arsinate (DMA)

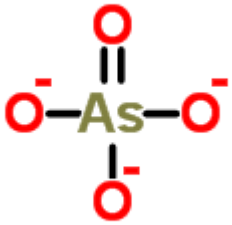


Monomethyl arsonate (MMA)

Inorganic arsenic (iAs)



Arsenite (AsIII)



Arsenate (AsV)

Increasing toxicity

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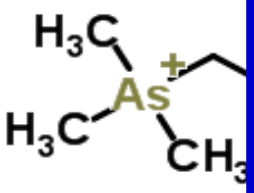
Examples of arsenic species in food

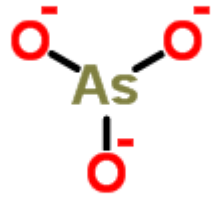


Arsenobetai

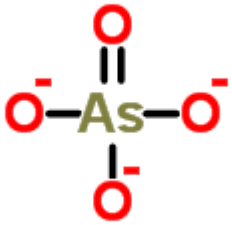
The European standard EN16802:2016

- **iAs most toxic As species**
- **EU legislation includes iAs**

Inorganic arsenic (iAs)



Arsenite (AsIII)



Arsenate (AsV)

Increasing toxicity

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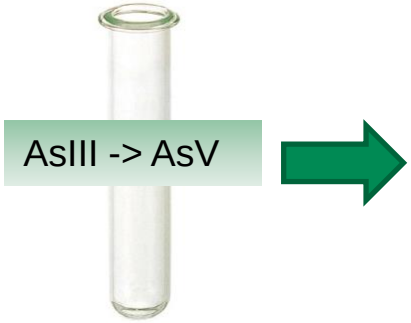
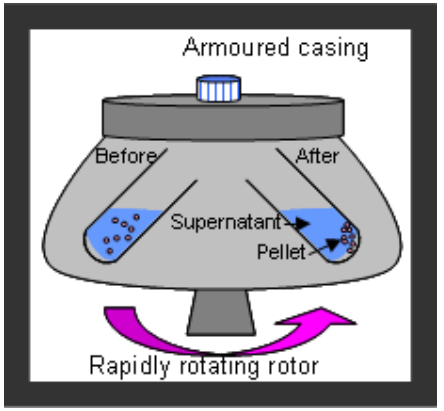
EN16802:2016. Foodstuffs. Determination of elements and their chemical species. Determination of inorganic arsenic in foodstuffs of marine and plant origin by anion-exchange HPLC-ICP-MS.

EUROPEAN UNION



Sample + 10 mL extractant
(0.1 M HNO_3, 3% H_2O_2)

90°C waterbath, 1h

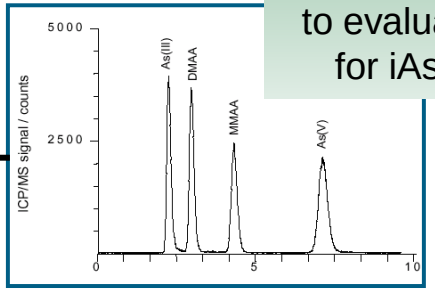


centrifugation

Anion-exchange chromatography HPLC-ICPMS

Only one peak (AsV) to evaluate for iAs.

HPLC
Dionex ICS5000
Thermo Scientific



Jens Sloth, Food Institute, Technical University of Denmark

EN16802:2016. Foodstuffs. Determination of elements and their chemical species. Determination of inorganic arsenic in foodstuffs of marine and plant origin by anion-exchange HPLC-ICP-MS.

