

# Detection of Polar and Nonpolar Compounds on TLC Plates Using Laser Desorption/Electrospray+Atmospheric Pressure Chemical Ionization/Mass Spectrometry (LD/ESI+APCI/MS)

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(2014 HPTLC Symposium)

**Two ambient ionization methods are currently used in TLC/MS:**

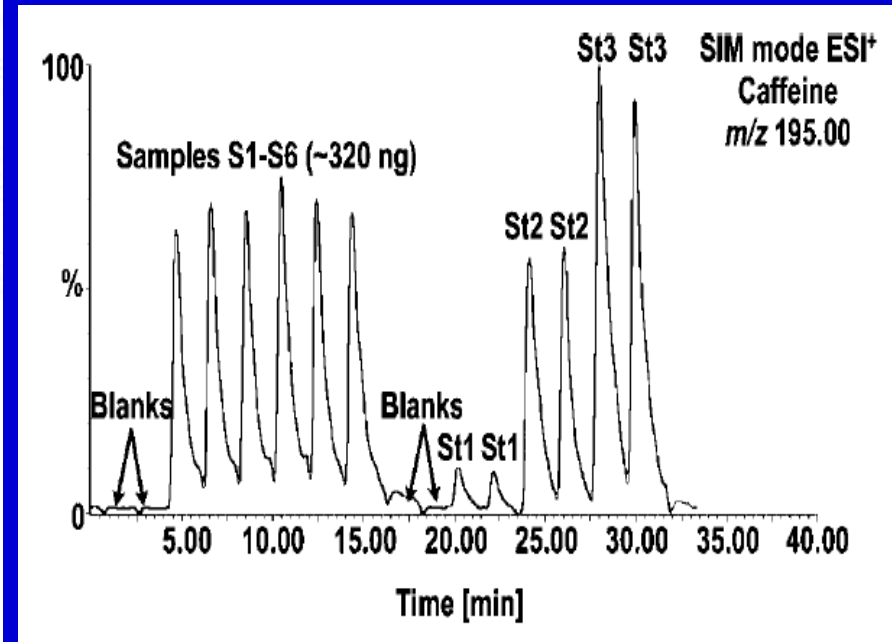
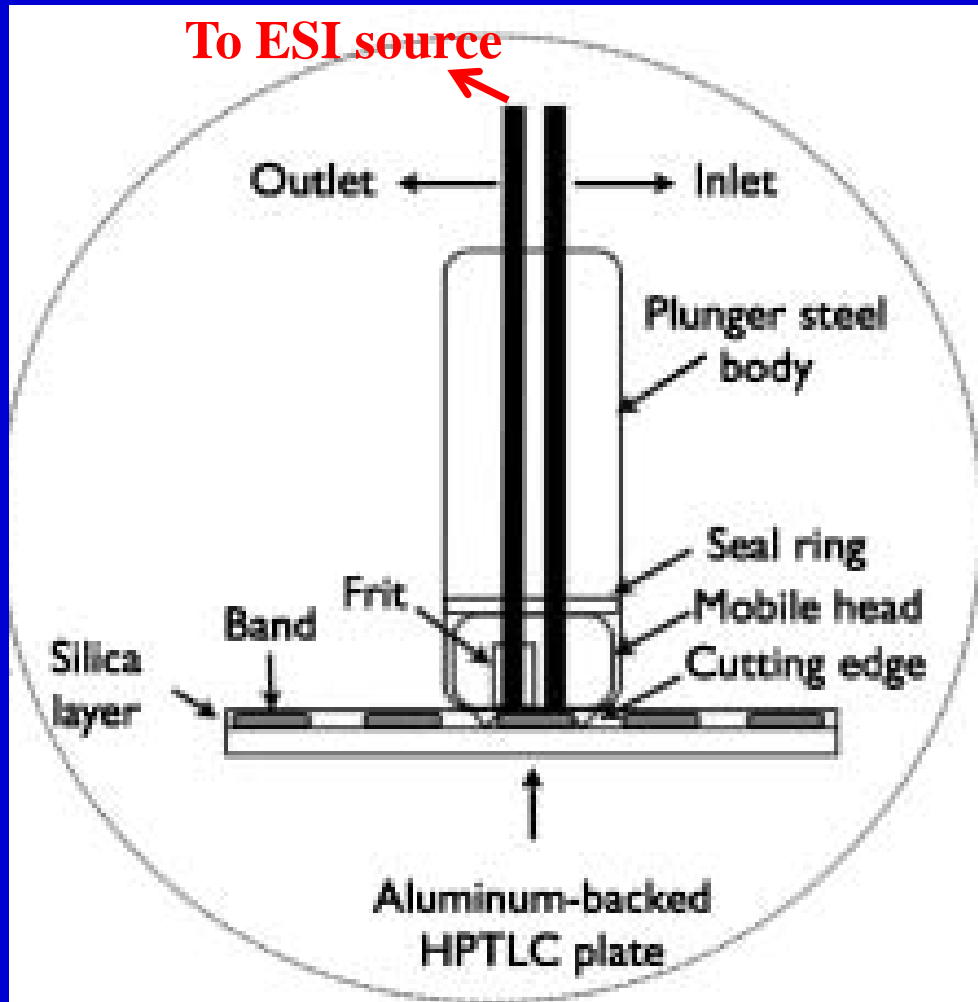
- **(1) Electrospray Ionization (ESI)**
- **(2) Atmospheric Pressure Chemical Ionization (APCI)**

