

FUMONISINS: THE HIDDEN MENACE

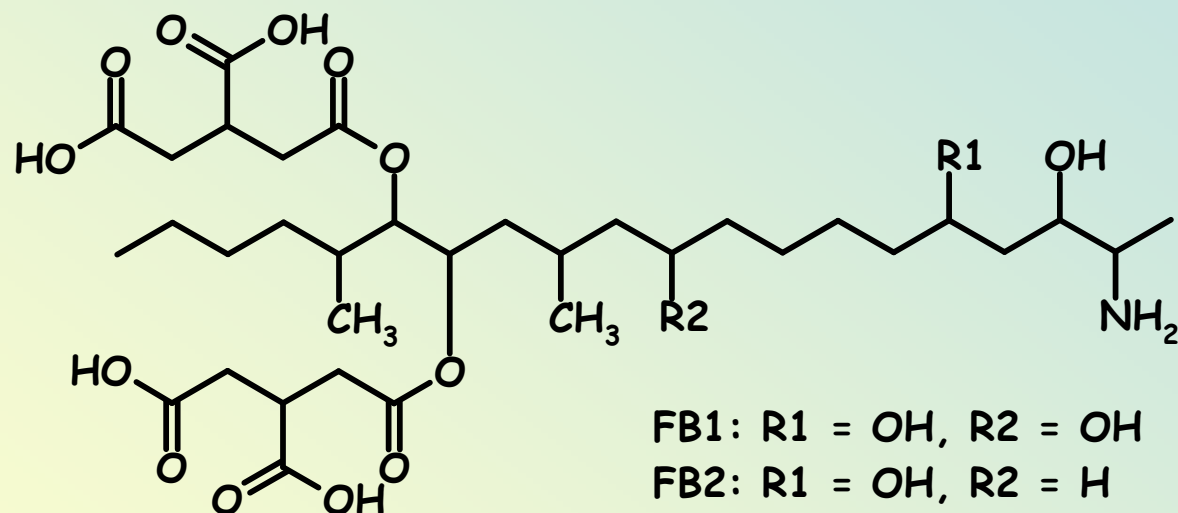
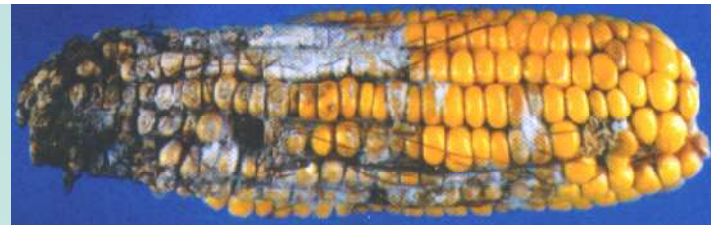
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Fumonisin



FB1: R₁ = OH, R₂ = OH

FB2: R₁ = OH, R₂ = H

FB3: R₁ = H, R₂ = OH

F. verticillioides, *F. proliferatum*

Worldwide
contaminants of corn
and corn-based
products.

Toxicity: Carcinogenic, hepatotoxic and nephrotoxic

FB1: IARC class 2B carcinogen (possible human carcinogen).

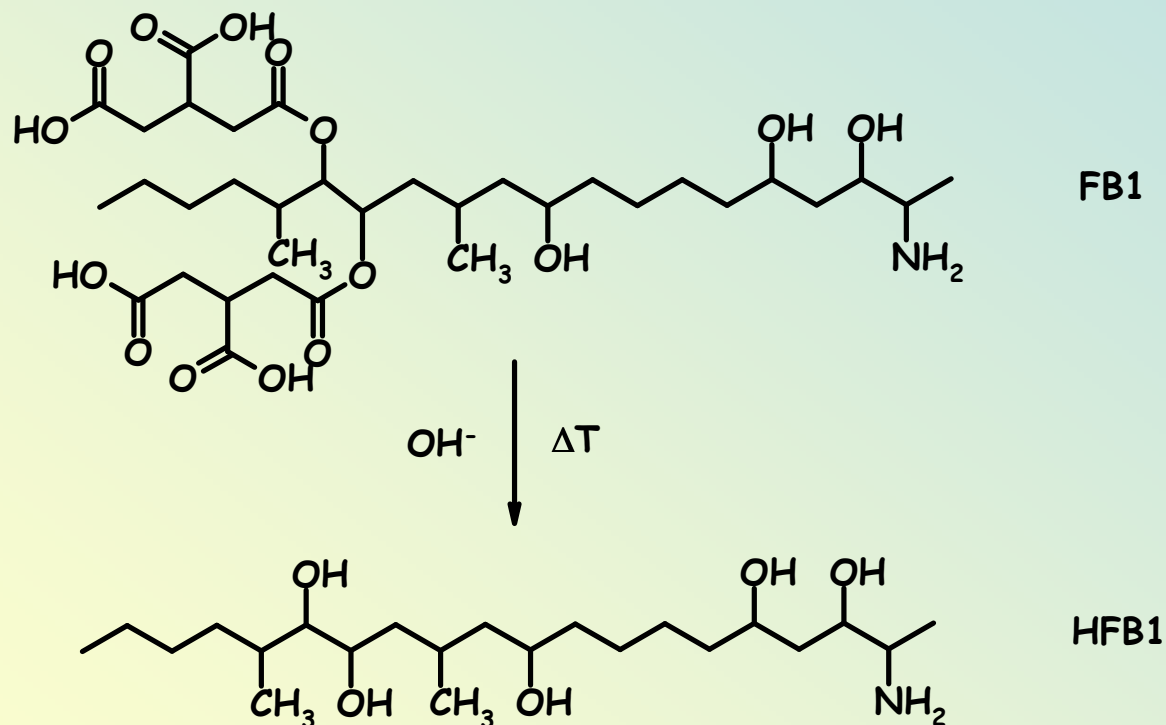
Legislation: Regulation EC No. 1126/2007 of 28 september 2007

Fumonisin: effect of processing

Degradation at $T > 100^{\circ}\text{C}$.

Contamination levels are higher in whole grain than in highly processed corn products: flakes, chips, etc.

Heat-treated or heat- plus alkali-treated products: partial hydrolysis to HFBs



Fumonisin: analytical problems

Poor recoveries, specially in heat treated products, lead to underestimation of the real contamination.

Possible binding to the food matrix?

Shier et al., J. Nat. Toxins, 1997, 6, 225-242

Addition of radioactive labelled FB1 to maize flour and oven cooking.

Only 37% of the radioactivity recovered by routine analytical methods

Another 46% closely associated with the protein fraction.

Hidden or bound fumonisins

Fumonisin: the paradox

Shier W T, *J. Toxicol. - Toxin Reviews*, 2000, 19, 161-187

Although FB1 shows low bioavailability, toxic effects are evident also after ingestion of foods apparently poorly or not contaminated.

