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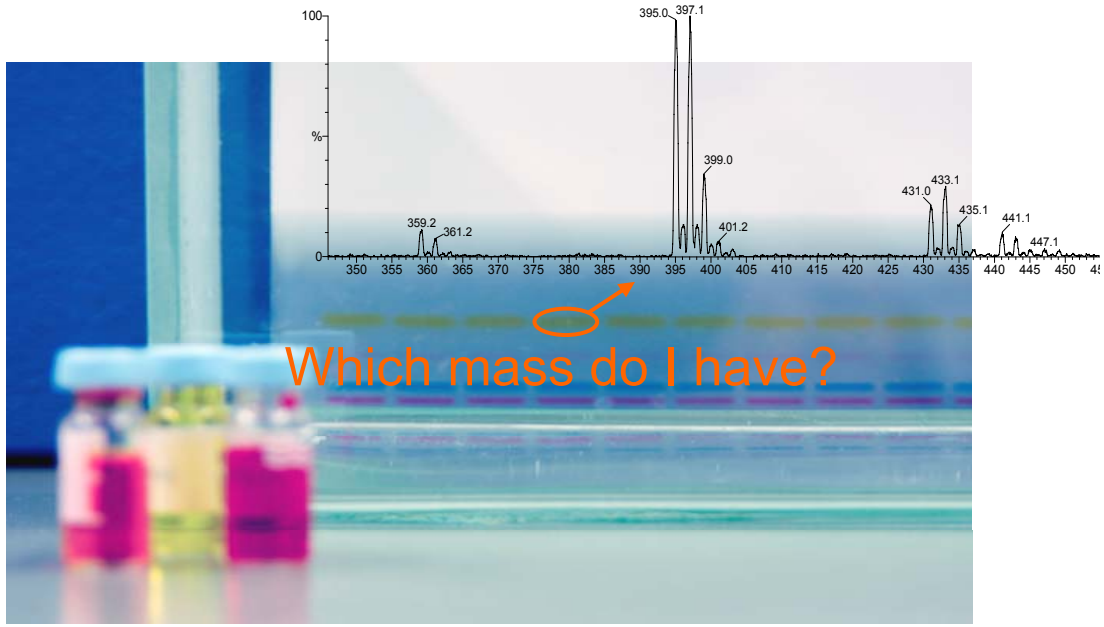
Coupling of planar chromatography with MS - comparison of three approaches DART, ESI and APGD



G. Morlock, Institute of Food Chemistry
University of Hohenheim, Stuttgart

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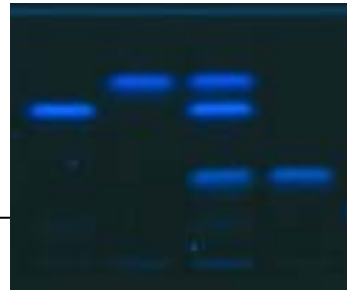
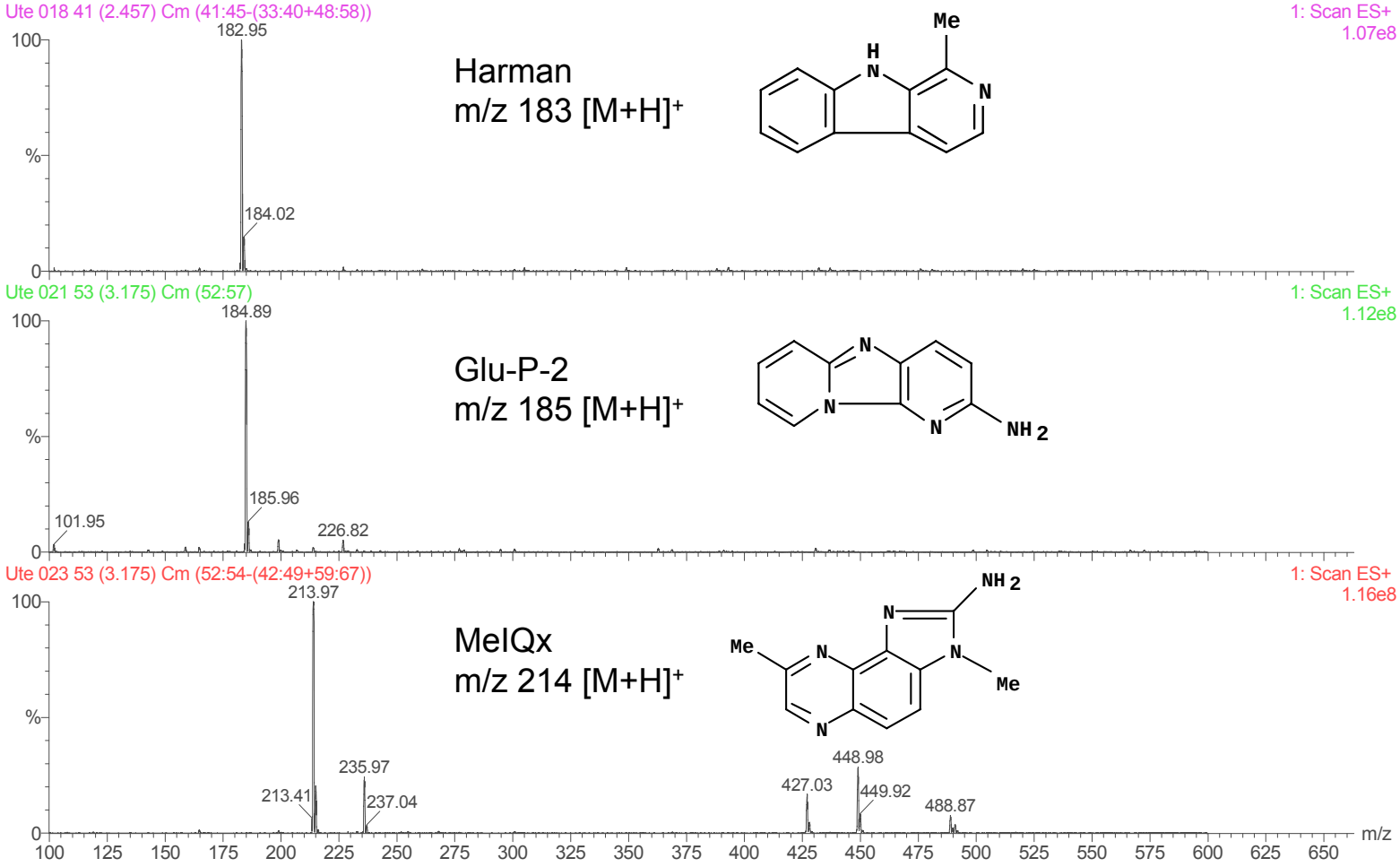
Heterocyclic aromatic amines





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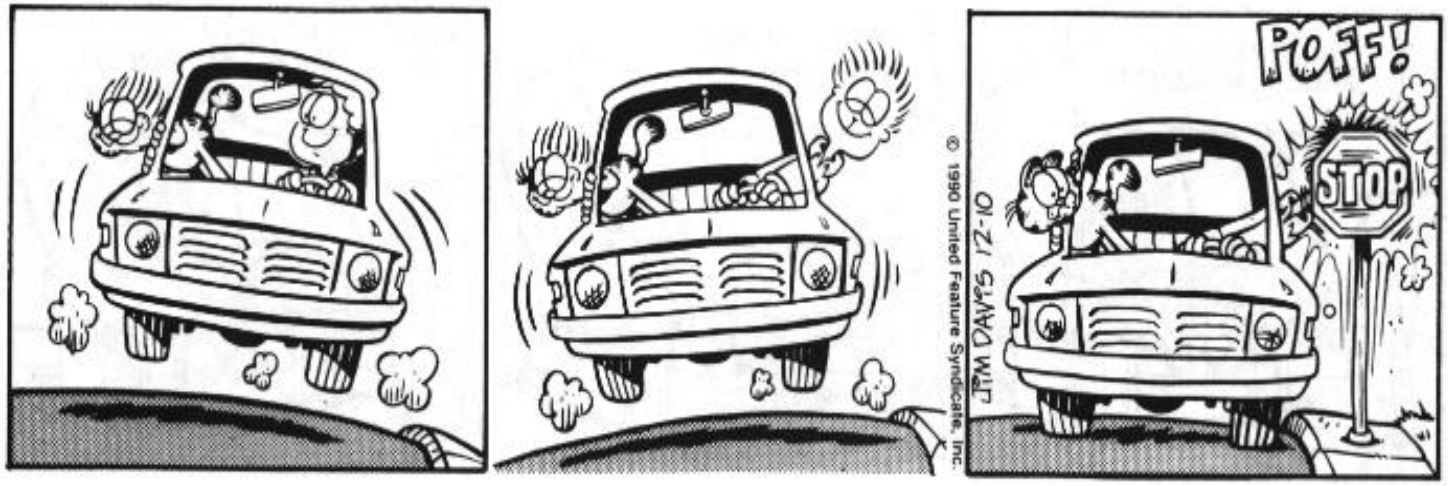
Various approaches…

What suits one analyst...



... might not suit the next!

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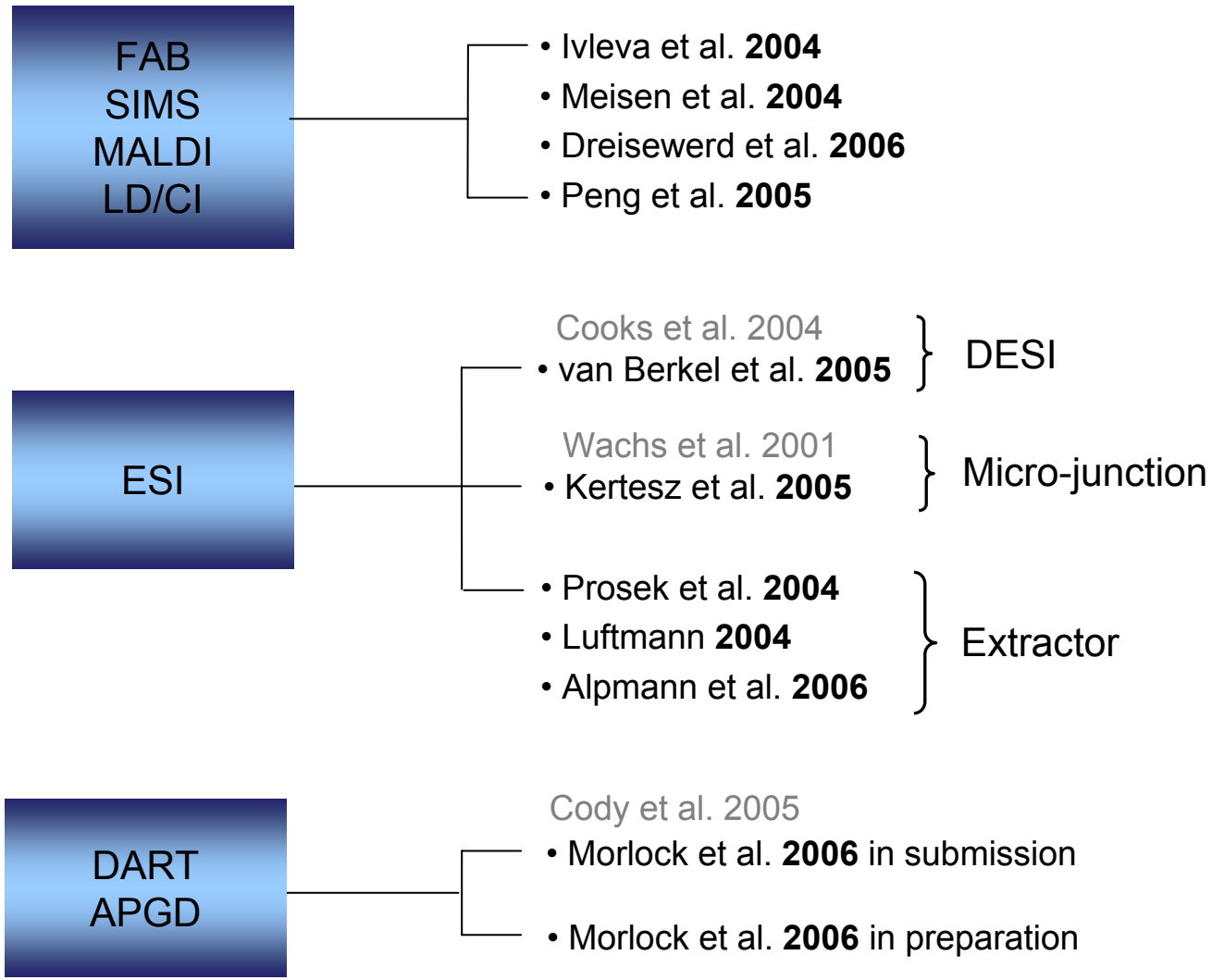
Various approaches of HPTLC/MS coupling



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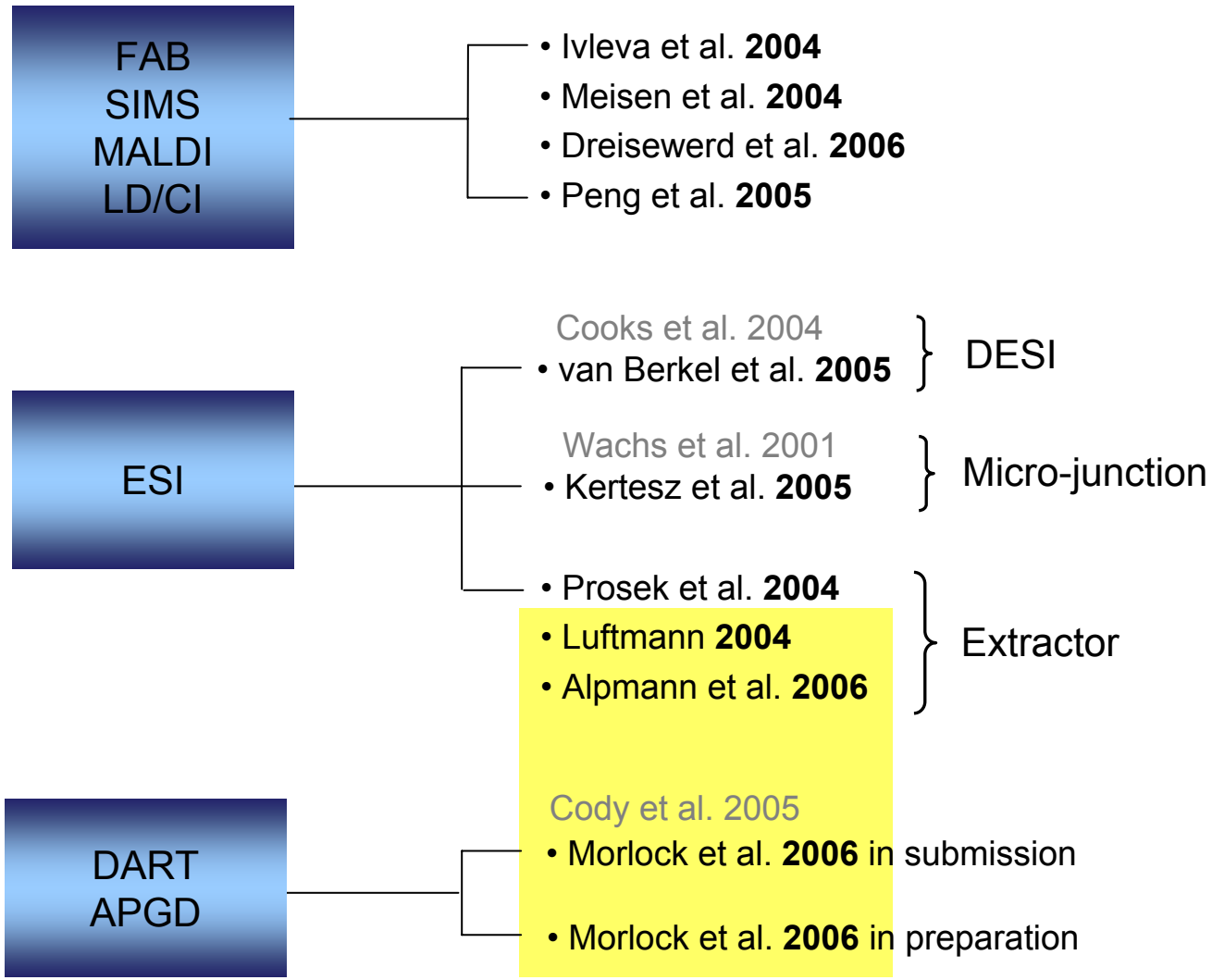
Various approaches of HPTLC/MS coupling



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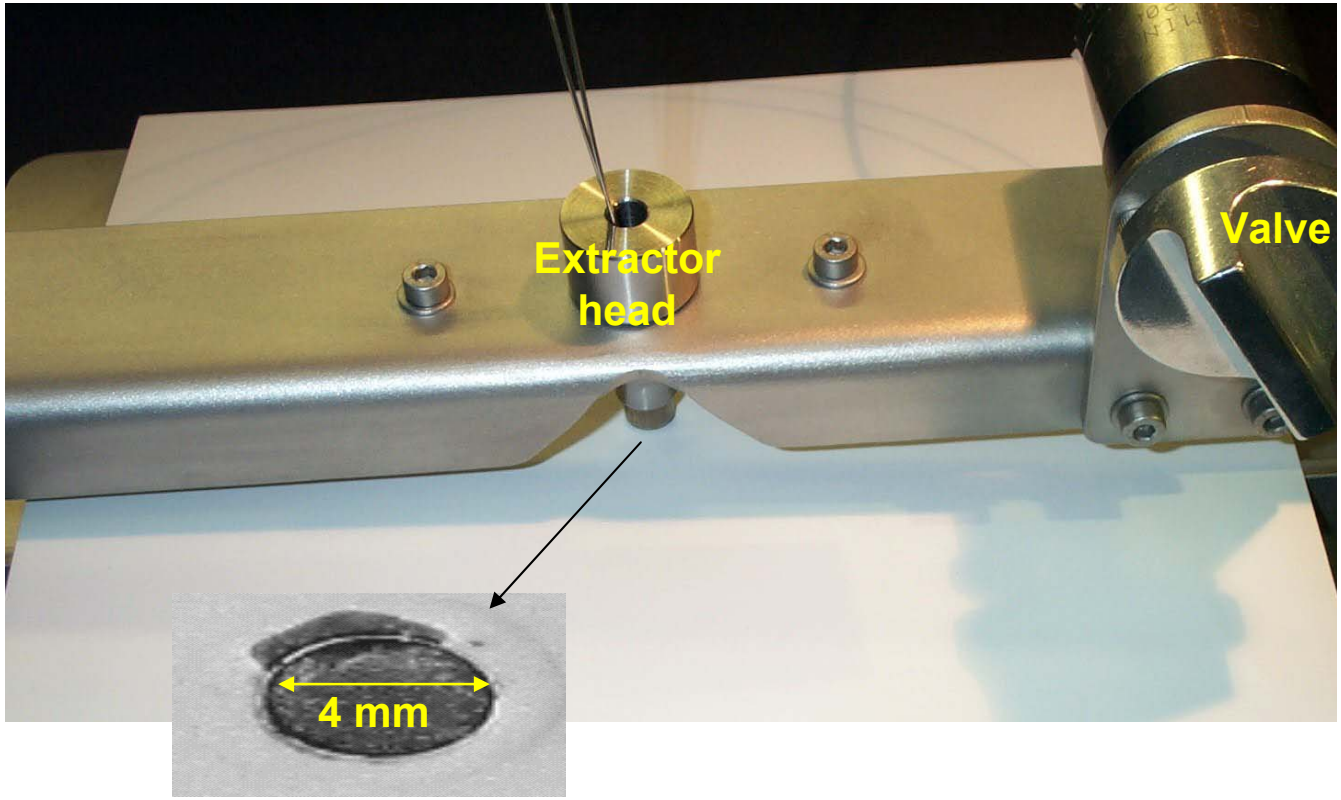
Online Extraction



