INSTITUTE OF CHEMICAL TECHNOLOGY PRAGUE

Planar chromatography meets direct ambient mass spectrometry: current trends

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Major Hyphenations of Open Air Ambient MS & (HP)TLC Separations

Thermal Desorption

- DART – Direct Analysis in Real Time
- FAPA – Flowing Atmospheric Pressue Afterglow

Laser Ablation

- LA-DART – Laser Ablation DART
- LAESI – Laser Ablation Electrospray Ionization

Liquid Spray

- DESI – Desorption Electrospray Ionization
- EASI – Easy Ambient Sonic-spray Ionization
- LESA – Liquid Extraction Surface Analysis

- TLC-CAMAG ESI Interface – main ESI based method

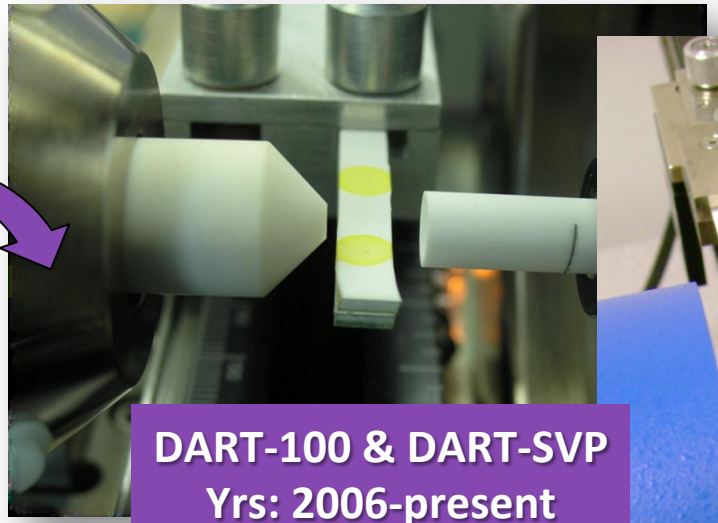
Focusing on *Open Air Thermal Ionization* Coupled with Mass Spectrometry

Major benefits **compared to liquid based methods:**

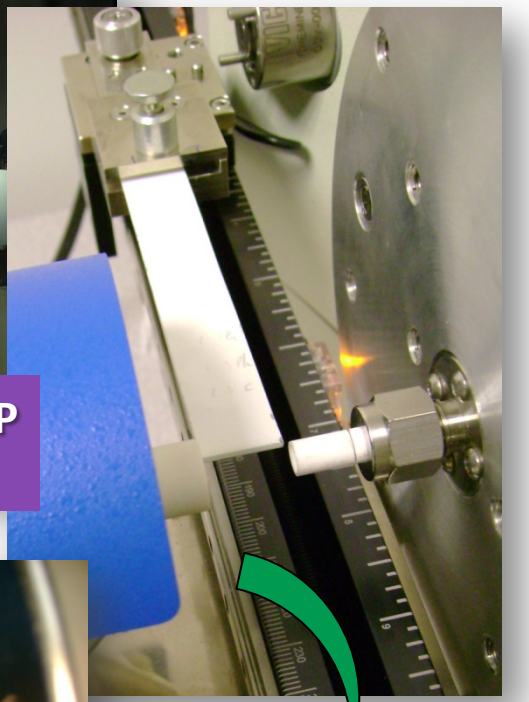
- **No use of solvents during ionization**
- **Only semi-destructive - all material not completely ablated → can run repeat analyses or other methods**
- **Complementary MS data compared with HPTLC ESI-MS – no salt adduct formation, potential thermal separation, both RP & NP plates**
  - **→ Heating Ramp (RT – 550° C)**
- **Silica gel not disturbed from plate surface → interaction only with heated gas → no source contamination**

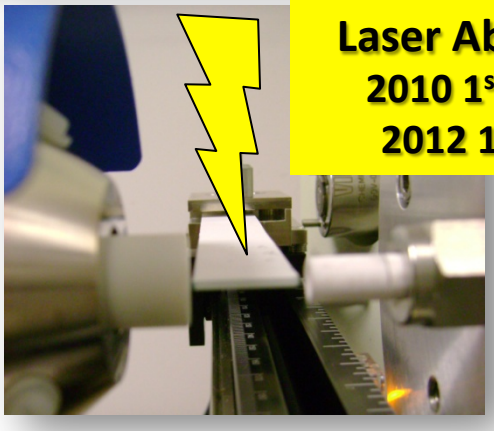
DART TLC Evolutions...

DART-100 Yrs: 2006-09

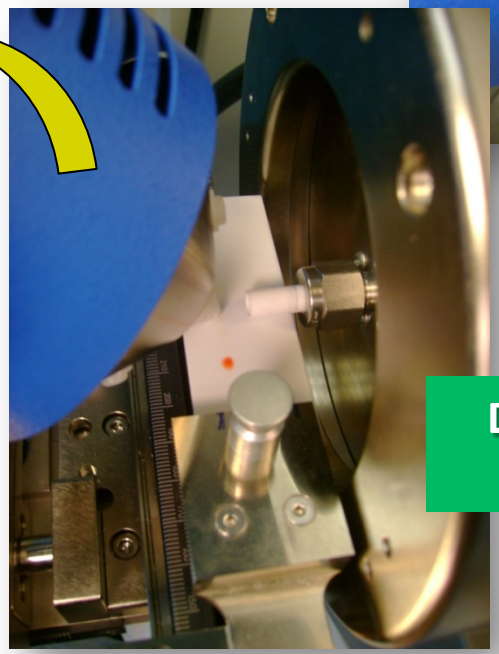


DART-100 & DART-SVP
Yrs: 2006-present



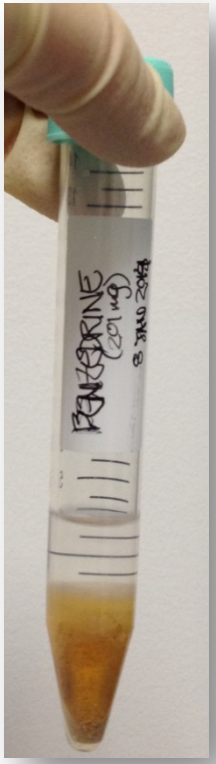


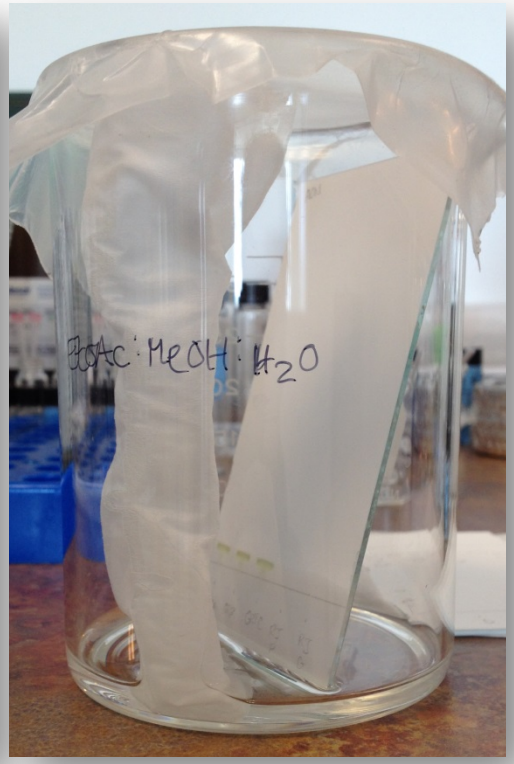
Laser Ablation DART
2010 1st Publication
2012 1st TLC DART