Hidden fumonisins: analytical approach

Park et al. *Food Add. & Contam.*, 2004, 21 (12), 1168-1178

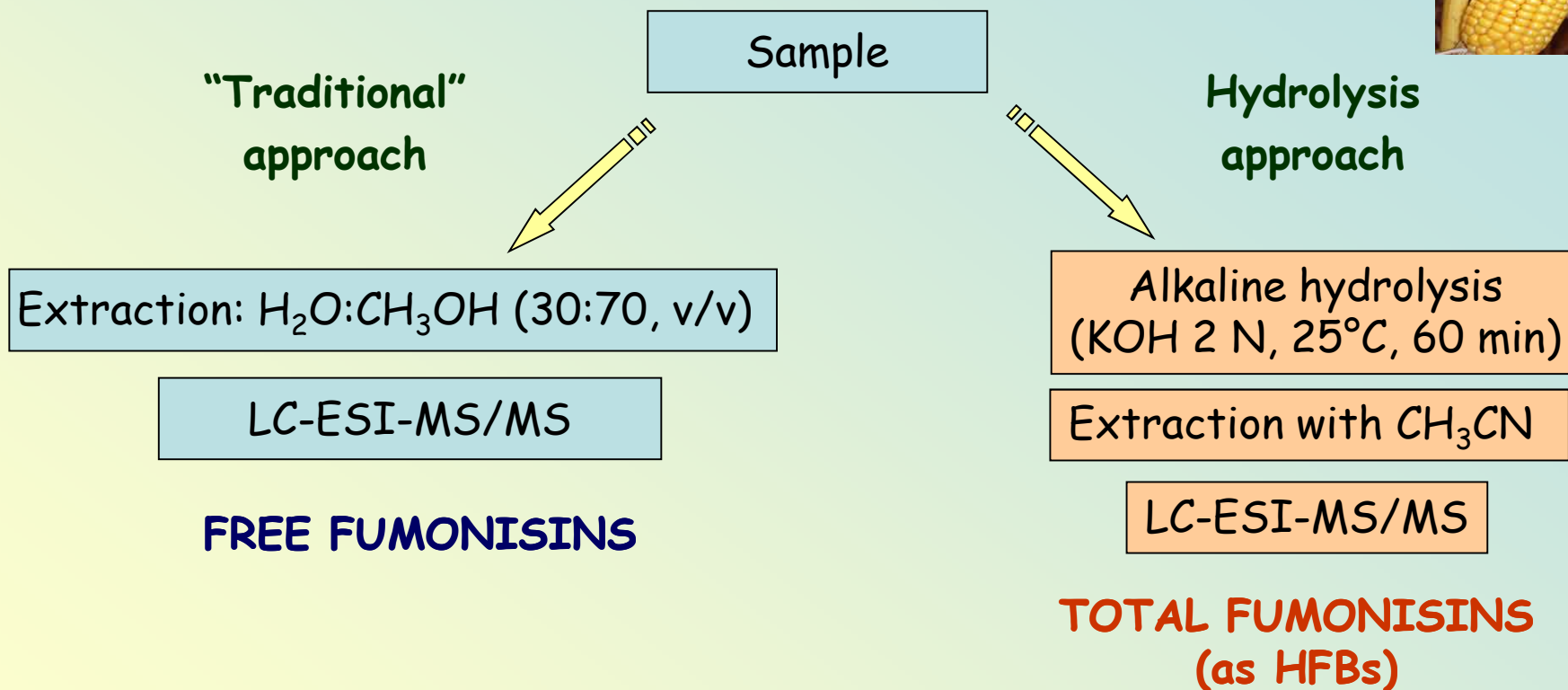
Extraction with SDS.

Alkaline hydrolysis.

Detection of released HFB1.



Hidden fumonisins: our approach



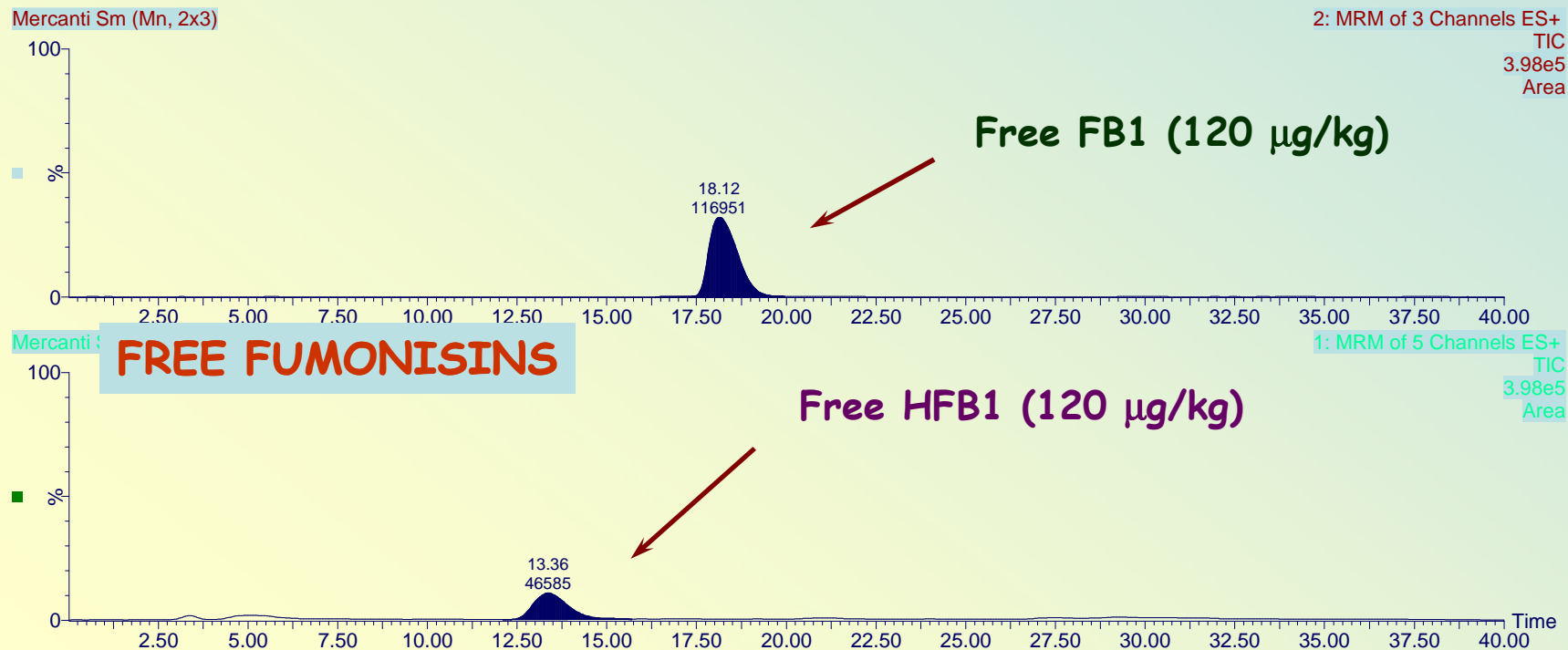
$$\text{HIDDEN FUMONISINS} = \text{TOTAL} - \text{FREE}$$

Dall'Asta, Galaverna, Mangia, Sforza, Dossena, Marchelli, *Mol. Nutr. Food Res.* 2009, 53, 492

Free and hidden fumonisins in corn-flakes

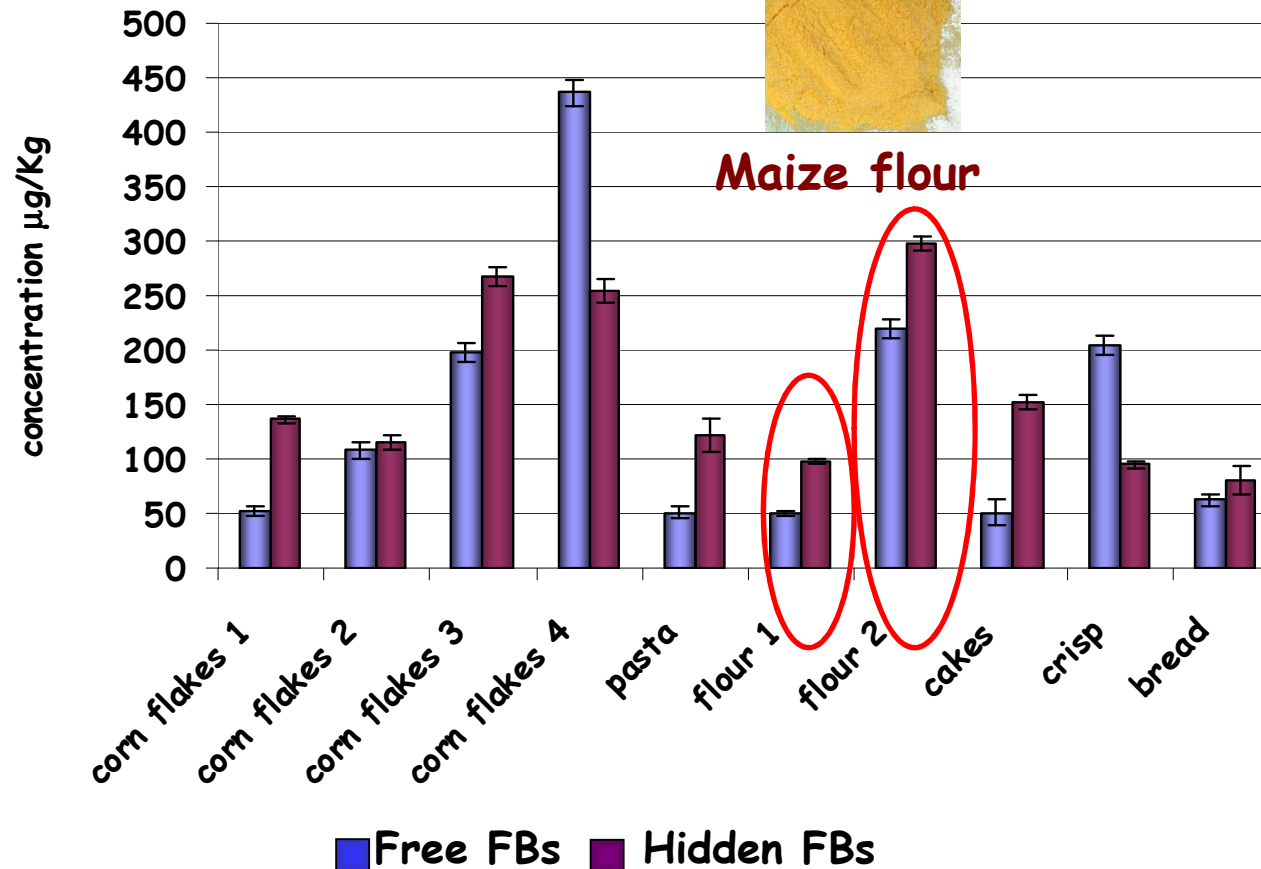


Dall'Asta, Galaverna, Mangia, Sforza, Dossena, Marchelli, *Mol. Nutr. Food Res.* 2009, 53, 492