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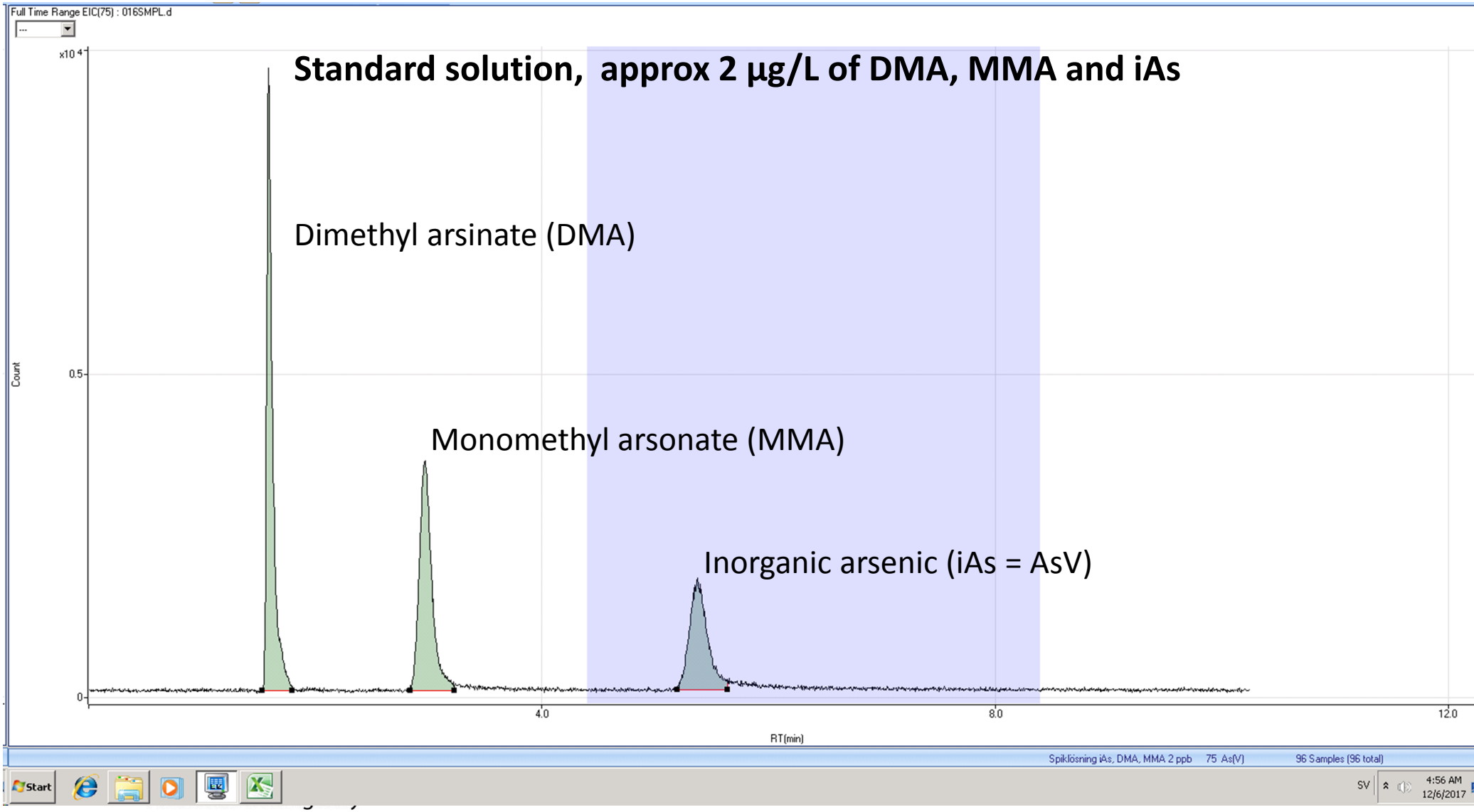
Analytical parameters at National Food Agency laboratory:

Instrument:
HPLC. Agilent Infinity 1260 Quaternary Pump
ICP-MS. Agilent 7700x

HPLC-ICP-MS
LOD: 0.5 - 3 µg iAs/kg food depending on dilution of the sample
Measurement uncertainty: +/- 18 % (95 %, coverage factor k=2)

Quality control:
Participation in iAs- proficiency tests (N=16)
11 with satisfactory z-scores within +/- 2 (ISO13528:2015)
3 with questionable results (z-score > 2 and < 3)
2 PT:s did not deliver results for iAs
Certified reference materials analysed and evaluated within each batch.

Example of Chromatogram



Consequences from eating sushi

- a small inhouse experiment to test the method for urine

Bachelor thesis by Philip Granqvist, UU, 2017

Outline:
5 participants
3 eating sushi for lunch
2 not eating sushi

Sampling urine
Before lunch
After lunch, approx 4-5 hours
After lunch, approx 20 hours (only 2 participants)

