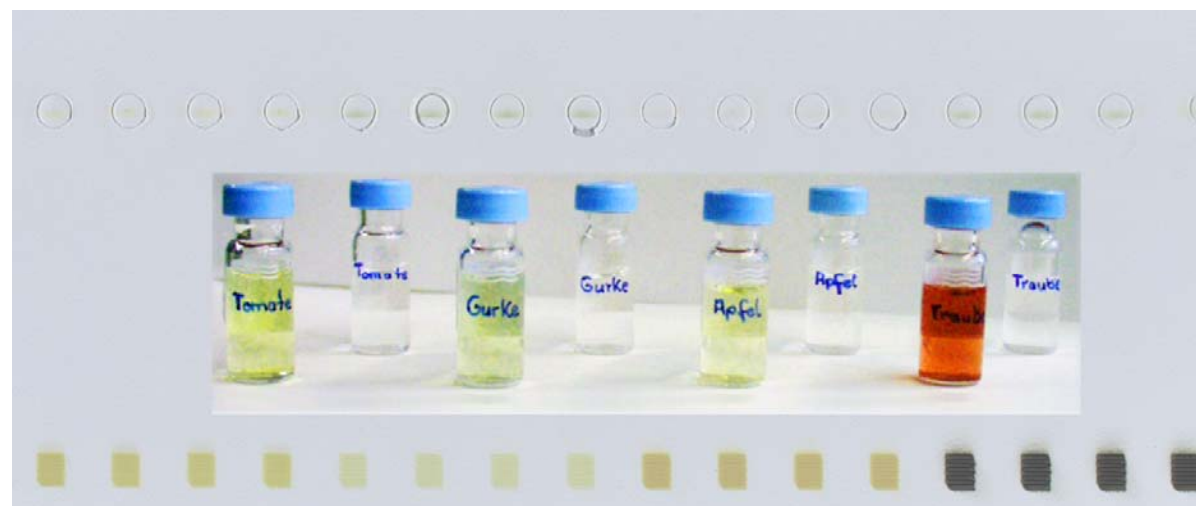


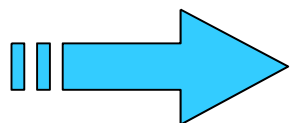
Planar solid phase extraction – a new clean-up concept in multi-residue analysis of pesticides

Wolfgang Schwack, Claudia Oellig
University of Hohenheim



Current problems in pesticide residue analysis of food

- a plenty of matrix compounds in fruits and vegetables, co-extracted with pesticides
- matrix effects: co-elution, retention time shifting, MS signal enhancement / suppression
- matrix-matched standards must be used (less-than-ideal solution)

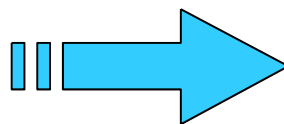


efficient clean-up methods are essential

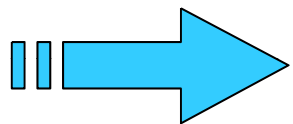
Current clean-up methods in pesticide residue analysis

- dispersive SPE (PSA, GCB, C18)
- cartridge SPE (same materials)
- GPC (gel permeation chromatography)

- time and solvent consuming
- clean-up insufficient
- loss of pesticides



many compromises

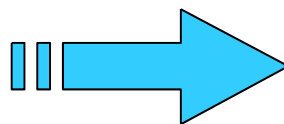


current clean-up methods are not really satisfactory

Current clean-up methods in pesticide residue analysis

- dispersive SPE (PSA, GCB, C18)
- cartridge SPE (same materials)
- GPC (gel permeation chromatography)

