Standard substance free quantification of LC/ESI/MS on example of pesticides in cereals

Jaanus Liigand[a], Tingting Wang[b], Piia Liigand [a], Mari Ojakivi [a], Anneli Kruve [a,c]

[a] Institute of Chemistry, University of Tartu, Estonia, kruvelab.com, jaanus.liigand@ut.ee
[b] National Food Institute, Technical University of Denmark, Denmark
[c] Department of Environmental Science and Analytical Chemistry, Stockholm University, Sweden

Introduction

LC/ESI/MS is increasingly applied for qualitative and quantitative analysis in food monitoring. However, analysis of a large number of compounds is a big challenge as standard substances are not always available. One of the possibilities is to use a quantification approach based on in silico predicted electrospray ionization efficiencies. The impediment of detection of food contaminants has been overcome by suspect and non-targeted analysis; still, solving the quantitation issues is still underway. Here we present the application of Quantem approach for pesticide analysis together with a interlaboratory comparison based on two different mass spectrometric setups (triple quadrupole and micro-TOFq) in two different laboratories.

Chemicals

139 pesticides and mycotoxins
- 6 concentration levels
  - 10 nM – 35 µM

Matrices

6 cereals (proficiency test materials EU-PTs):
- Barley C6
- Wheat CF8
- Rye CF10
- Oat C3
- Maize CF9
- Rice SRM6

QuEChERS sample preparation

Instrumentation

University of Tartu - UT
- Agilent 1290 UPLC with Agilent 6495 **Triple Quadrupole**
  - Agilent Zorbax RRHD SB-C18 (1.8 µm, 2.1 × 50 mm)
  - A 0.1% formic acid
  - B Acetonitrile

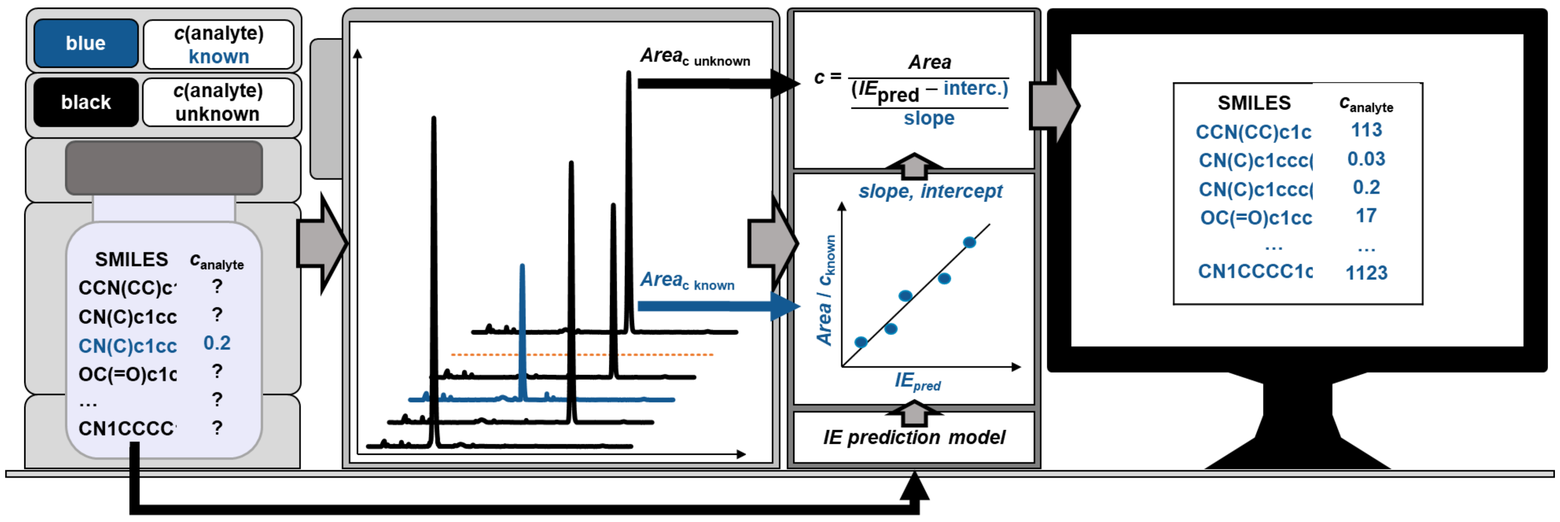
Technical University of Denmark - DTU
- Agilent 1200 HPLC with Bruker Daltonics **micro-TOFq**
  - Nucleoshell C18 (2.7 µm, 2 × 100 mm)
  - A 2.5 mM ammonium formate pH = 3.0
  - B Acetonitrile

Quantification

ESI ionization efficiency predictions
- **Quantem** approach
  - PaDEL Descriptors for Compound
  - Viscosity, surface tension, polarity, pH for eluent
  - **Random Forest Regression**