# **ESI-based TLC/MS:**

- 1. Solvent elution followed by ESI/MS**
- 2. Desorption/ionization by charged droplets impact (DESI)**
- 3. Over-run TLC followed by ESI/MS**
- 4. Two-Step ionization: pulsed laser for sampling and ESI for ionization**

# (1) Automated interface for hyphenation of planar chromatography with mass spectrometry

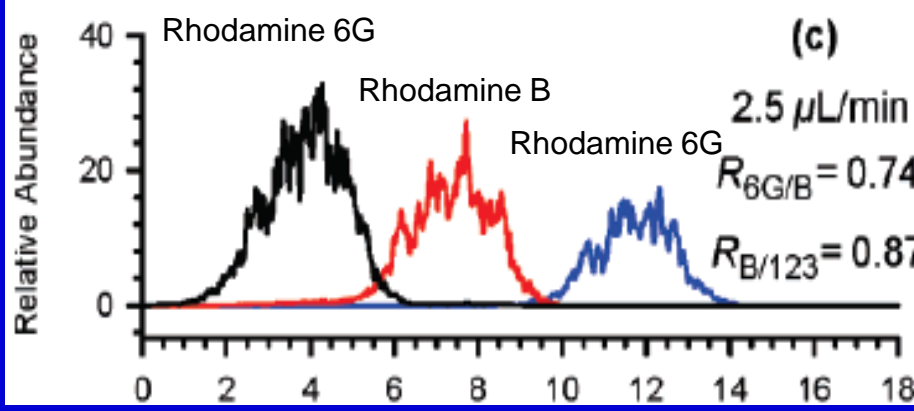
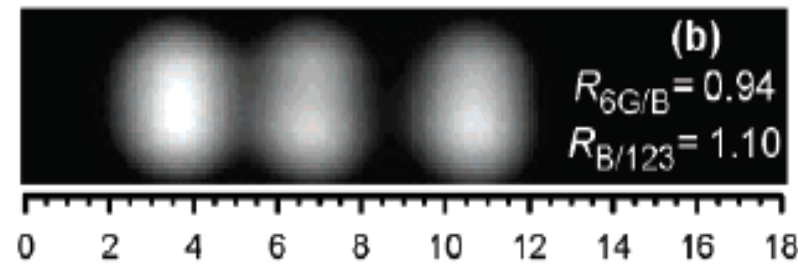
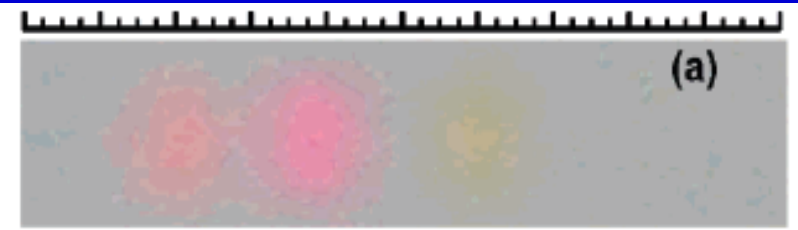
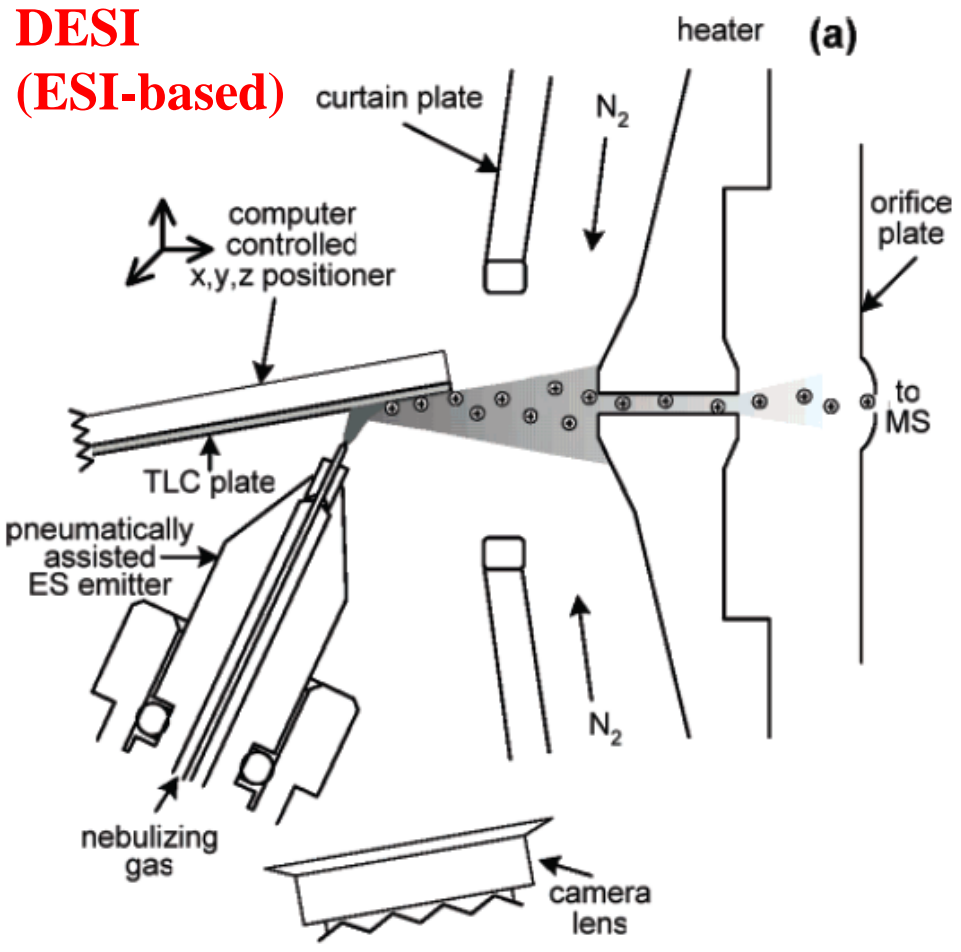
Luftmann and Morlock *Rapid Commun. Mass Spectrom.* 2007; 21, 3772