H. Luftmann, Anal Bioanal Chem 378 (2004) 964-968

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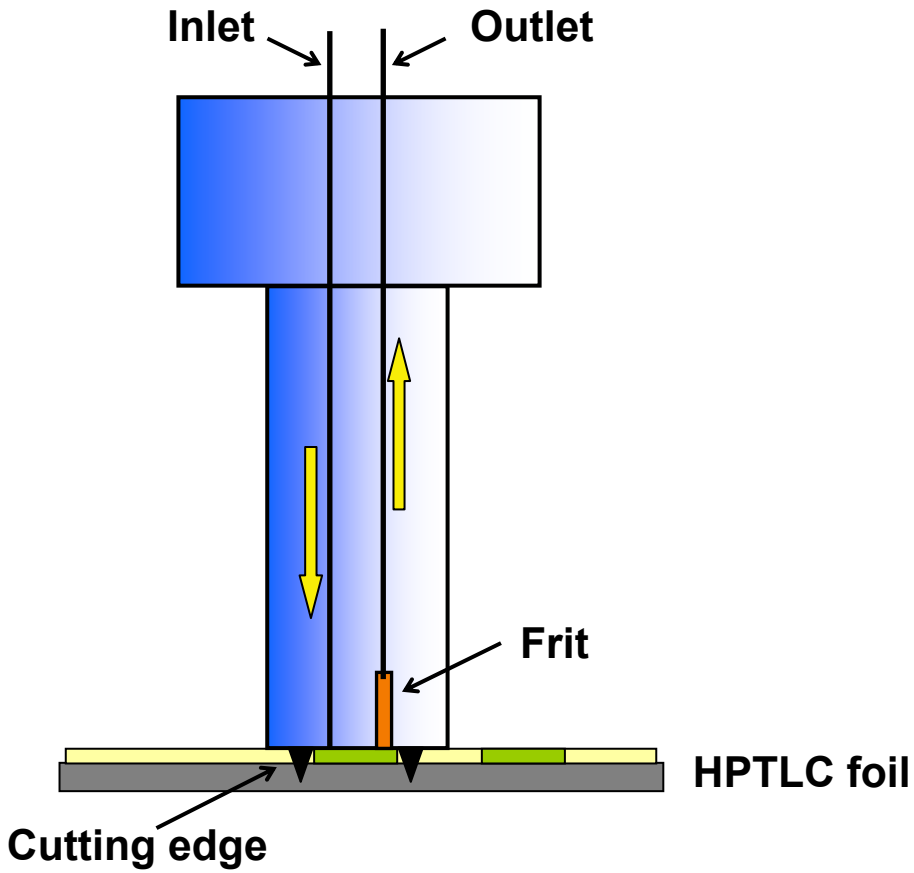
Extractor head



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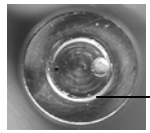
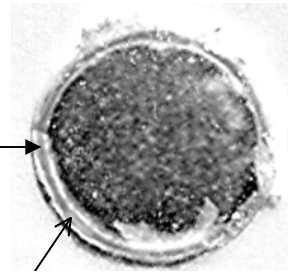
Plunger modification ⇒ enabled extraction from glass plates

1.

2.





3.

Shortened cutting edge for plates with 100 µm layer thickness

A. Alpmann, G. Morlock, Anal Bioanal Chem (2006) DOI 10.1007/s00216-006-0692-y

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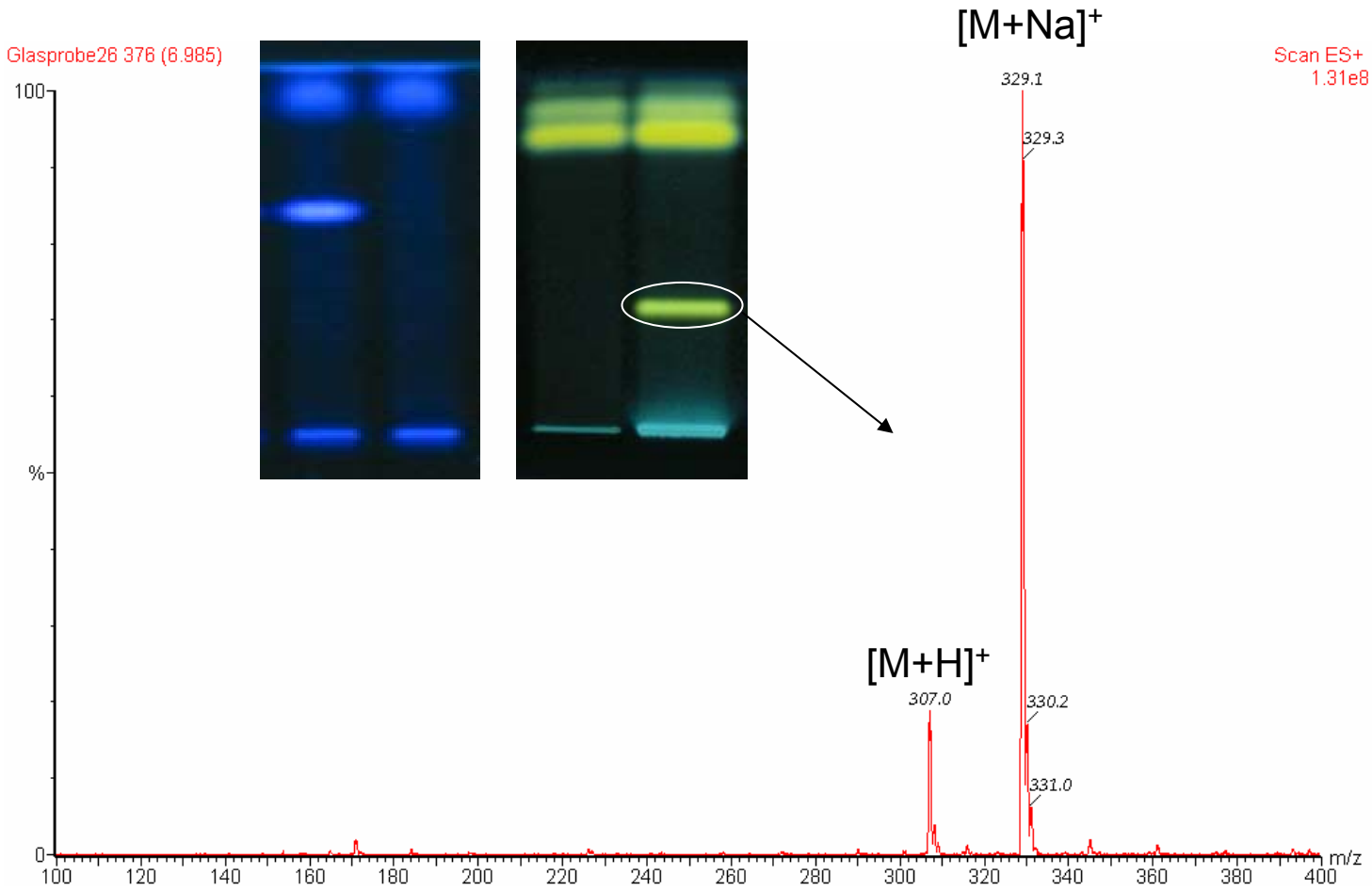
Products of synthesis with acrylamide



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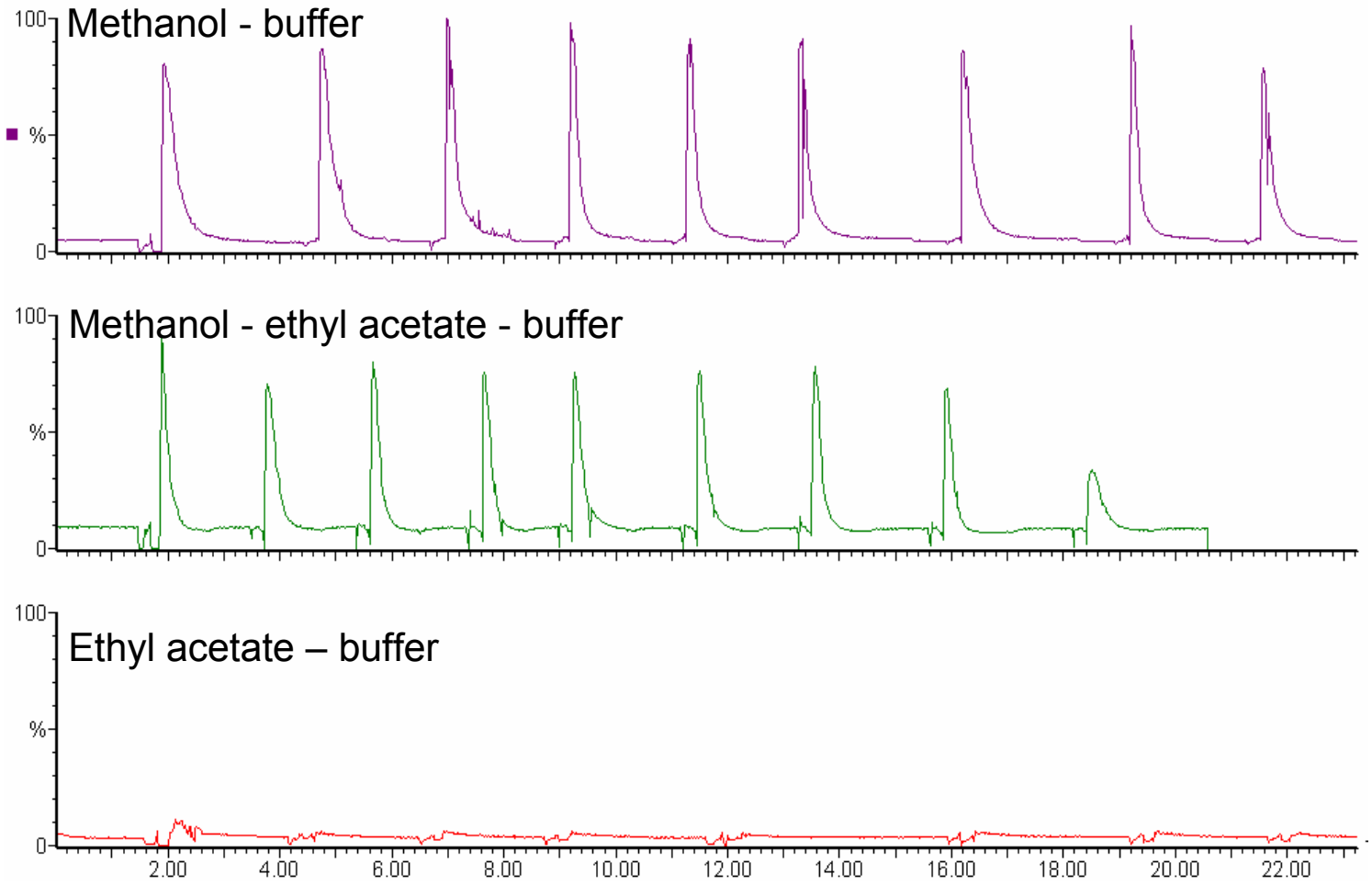
Elution profiles of various extraction solvents



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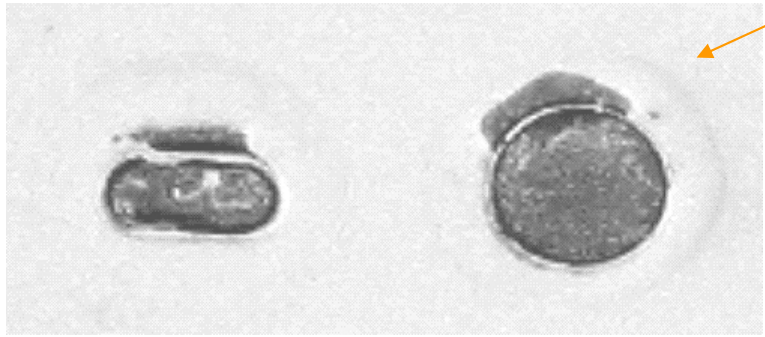
Comparison of different cutting edges



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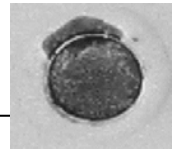
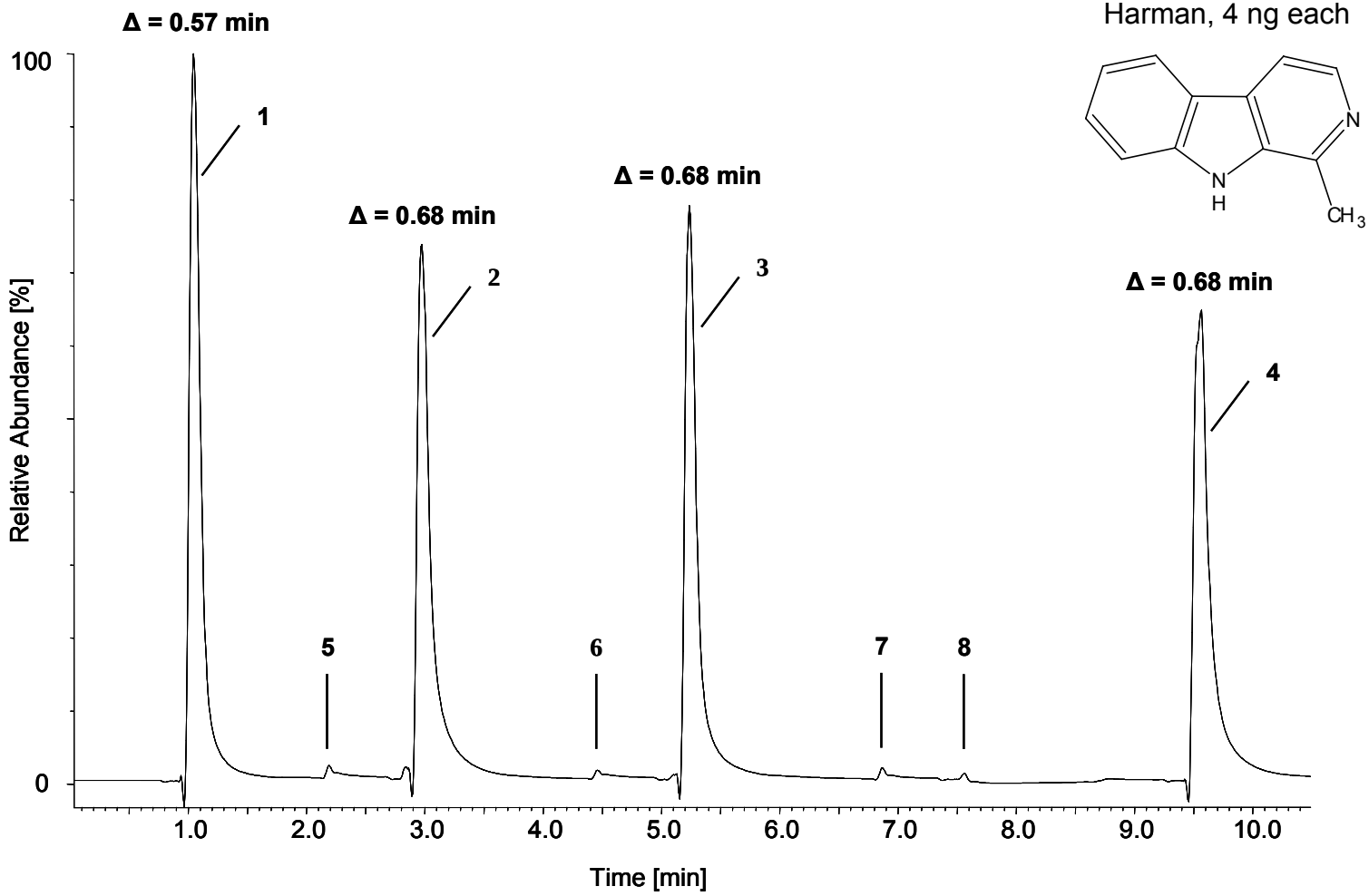
Extraction using a round cutting edge





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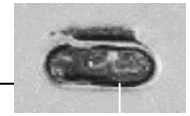
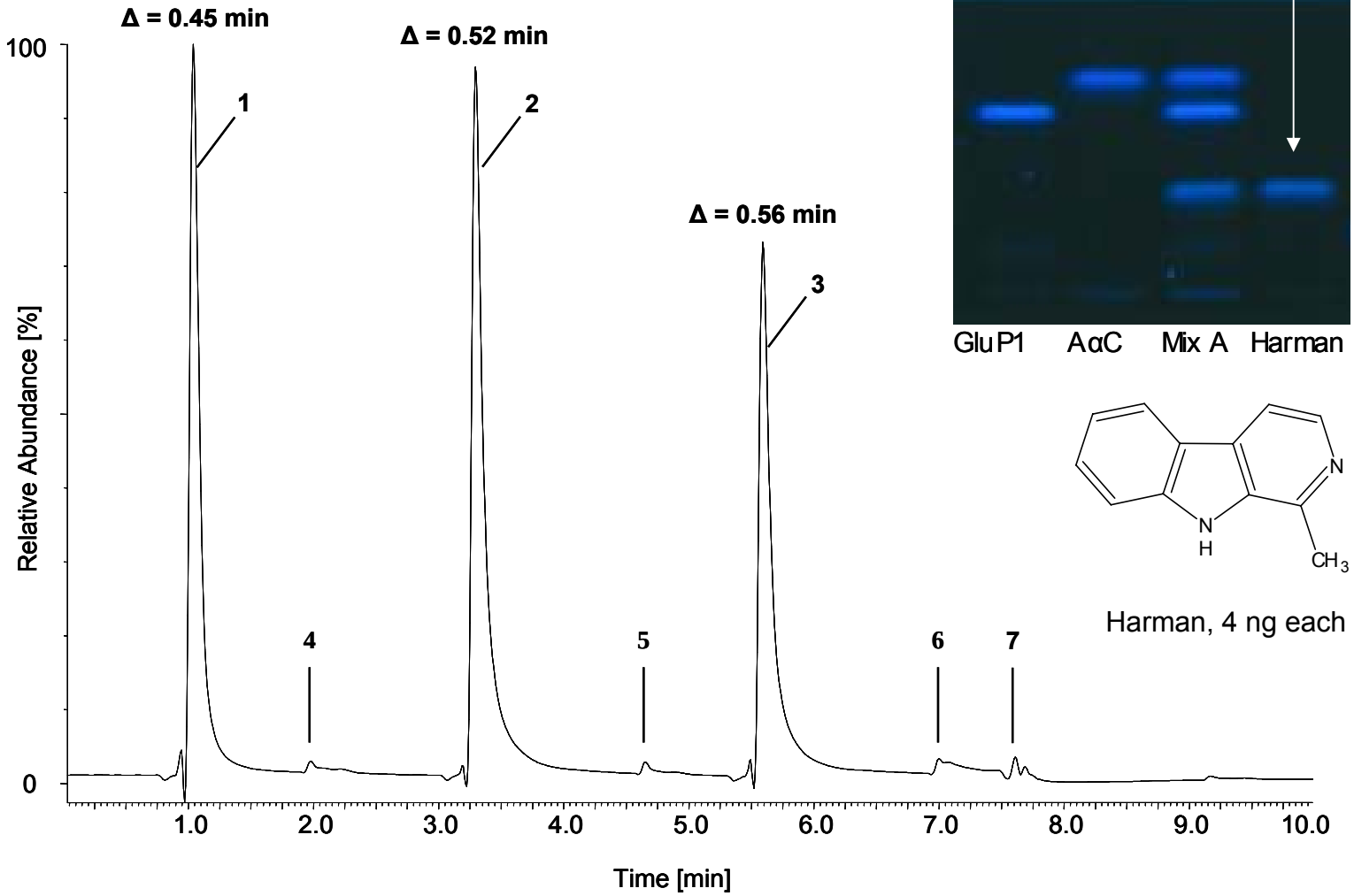
Extraction using an oval cutting edge