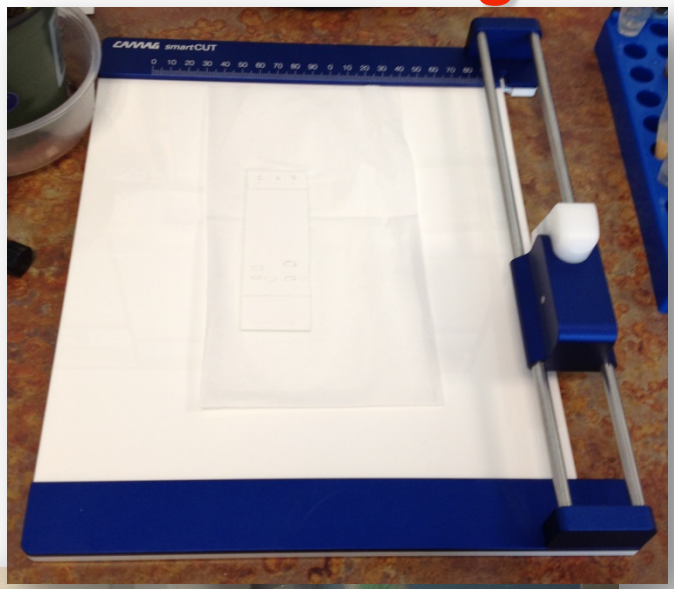


DART-SVP at Angle
Yrs: 2009-present

Direct TLC Analysis: *Vertical On-Edge* Method







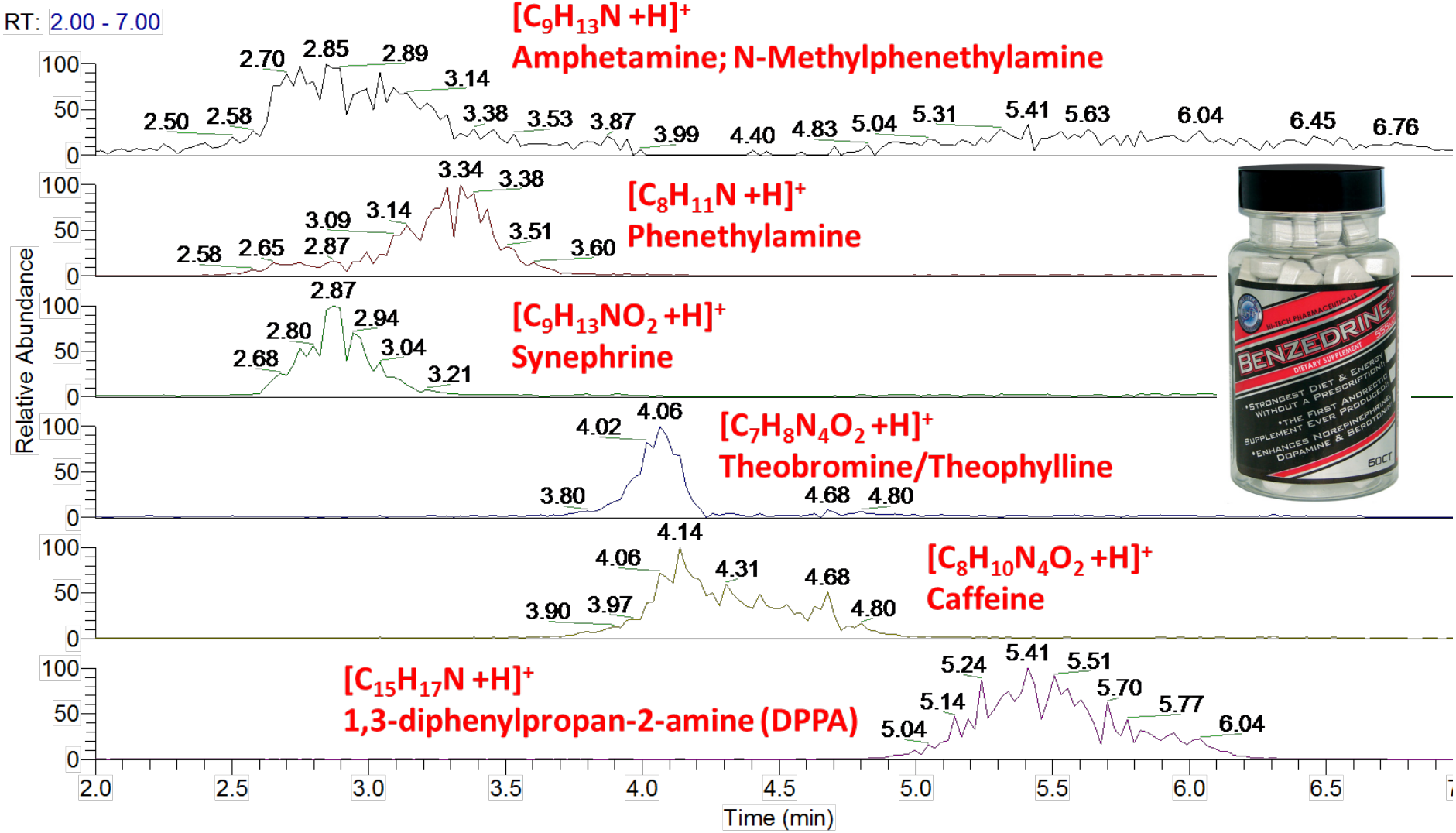
Sample preparation & separation via HPTLC (Methanolic Extract)
(Silica gel 60 F_{254} at thickness of 200 µm)

Helium at 350° C
0,5 mm/s speed

First coupling of DART with TLC: Morlock, G.; Schwack, W. Determination of isopropylthioxanthone (ITX) in milk, yoghurt and fat by HPTLC-FLD, HPTLC-ESI/MS and HPTLC-DART/MS. Anal. Bioanal. Chem. **2006**, 385(3): 586-595.