- time and solvent consuming
- clean-up insufficient
- loss of pesticides



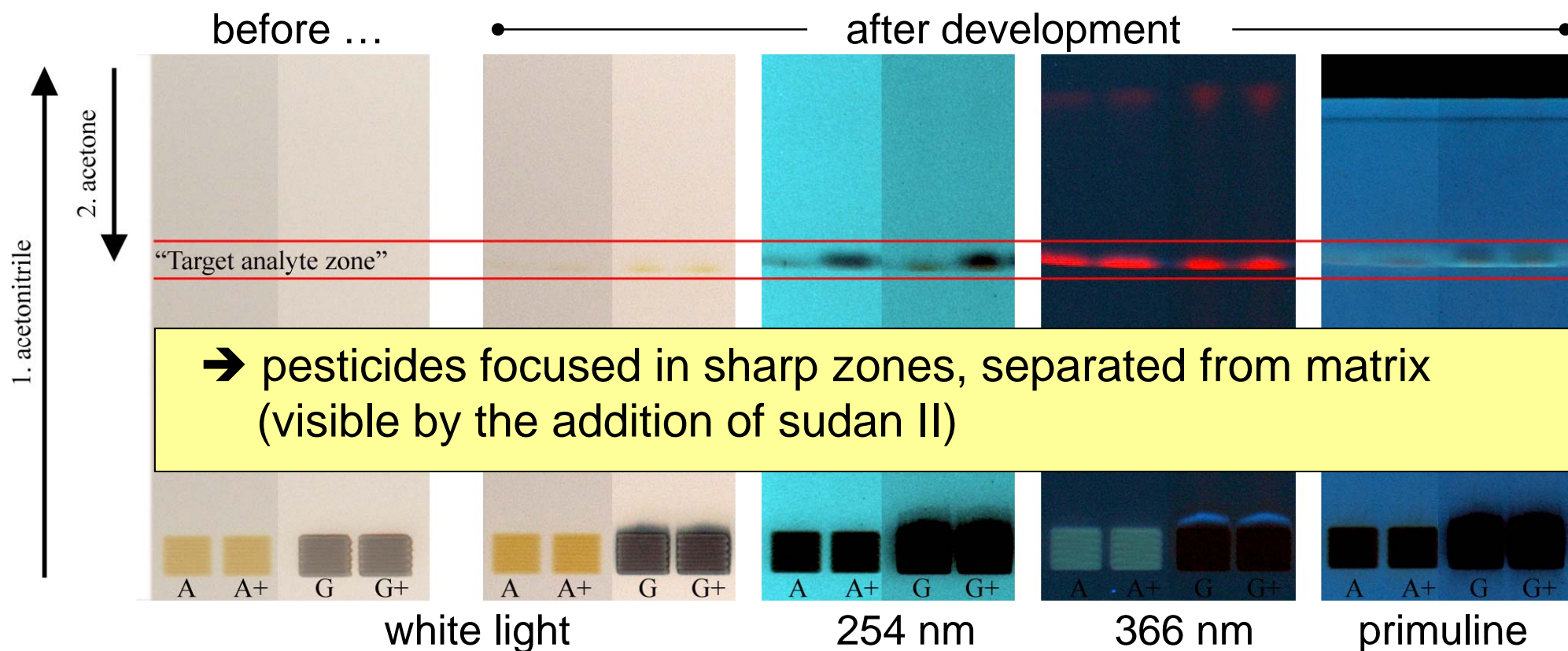
many compromises



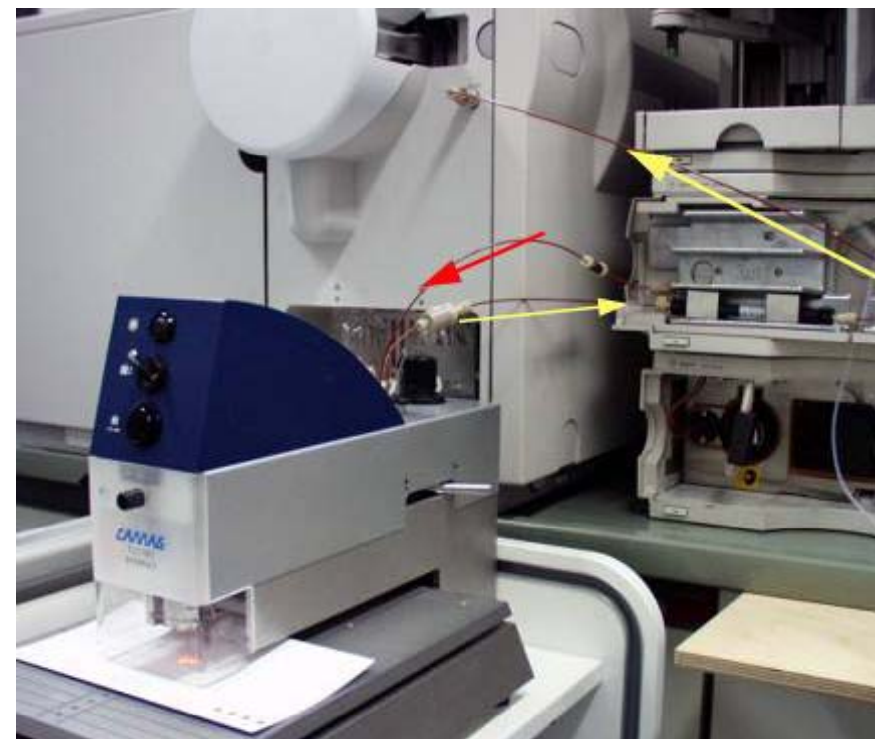
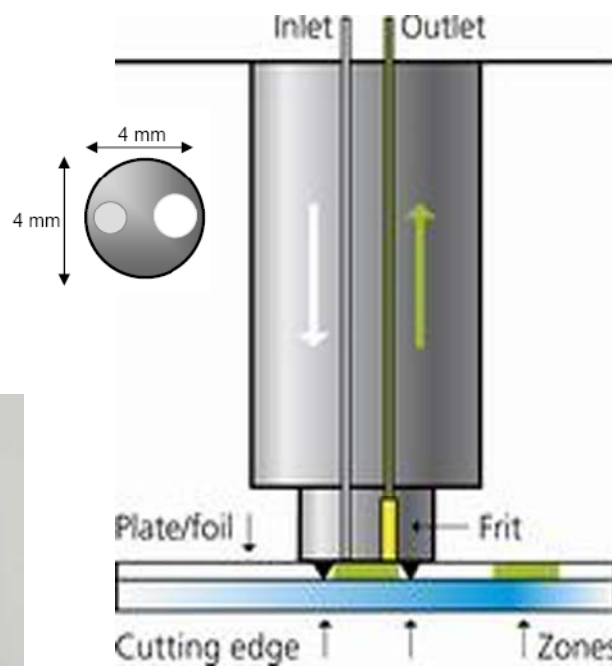
New approach