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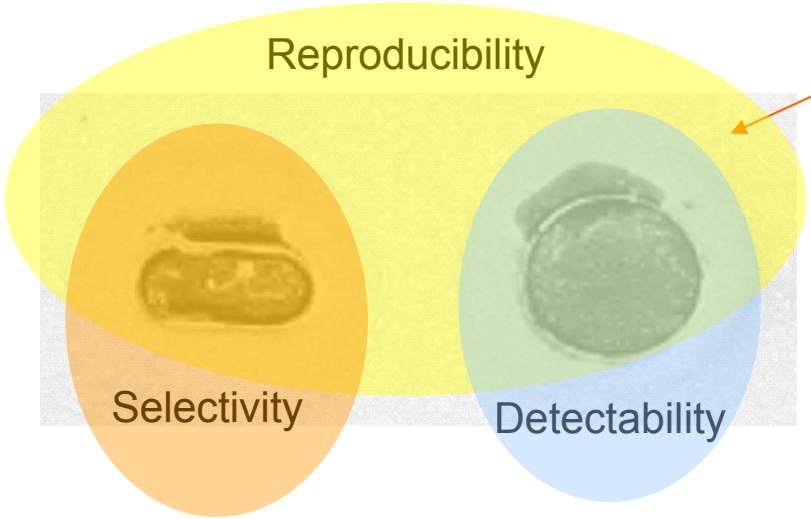
Comparison of different cutting edges



U. Jautz, G. Morlock, Comparison of two extraction heads of a plunger-based extraction device for HPTLC/ESI-MS coupling, in preparation

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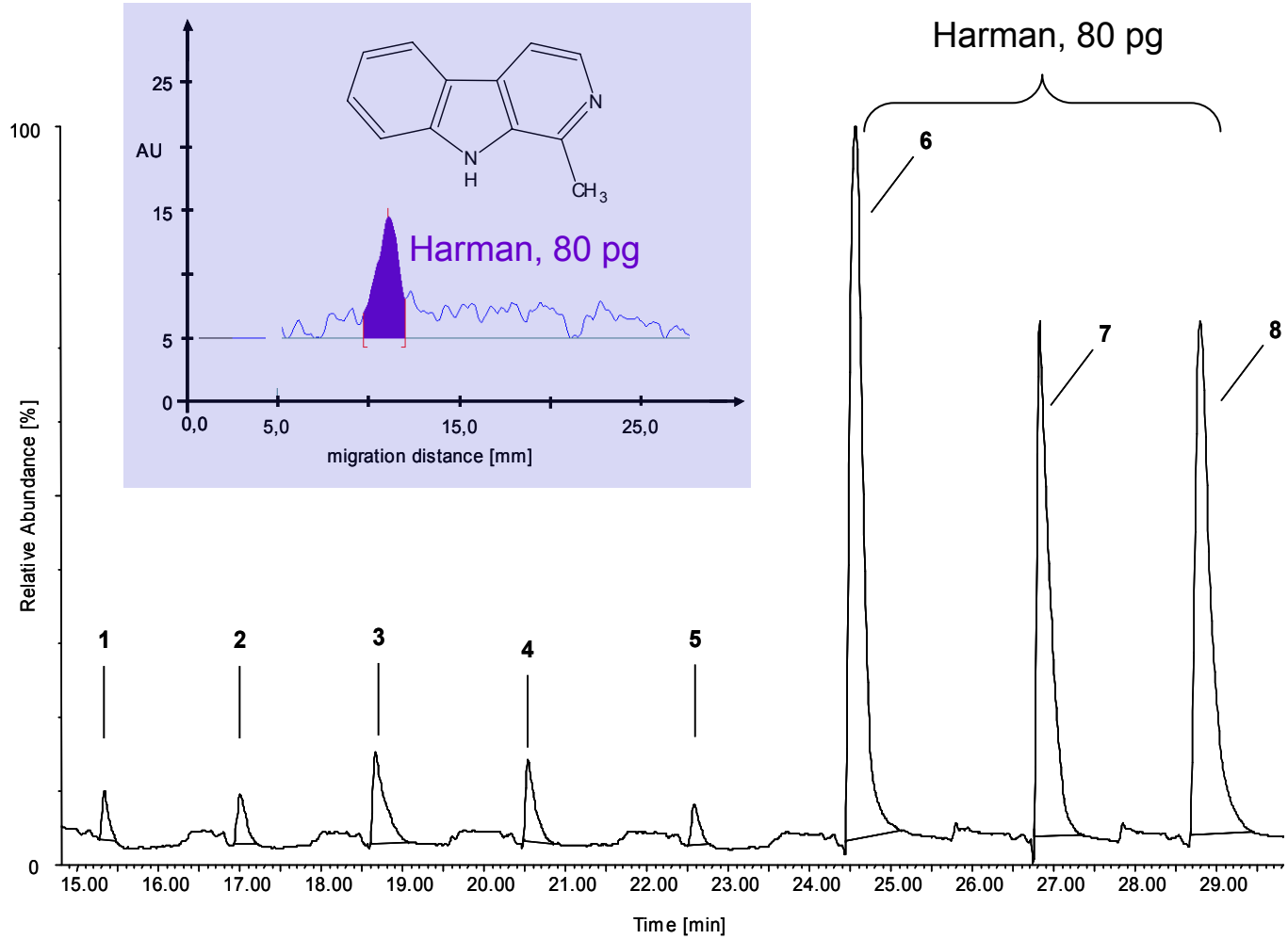
Detectability: FLD versus MSD



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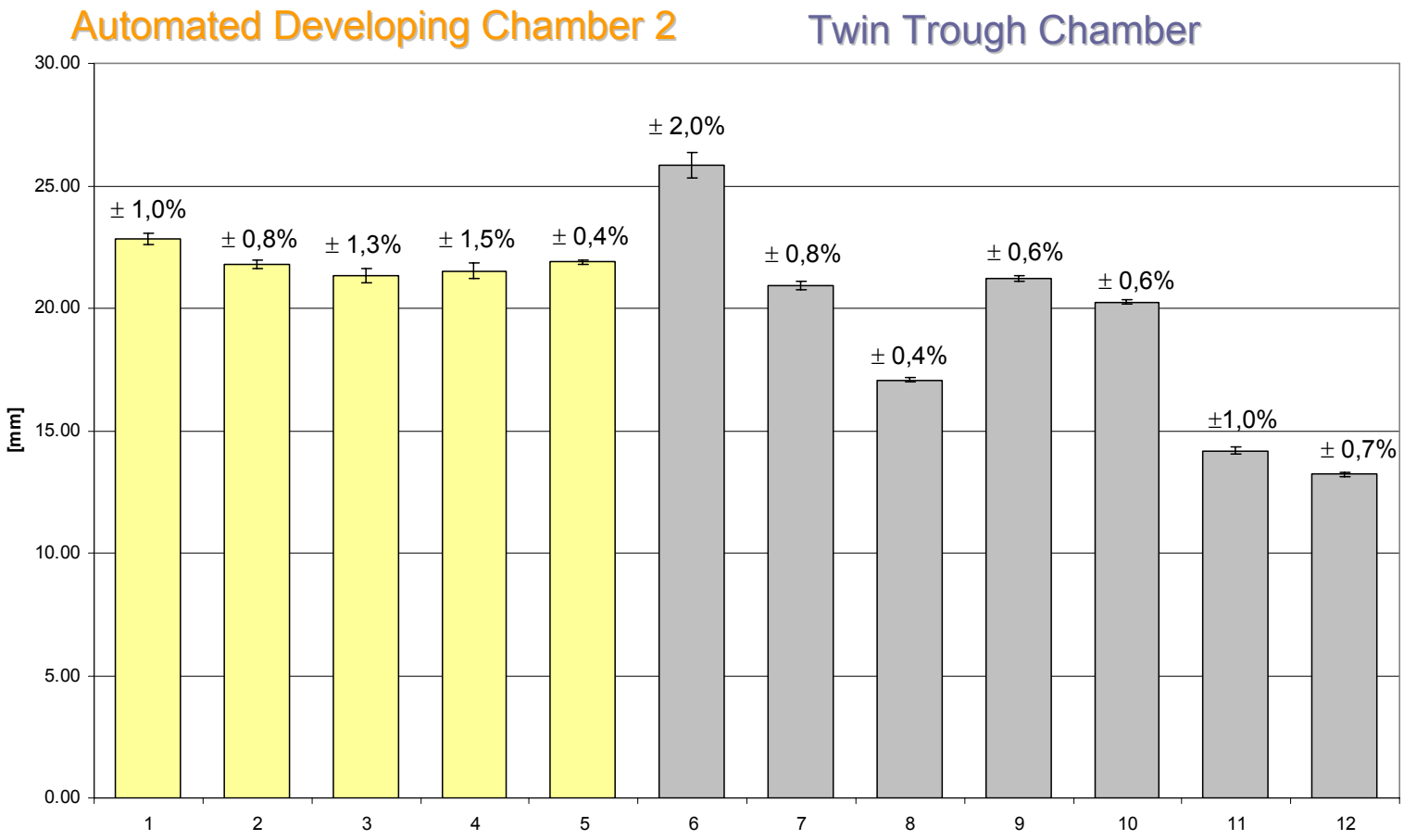
Reproducibility of migration distance



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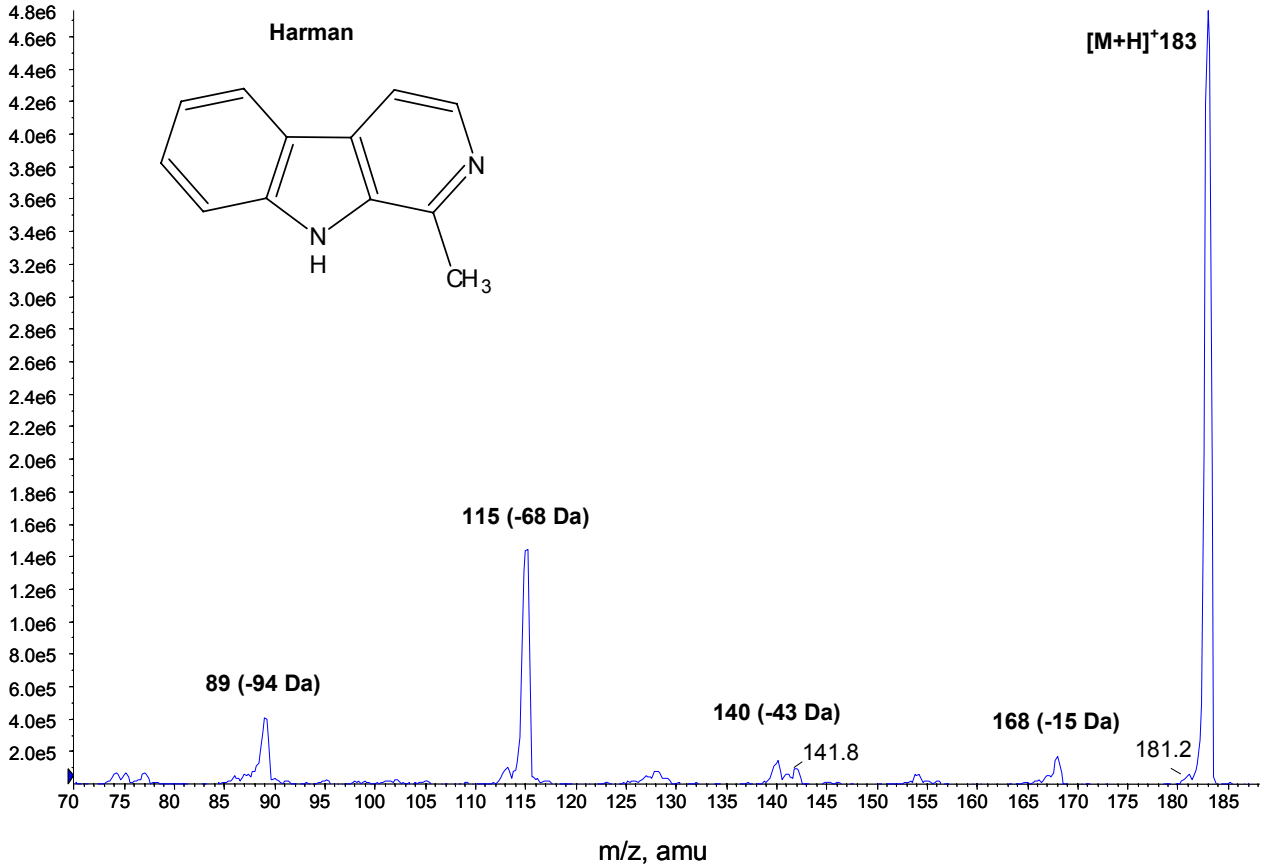
Detectability by HPTLC/ESI-MS-MS

Product Ion Intensity	m/z	rel. Abundance [%]	Tentative Assignation
306700	115	100.00	$[M+H-CH_3CN-HCN]^+$
66890	89	11.81	$[M+H-CH_3CN-HCN-C_2H_2]^+$
49420	168	16.11	$[M+H-CH_3]^+$
22280	140	7.26	$[M+H-CH_3-H-HCN]^+$



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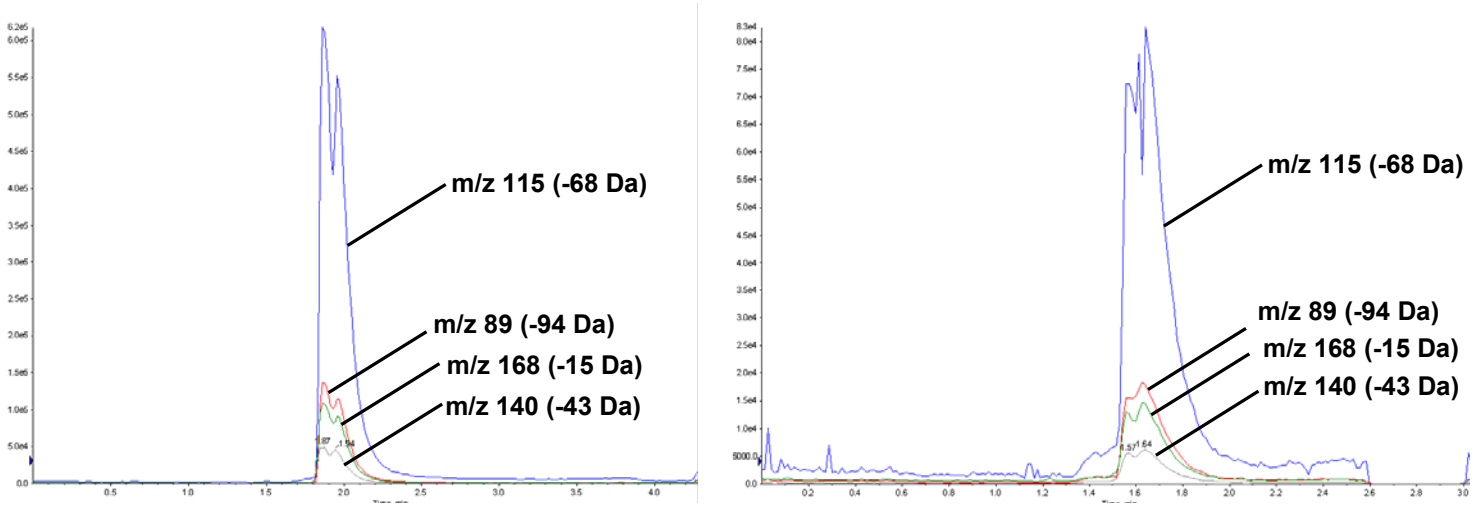
Detectability by HPTLC/ESI-MS-MS

200 pg Harman → 20 pg Harman



U. Jautz, G. Morlock, J Chromatogr A 58 (2006) 244-250

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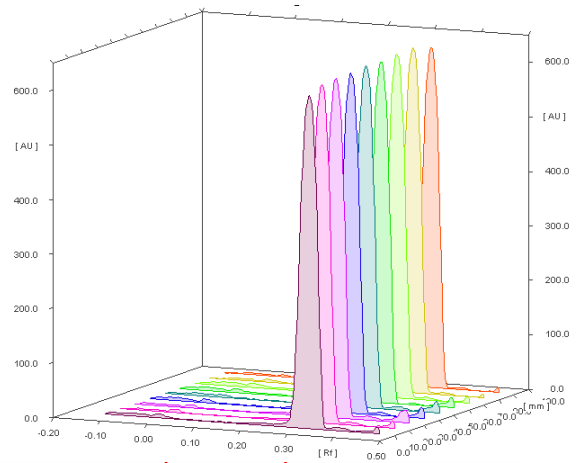
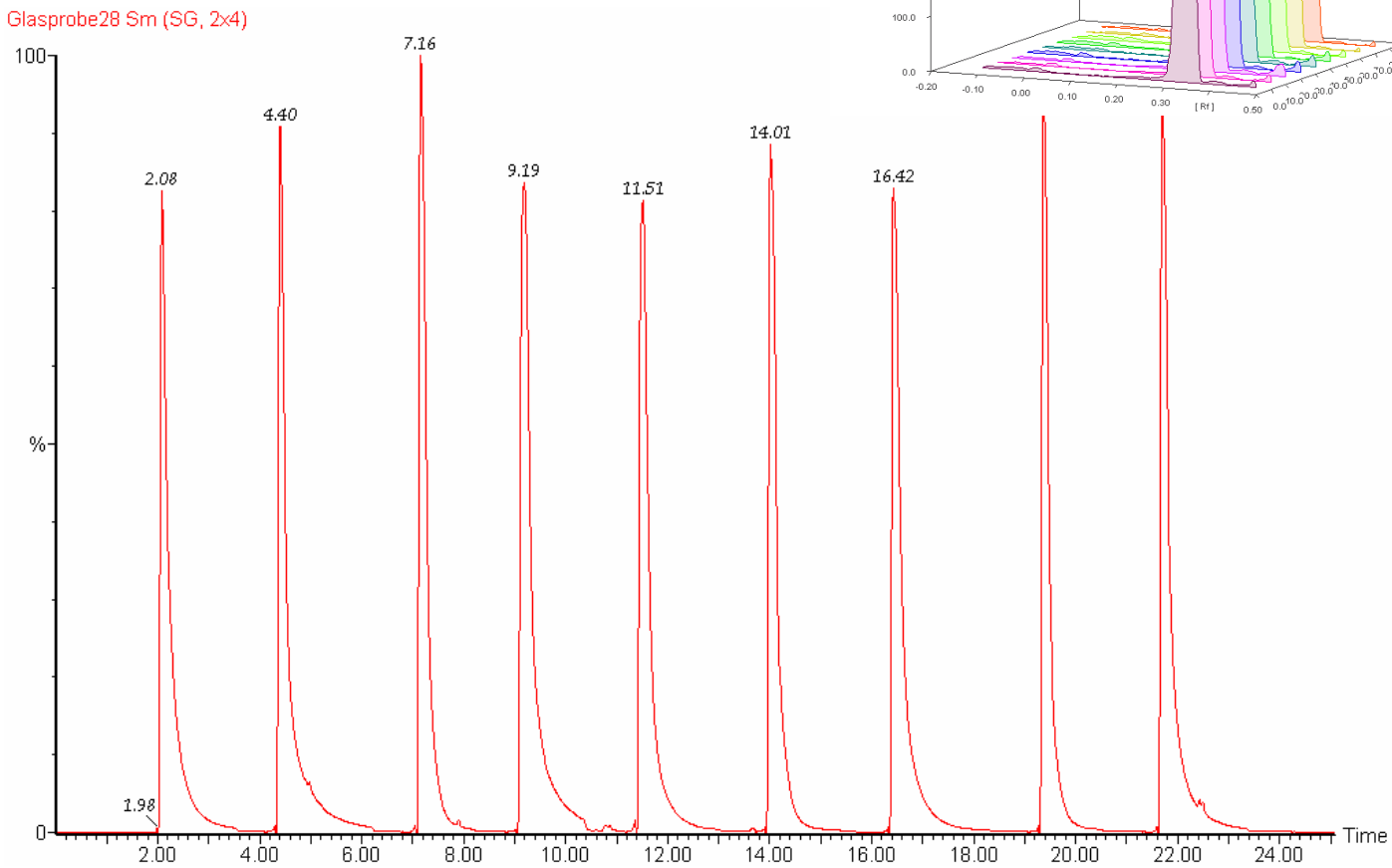
Repeatability of extraction