# (2) Thin-Layer Chromatography and Mass Spectrometry Coupled Using Desorption Electrospray Ionization (TLC-DESI/MS)

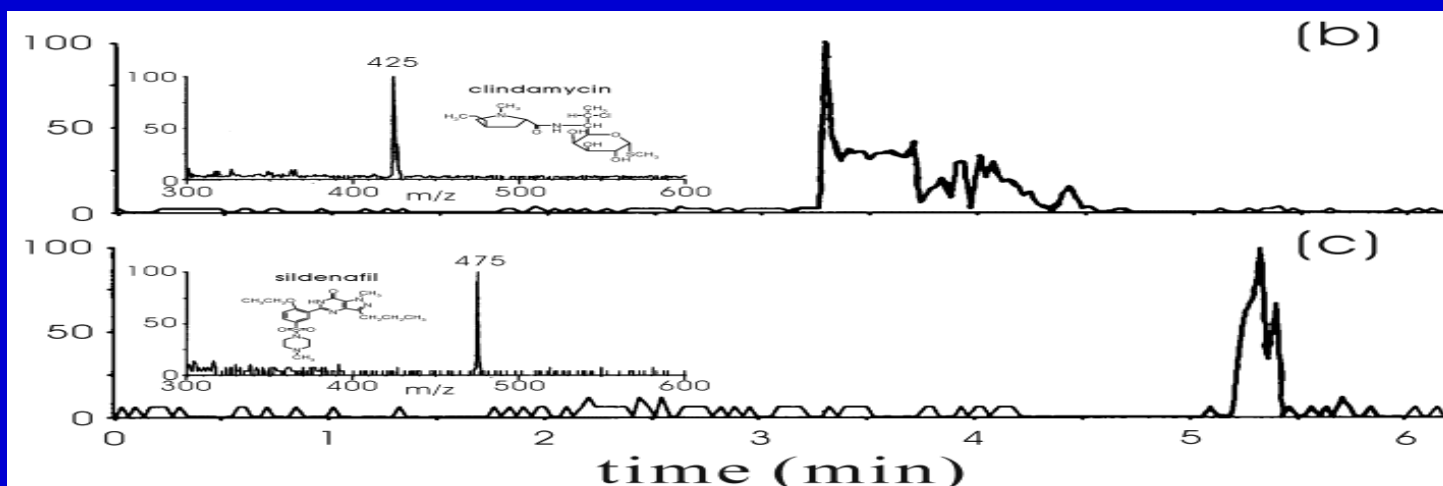