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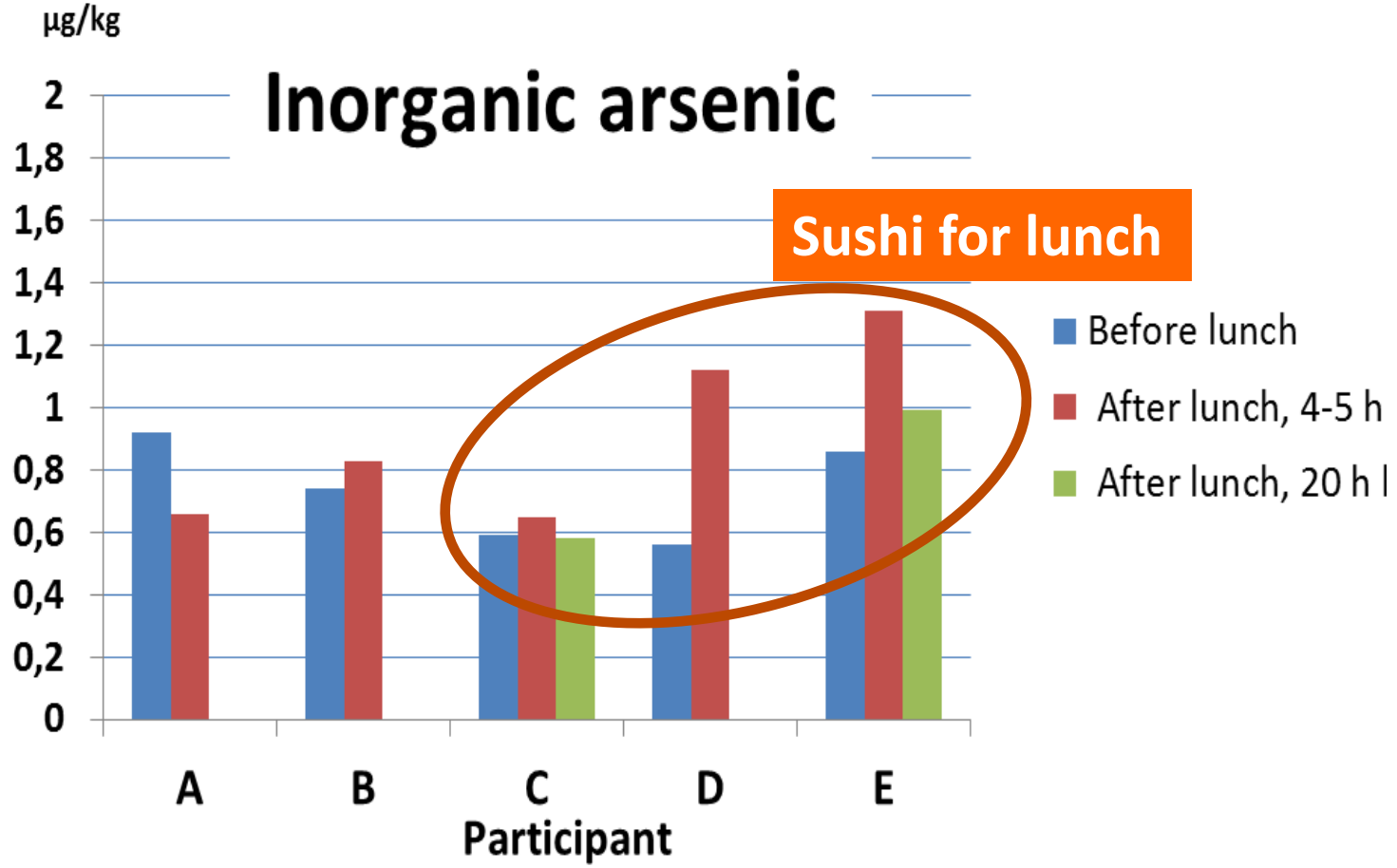
Consequences from eating sushi

- a small inhouse experiment to test the method for urine

Bachelor thesis by Philip Granqvist, UU, 2017



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Consequences from eating sushi

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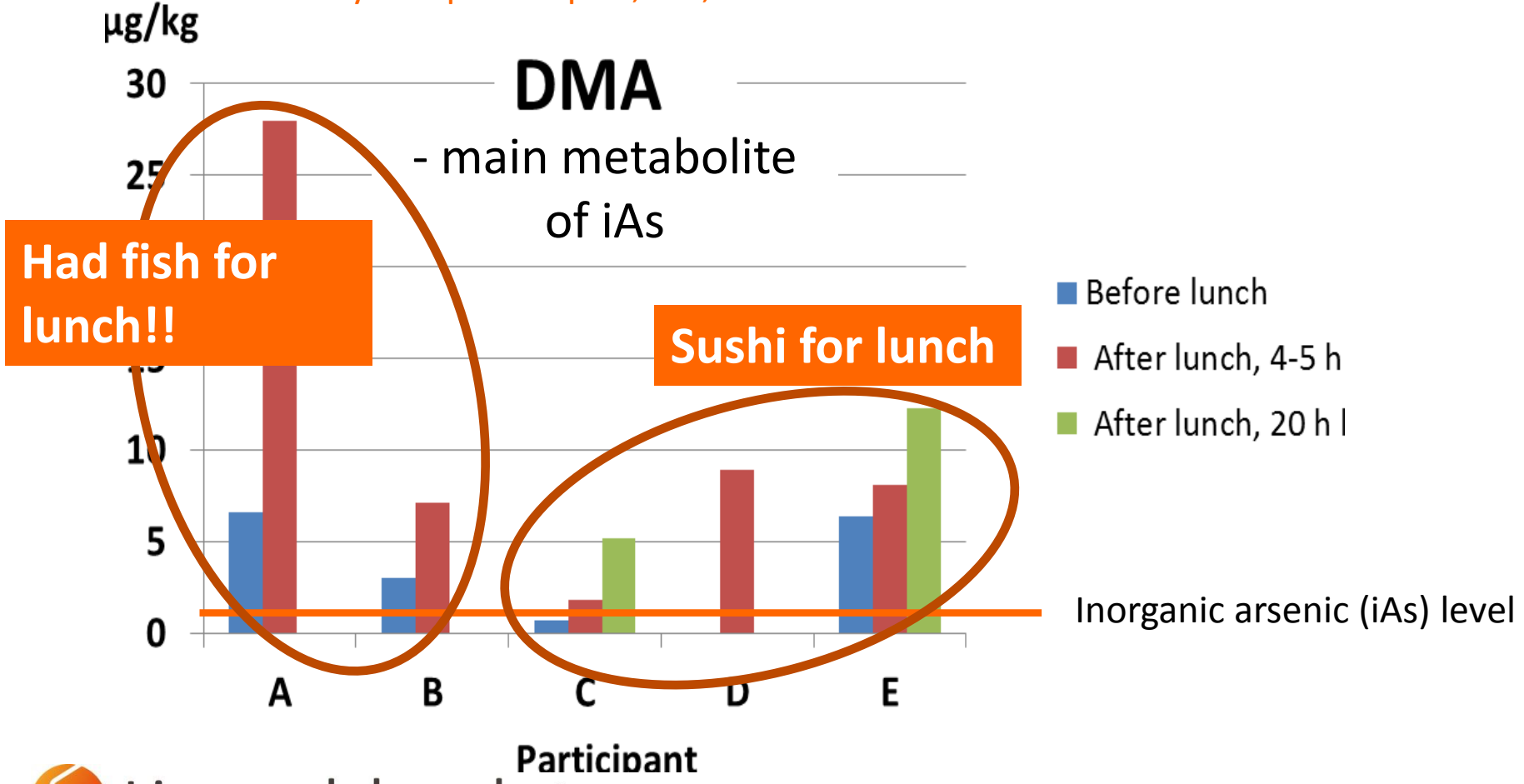