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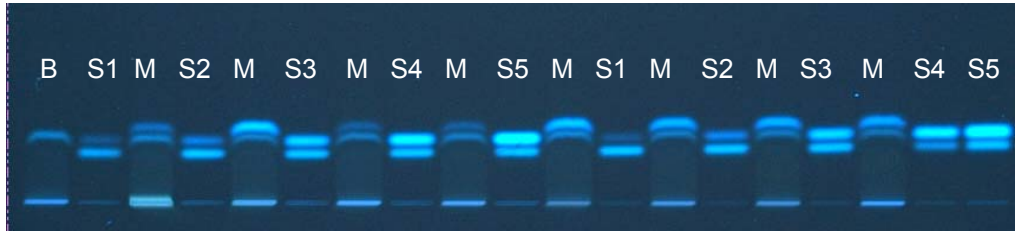
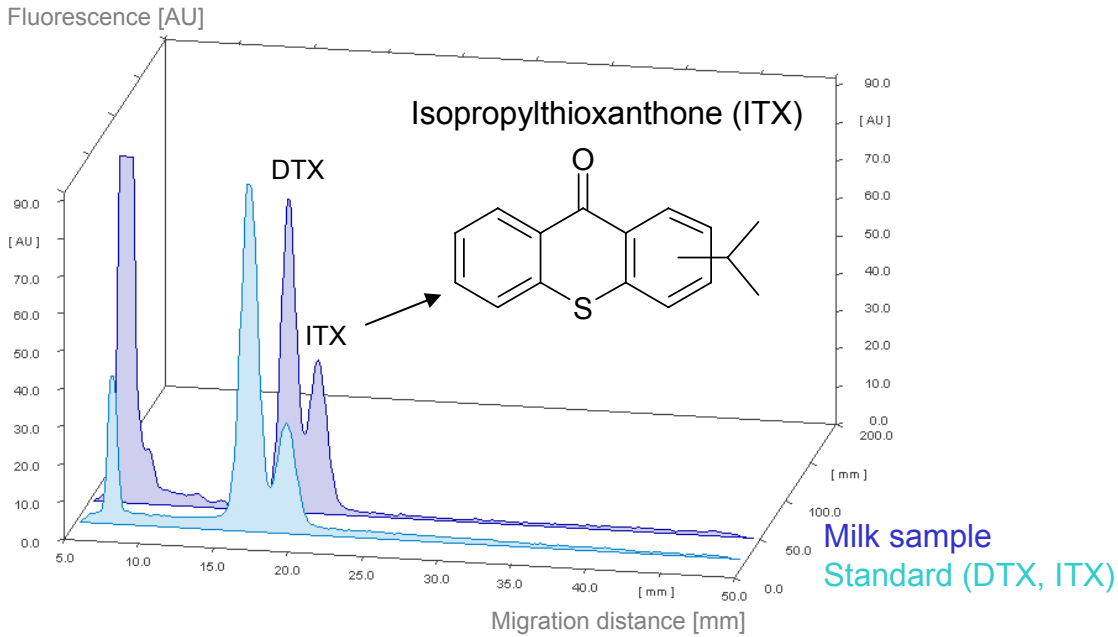
Trace analysis: Food contaminant ITX





G. Morlock, W. Schwack, Anal Bioanal Chem 385 (2006) 586-595

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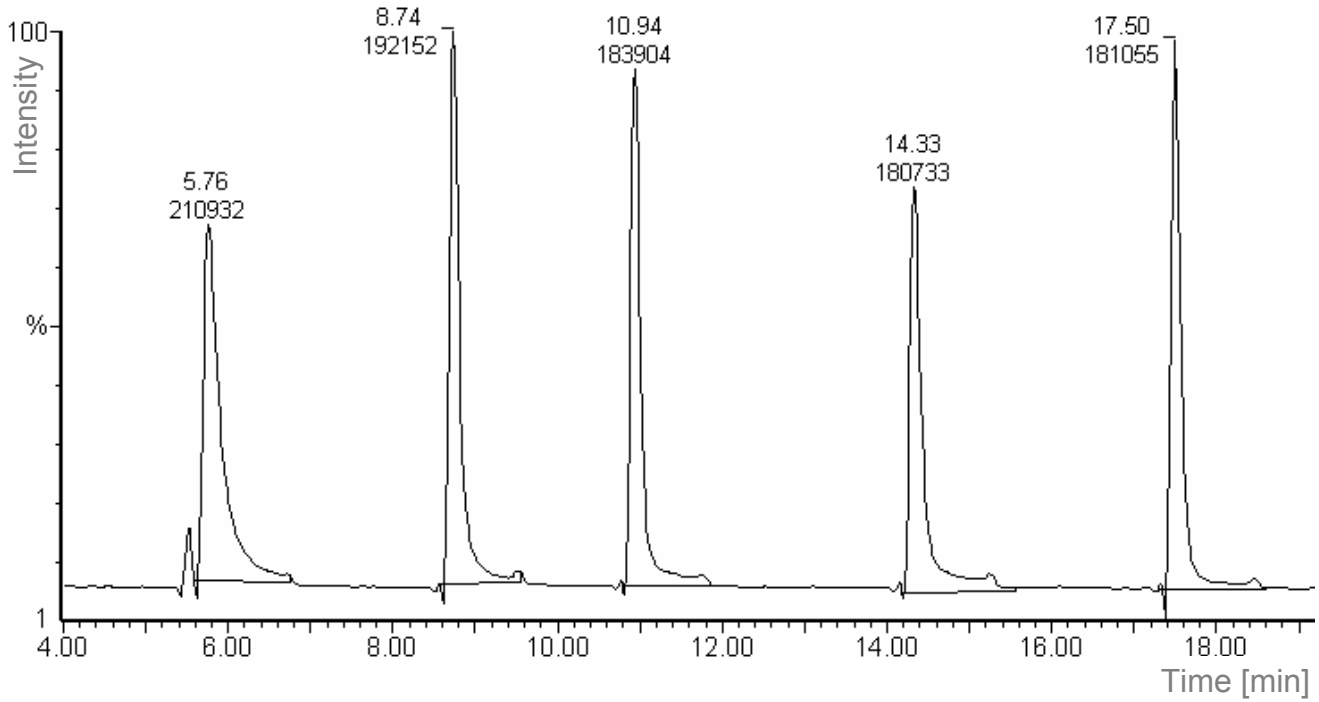
University of Hohenheim, Stuttgart

Repeatability

Elution profiles of 6 ng ITX each (SIM at *m/z* 255 $[M+H]^+$ and 277 $[M+Na]^+$)

RSD = ± 6.7 % (*n* = 5)



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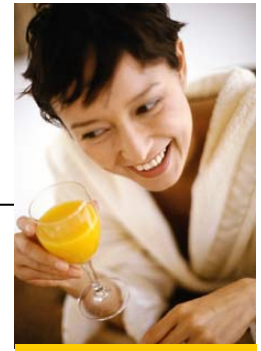
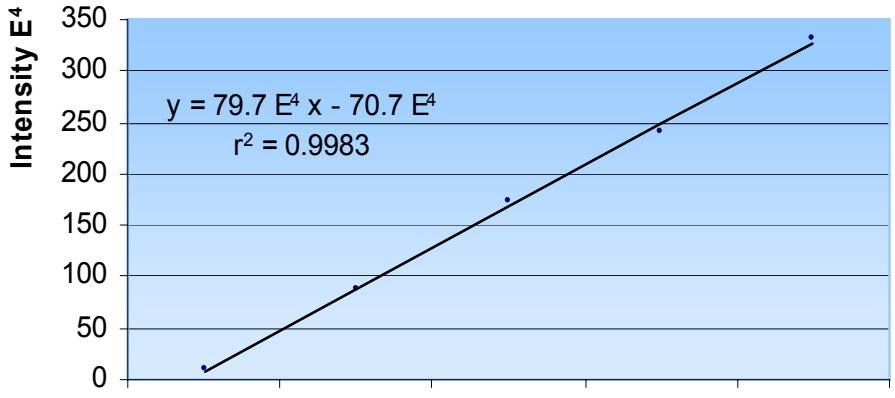
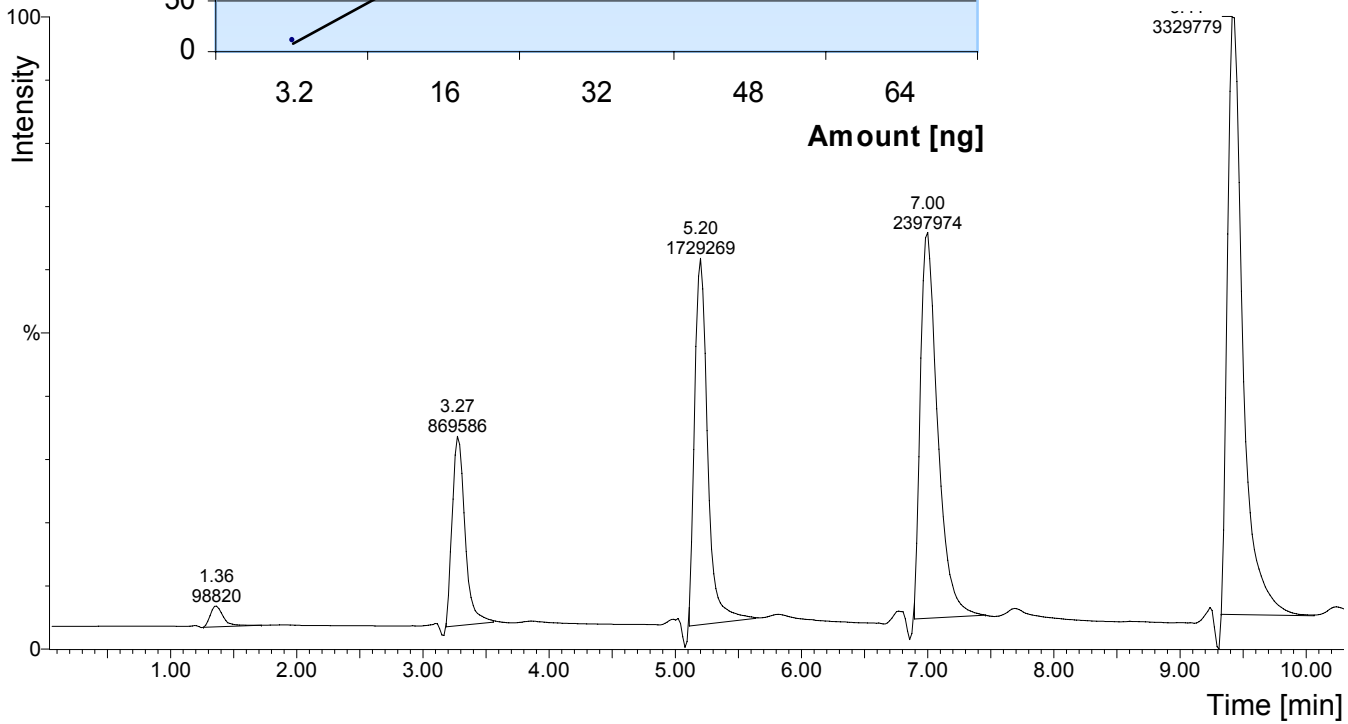
Analytical response



It is orange juice, but with ITX.





Elution profiles of ITX (SIM at *m/z* 255 $[M+H]^+$ and 277 $[M+Na]^+$)

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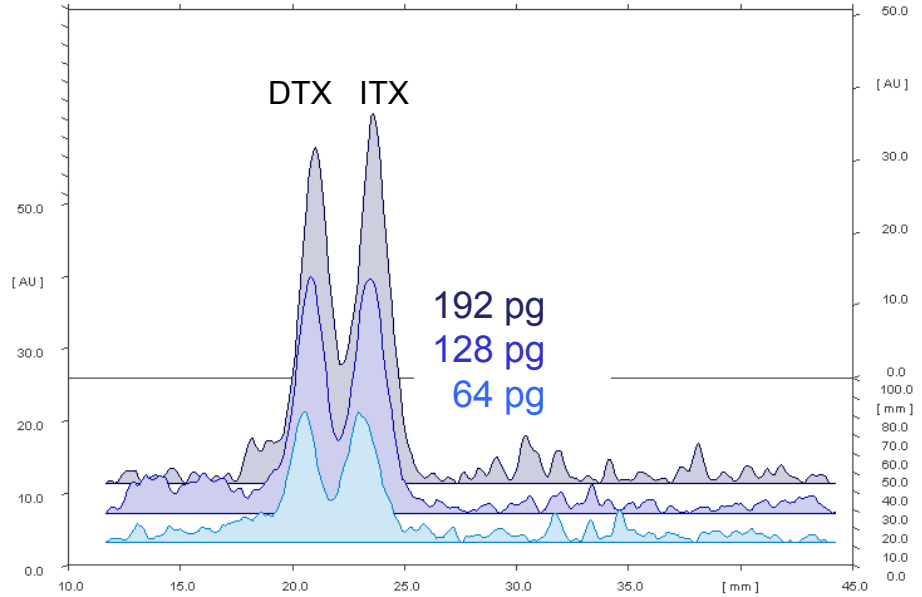
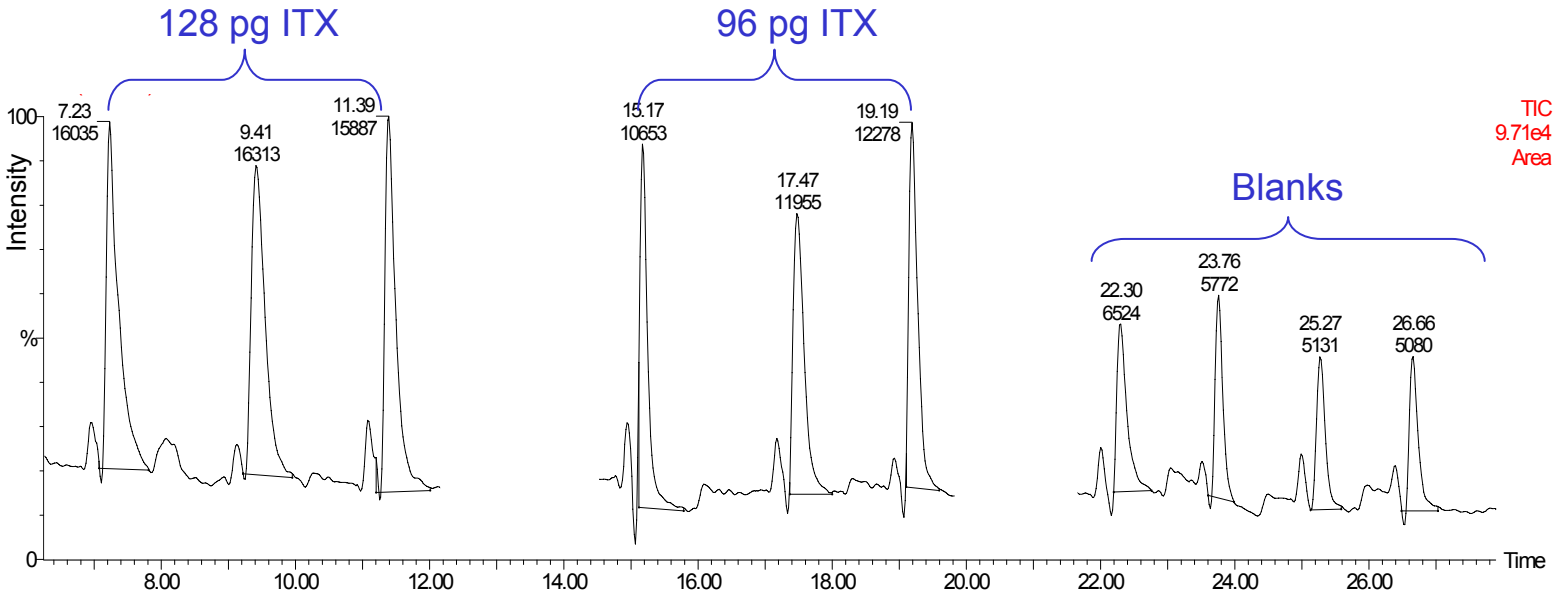
FLD ↔ MSD





Elution profiles of ITX (SIM at *m/z* 255 $[M+H]^+$ and 277 $[M+Na]^+$)

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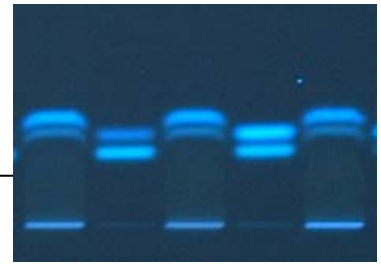
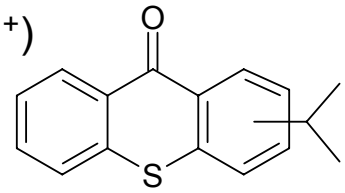
Confirmation by HPTLC/ESI-MS