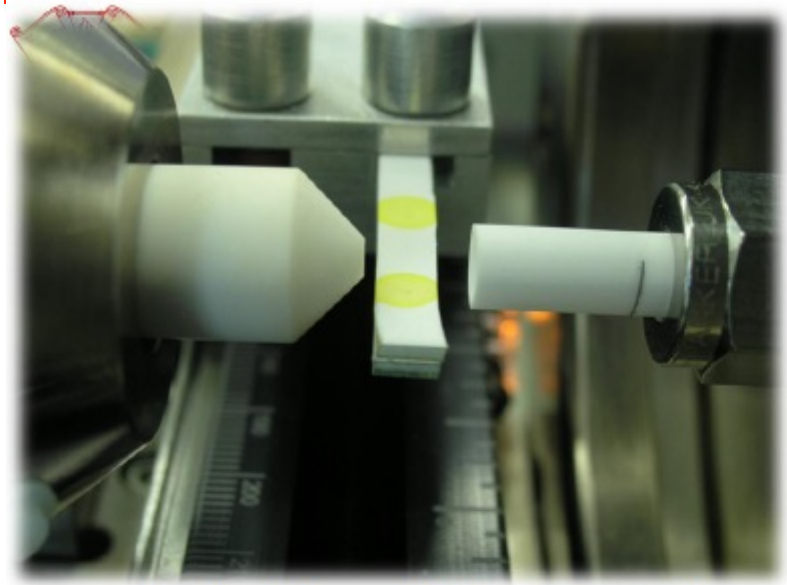
Direct analysis *vertical edge* of HPTLC plate

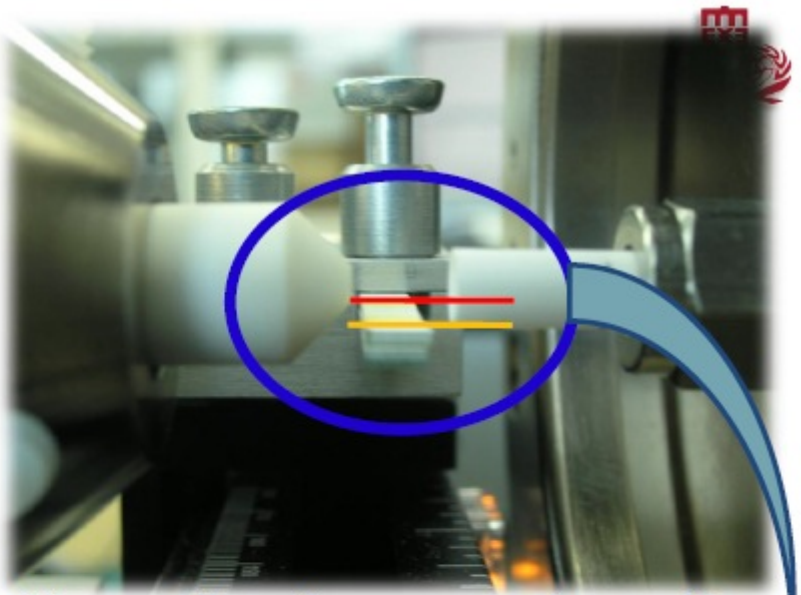
Benzedrine Tablet: MeOH extract separated by HPTLC (silica gel 60 F_{254} at thickness of 200 µm)