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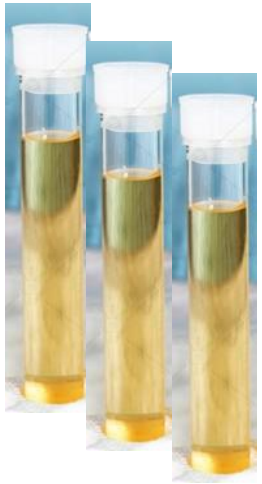
Biomonitoring of As species in urine

150 urine samples from the Swedish survey “Riksmaten ungdom” - a national dietary survey of children and adolescents. Recording of intake of food, weight and height, physical activity. In total 3000 individuals and blood and urine samples from 1200 of those. Examples of analytes: Toxic elements, PCB, Dioxins, flame retardants, mycotoxins, vitamins, iodine, ferritin.

Individual samples for arsenic analysis selected after



source of drinking water => private wells with different As content

Target analytes:
iAs
DMA (dimethyl arsinate): Main metabolite of iAs
MMA (monomethyl arsonate): Minor metabolite of iAs

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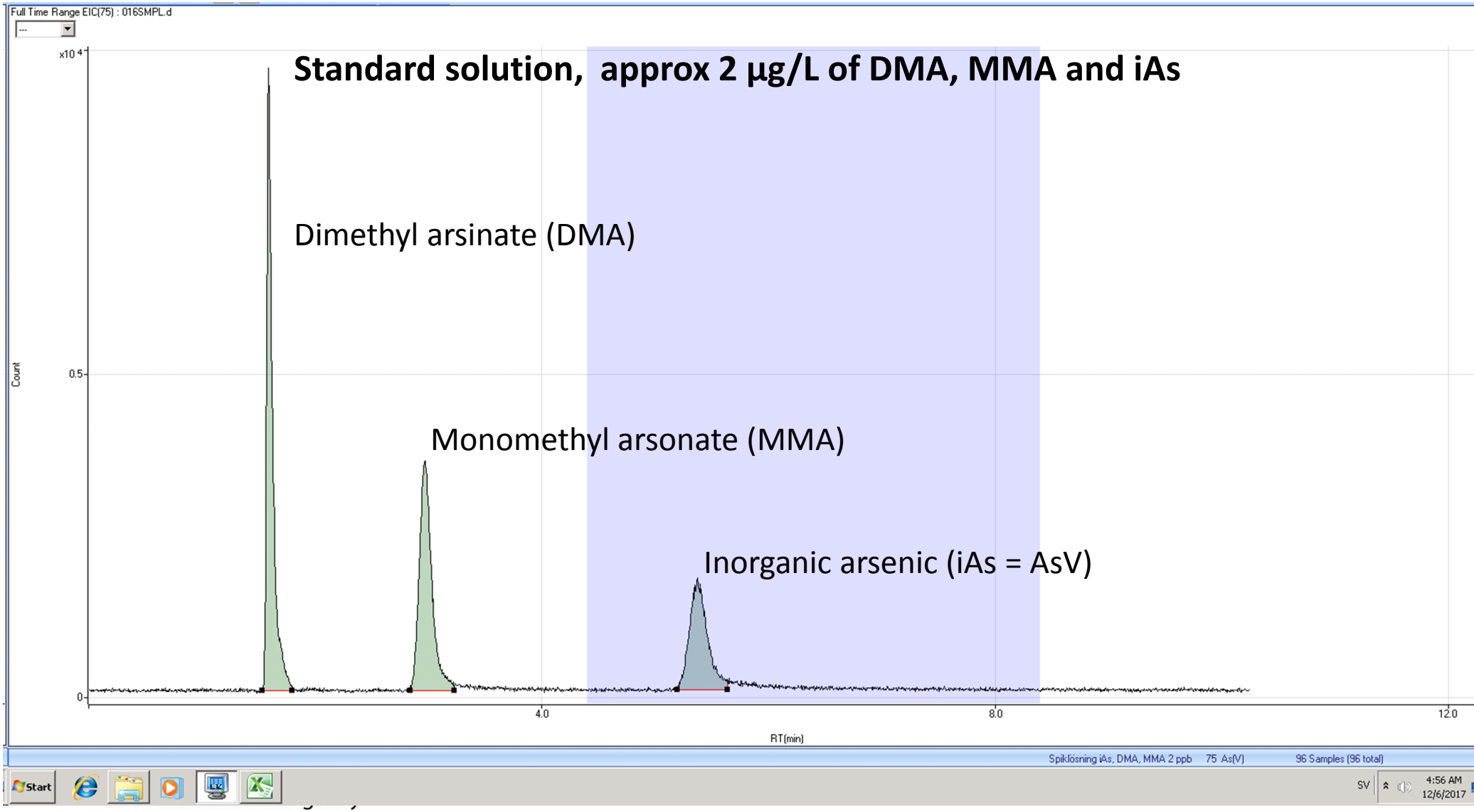
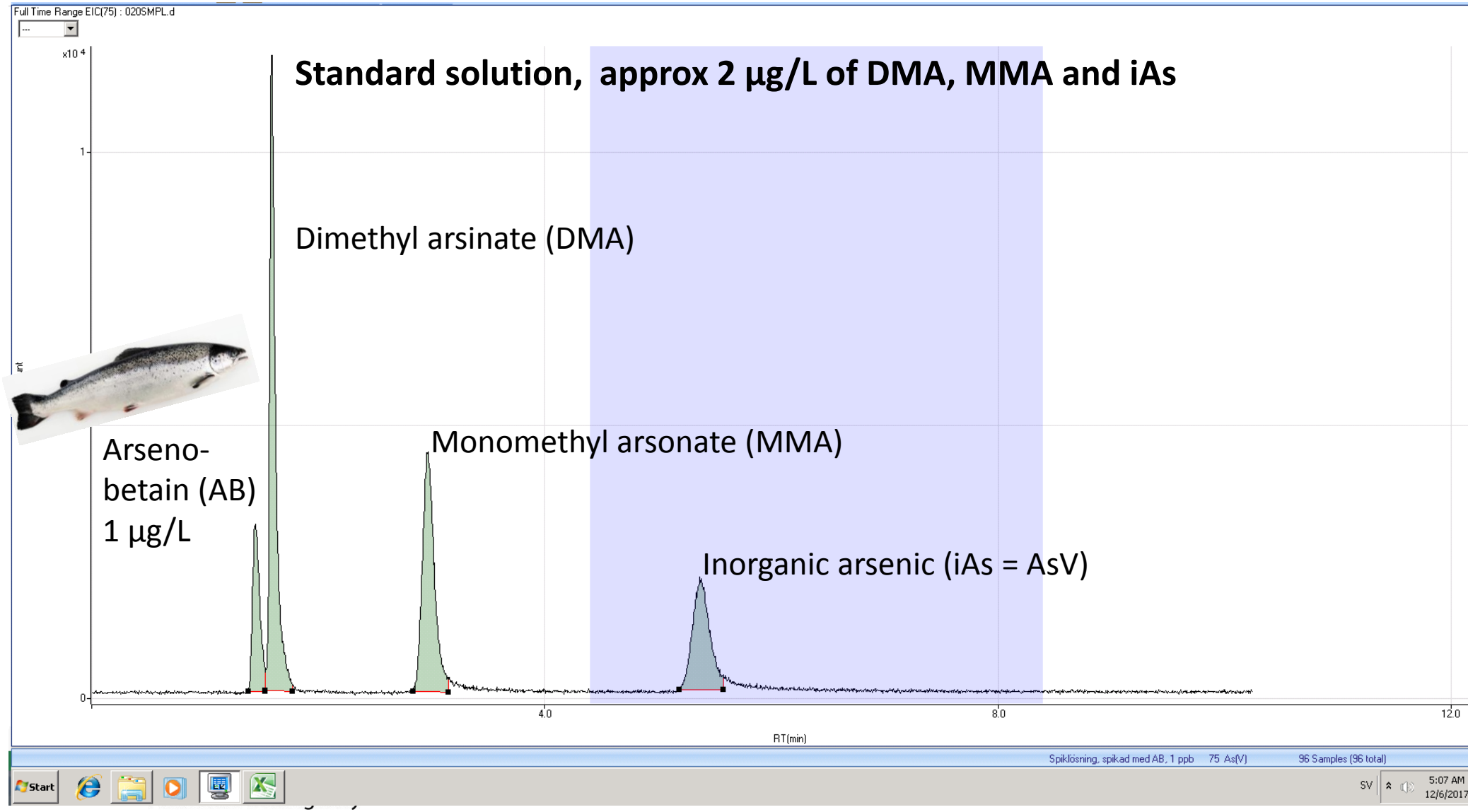
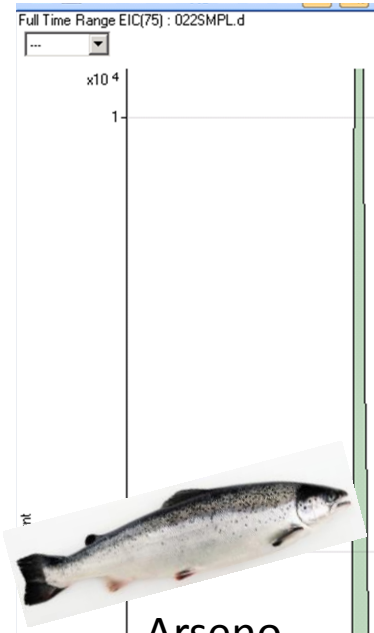
Biomonitoring of As species in urine