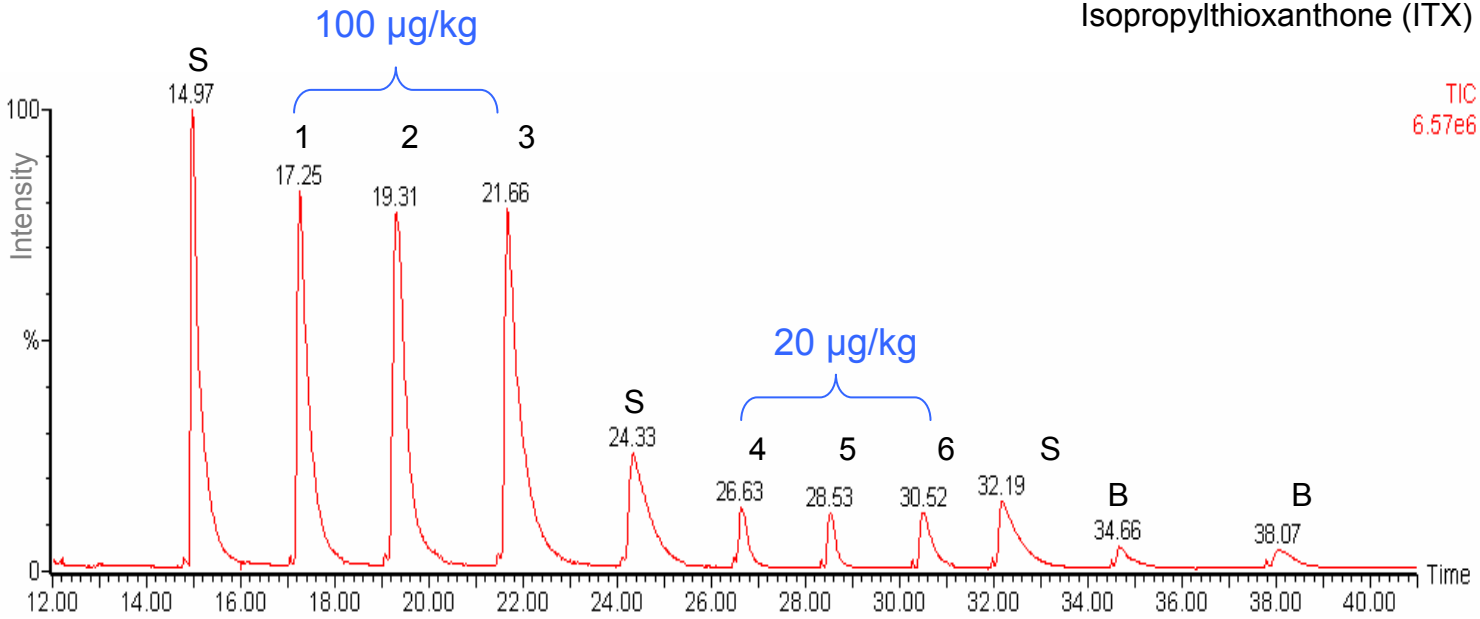


Elution profiles (SIM at *m/z* 255 $[M+H]^+$ and 277 $[M+Na]^+$)

→ Yoghurt samples spiked with ITX



Isopropylthioxanthone (ITX)



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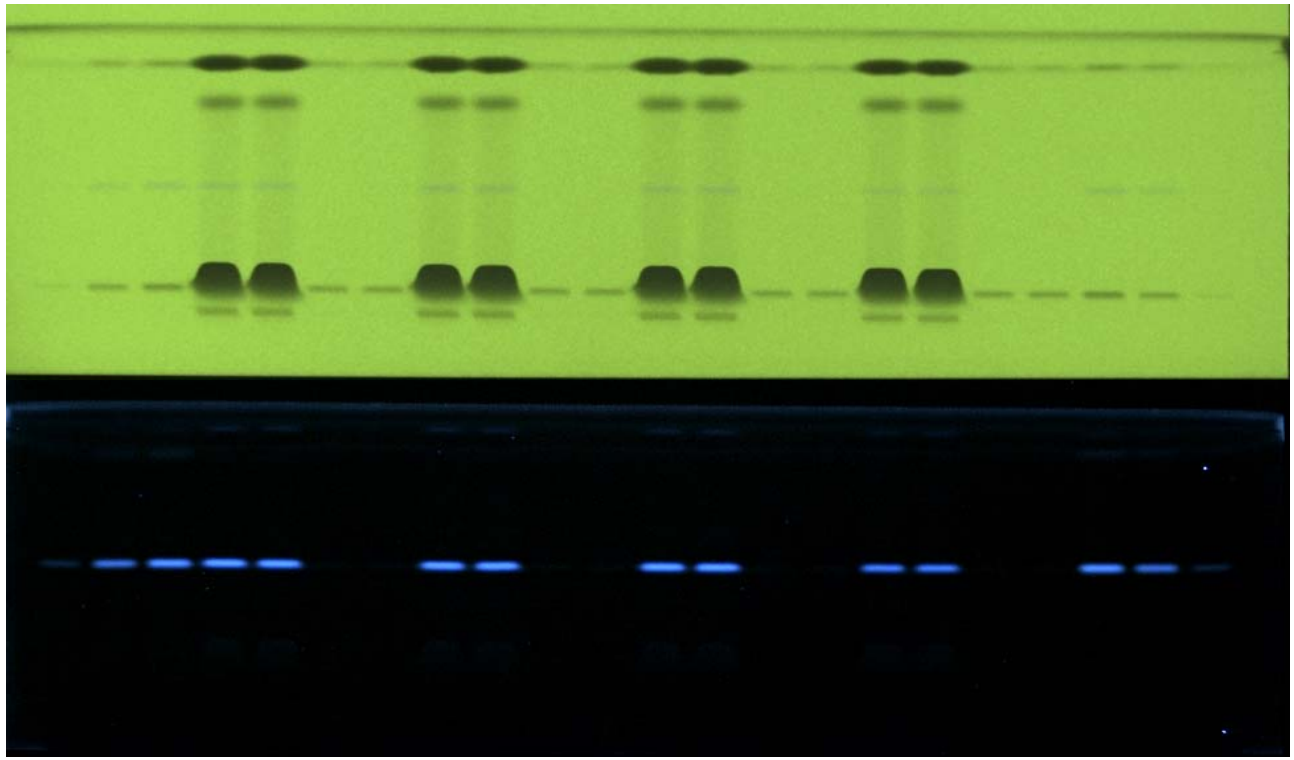
Confirmation by HPTLC/ESI-MS

→ Simultaneous Determination of Caffeine, Ergotamine and Metamizol



M. Aranda and G. Morlock (2006) in submission

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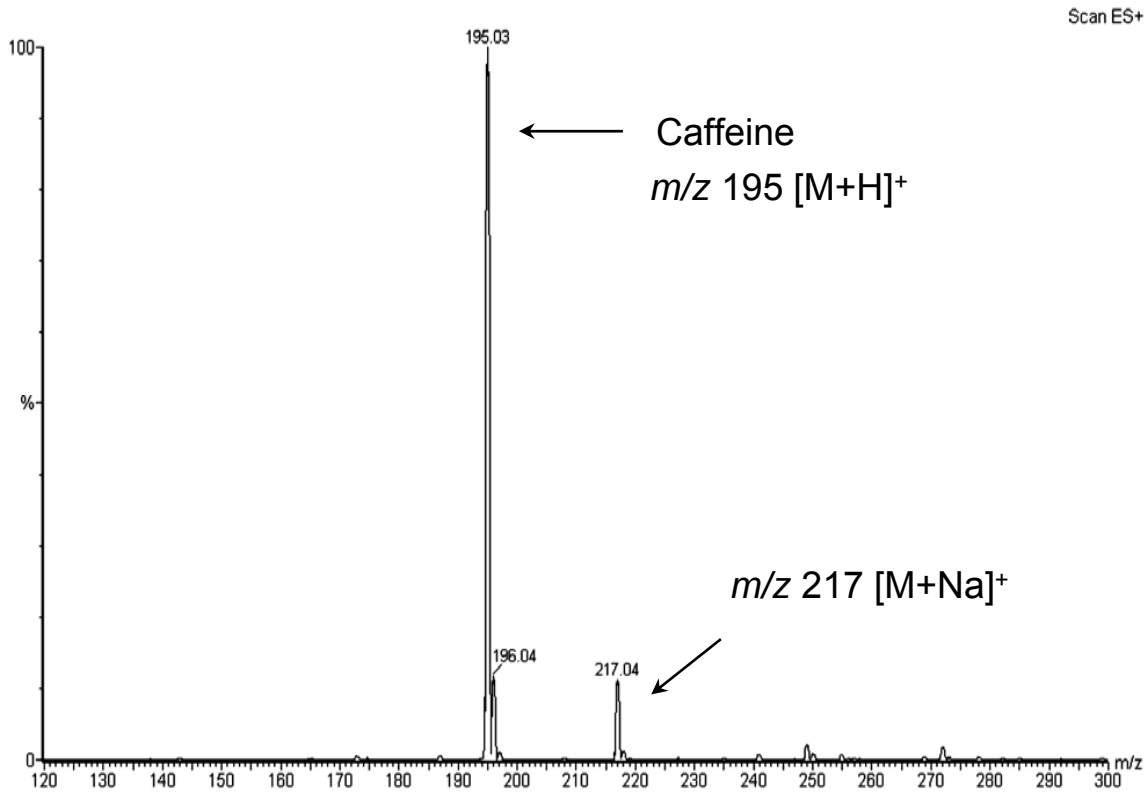
Confirmation by HPTLC/ESI-MS

→ Simultaneous Determination of Caffeine, Ergotamine and Metamizol



M. Aranda and G. Morlock (2006) in submission

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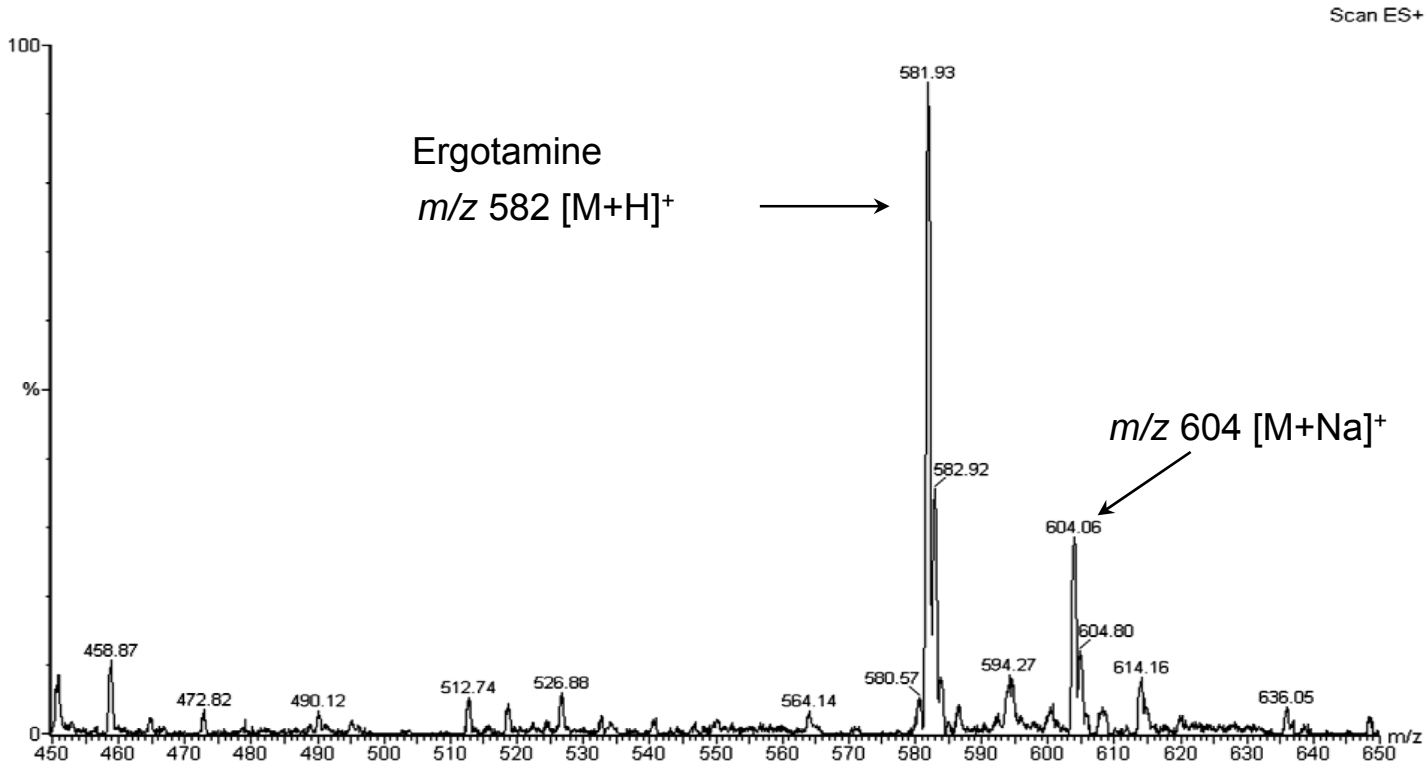

M. Aranda and G. Morlock (2006) in submission

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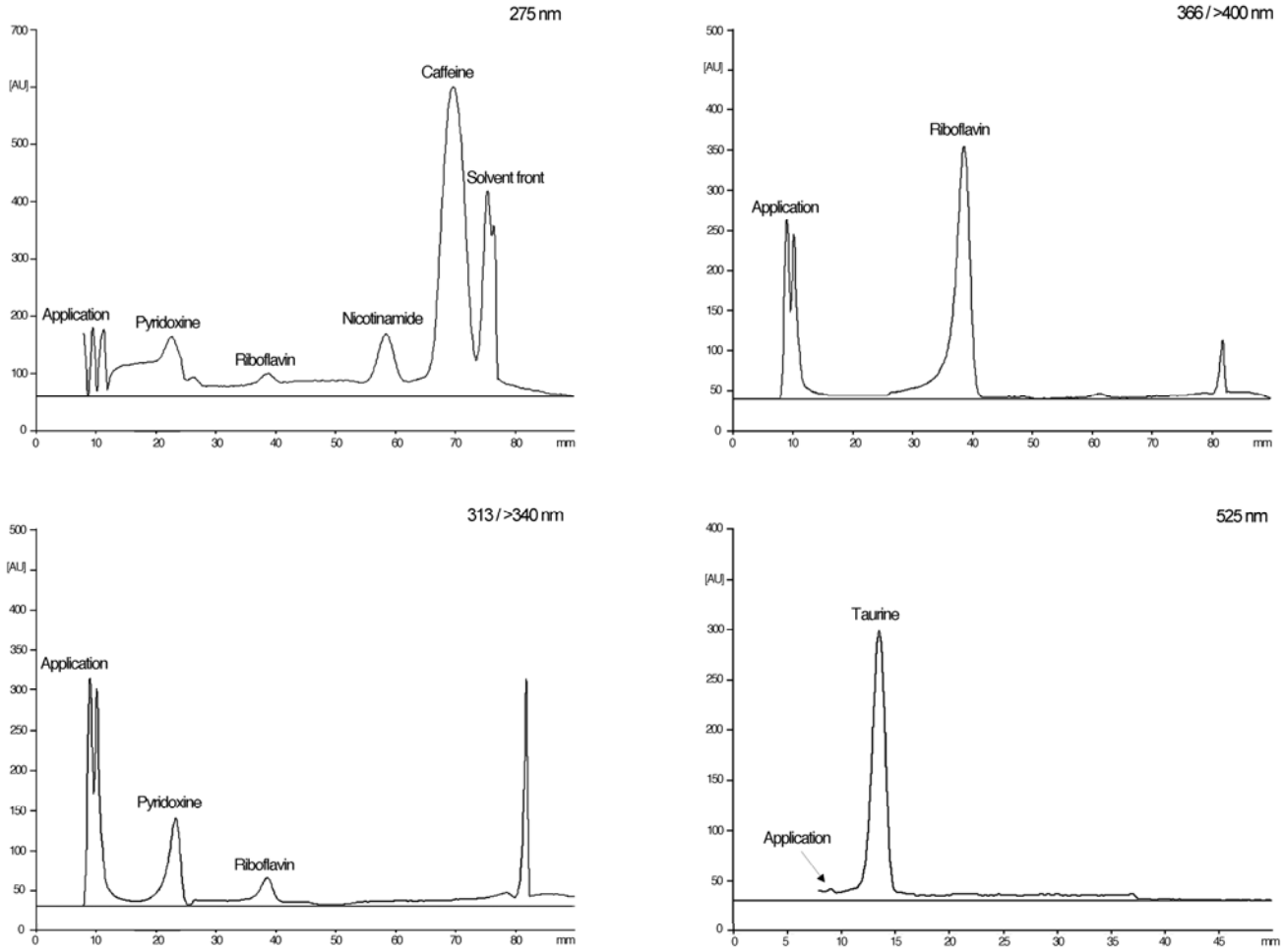
Confirmation by HPTLC/ESI-MS

→ Simultaneous determination of riboflavin, pyridoxine, nicotinamide, caffeine and taurine in energy drinks



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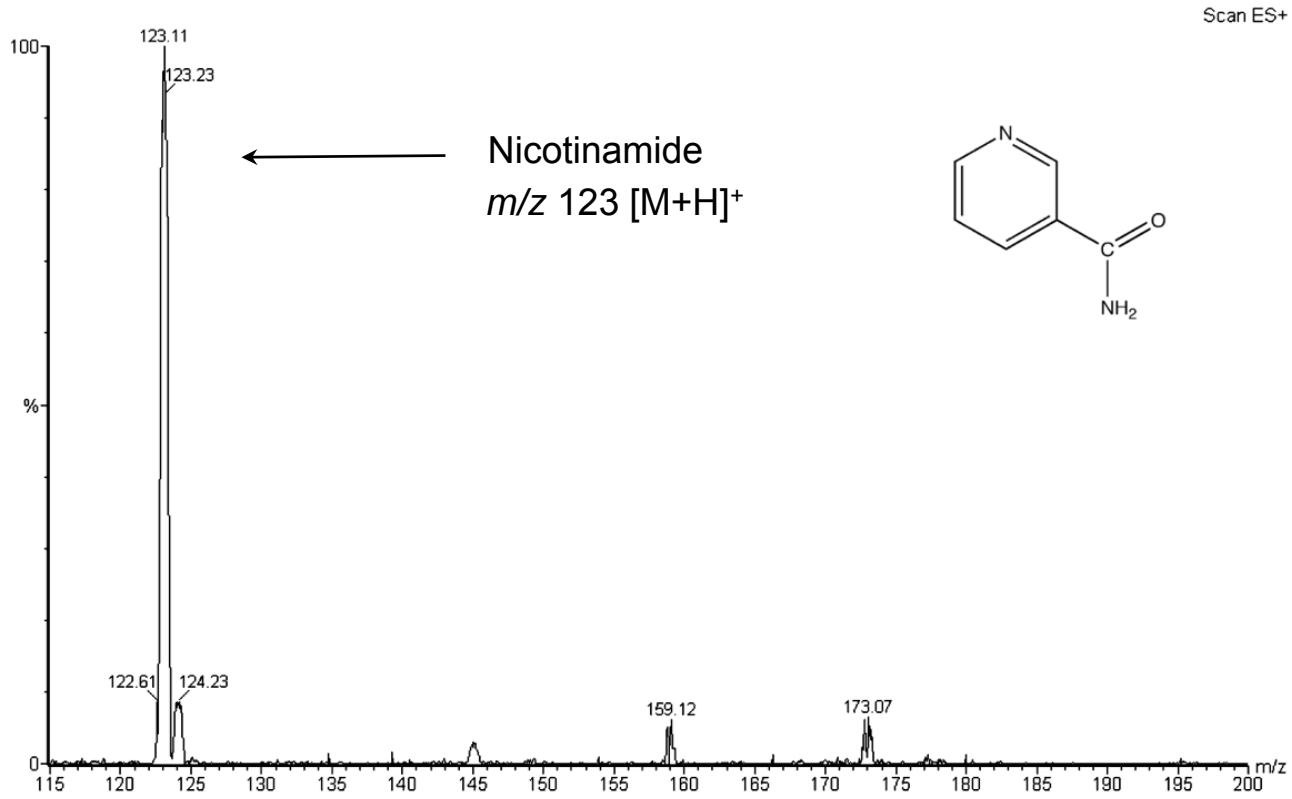