E. Crawford *et al*. ASMS 2014 ThP 413. Samples provided by Prof. Jason Shepard; University at Albany, SUNY, Albany, NY

Direct TLC Analysis: *Horizontal* Method

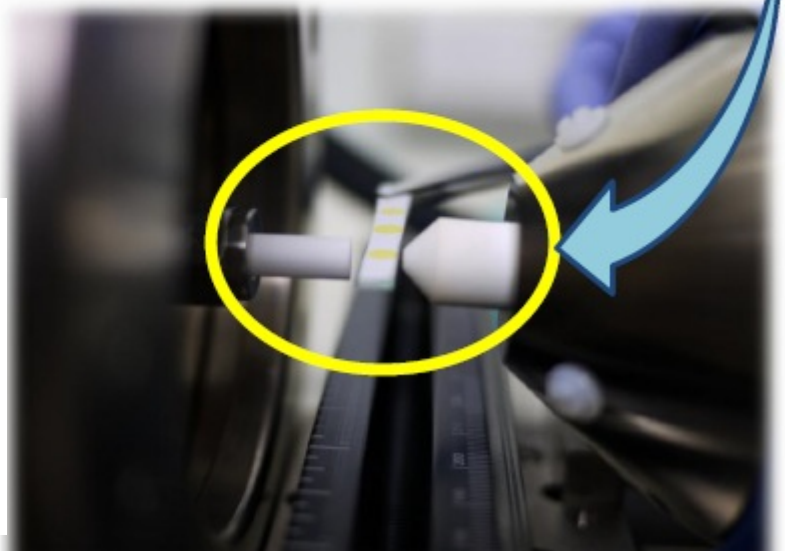




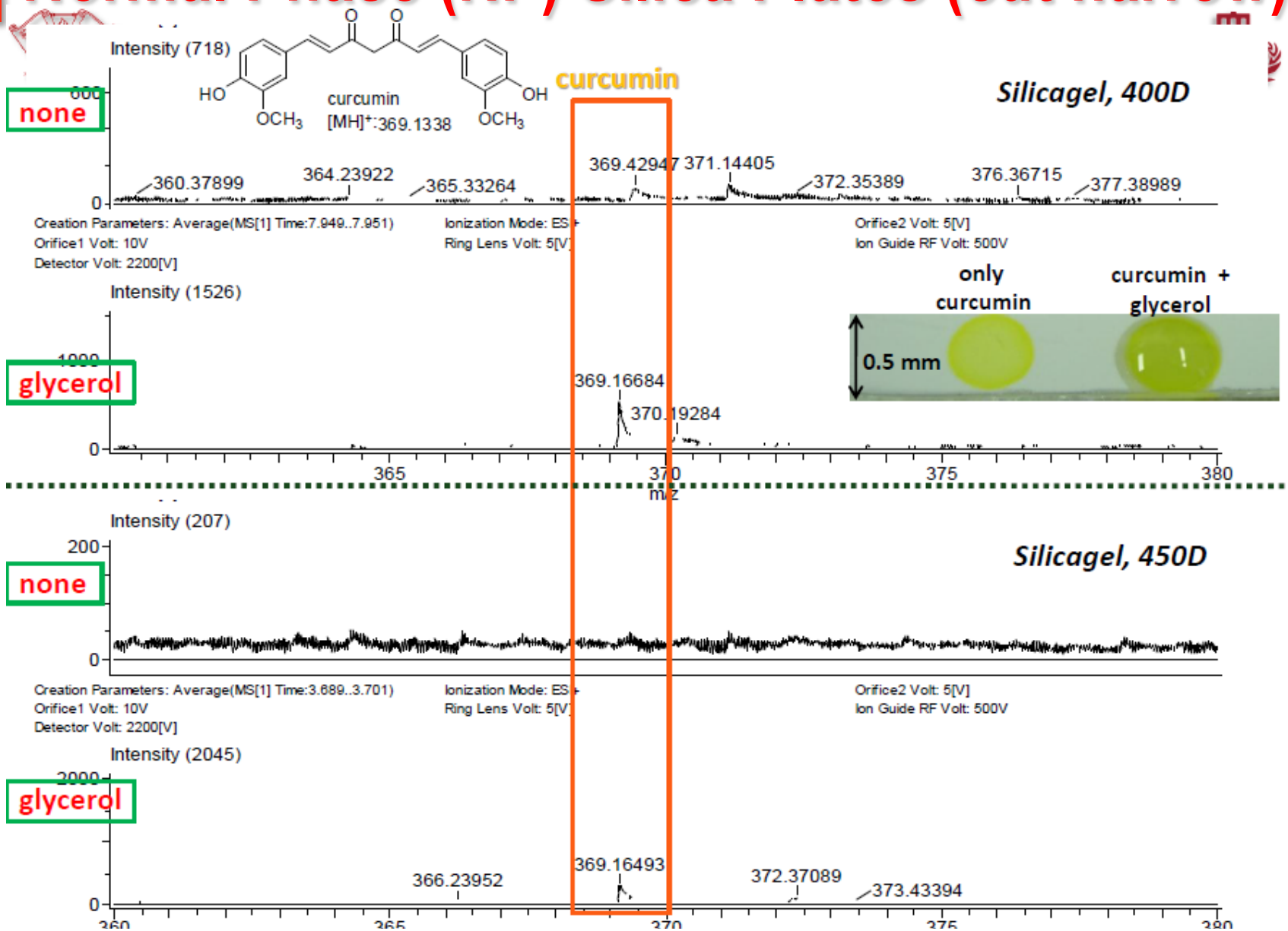
The height of TLC plate is lower than the He gas flow from ceramic cap !!

He gas flow and TLC plate must be arranged in a straight line

Optim. by J.P. Yang *et al.* at Kyung Hee University Seoul, South Korea

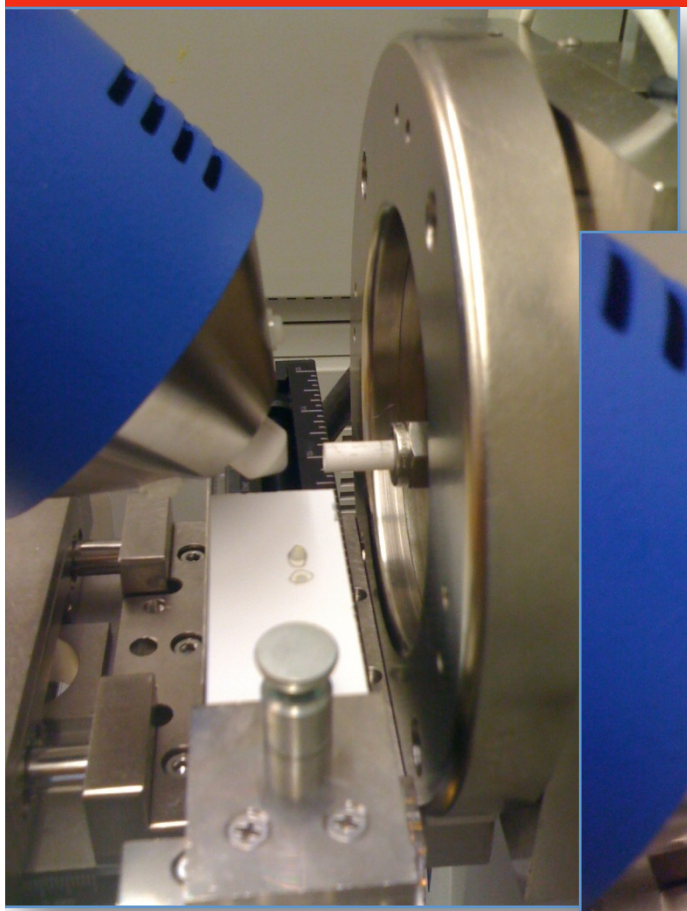


Normal Phase (NP) Silica Plates (cut narrow)

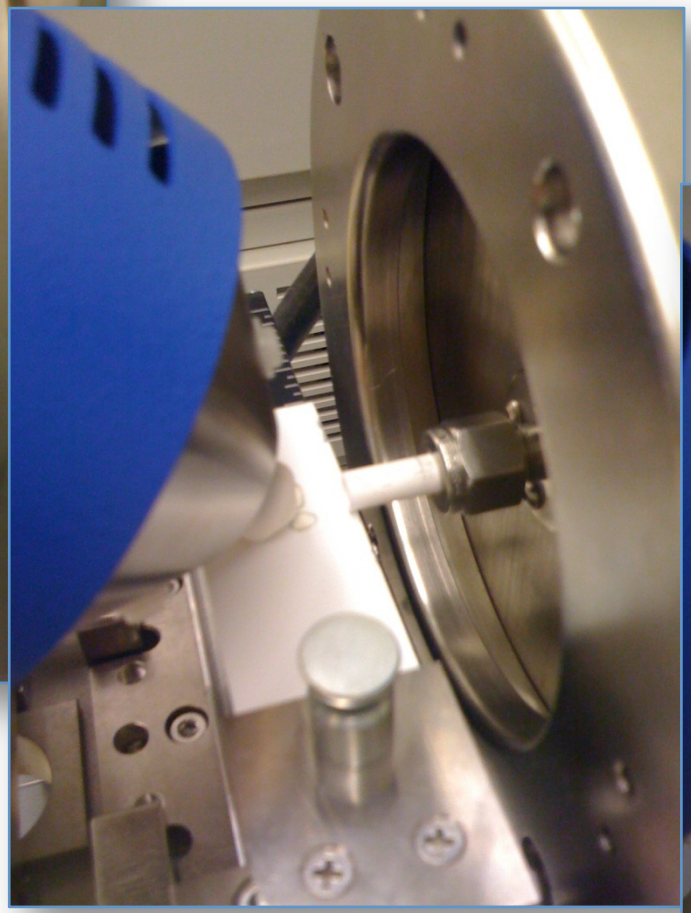


Data provided by H.J. Kim and Dr. Y.P. Jang (2011) ; College of Pharmacy Kyung Hee University Seoul, South