Biomonitoring of As species in urine



Biomonitoring of As species in urine



Arseno-
betain (AB)
5 µg/L

Dimethyl arsinate (DMA)

Monomethyl arsona

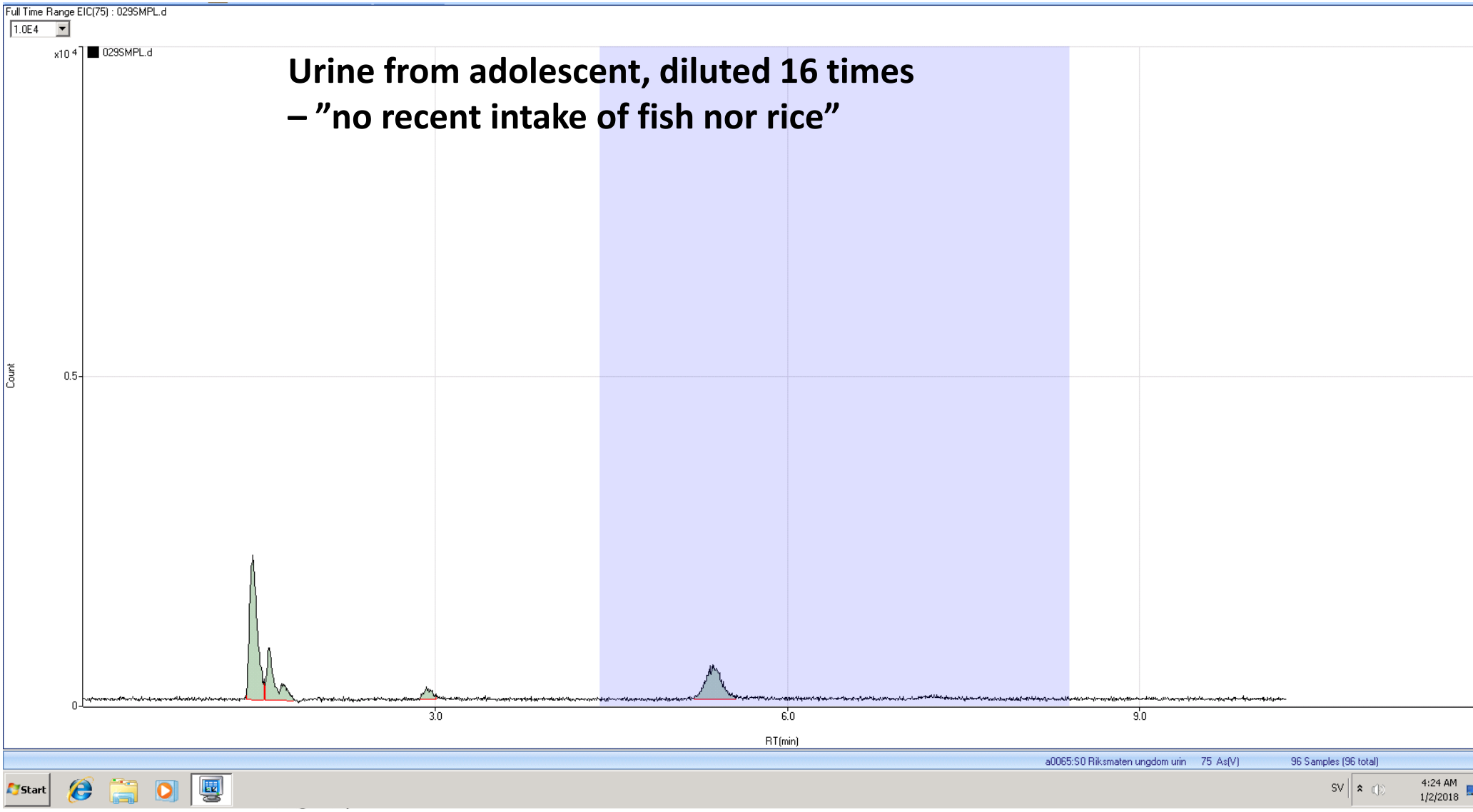
Standard solution, approx 2 µg/L of DMA, MMA and iAs