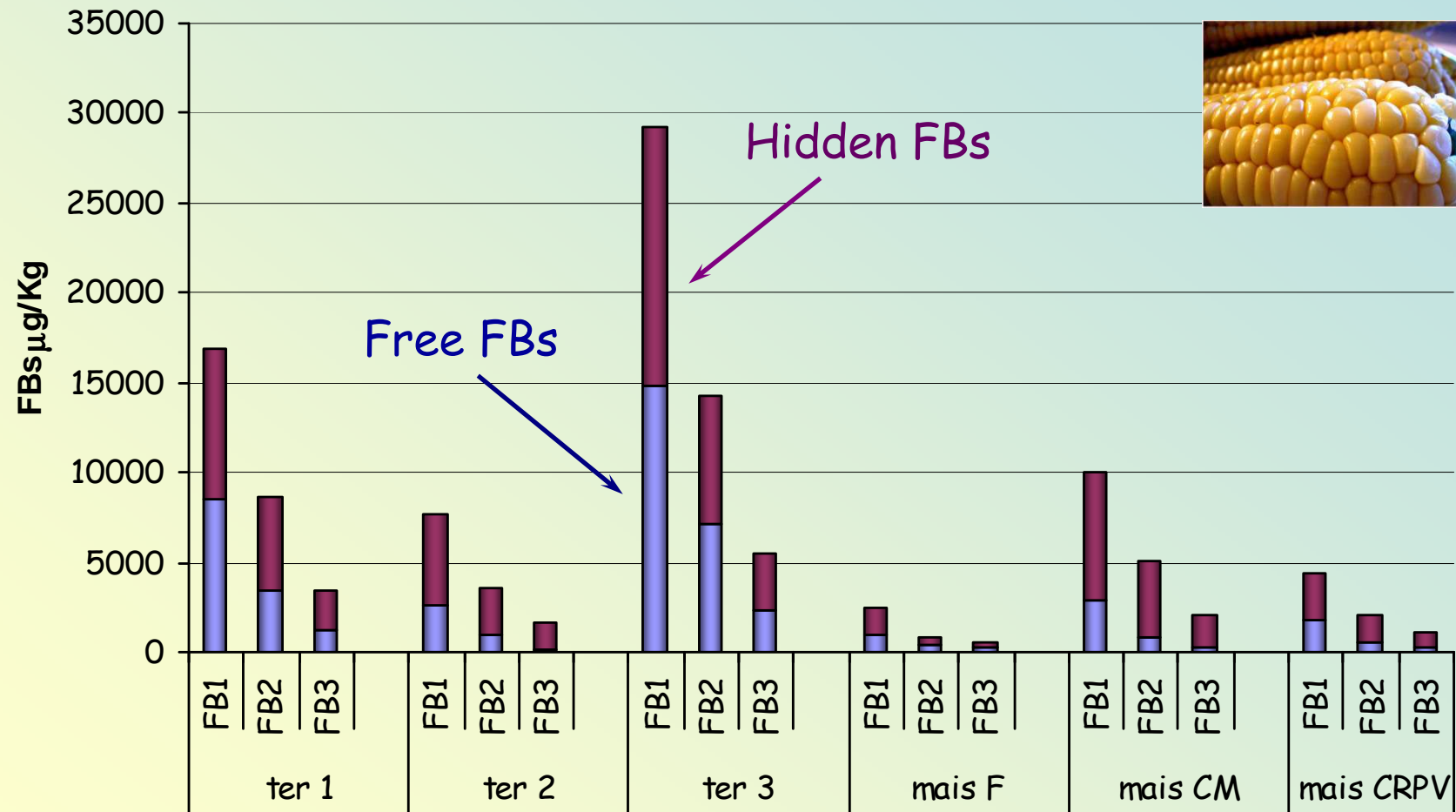
Free and hidden fumonisins in maize products

Dall'Asta, Galaverna, Mangia, Sforza, Dossena, Marchelli, *Mol. Nutr. Food Res.* 2009, 53, 492



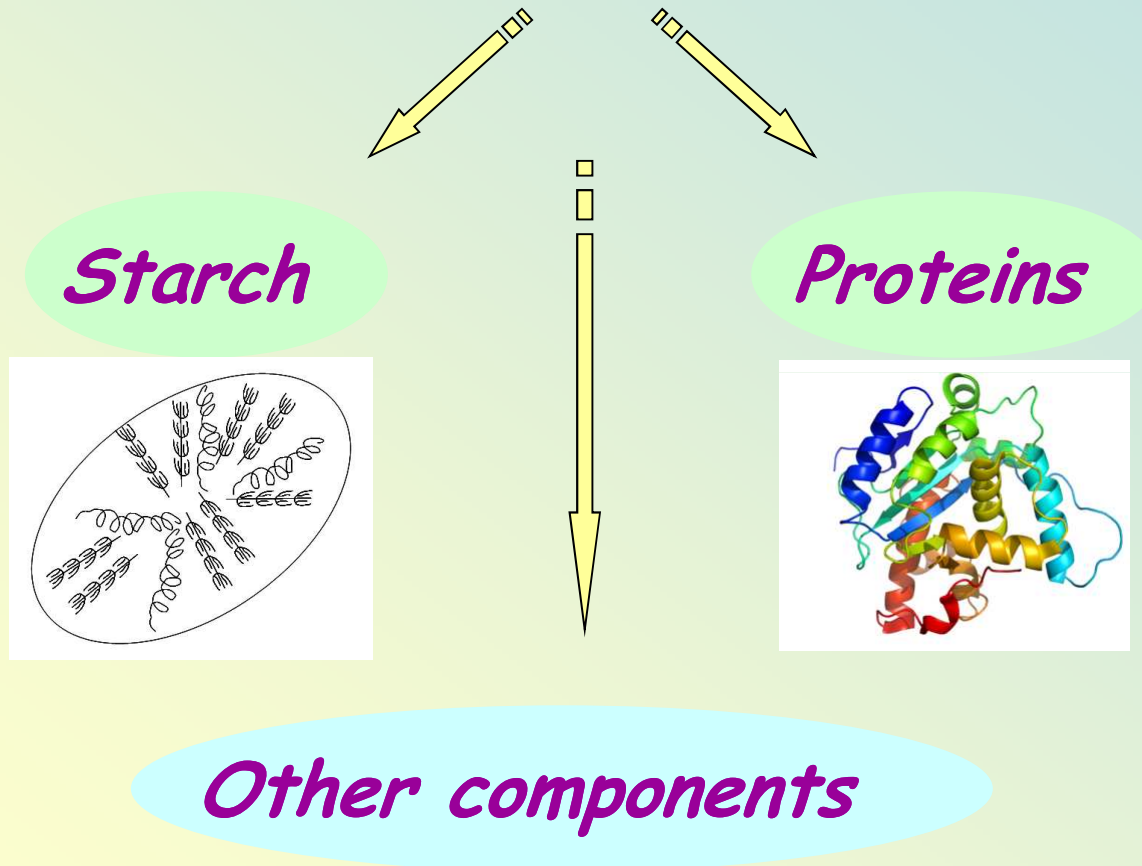
Hidden forms in comparable amount with free forms.