M. Aranda, G. Morlock, J Chromatogr A (2006) DOI 10.1016/j.chroma.2006.07.018

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Confirmation by HPTLC/ESI-MS

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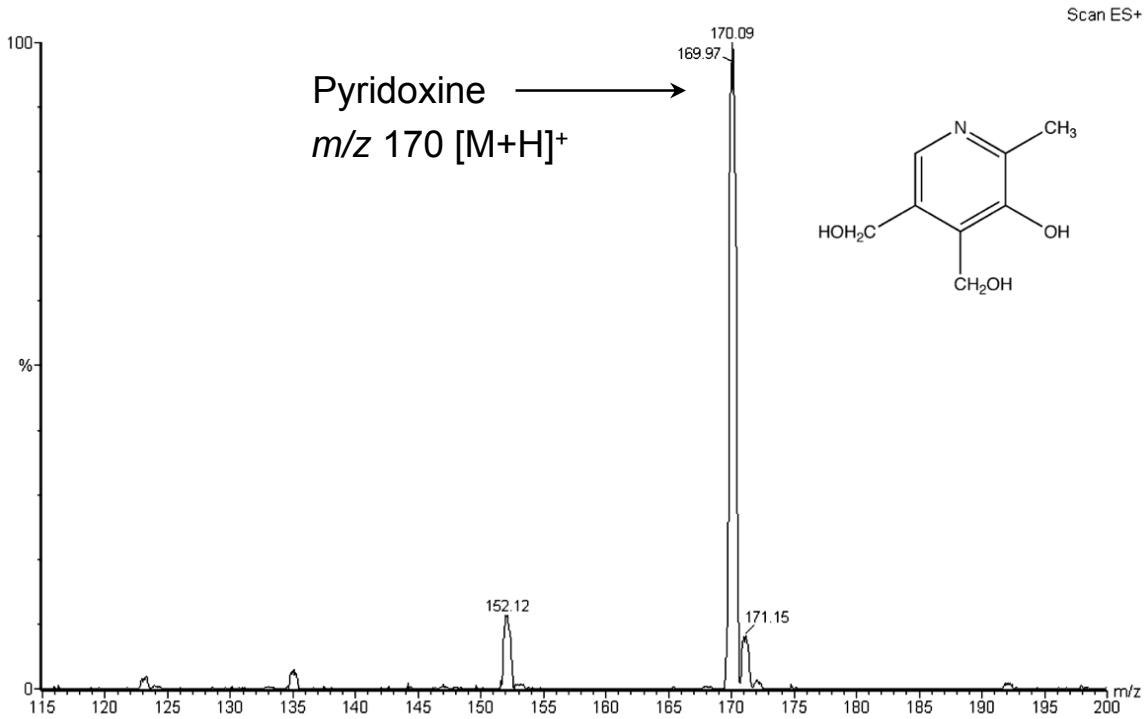

M. Aranda, G. Morlock, J Chromatogr A (2006) DOI 10.1016/j.chroma.2006.07.018

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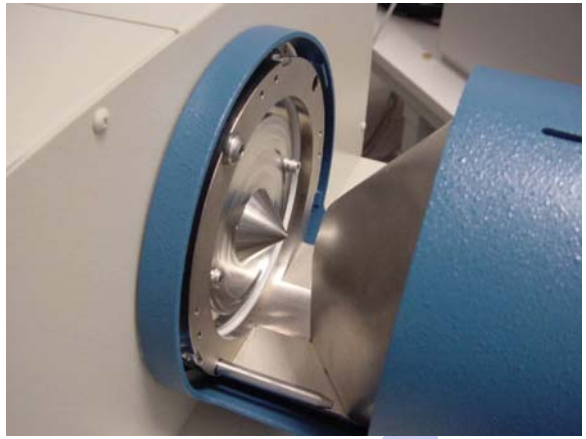
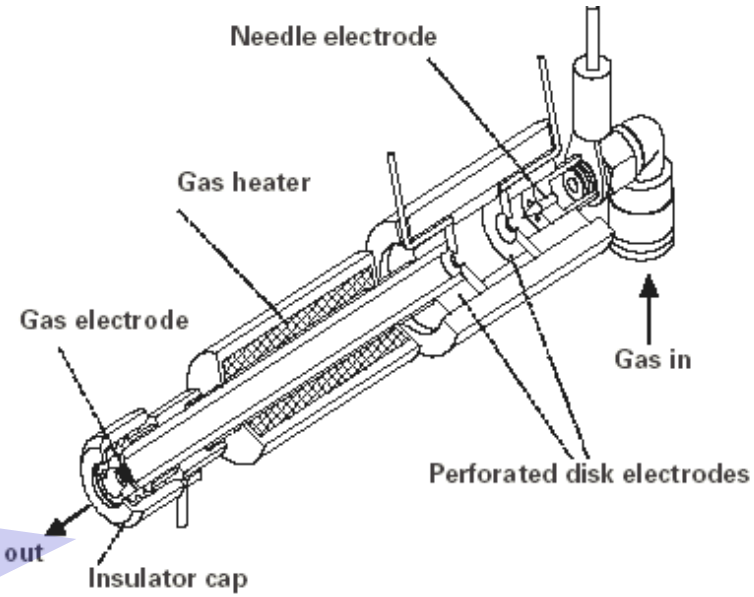
DART: Direct Analysis in Real Time





$$He(2^3S) + H_2O \rightarrow H_2O^{+\cdot} + He(1^1S) + electron^-$$
$$H_2O^{+\cdot} + H_2O \rightarrow H_3O^+ + OH^\cdot$$
$$H_3O^+ + n\ H_2O \rightarrow [(H_2O)nH]^+$$
$$[(H_2O)nH]^+ + M \rightarrow MH^+ + nH_2O$$

$$M^* + S \rightarrow S^{+\cdot} + M + electron^-$$

R. Cody, J. Laramée, H. Dupont Durst Anal Chem 77 (2005) 2297-2302

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DART-AccuTOF (JEOL)

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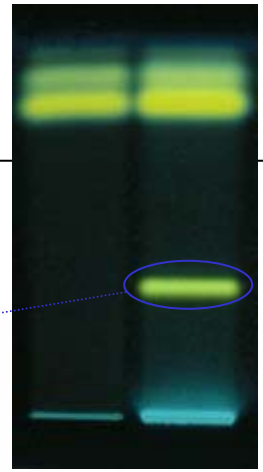
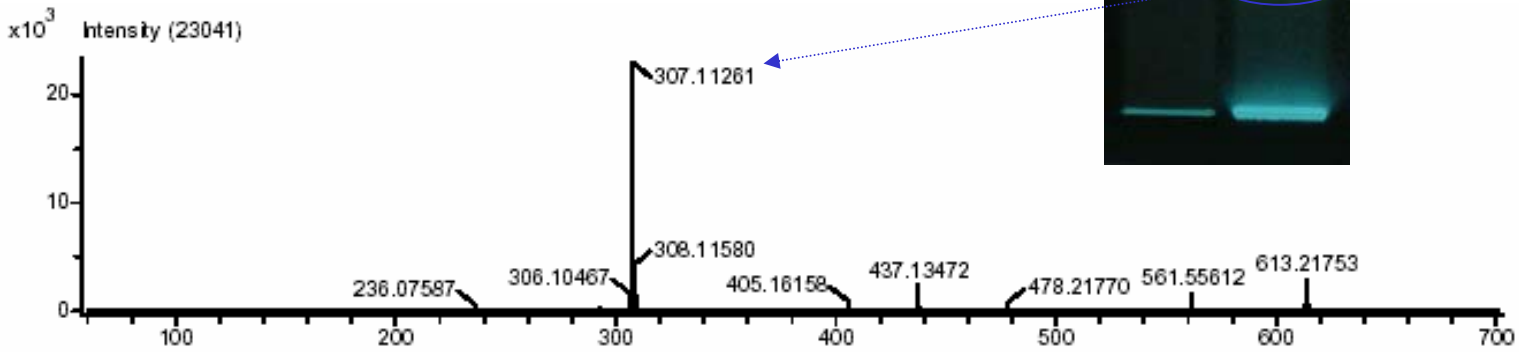
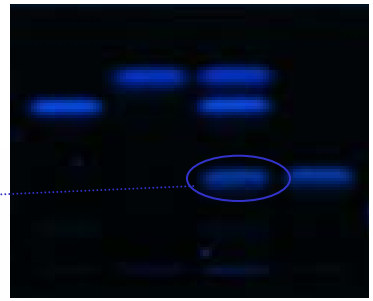
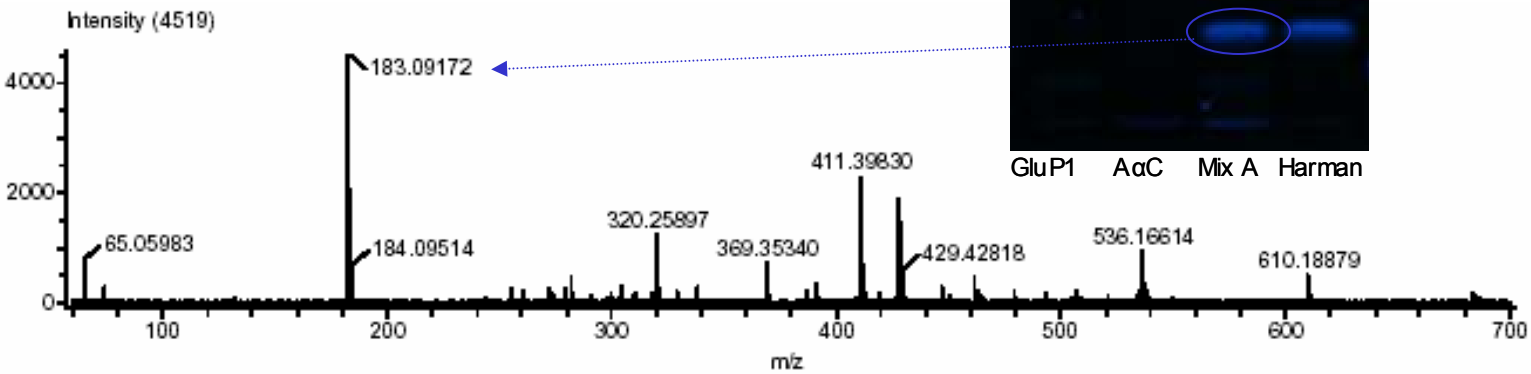
HPTLC/DART-TOF









recorded by Robert Cody, JEOL USA

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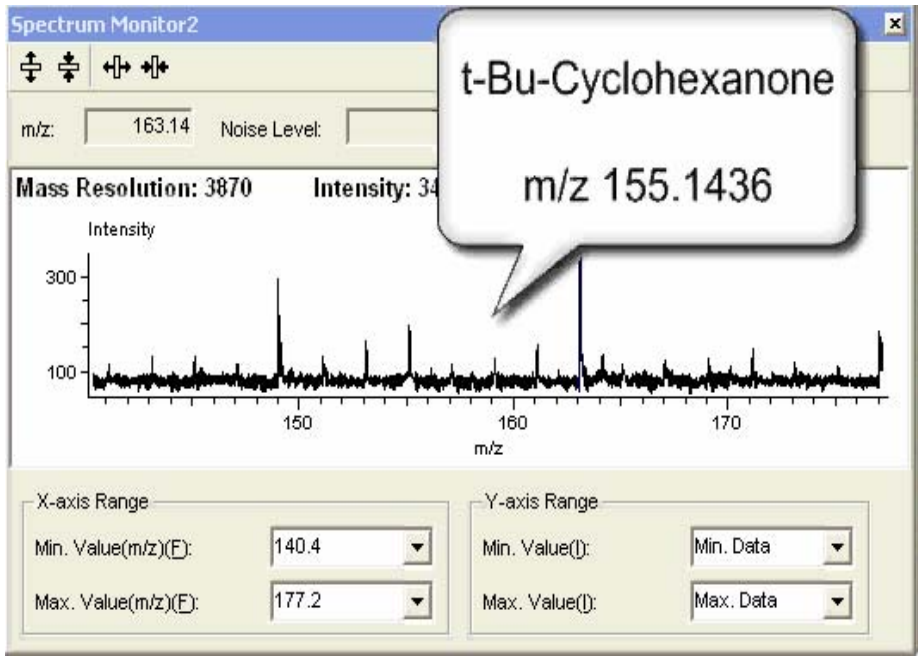
HPTLC/DART coupling



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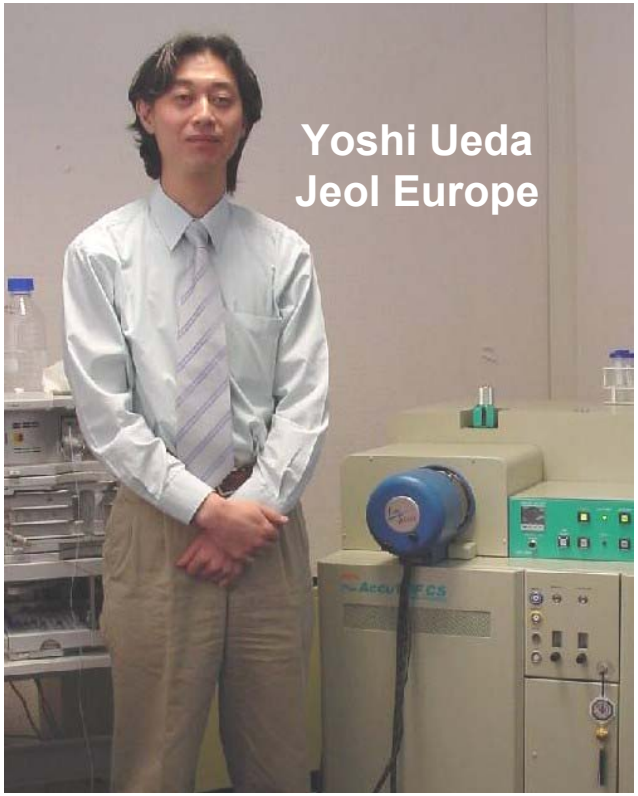
HPTLC/DART-TOF



G. Morlock, Y. Ueda, Coupling of planar chromatography with DART (2006) in submission

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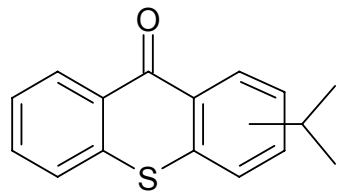
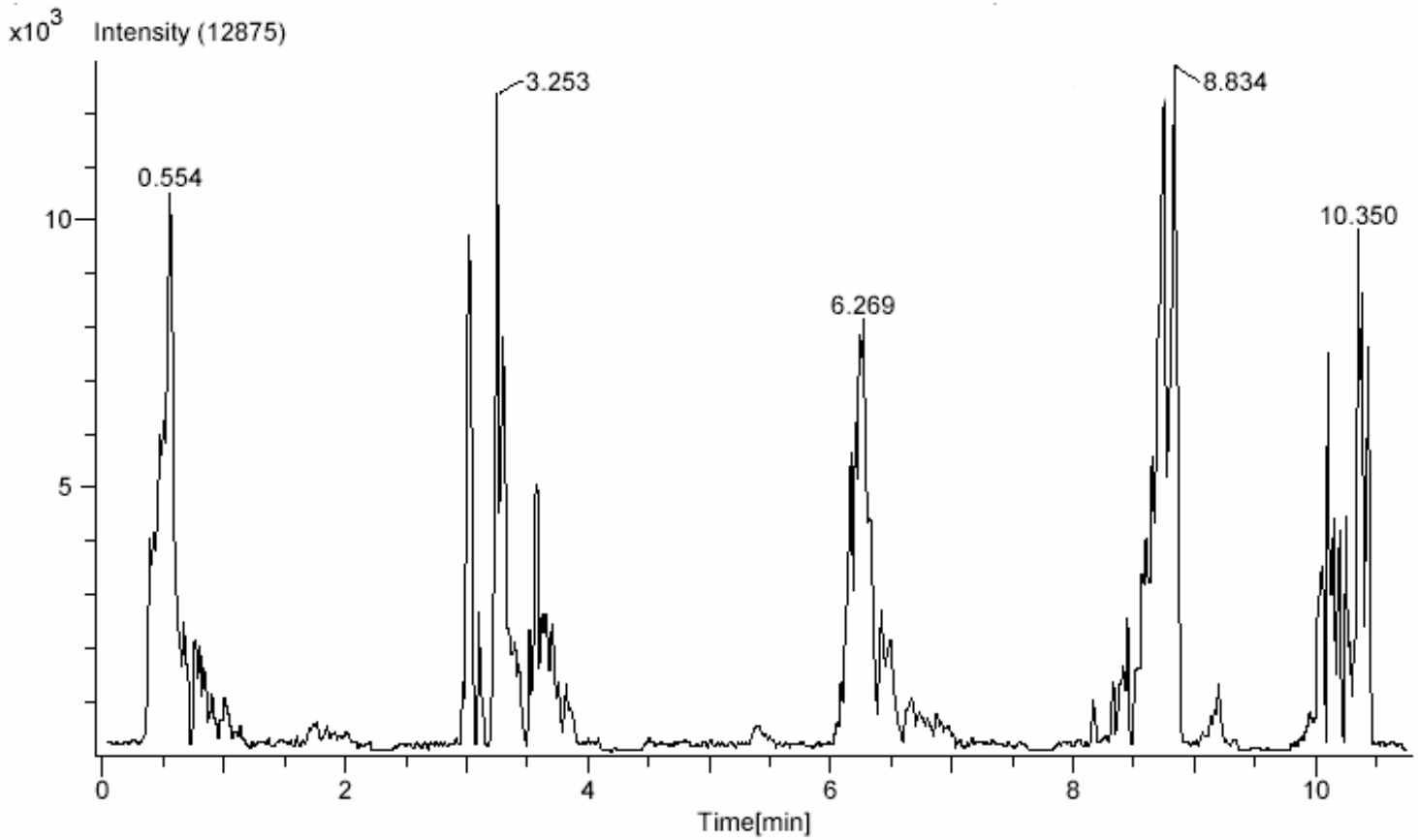
Repeatability



Isopropylthioxanthone (ITX)

5 zones, 32 ng ITX each: CV = ± 71.1 % (18.3 %)