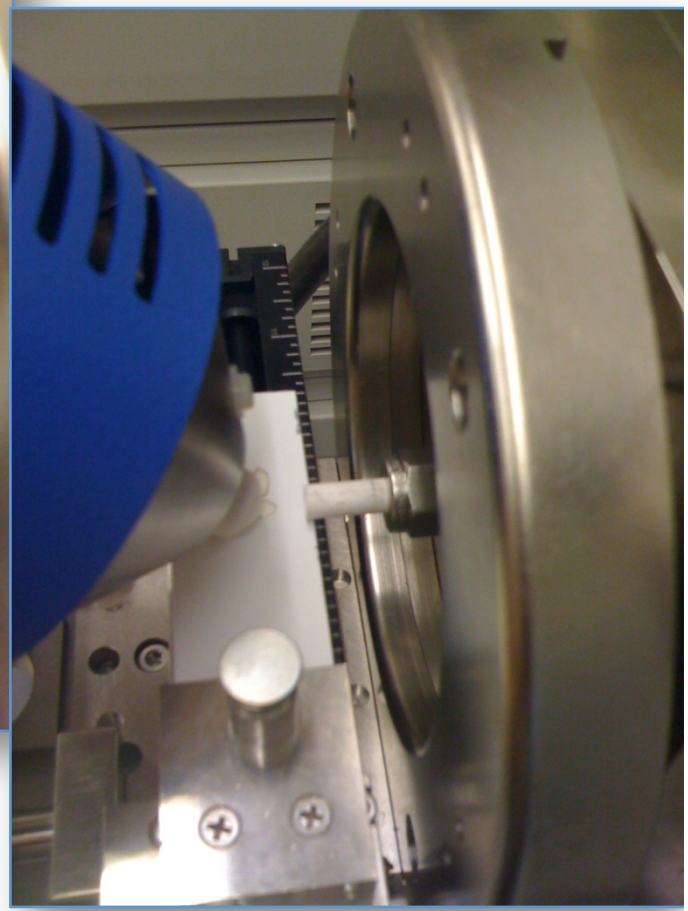
Direct TLC Analysis:
45° Angle



A small dab of glycerol was added to the surface of the TLC plate to enhance the heating of the target area on the TLC plate.



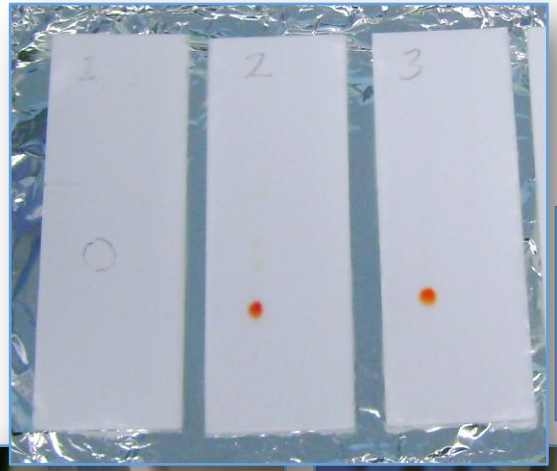
The TLC plate was mechanically moved under the DART-SVP source at 0.3 mm/s speed.



Chernetsova, E.S.; Revelsky, A.I.; Morlock, G.E. Some new features of Direct Analysis in Real Time mass spectrometry utilizing the desorption at an angle option. Rapid Comm. Mass Spec., 2011, 25(16): 2275-2282.

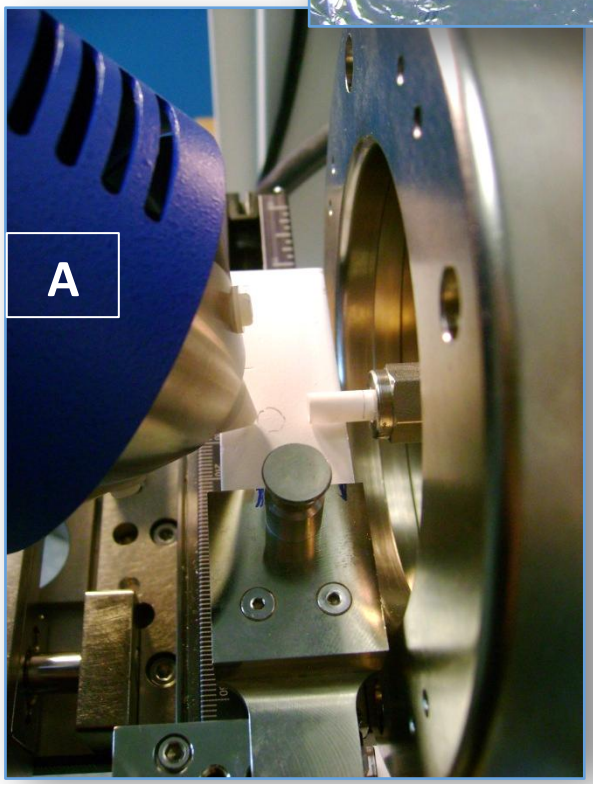
Direct TLC Plate Analysis Workflow

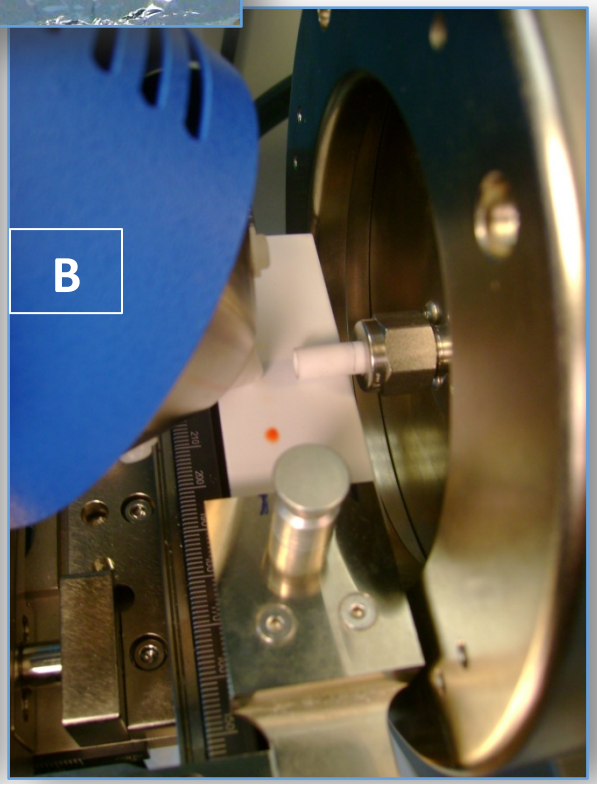
Developed TLC plates are **ready** for **direct** mass spectrometric **analysis**