Hidden fumonisins in raw maize



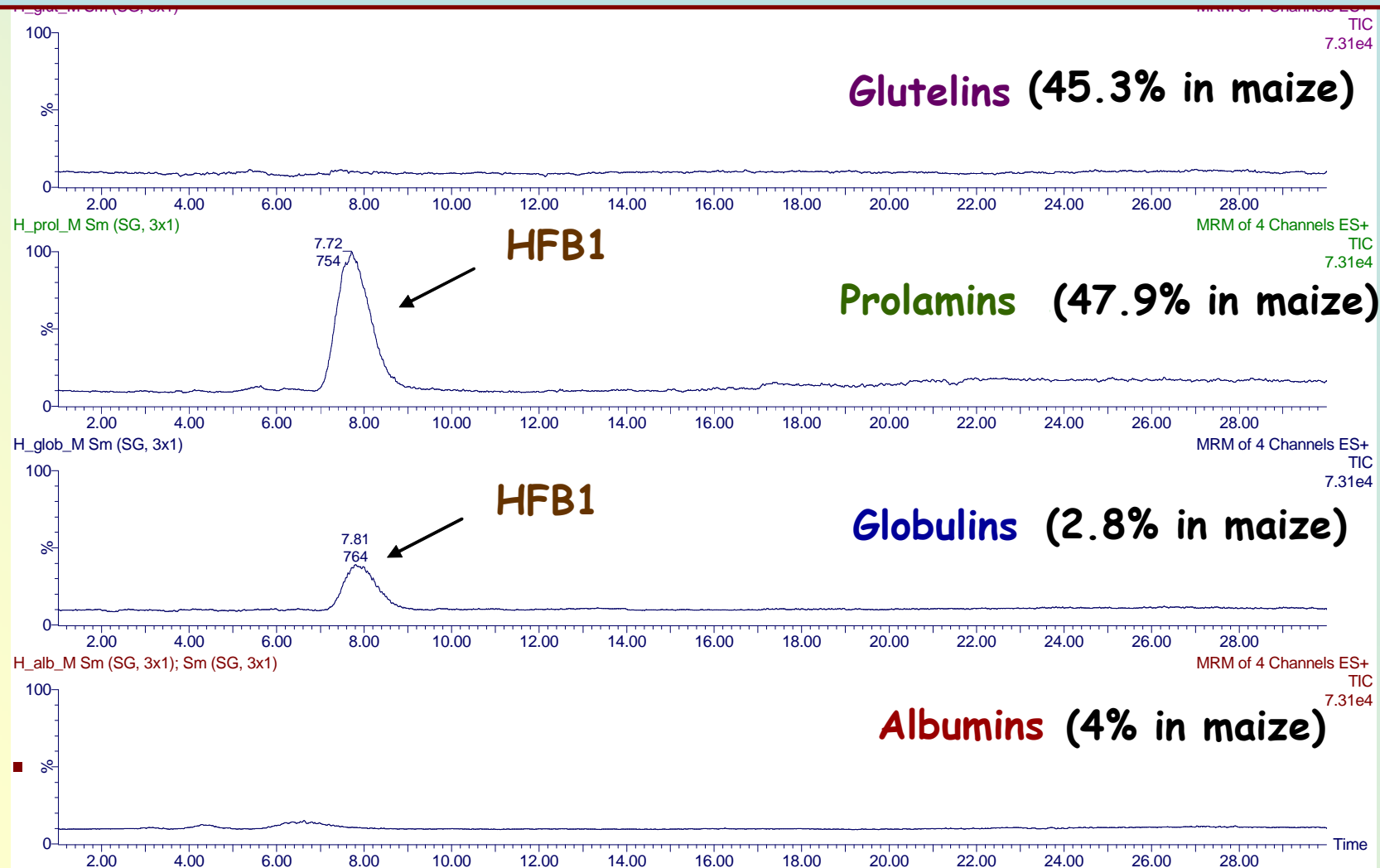
The presence of hidden fumonisins in raw maize cannot be ascribed to thermal treatment.

Hidden fumonisins: where?



Alkaline hydrolysis of Osborne fractions of maize proteins

Dall'Asta, Galaverna, Aureli, Dossena, Marchelli *World Mycotoxin Journal*, 2008, 1(3), 1-10.

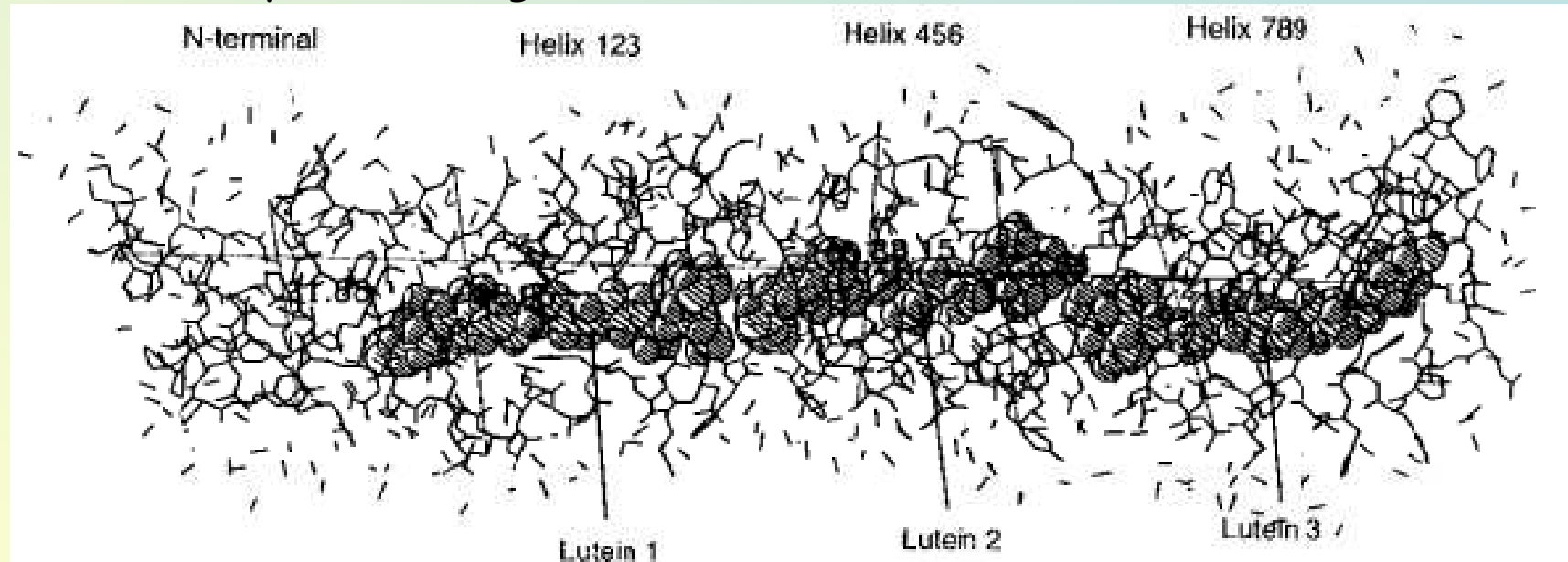


Hidden fumonisins are mainly associated with prolamins (maize zeins).

Hidden fumonisins: which kind of interaction?

Structural characterization of α -Zein

F.A. Momany et al., *J. Agric. Food Chem.* 54 (2006) 543-547.



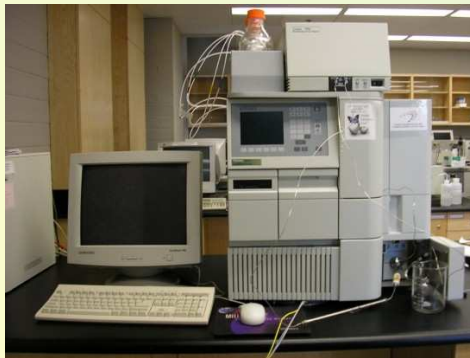
Prolamins (zeins) are able to bind/complex different kind of molecules (xanthophylls, fatty acids).

Physical entrapment/complexation into the protein bodies?