Planar chromatography for the separation of target pesticides from matrix compounds (HTpSPE)

- layer type: TLC silica gel 60 NH₂ F₂₅₄s aluminum sheets
- layer modification: dipping (2 cm) into 2% formic acid in acetonitrile
- area application: 3 x 4 mm (50 μL)
- 2-fold development: 1. acetonitrile (75 mm)
2. acetone (45 mm, back direction)

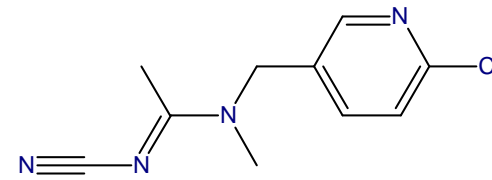


TLC-LC/MS

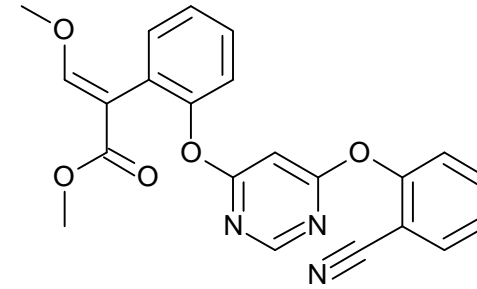


- **Extraction of target zones** (acetonitrile/10 mM ammonium formate)
 - **on-line coupling to LC column** (Chromolith RP-18)
 - **elution into autosampler vials** (LC/MS or GC/MS)

- different pesticide groups
- various chemical classes
- different in polarity/acid constants
- internal standard: **TDCPP** (tris(1,3-dichloropropan-2-yl)-phosphate)

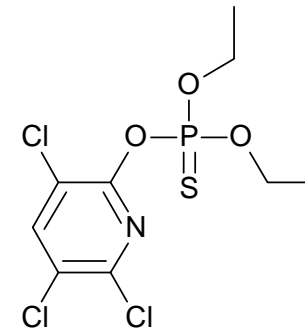
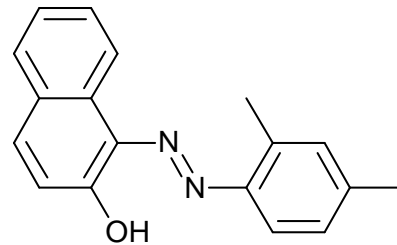