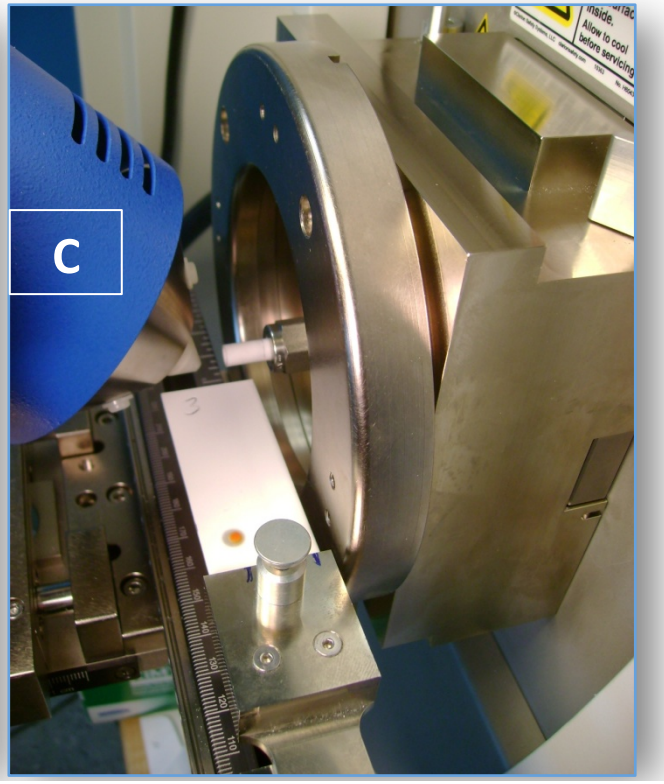


TLC plate is placed into the **holder**, which is mounted onto a **motorized linear rail**

A: 350° C heater setting **(Compound 1)**
B: 450° C heater setting **(Compound 2)**
C: 450° C plus **glycerol** on spot **(Cmpds 2&3)**