*Which kind of evidences?
Which kind of implications?*



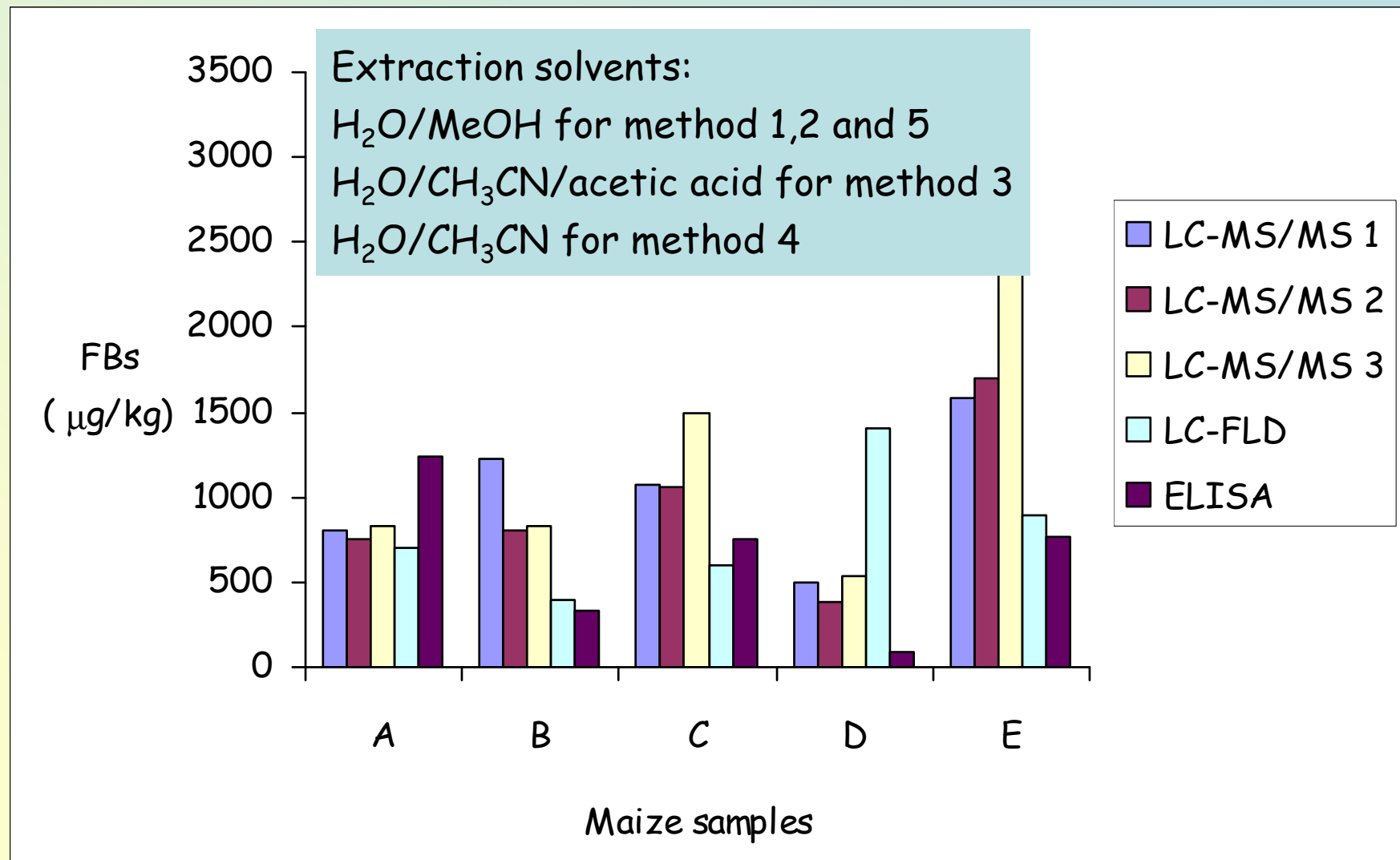
*Analytical
problems?*



*Potential risk
for consumers?*

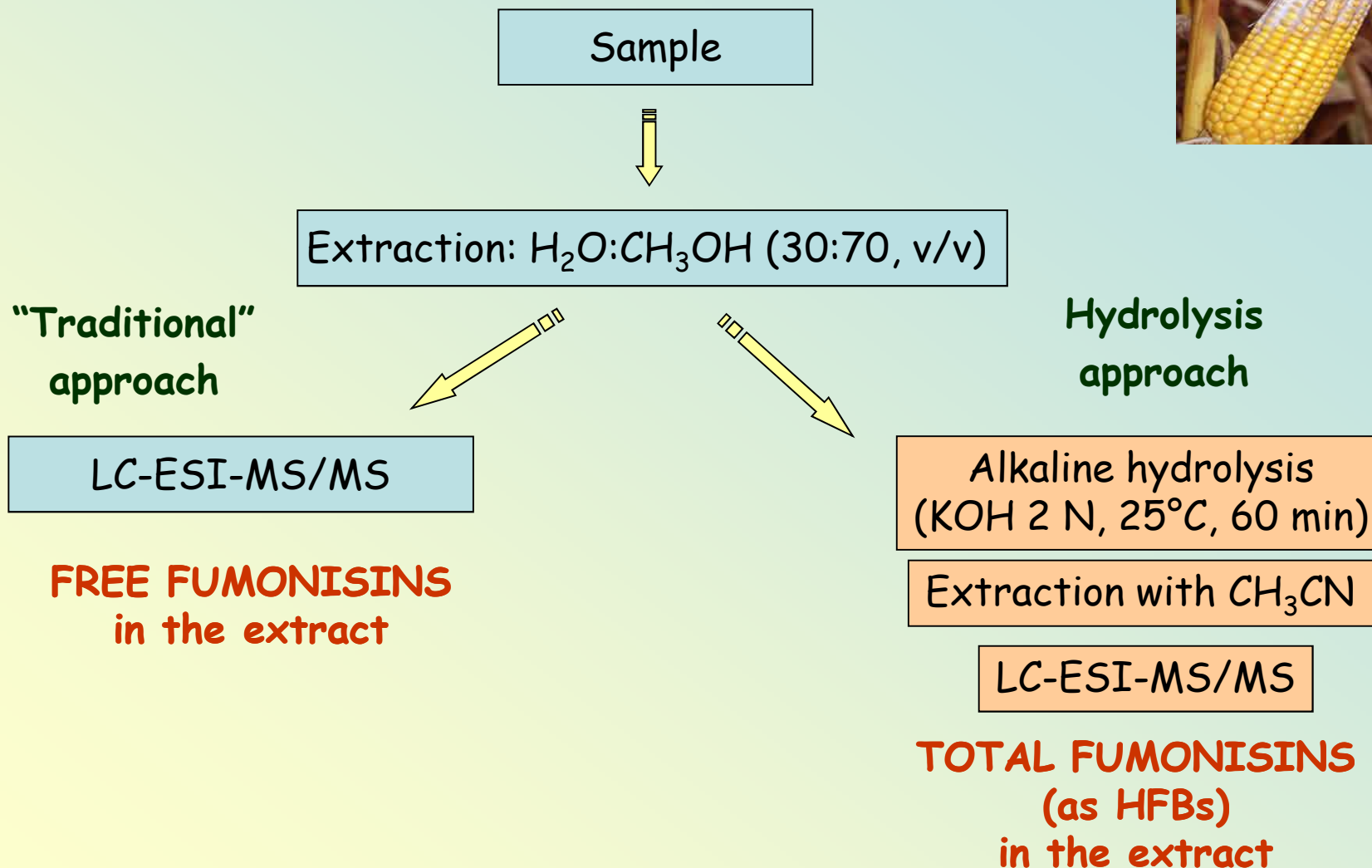


Poor consistency between different methods



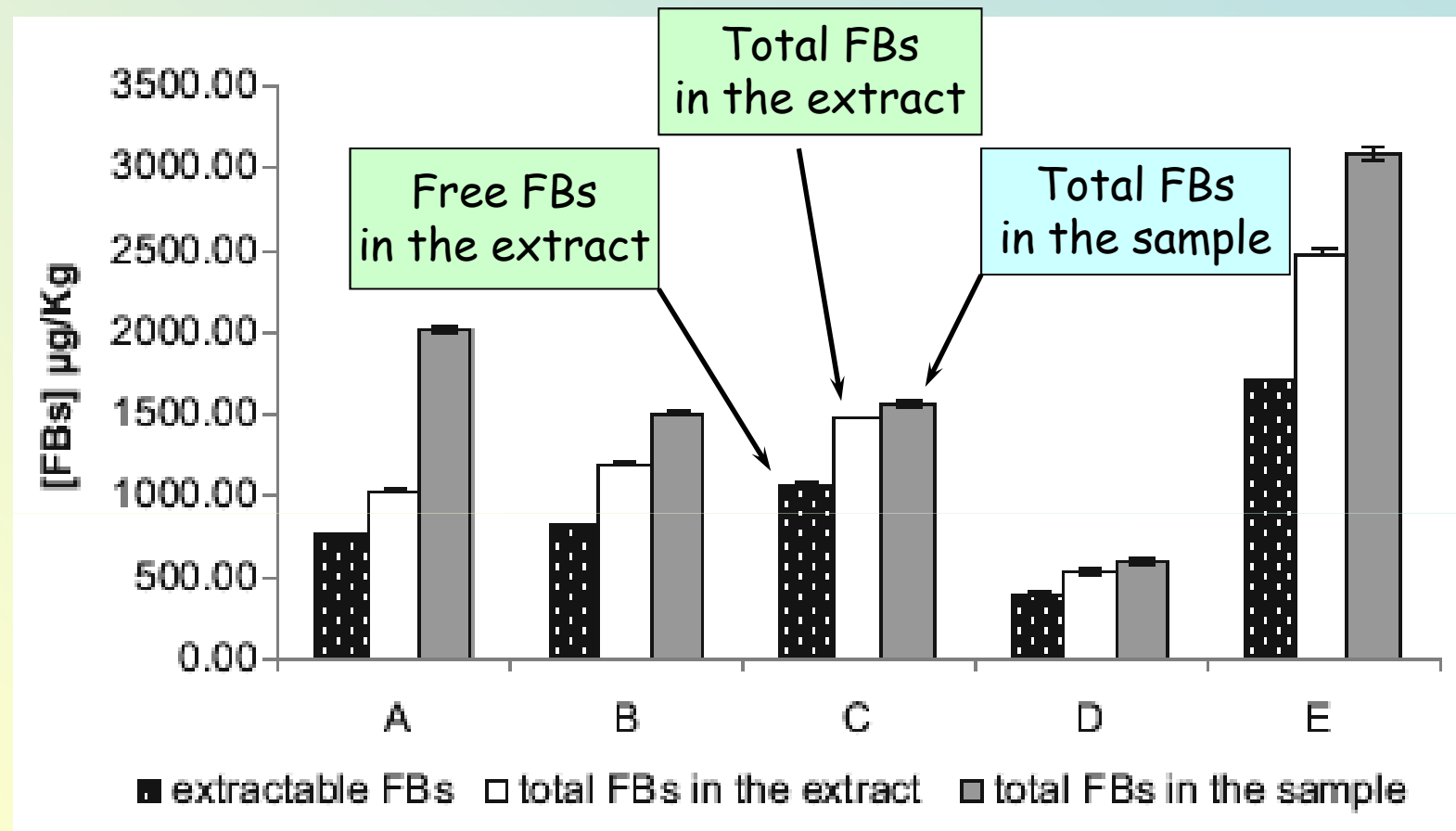
Dall'Asta, Mangia, Berthiller, Molinelli, Sulyok, Schuhmacher, Krska, Galaverna, Dossena, Marchelli, *Anal. Bioanal. Chem.*, 2009, 395, 1335-1345

Hidden fumonisins in the extract?



Dall'Asta, Mangia, Berthiller, Molinelli, Sulyok, Schuhmacher, Krska, Galaverna, Dossena, Marchelli, *Anal. Bioanal. Chem.*, 2009, 395, 1335-1345