Transformation with 6 compounds

Workflow



UT

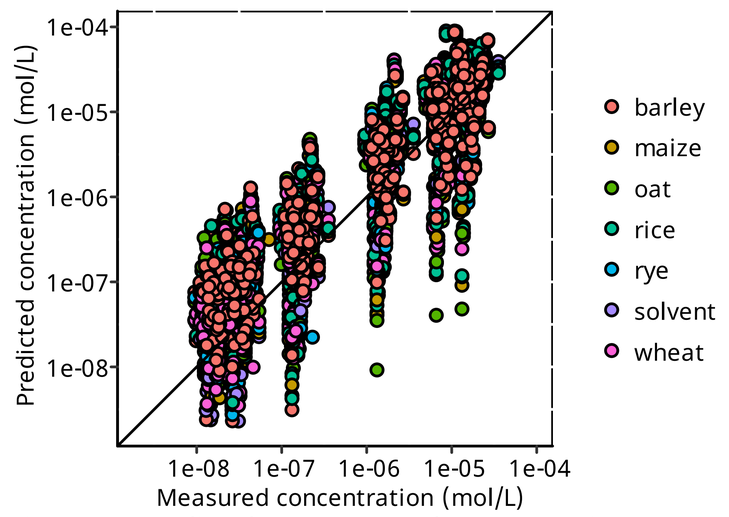


Figure 1 Predicted vs measured concentrations on triple quadrupole in University of Tartu. Black line denotes ideal fit

DTU

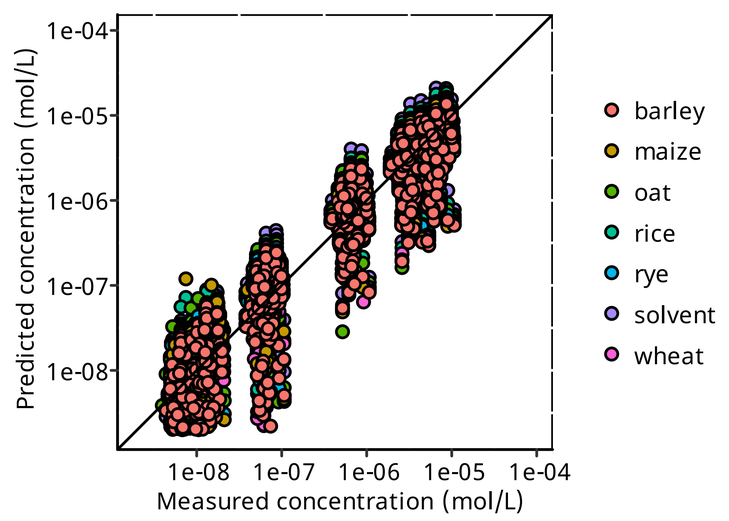


Figure 2 Predicted vs measured concentrations on micro TOFq in Technical University of Denmark. Black line denotes ideal fit

UT vs DTU

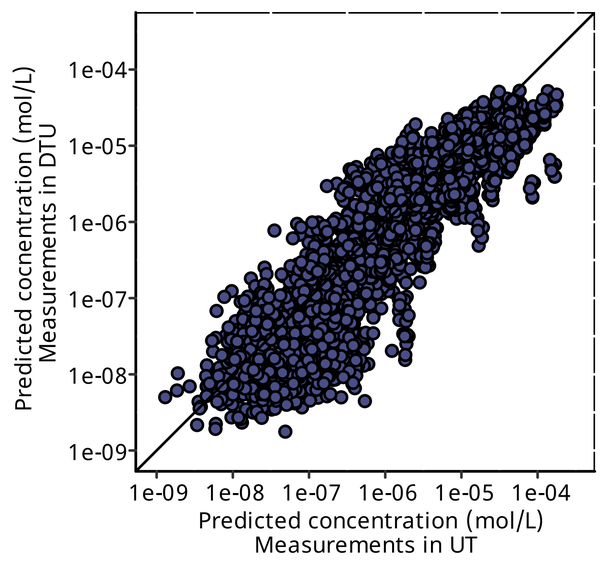


Figure 3 Comparison of predicted concentrations on micro TOFq vs triple quadrupole. Black line denotes ideal fit

Conclusions

Standard substance free quantification in LC/ESI/MS analysis using Quantem approach is feasible

Average concentration prediction error **3.8-times**

Average difference on two instruments **3.2-times**

References

- Kruve and Kaupmees *Anal Chem* 89(9), 2017
- Liigand J et al submitted 2019
- Liigand P et al submitted 2019
- Wang T et al submitted 2019
- quantem.co

Acknowledgement

This work has been supported by PRG 300 from Estonian Research Council, by the institutional funding IUT20-14 (TLOKT14014I) from the Ministry of Education and Research of Estonia and by smart specialization doctoral stipend.