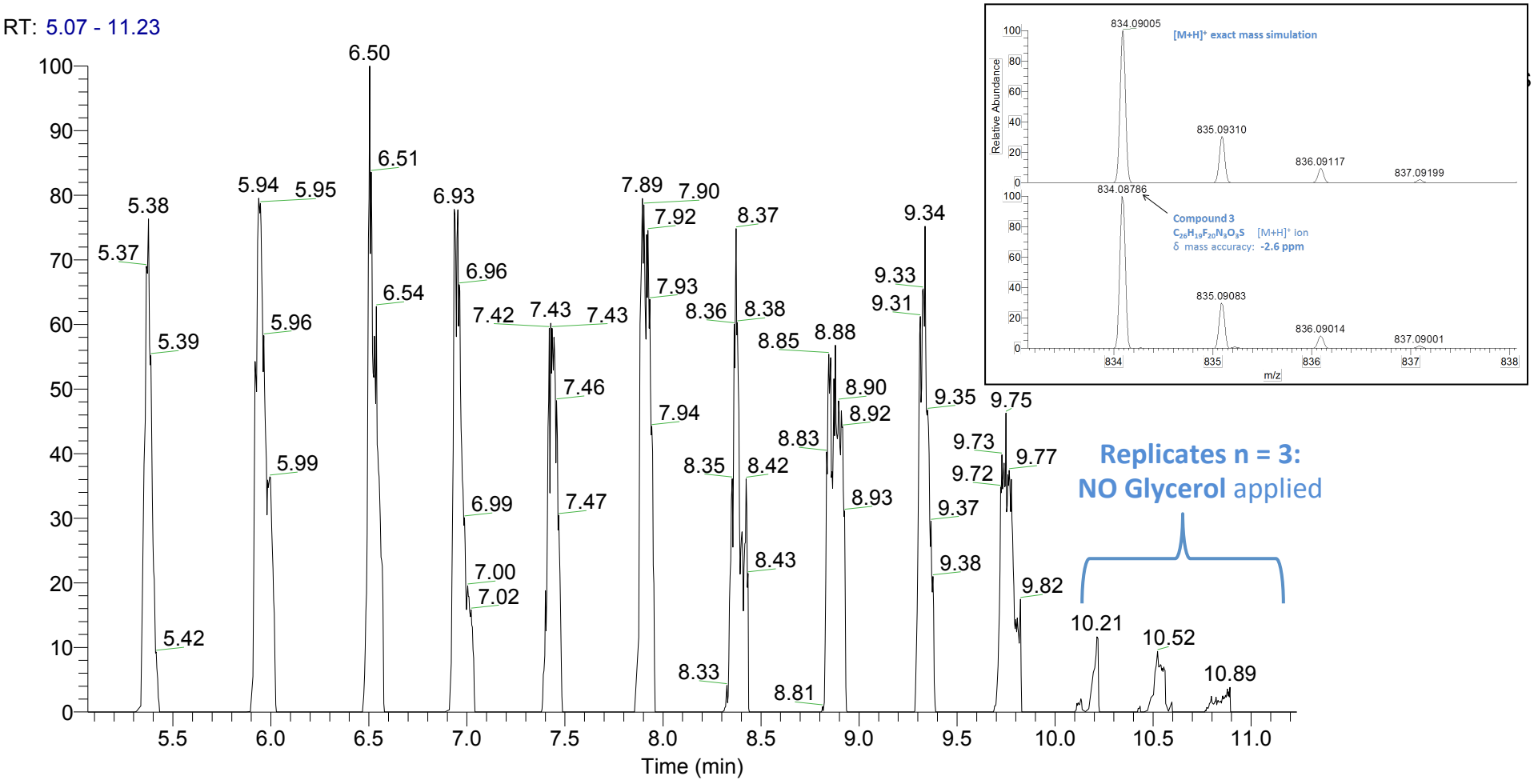




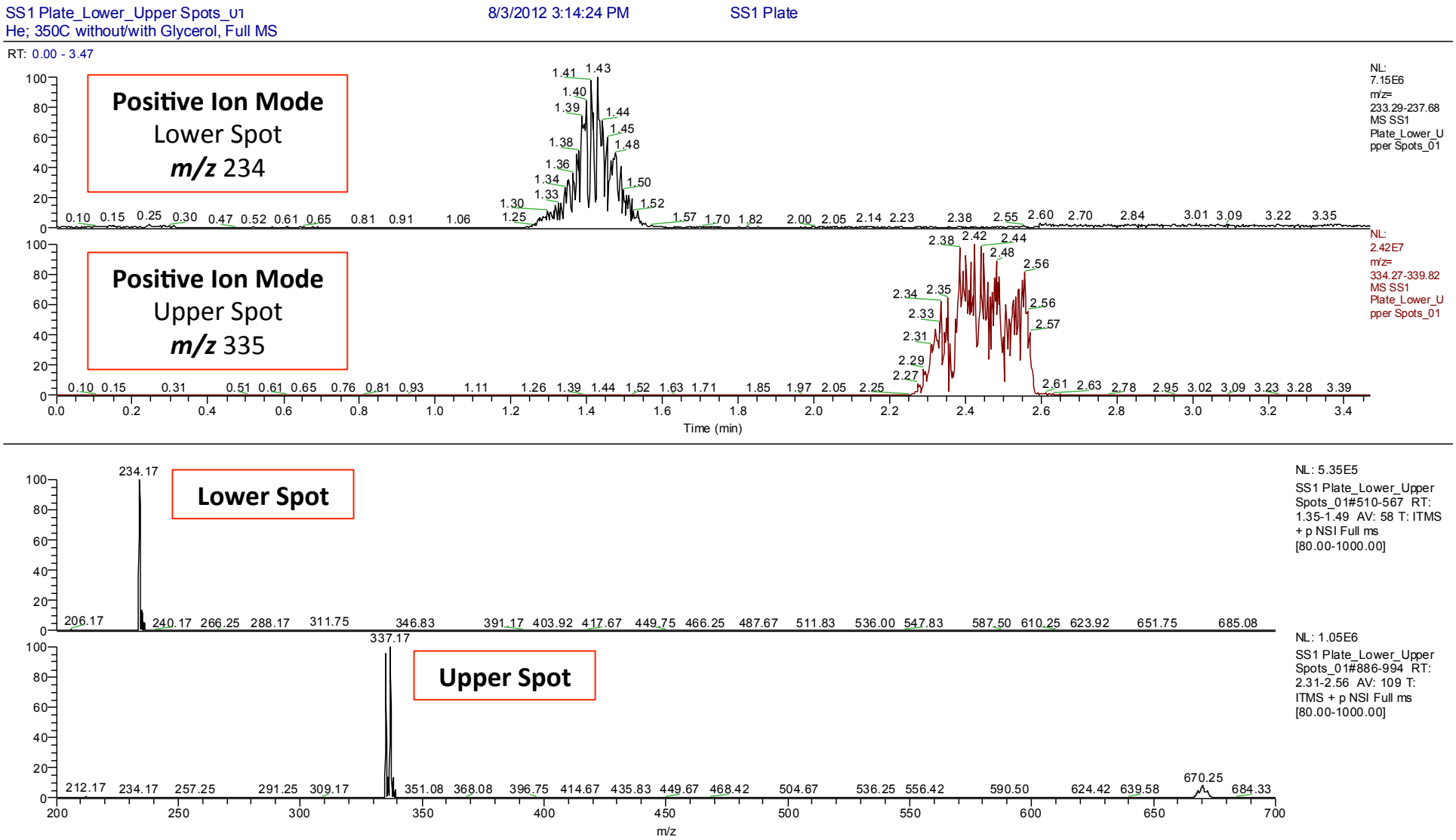
TLC Plate: Pharma Compound 3

Replicate of **10 Repeat Sampling** of the **Same TLC Spot**:
Glycerol reapplied to single TLC spot before reintroducing the spot to the DART source

450° C

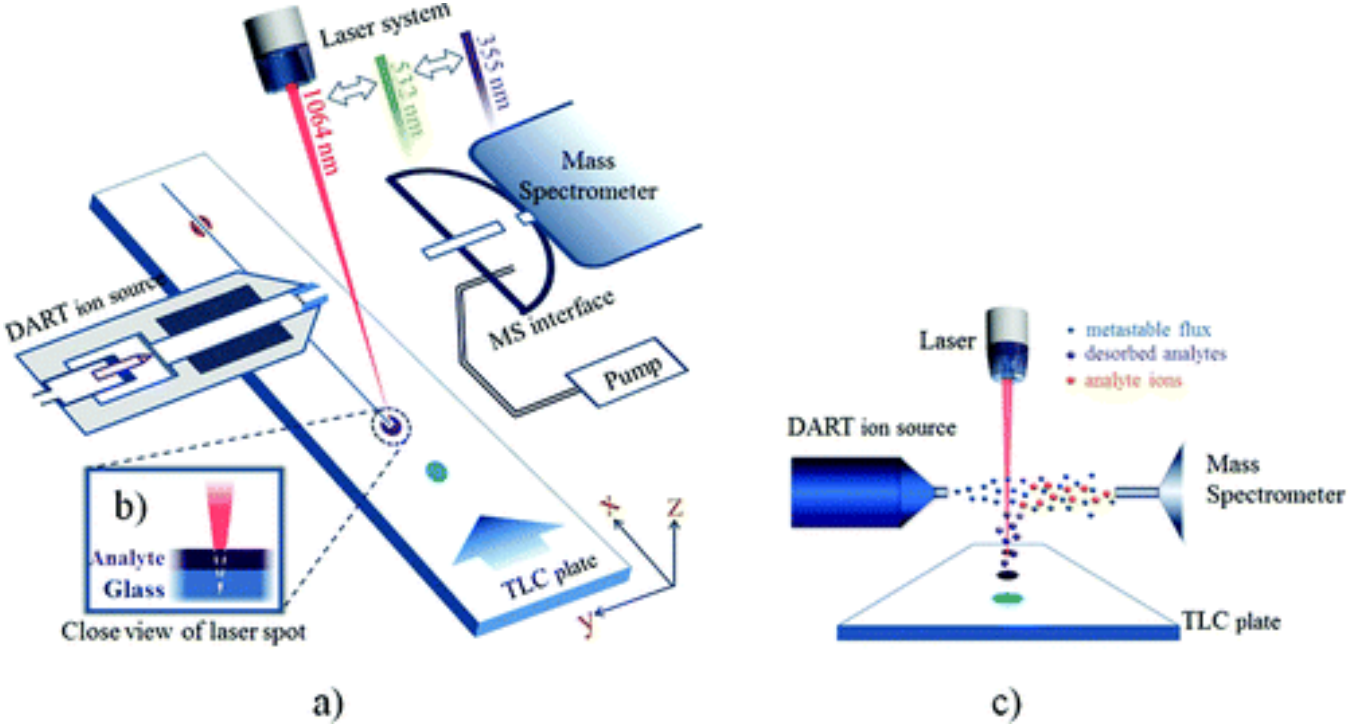


SS1: Well Separated - Lower & Upper Spots



For the Next Generations: Laser Ablation TLC Plasma (DART) Ionization

Abstract:
"The PAMLDI-MS system was successfully applied in the detection of low molecular weight compounds from different kinds of samples separated on a normal-phase silica gel, such as dye mixtures, drug standards, and tea extract, with the detection level of 5 ng/mm^2."



Zhang, J.; Zhou, Z.; Yang, J.; Zhang, W.; Bai, Y.; Liu, H. Thin Layer Chromatography/Plasma Assisted Multiwavelength Laser Desorption Ionization Mass Spectrometry for Facile Separation and Selective Identification of Low Molecular Weight Compounds. Anal. Chem., **2012**, 84(3): 1496–1503.