Mass chromatogram at m/z 255 $[M+H]^+$

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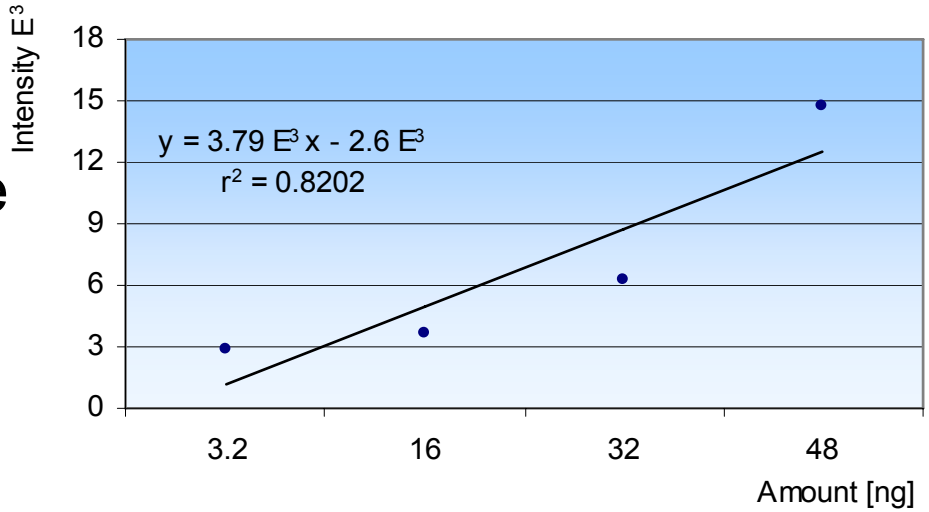
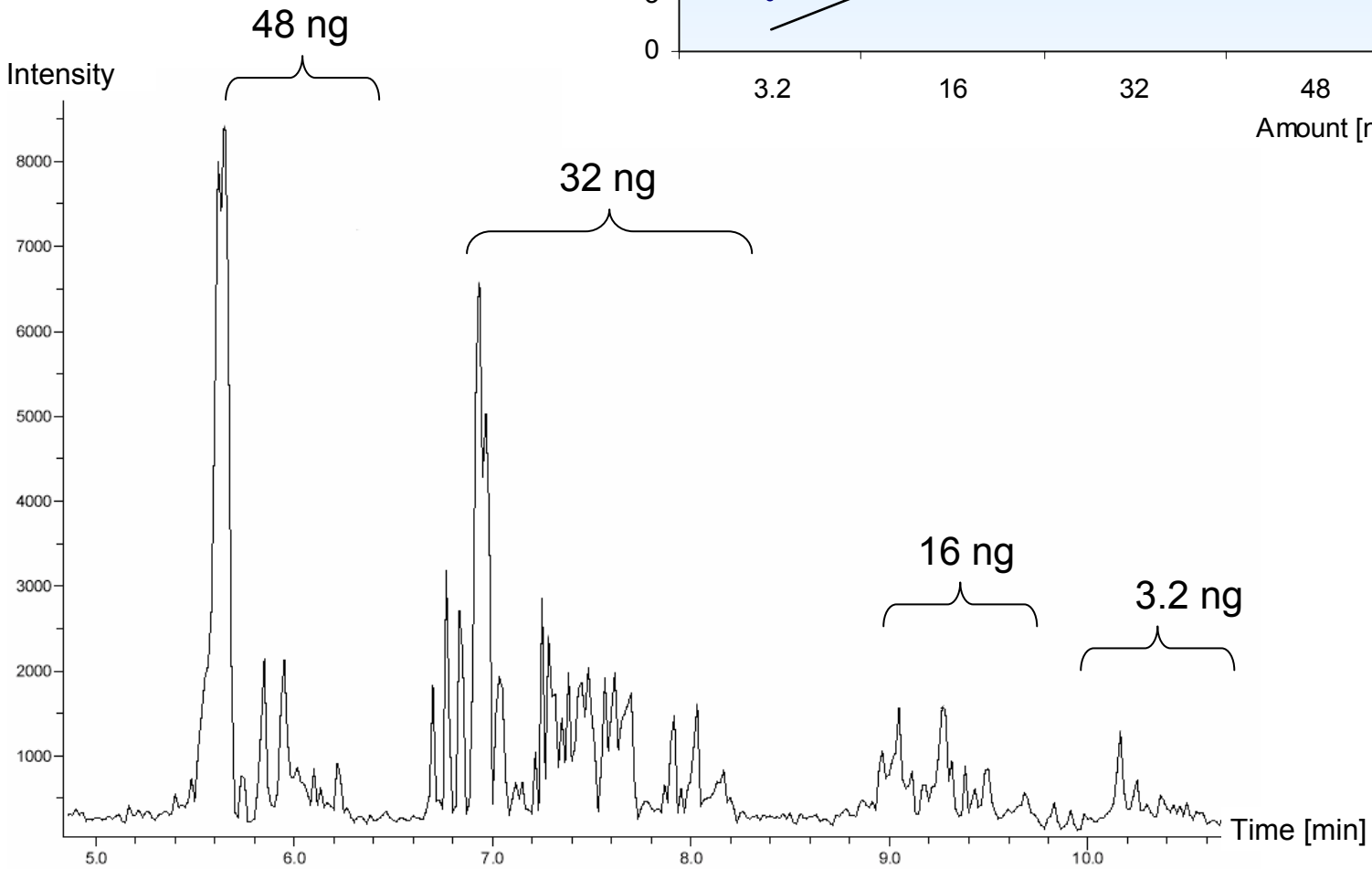
Analytical response





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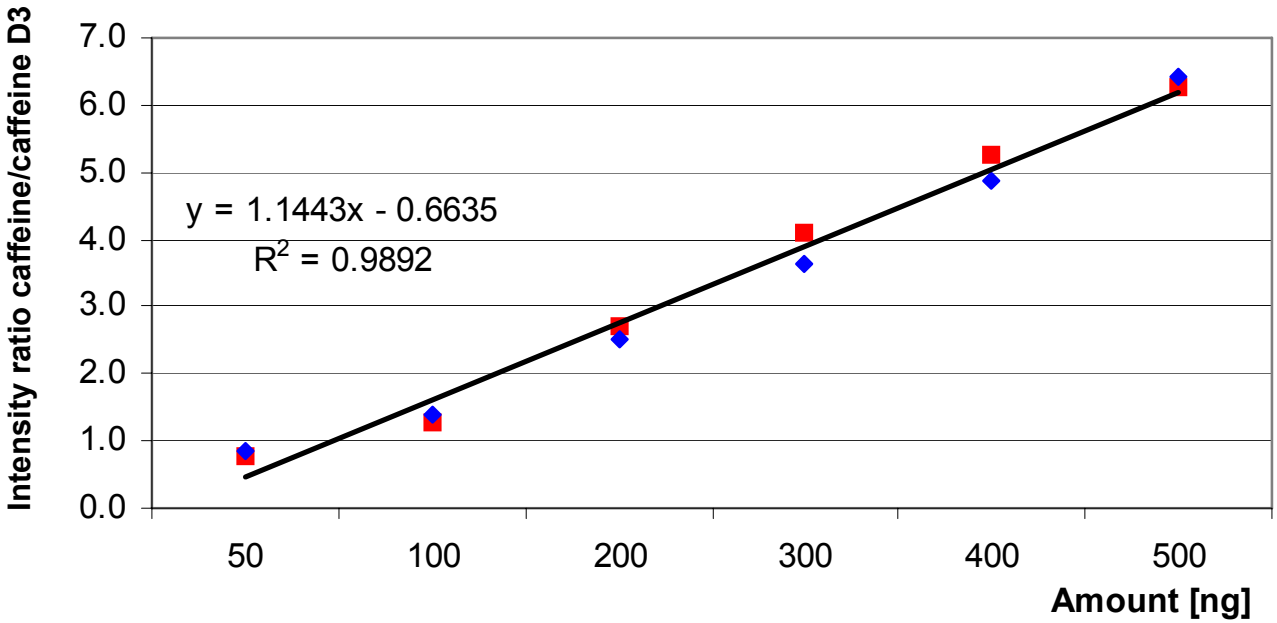
HPTLC/DART-IDA-TOF

- Caffeine at *m/z* 195 $[M+H]^+$ corrected by the stable isotope labeled internal standard caffeine D3 at *m/z* 198 [M+H]+



- Repeatability RSD < ±5.4 %, *n* = 6

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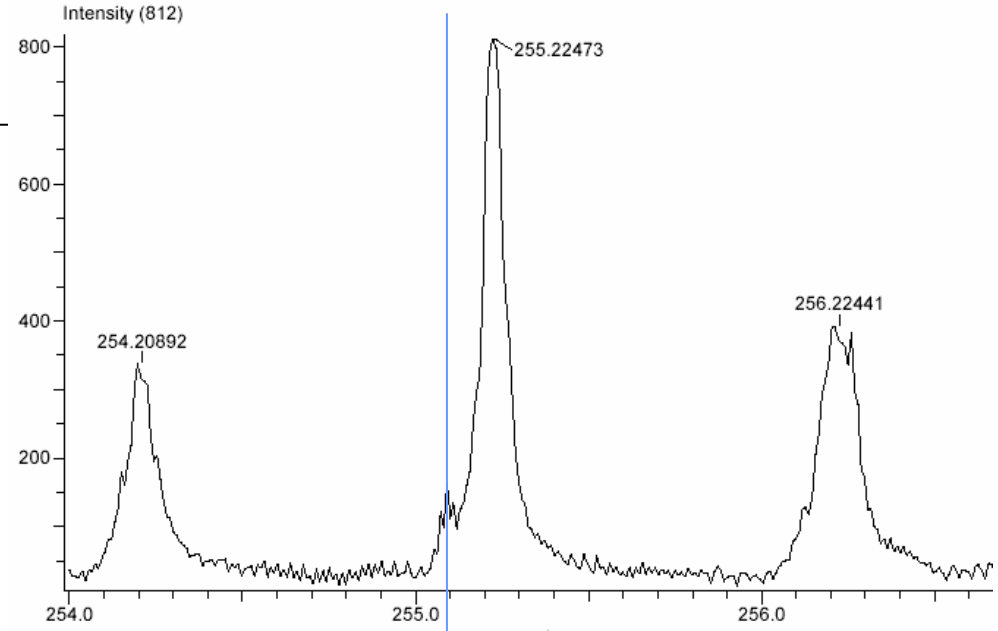
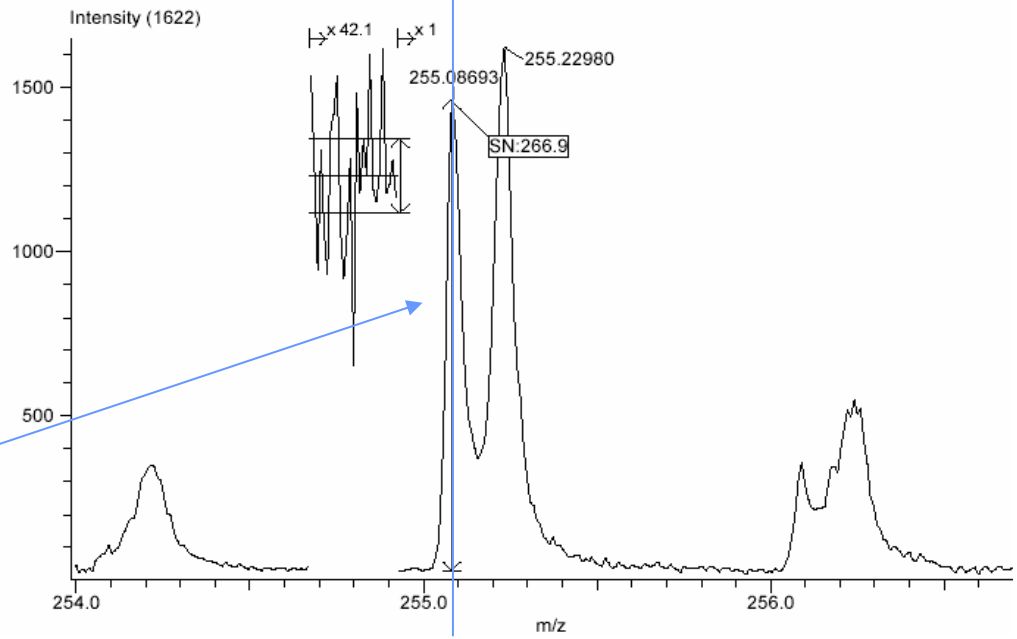
Detectability

Blank
m/z 255.08693



3.2 ng ITX zone
m/z 255.08693
S/N of 267



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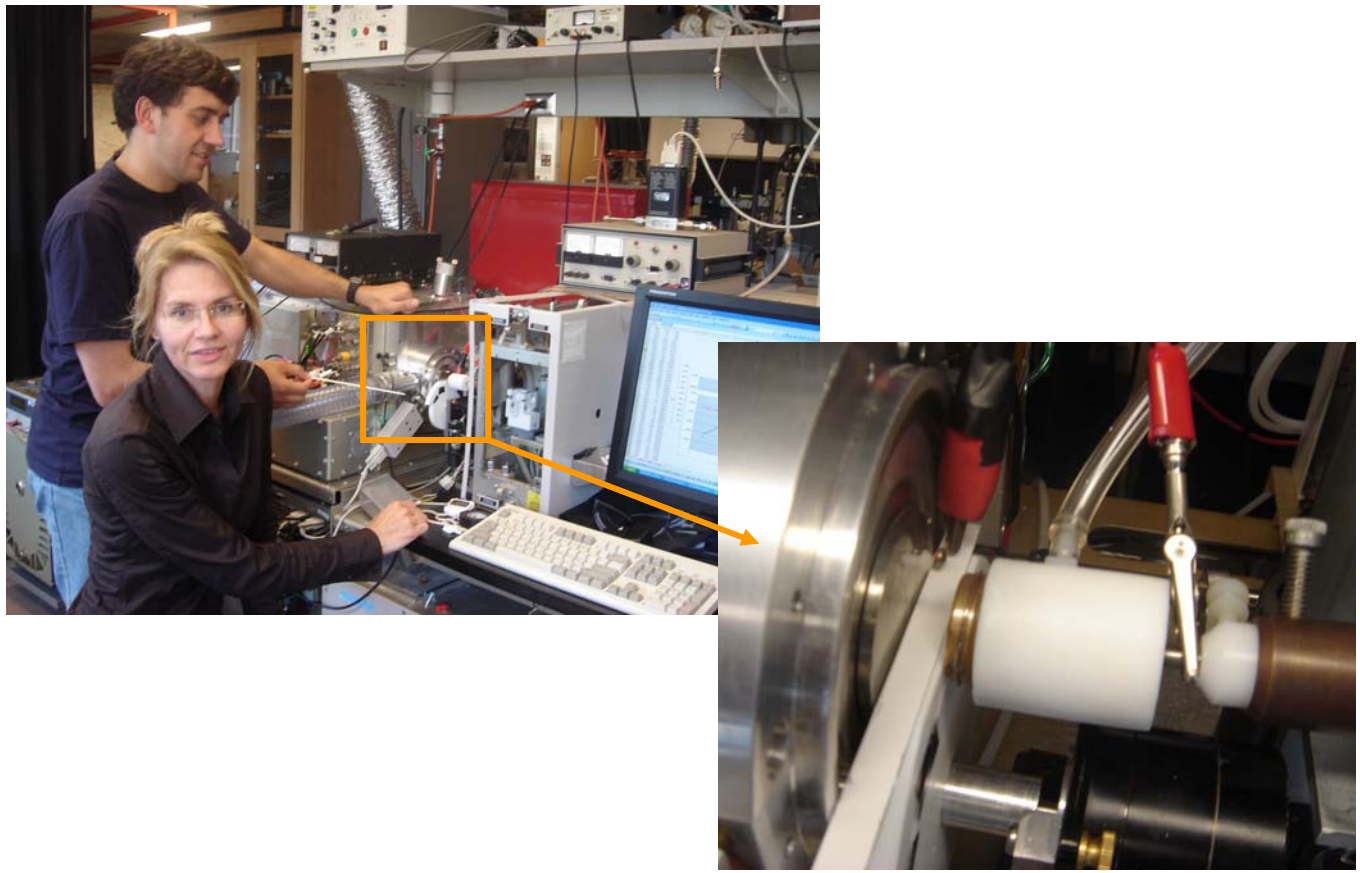
HPTLC/APGD coupling



G. Morlock, F. Andrade, G. Hieftje: Coupling of planar chromatography with atmospheric pressure glow discharge mass spectrometry (2006) in preparation

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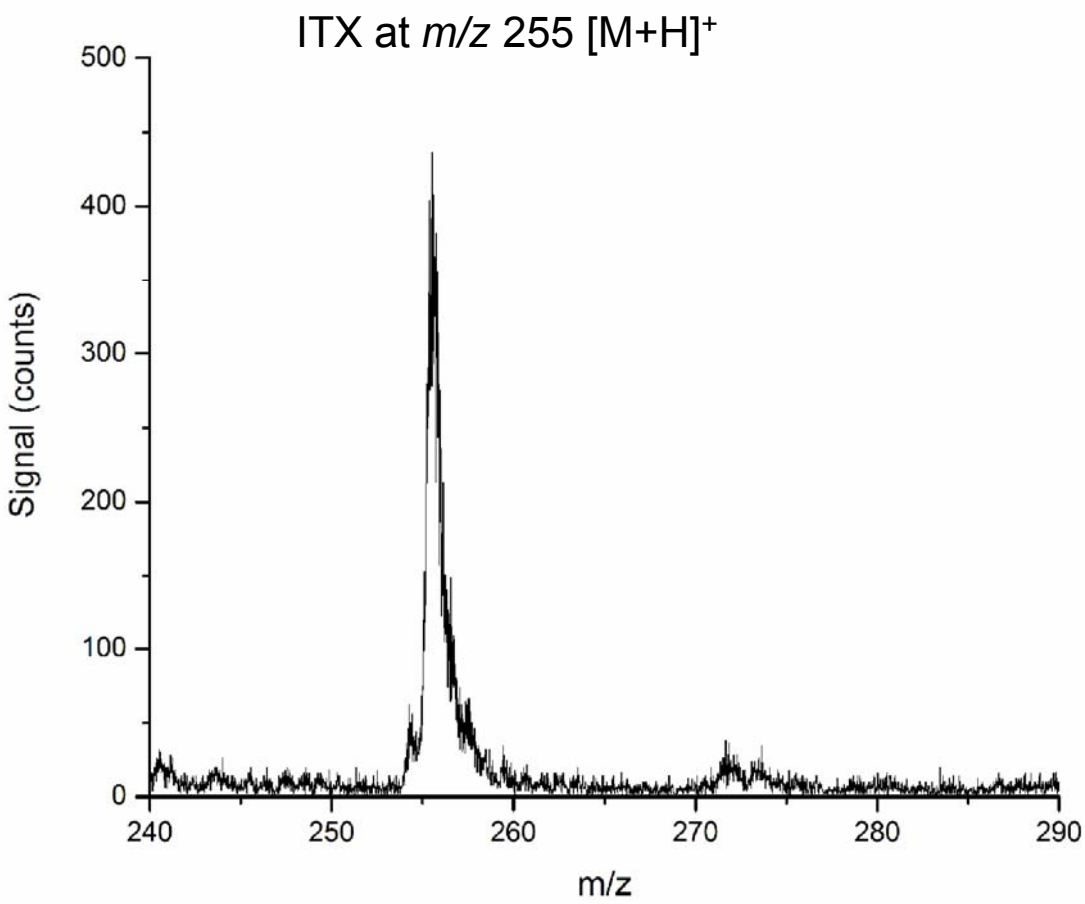
HPTLC/APGD coupling