Acetamiprid

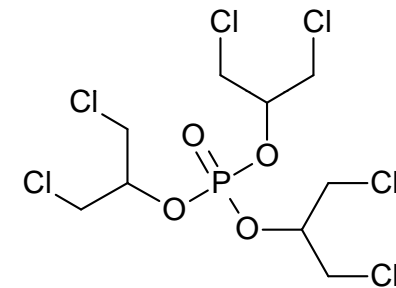


Azoxystrobin

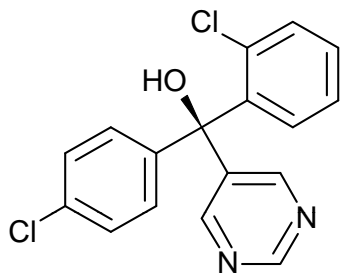
Sudan II



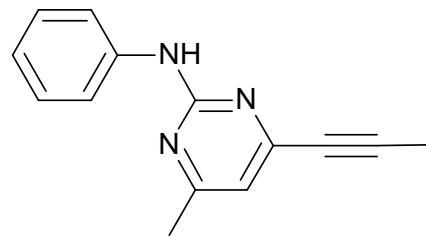
Chlorpyrifos



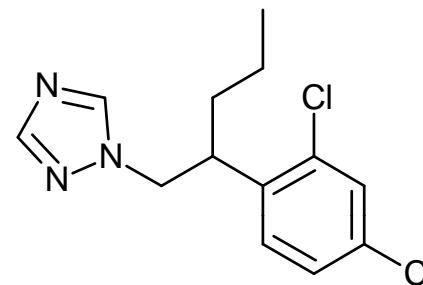
TDCPP



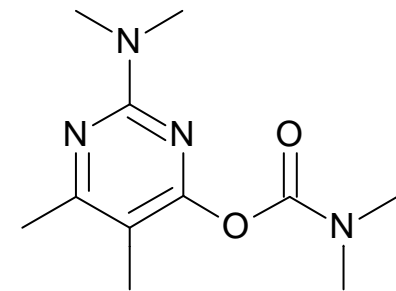
Fenarimol



Mepanipyrim



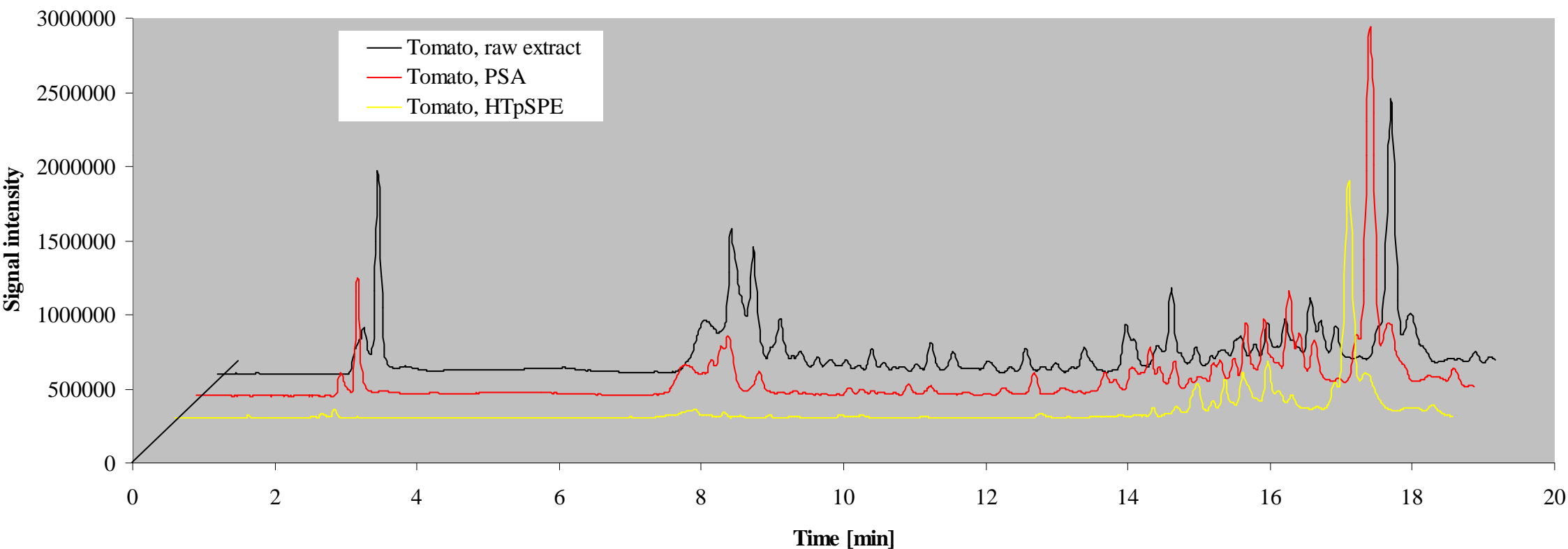
Penconazole