Conclusions

- Both RP & NP plates (glass backed) can be directly analyzed without source contamination
- Plates can be cut thin (5 mm wide) and run with DART source in-line with MS
- To analyze intact large format plates, set the DART-SVP source at an angle (45° angle) to the plate
- Resolution of DART gas beam 3-4 mm, with laser target area becomes nm spot size
- Coupling with high resolution accurate mass (HRAM) MS is major trend with coupling TLC and ambient MS.
- Direct quantitation of HPTLC plates with DART-MS…Tim Häbe & Prof. G. Morlock
  - O15 today at 14.45

DART (HP)TLC Publications

2006

Morlock, G.; Schwack, W. Determination of isopropylthioxanthone (ITX) in milk, yoghurt and fat by HPTLC-FLD, HPTLC-ESI/MS and HPTLC-DART/MS. Anal. Bioanal. Chem., **2006**, 385(3): 586-595.

2007

Morlock, G.; Ueda, Y. J. New coupling of planar chromatography with direct analysis in real time mass spectrometry. Chromatogr. A, **2007**, 1143: 243–251.

2008

Dytkiewitz, E. and Morlock, G.E. Analytical strategy for rapid identification and quantification of lubricant additives in mineral oil by high-performance thin-layer chromatography with UV absorption and fluorescence detection combined with mass spectrometry and infrared spectroscopy. Journal of AOAC International, **2008**, 91(5): 1237-1243.

Smith, N.J.; Domin, M.A.; Scott, L.T. HRMS Directly From TLC Slides. A Powerful Tool for Rapid Analysis of Organic Mixtures. Org. Lett., **2008**, 10(16): 3493-3496.

2009

Jee, E. H.; Jeong, C. W.; Jeong, S. D.; Kim, H. J.; Jang, Y. P., Detection of characterising compounds on TLC by DART-MS. Planta Med, **2009**, 75(9): 38.

2010

Kim, H. J.; Jee, E. H.; Ahn, K. S.; Choi, H. S.; Jang, Y. P. Identification of marker compounds in herbal drugs on TLC with DART-MS. Archives of Pharmacal Research, **2010**, 33(9): 1355-1359.

Kim, H. J.; Oh, M. S.; Hong, J.; Jang, Y. P., Quantitative analysis of major dibenzocyclooctane lignans in schisandrae fructus by online TLC-DART-MS. Phytochemical Analysis, **2010**, 22(3): 258-262.

2011

Cheng, S.-C.; Huang, M.-Z.; Shiea, J. Thin layer chromatography/mass spectrometry. Journal of Chromatography A, **2011**, 1218(19): p. 2700-2711.

Chernetsova, E.S.; Revelsky, A.I.; Morlock, G.E. Some new features of Direct Analysis in Real Time mass spectrometry utilizing the desorption at an angle option. Rapid Comm. Mass Spec., **2011**, 25(16): 2275-2282.

Howlett, S.E.; Steiner, R.R., Validation of Thin Layer Chromatography with AccuTOF-DART™ Detection for Forensic Drug Analysis. Journal of Forensic Sciences, 2011, 56(5): 1261-1267.

Kim, H.J.; Oh, M.S.; Hong, J.; Jang, Y.P. Quantitative analysis of major dibenzocyclooctane lignans in schisandrae fructus by online TLC-DART-MS. Phytochemical Analysis, **2011**, 22(3): 258-262.

Wood, J.L.; Steiner, R.R. Purification of pharmaceutical preparations using thin-layer chromatography to obtain mass spectra with Direct Analysis in Real Time and accurate mass spectrometry. Drug Testing and Analysis, 2011, 3(6): 345-351.

2012

Morlock, G.E.; Chernetsova, E.S. Coupling of planar chromatography with direct analysis in real time mass spectrometry (DART-MS). Cent Eur J. Chem. **2012**, 10(3): 703-710.

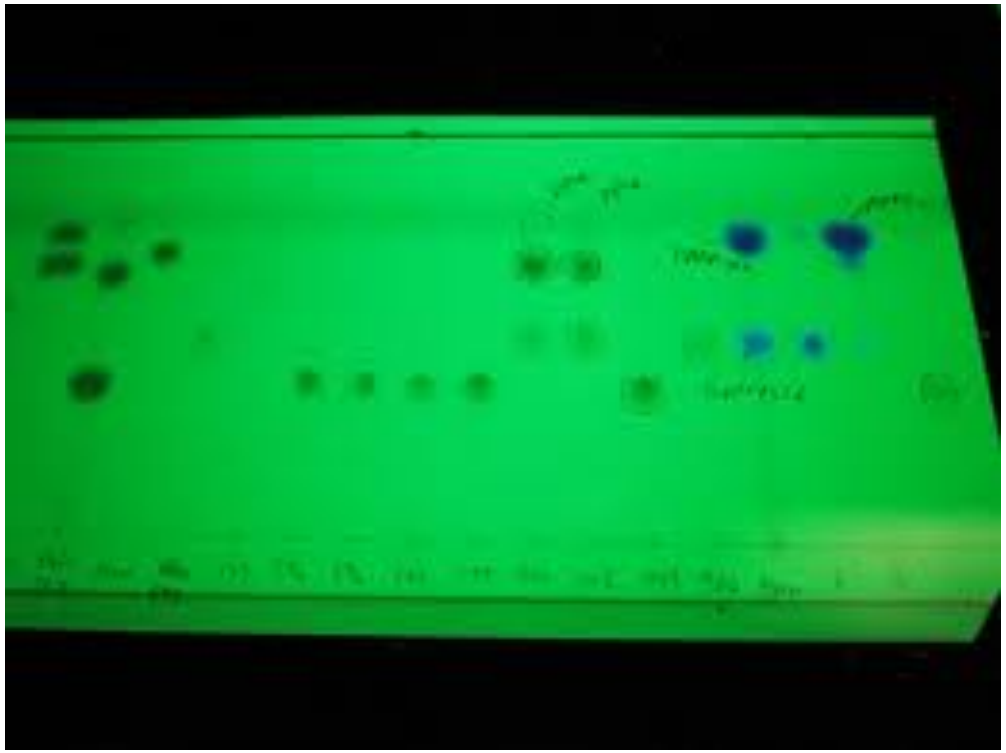
Zhang, J.; Zhou, Z.; Yang, J.; Zhang, W.; Bai, Y.; Liu, H. Thin Layer Chromatography/Plasma Assisted Multiwavelength Laser Desorption Ionization Mass Spectrometry for Facile Separation and Selective Identification of Low Molecular Weight Compounds. Anal. Chem., **2012**, 84(3): 1496–1503.

2013

Djelal, H.; Cornée, C.; Tartivel, R.; Lavastre, O.; Abdeltif, A. The use of HPTLC and Direct Analysis in Real Time-Of-Flight Mass Spectrometry (DART-TOF-MS) for rapid analysis of degradation by oxidation and sonication of an azo dye. Arabian Journal of Chemistry, **2013**, (0).

Questions?

Are your spots ‘priceless’?



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