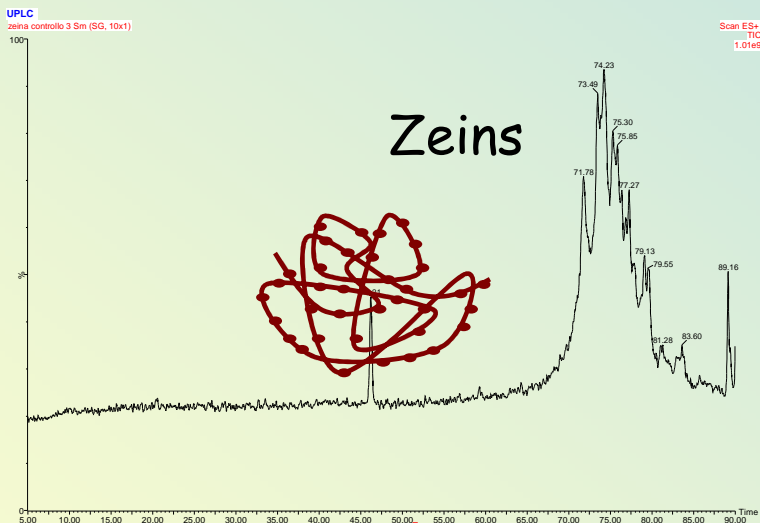
Hidden fumonisins in the extract



A certain amount of hidden fumonisins are already present in the extract, closely associated with the protein fraction.

Dall'Asta, Mangia, Berthiller, Molinelli, Sulyok, Schuhmacher, Krska, Galaverna, Dossena, Marchelli, *Anal. Bioanal. Chem.*, 2009, 395, 1335-1345

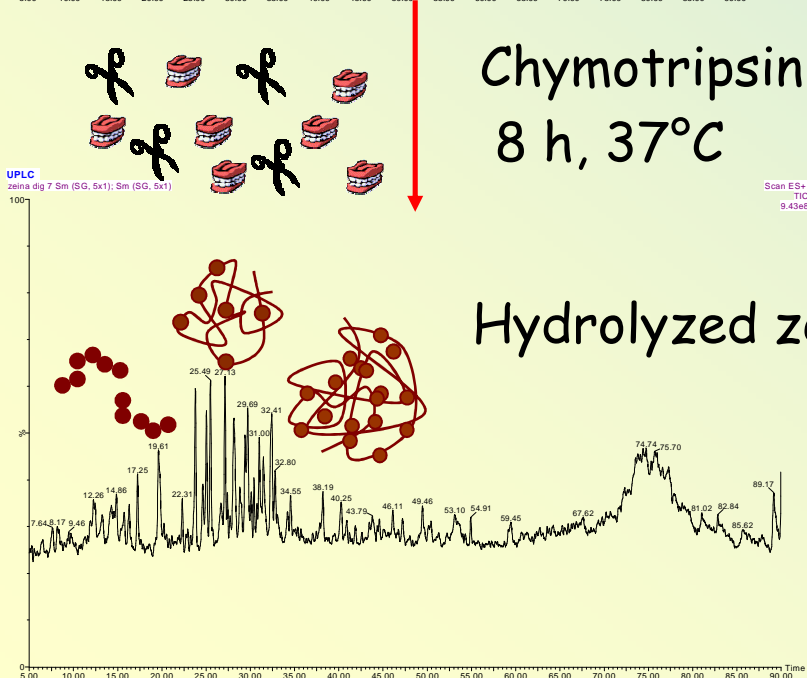
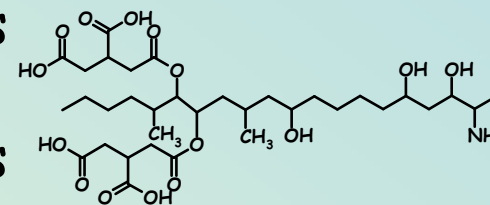
Chymotryptic digestion of the protein fraction



Extraction of the prolamin fraction (EtOH/H₂O = 70:30)