Pirimicarb

HTpSPE – Clean-up effect

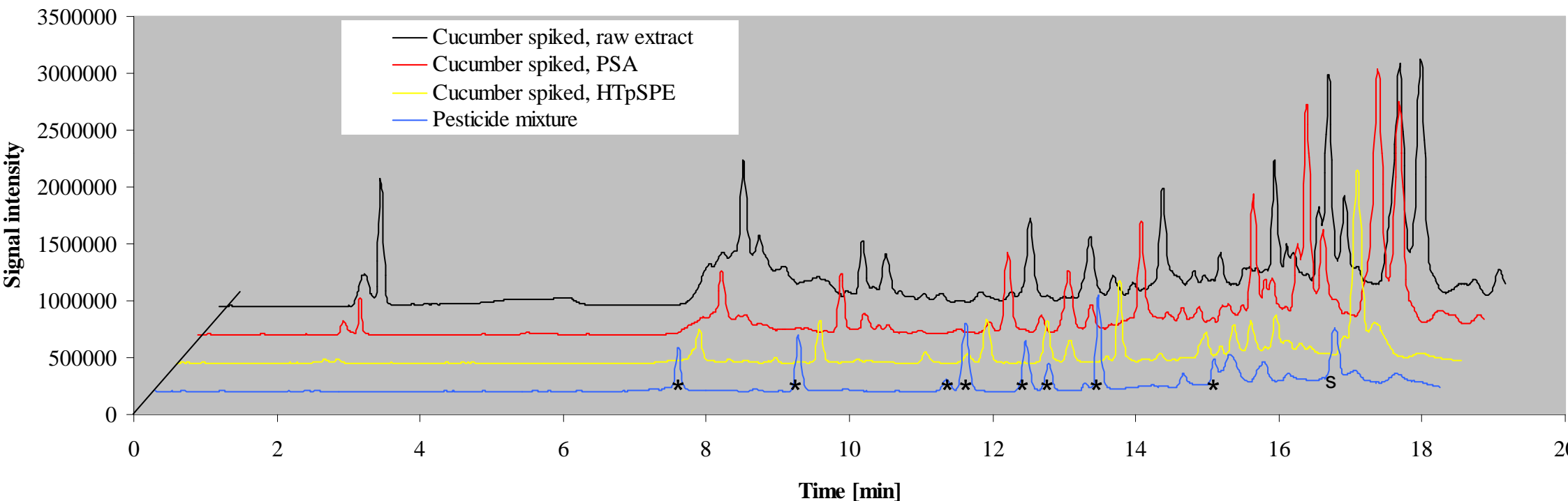
- total ion chromatograms (TICs) of tomato extracts



➔ HTpSPE extracts are very clean as compared to current clean-up methods

HTpSPE – Clean-up effect

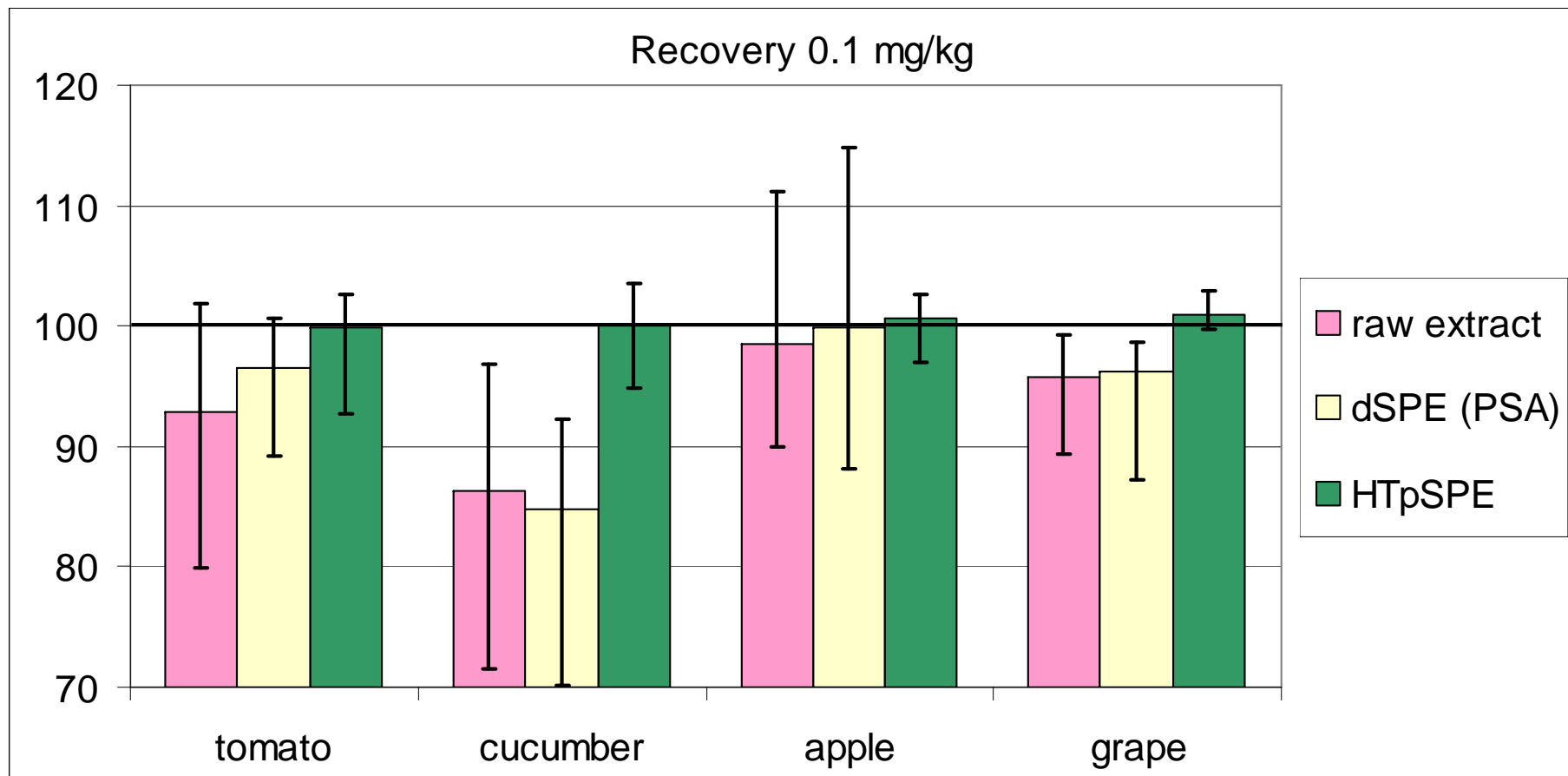
- TICs of spiked cucumber extracts and a pesticide standard mix