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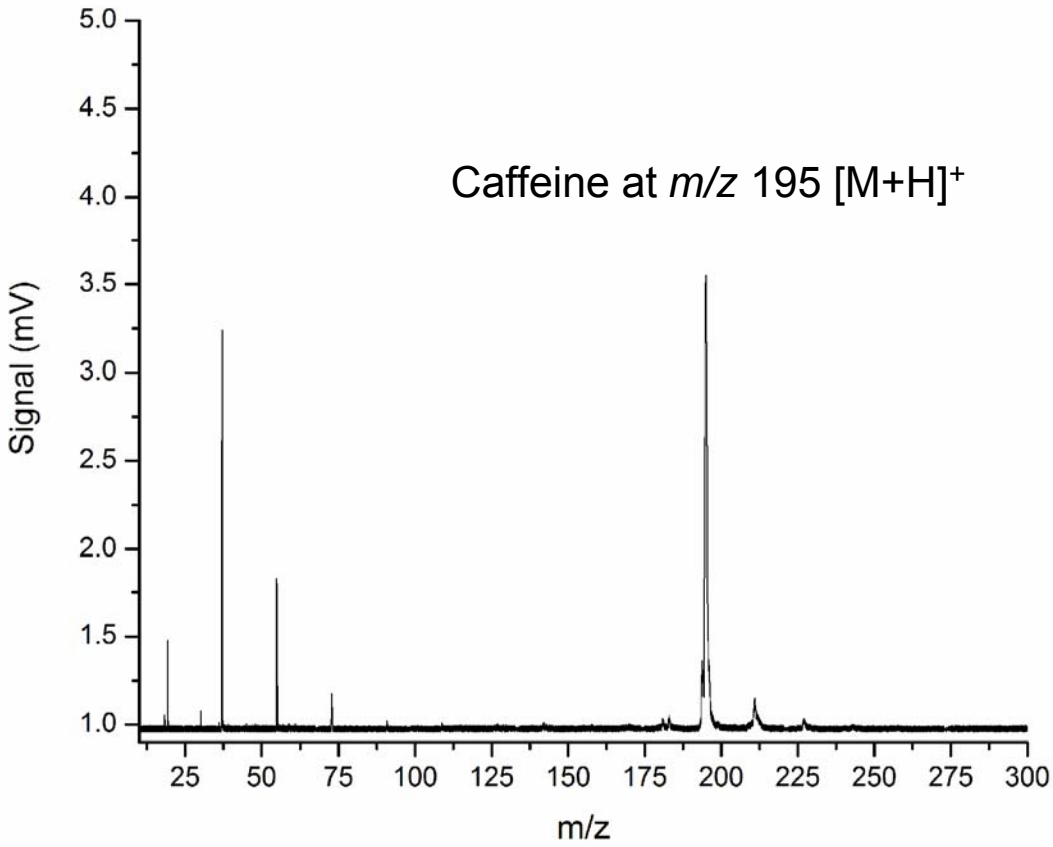
HPTLC/APGD coupling



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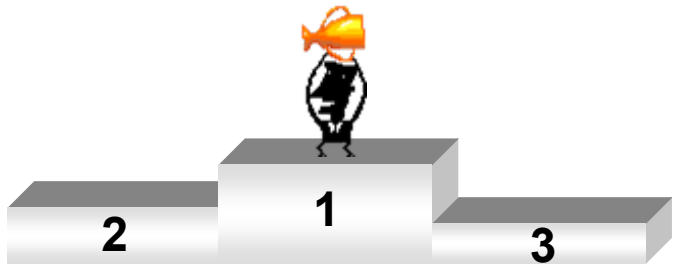
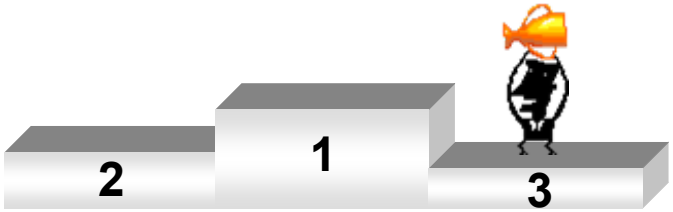
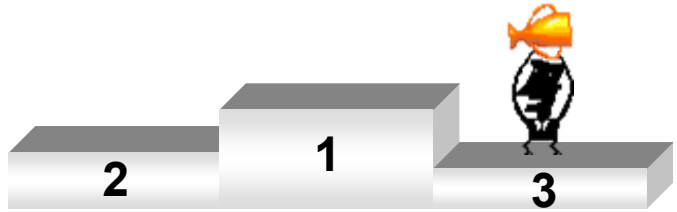
To conclude…



HPTLC/ESI-MS(-MS)



HPTLC/DART-TOF



HPTLC/APGD-TOF

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Special thanks go to …

Prof. Dr. W. Schwack

Dr. Luftmann, Münster

W. Seitz, LW Langenau

CAMAG, Muttenz, CH

Merck, Darmstadt

ChromAn, Holzhausen

Jeol (Europe) S.A., Paris

Landesstiftung BW

Project No. P-LS-E2/25

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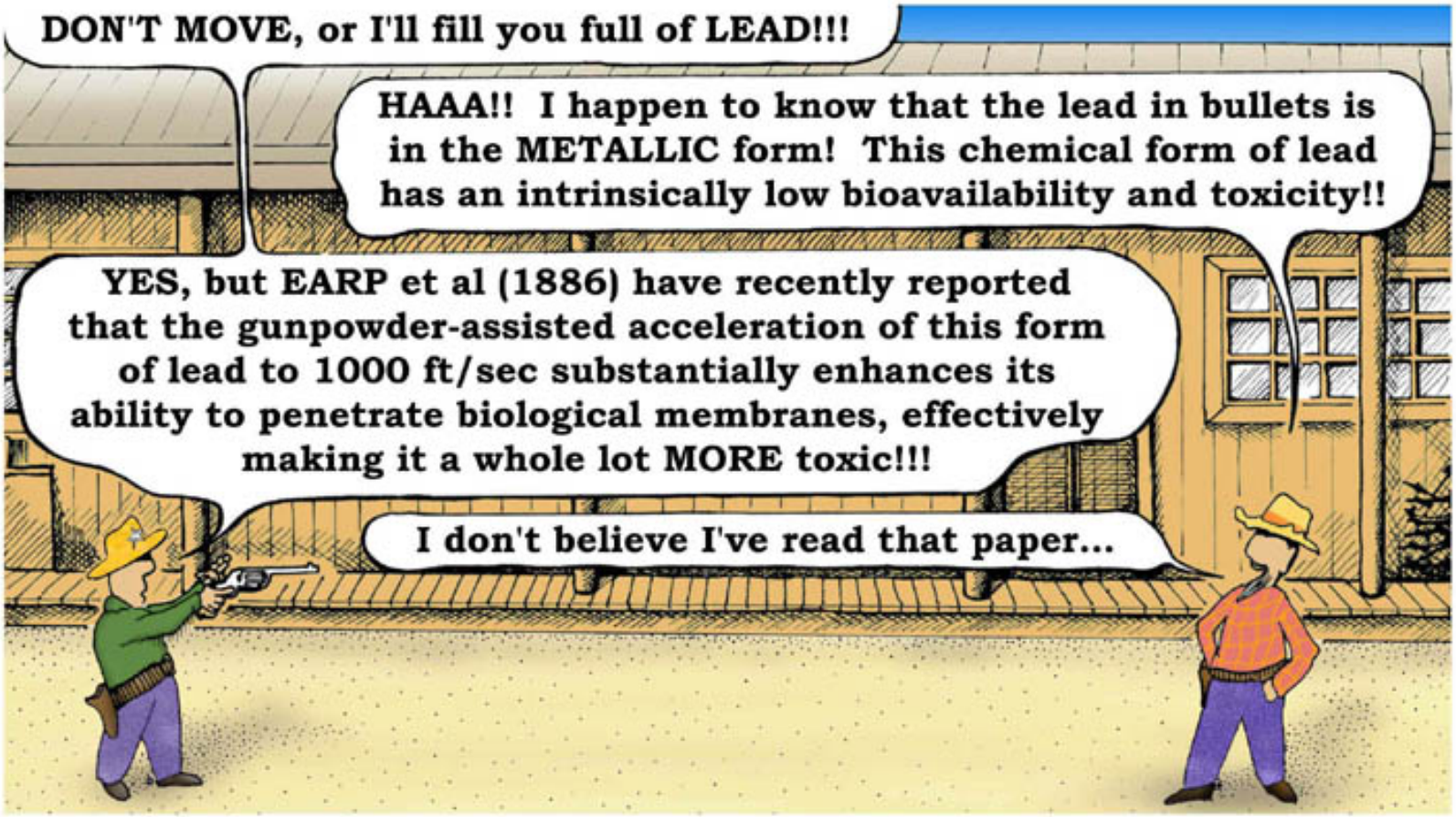
Discussion



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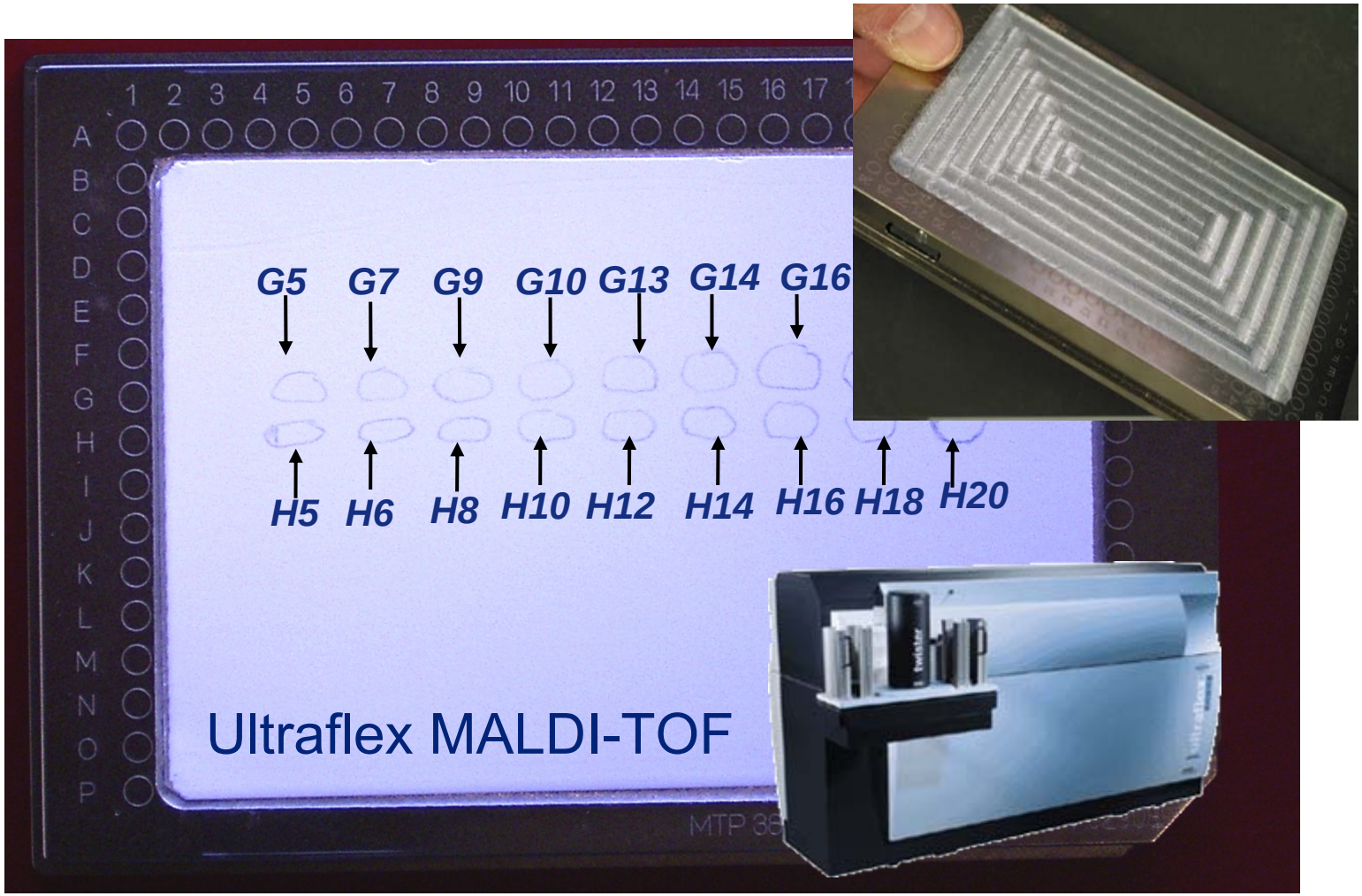
Microtiter plate target used for HPTLC foils



recorded by Dr. Franz Mayer-Posner, Bruker Daltonic, Bremen

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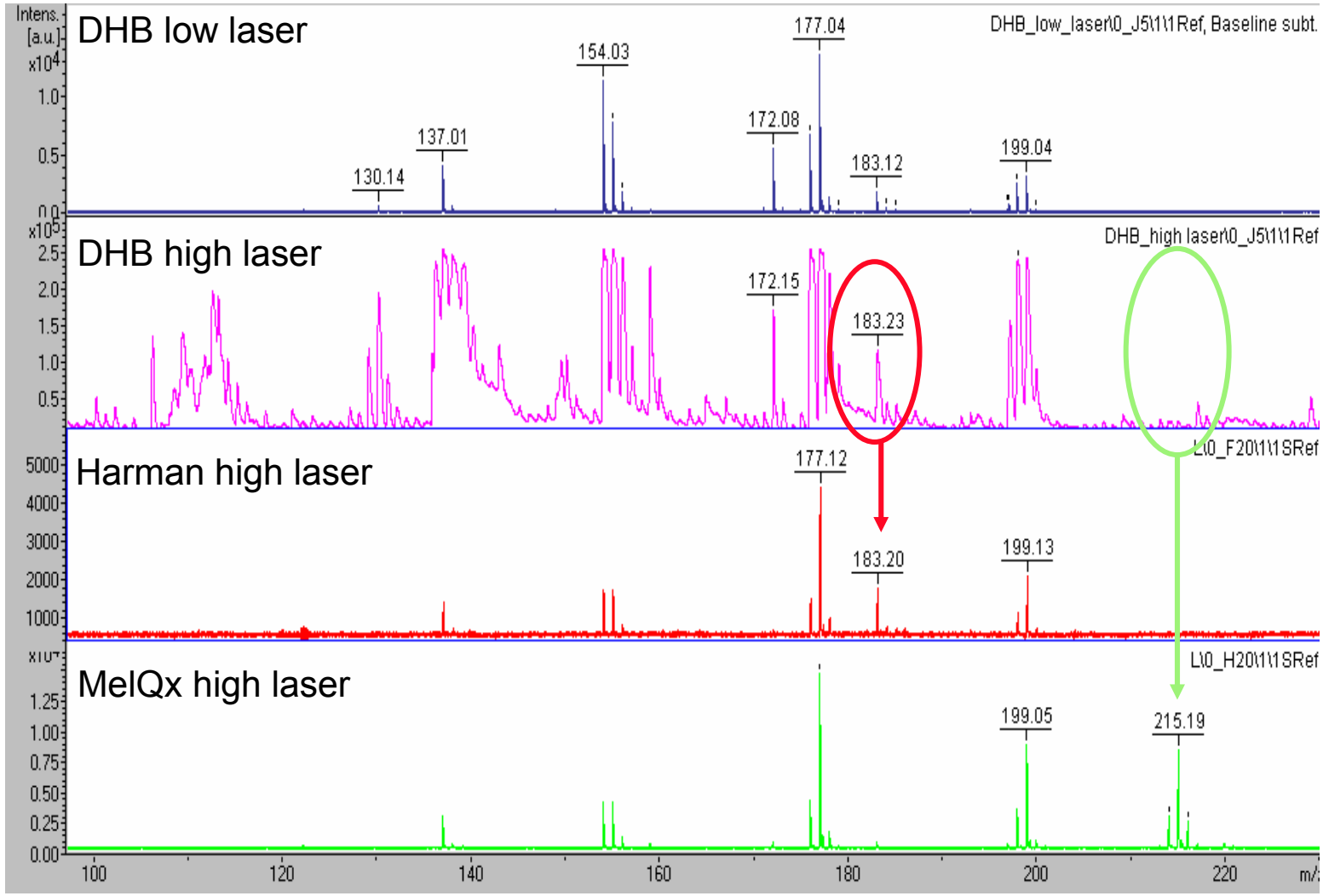
Comparison with DHB matrix



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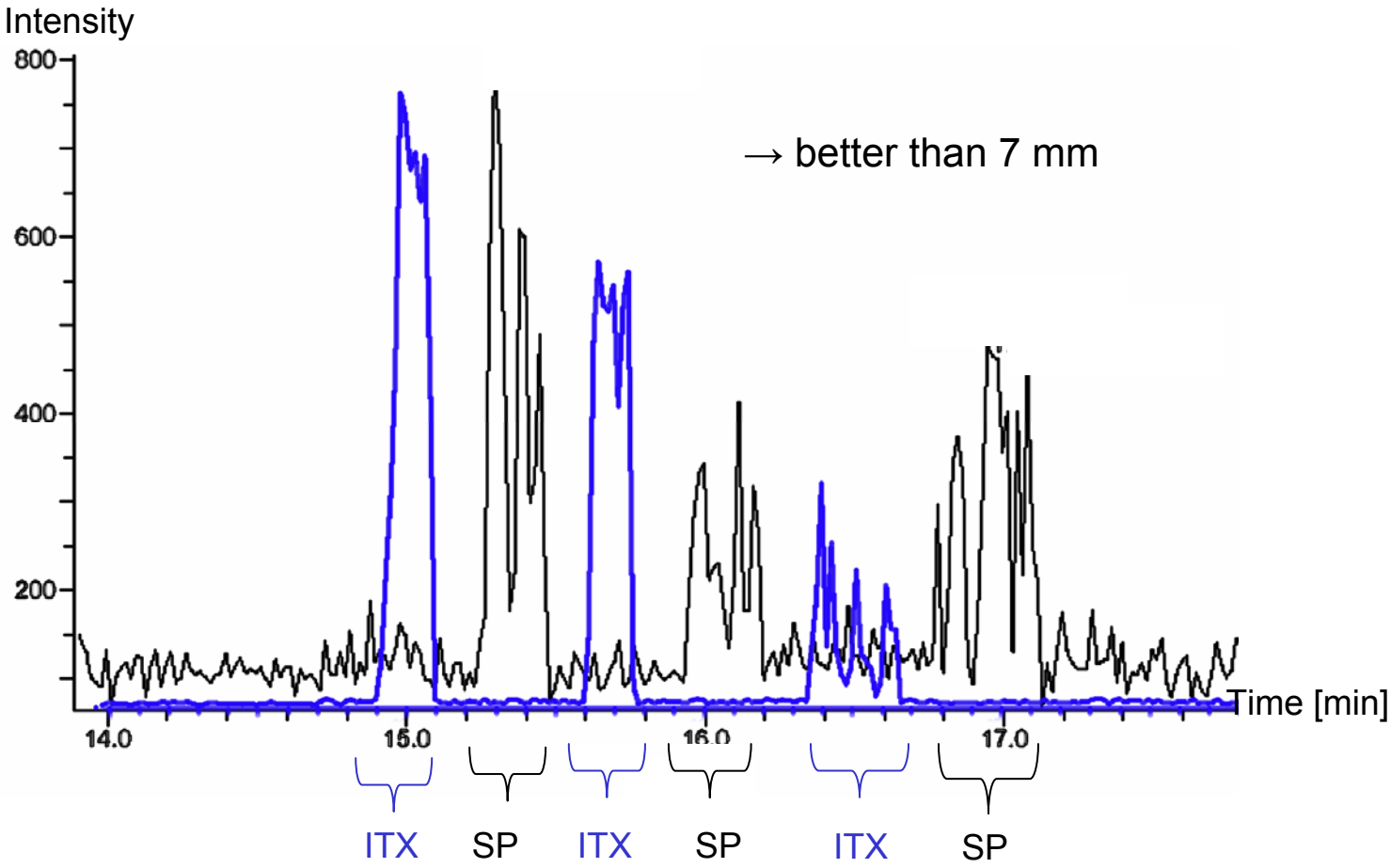
Spatial resolution



Overlaid mass traces of the adjacent zones ITX (16 ng, *m/z* 255 $[M+H]^+$) und SP (5 ng, *m/z* 264 $[M+H]^+$) applied in 7 mm distance