Planar chromatography meets direct ambient mass spectrometry: current trends

Elizabeth Crawford\textsuperscript{1,2}, Brian Musselman\textsuperscript{1}

\textsuperscript{1} IonSense, Inc. Saugus, MA, USA
\textsuperscript{2} Institute of Chemical Technology, Prague, Czech Republic
Major Hyphenations of Open Air Ambient MS & (HP)TLC Separations

- **DART** – Direct Analysis in Real Time
- **FAPA** – Flowing Atmospheric Pressure Afterglow
- **LA-DART** – Laser Ablation DART
- **LAESI** – Laser Ablation Electrospray Ionization
- **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 F254 at thickness of 200 µm)

Direct analysis of 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 Korea
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.

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

**RT:** 5.07 - 11.23

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**Replicates n = 3:**
NO Glycerol applied

**DART_SVP_In-line_Millennium TLC Plate_MPI 3_450C_with Glycerol_20120404**

**NL:** 2.84E5

**m/z= 833.99-834.19 MS**
**SS1: Well Separated - Lower & Upper Spots**

**He; 350°C without/with Glycerol, Full MS**

**RT:** 0.00 - 3.47

**Relative Abundance**

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**NL:** 7.15E6

**m/z = 233.29-237.68**

**MS SS1 Plate_Lower_Upper Spots_01**

**NL:** 2.42E7

**m/z = 334.27-339.82**

**MS SS1 Plate_Lower_Upper Spots_01**

**Positive Ion Mode**

**Lower Spot**

**m/z 234**

**Upper Spot**

**m/z 335**
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/mm².”
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**
2006

2007

2008


2009

2010


2011


2012


2013
Questions?

Are your spots ‘priceless’?

Email: crawford@ionsense.com