Hypothesis:

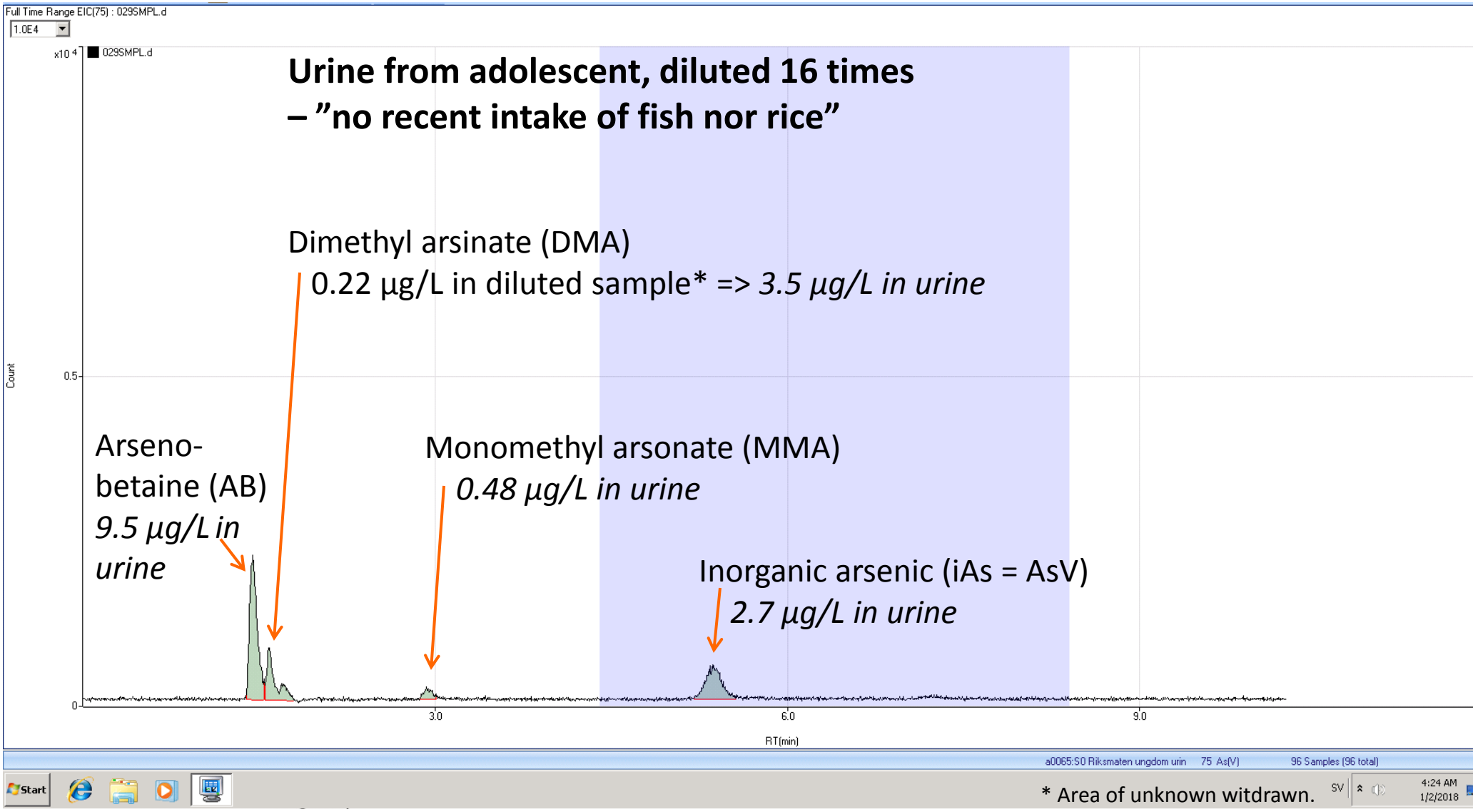
1. Urine from adolescents not eating too much fish could be analysed regarding DMA, MMA and iAs by this method, approx 70-90 % of samples.