- ➔ Nearly identical profiles of the pesticide standard mix and spiked extracts after HTpSPE (calibration with solvent standards possible)

Recovery experiments by LC/MS : 0.5 mg/kg and 0.1 mg/kg

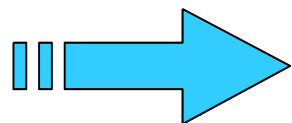
- mean recoveries of seven pesticides in raw extracts and after clean-up (n=5)



➔ no matrix effects, higher recoveries after HTpSPE, lower SD

HTpSPE clean-up benefits

- very clean extracts -> **equipment-friendly**
- no loss of pesticides, no matrix effects, excellent recoveries
- 80 % automated (instrumental HPTLC)
- 20 extracts simultaneously
- time-saving, only 5 min/sample
- low solvent consumption, 1 mL/sample



HTpSPE is a rapid, cost-efficient, and effective alternative to currently used clean-up methods (dSPE, cSPE, or GPC)

Many thanks for your attention !

Thanks to CAMAG (Berlin, Germany) and Merck (Darmstadt, Germany) for equipment and plate material.



extraction

matrices:

- tomato
- cucumber
- apple
- grape



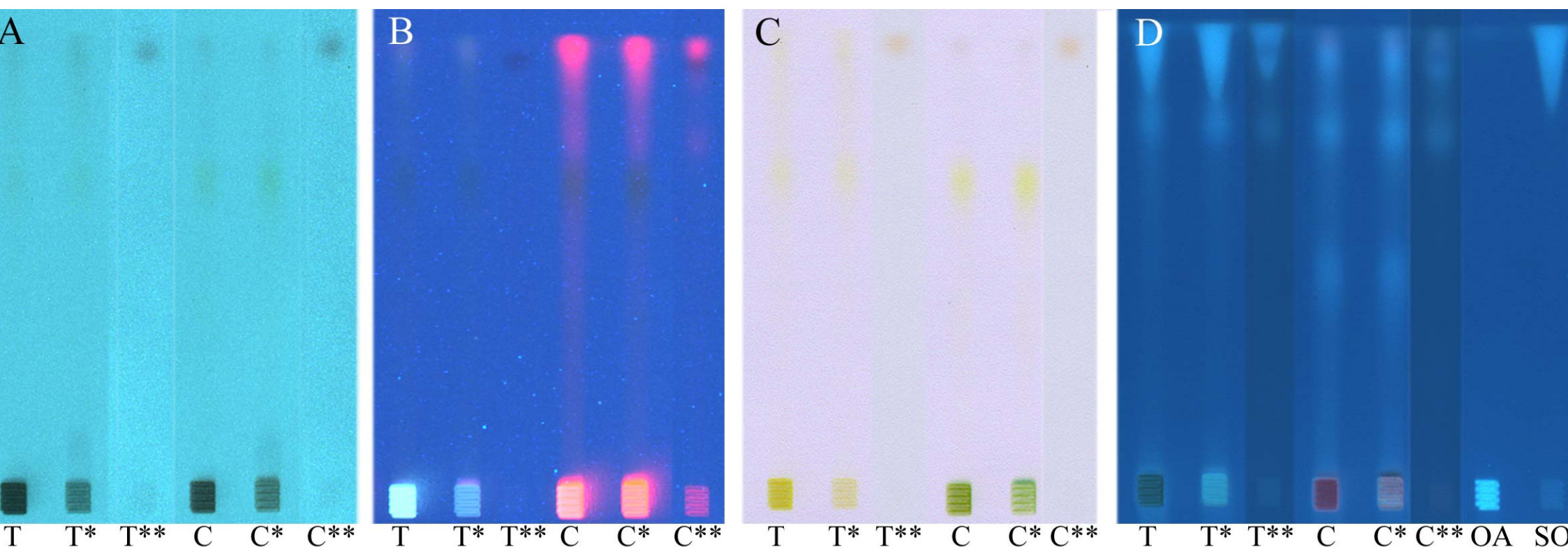
HTpSPE clean-up



TLC-LC/MS



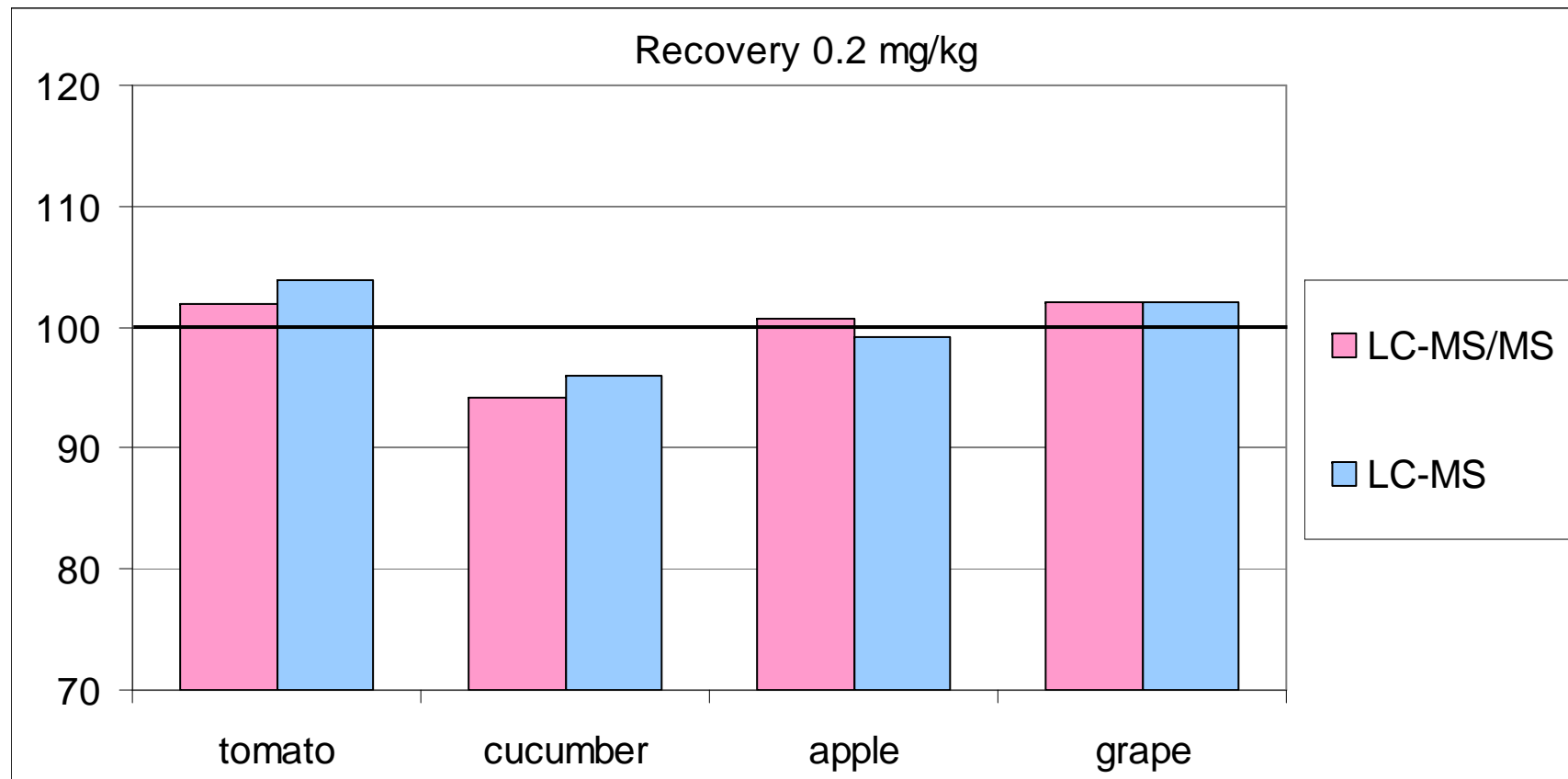
HTpSPE Clean-up – cleaning effect



Matrix load of extracts: tomato (T) and cucumber (C) raw extracts, after dSPE with PSA (*) and after HTpSPE (**) on TLC silica gel 60 NH₂ F₂₅₄s aluminum sheets; oleic acid (OA) and soy oil (SO); after development with acetonitrile to a migration distance of 75 mm, UV 254 (A), UV 366 (B), white light (C), and UV 366 after dipping in primuline solution (D))

Recoveries after HTpSPE clean-up: LC-MS vs. LC-MS/MS; 0.2 mg/kg

- average recovery over seven pesticides (n=1)



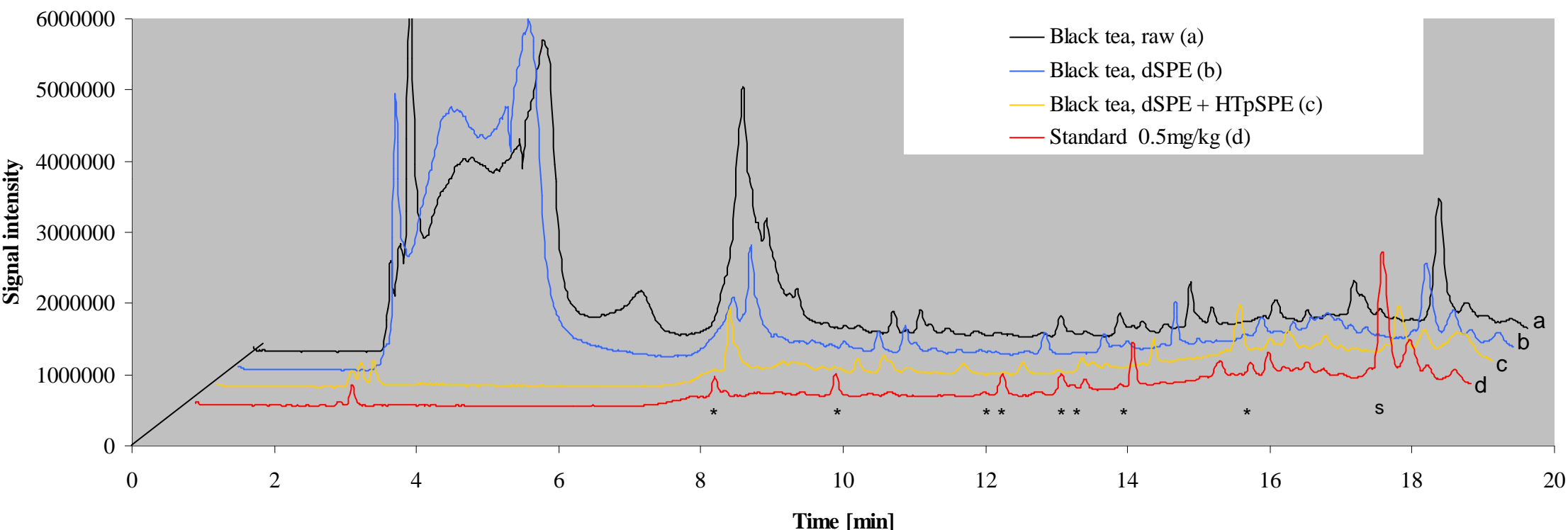
- LC/MS and LC/MS-MS show identical results (higher recoveries for HTpSPE extracts)



HTpSPE – Modification for black tea

- Very difficult matrix
- High matrix amount many interfering compounds
- High amount of co-extractive substances (additional step before HTpSPE to reduce the high matrix amount to use analytic plates, otherwise prep. Layers!
- Pre-clean up with dSPE (PSA + C18 material), caffeine is not separated
- High amount of caffeine (caffeine not separated from pesticides on amino modified layers! -> change separation strategy)
- layer material and solvent change (silica layer, solvent for 2. development: acetone/water 9/1)

- TICs of spiked matrix and a pesticide standard
- dSPE + HTpSPE extracts, dSPE (PSA + c18) extracts and raw extracts



- ➔ dSPE + HTpSPE extracts show lowest baseline
- ➔ TICs of spiked dSPE + HTpSPE extracts show nearly similar profile as a pesticide standard
- ➔ identical result for different teas (green and black tea)