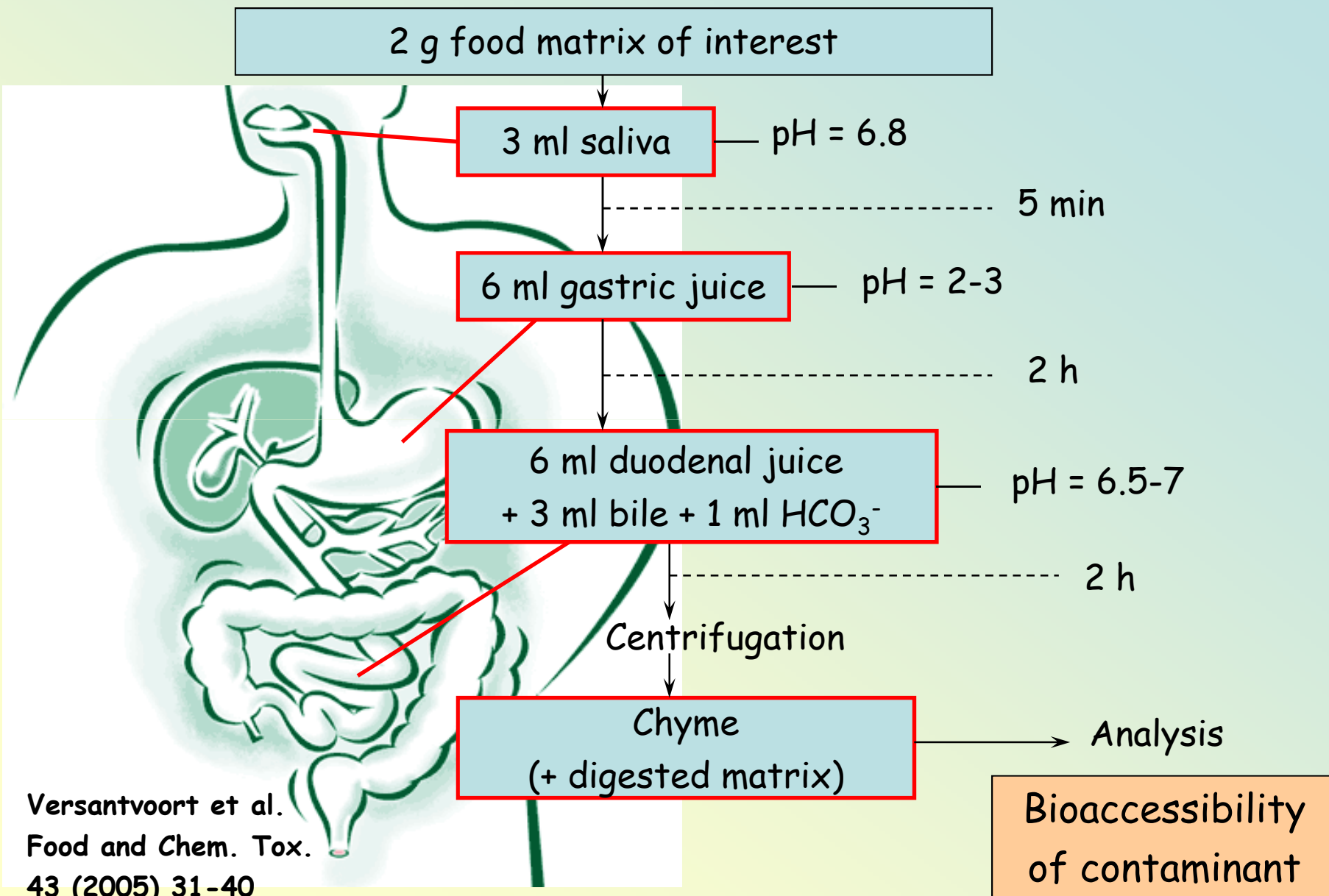
Analysis of free FBs

Analysis of free FBs after digestion



Chymotripsin
8 h, 37°C

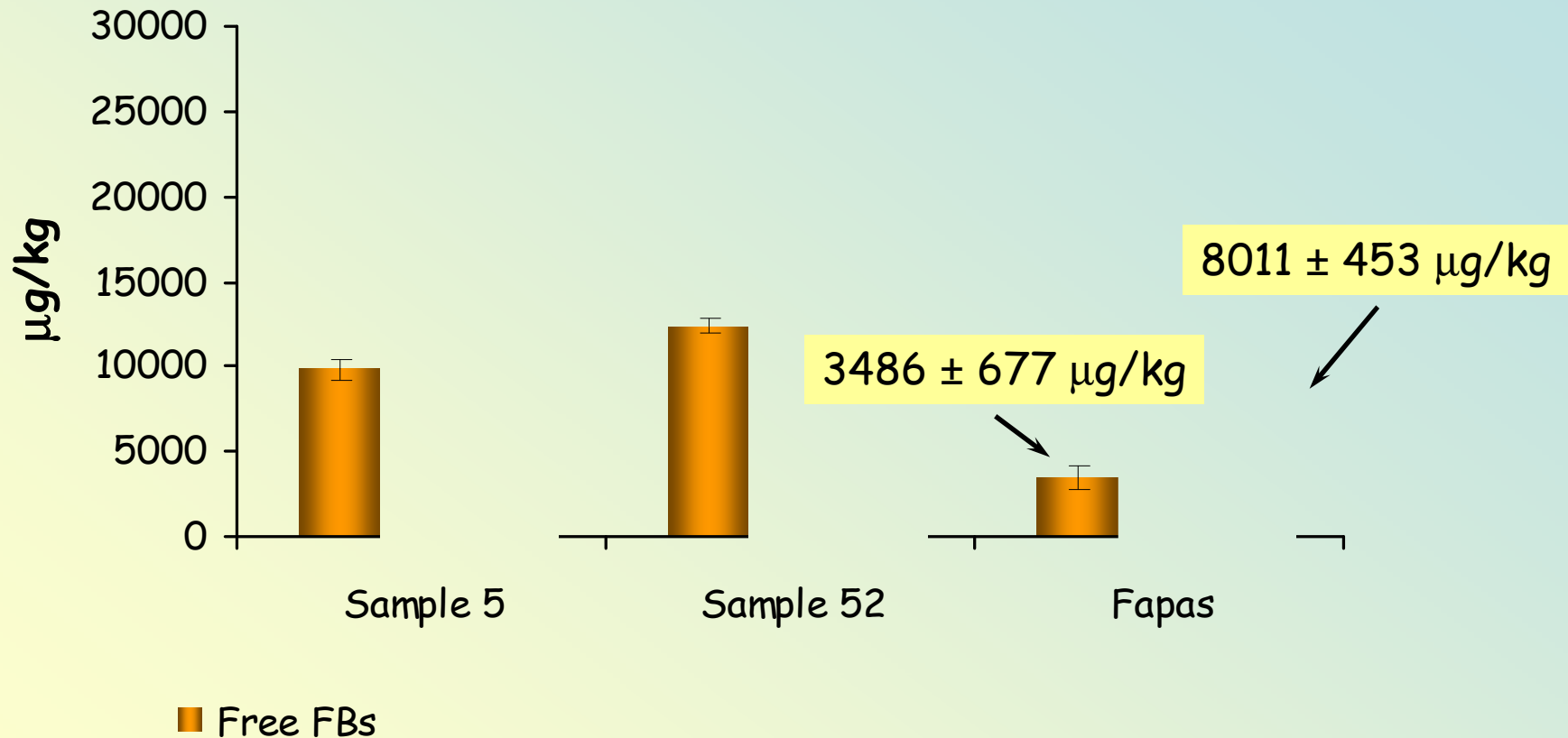
In vitro digestion model



Versantvoort et al.
Food and Chem. Tox.
43 (2005) 31-40

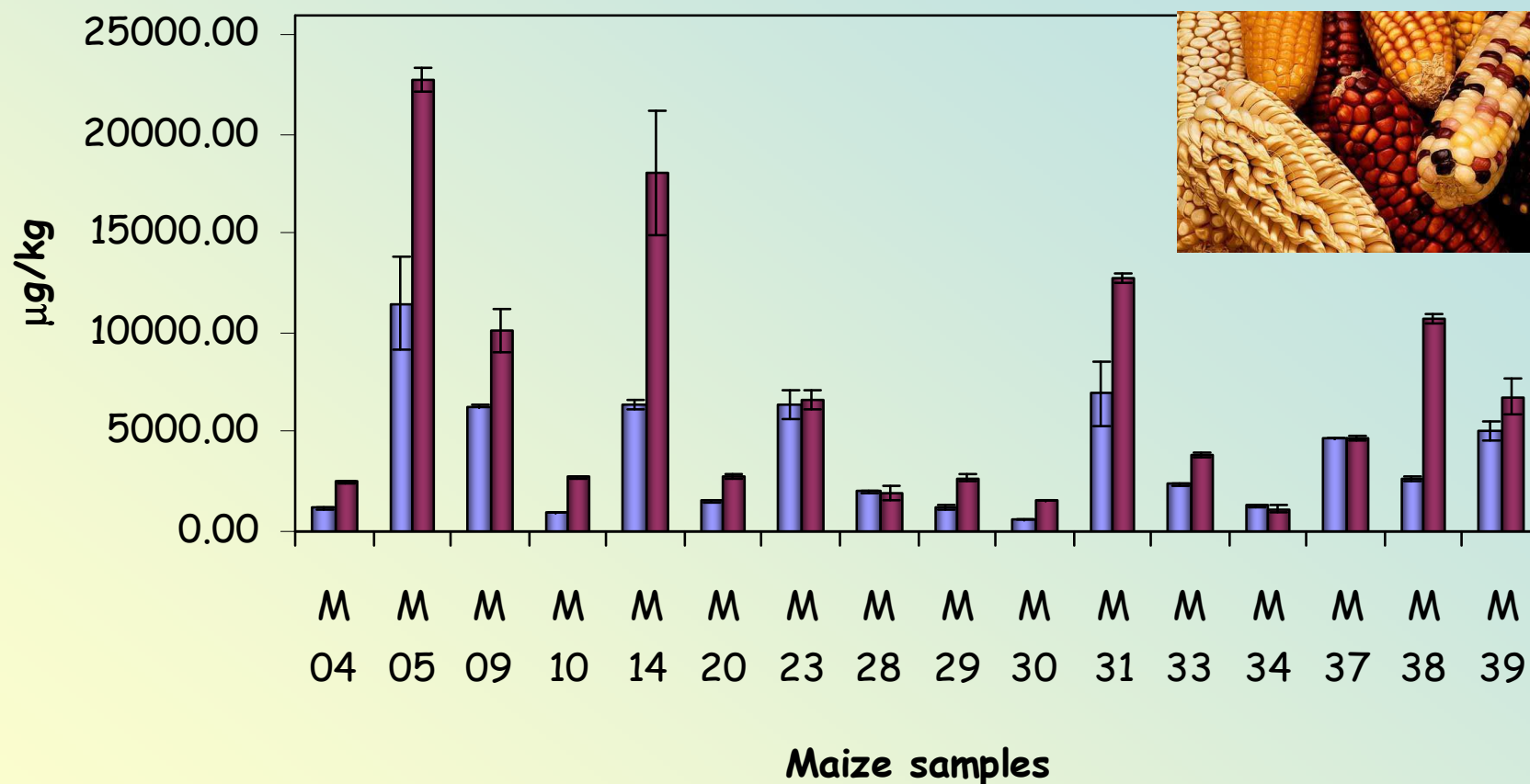
Free and hidden FBs in raw maize samples