2. Urine containing AB will be additionally analysed with cation exchange ICP-MS method, approx 10-30% of samples?

Biomonitoring of As species un urine

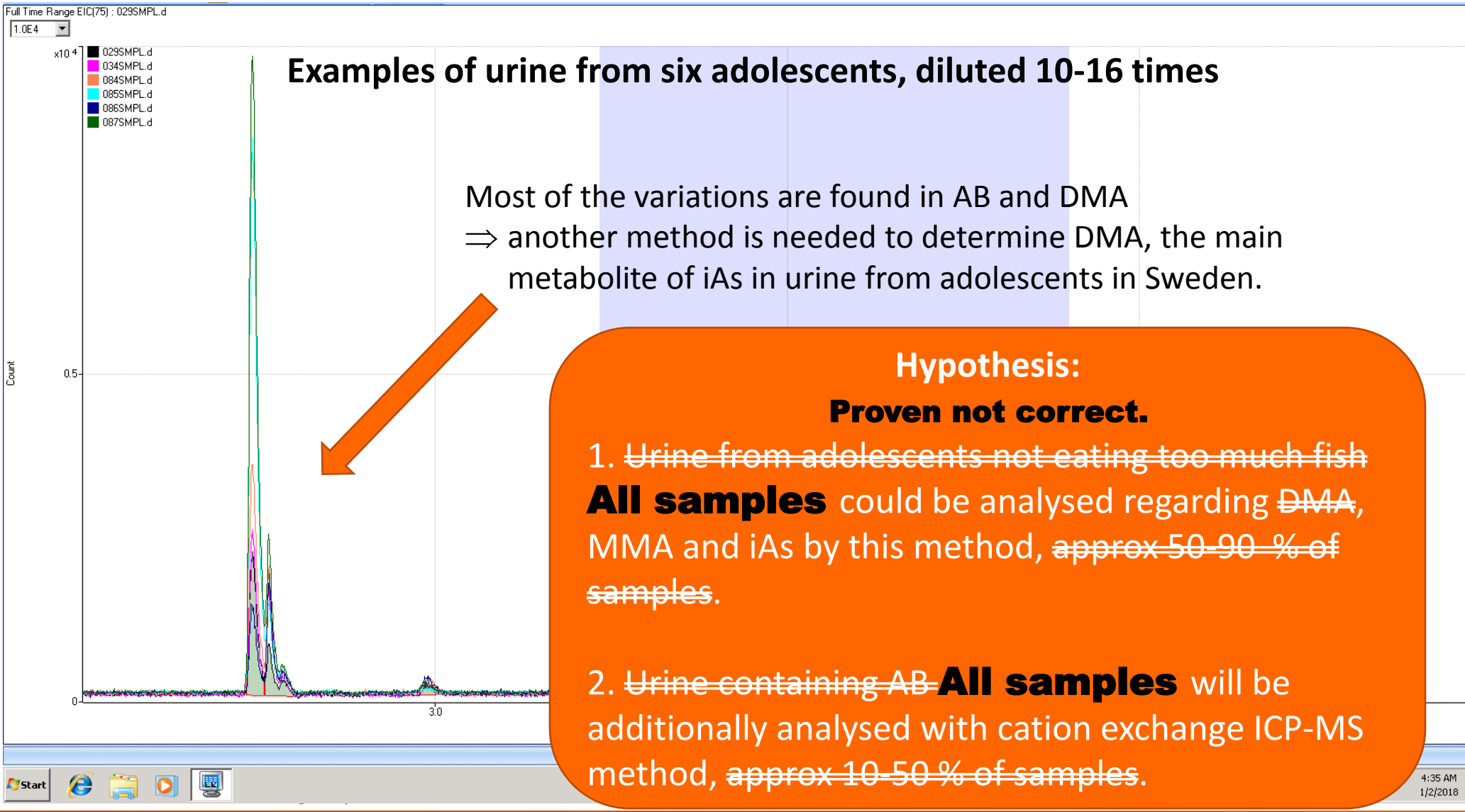


Biomonitoring of As species un urine



* Area of unknown witdrawn.

Biomonitoring of As species in urine



Conclusions and outlook

1. Everything is always taking much longer time than planned – ALWAYS!

2. The Standard EN 16802:2016 works well for iAs and MMA and in some matrices also for DMA.

3. Adolescents in Sweden eat enough fish to have measurable levels of arsenobetaine in their urine => cation exchange method needed to determine DMA.

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Acknowledgements

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(NIFES), Bergen, Norway

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Thank you for your kind attention!

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