Dall'Asta, Mangia, Berthiller, Molinelli, Sulyok, Schuhmacher, Krska, Galaverna, Dossena, Marchelli, *Anal. Bioanal. Chem.*, 2009, 395, 1335-1345



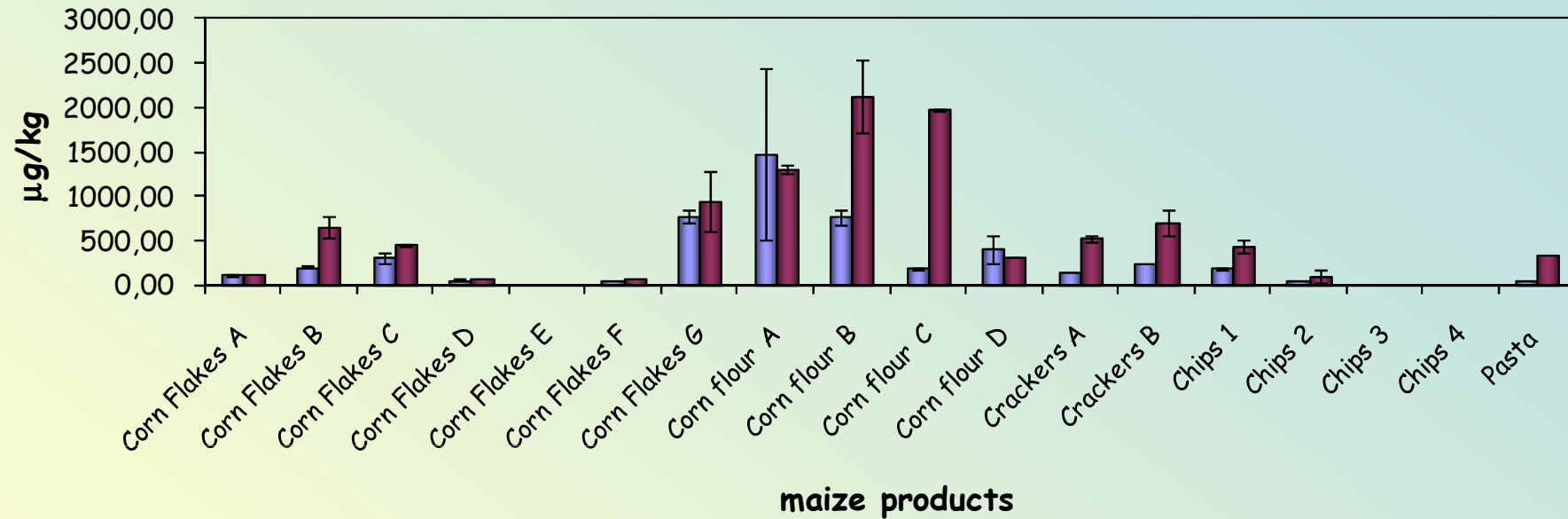
The amount of detectable FBs upon digestion is almost double that of free FBs determined with standard protocol!!!!

Digestion protocol applied to raw maize samples: a survey



A survey on different raw maize samples confirmed the observed general trend: occurrence of hidden fumonisins.

A survey of maize products



■ Free fumonisins ■ Fumonisin after digestion

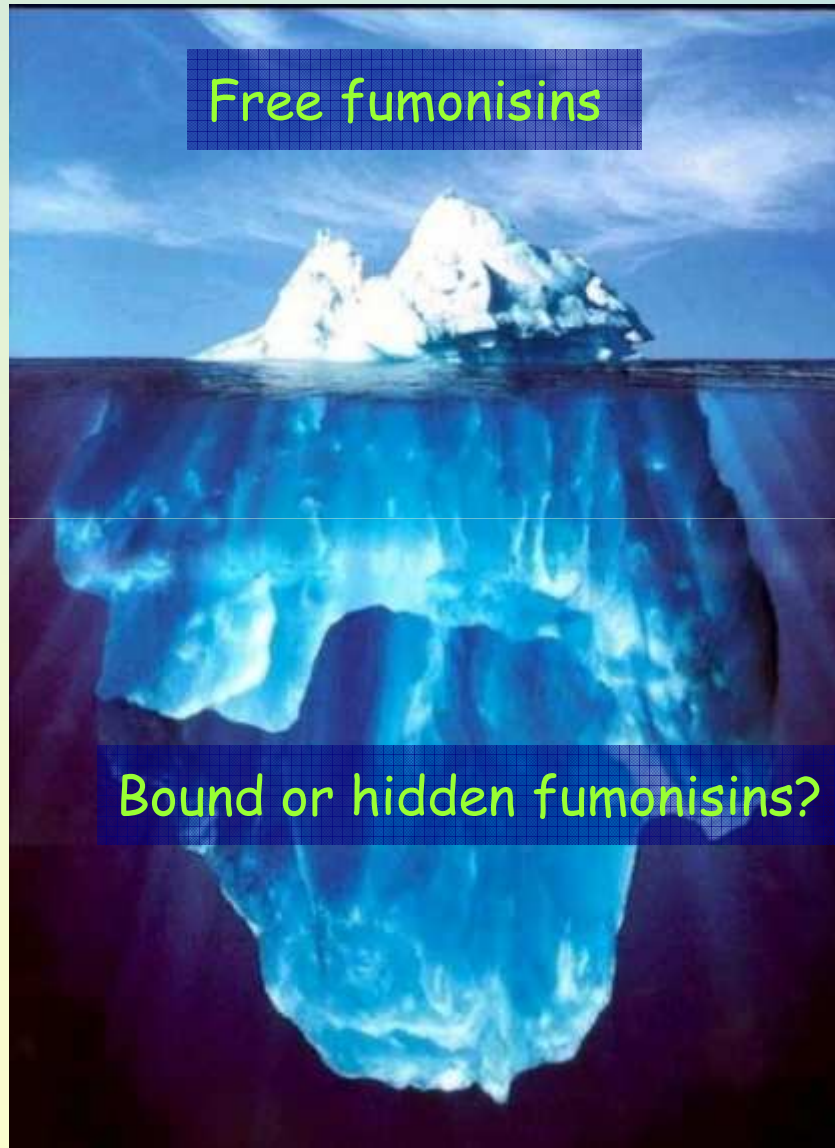


A similar situation is also observed in different maize products.

Conclusions and perspectives

Nature of the matrix-component interactions?

Fate of free fumonisins and their hidden forms during processing?



Toxicity and bioavailability of hidden forms?

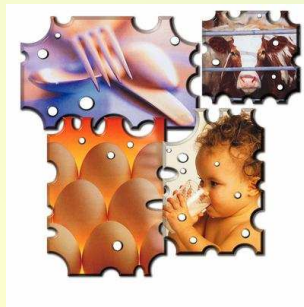
Effects upon:
Stakeholders
Regulators
Exposure data

Acknowledgments



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