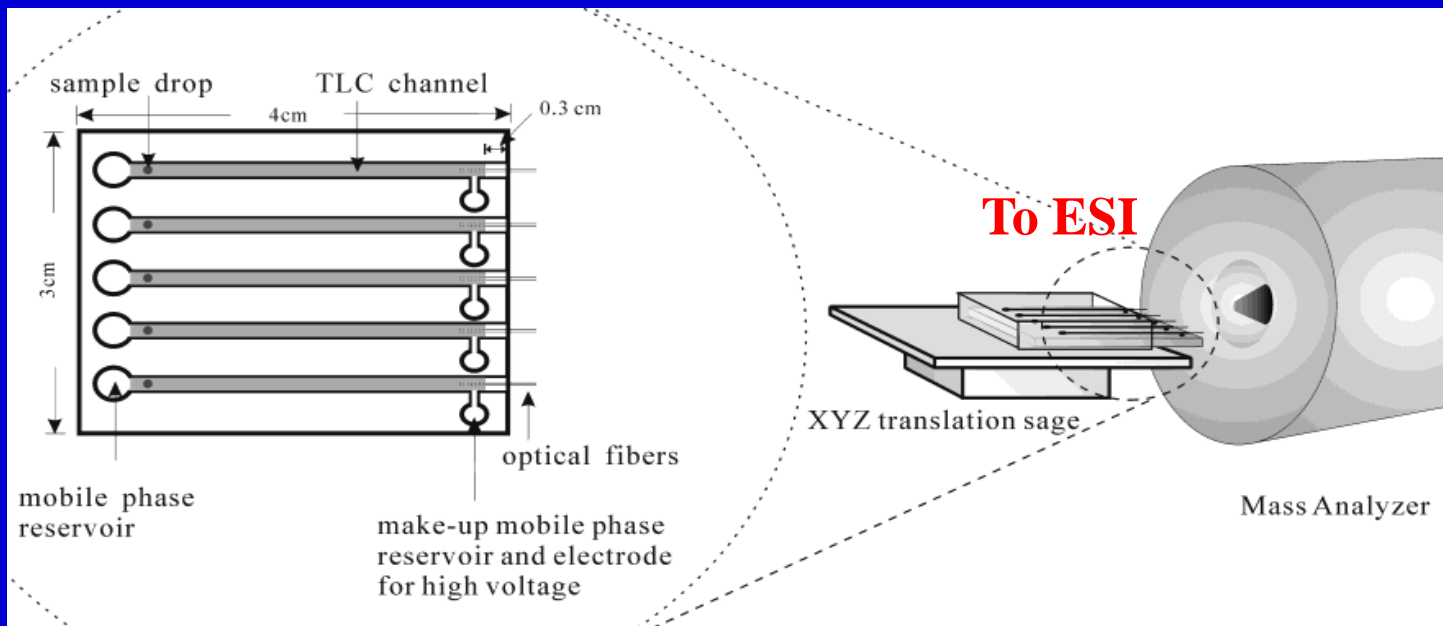
Van Berkel et al. *Anal. Chem.* 2005, 77, 1207

## DESI (ESI-based)



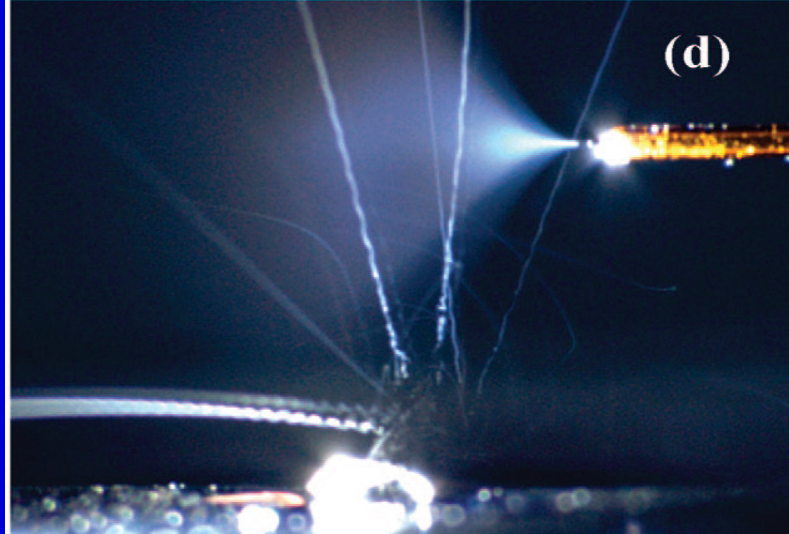
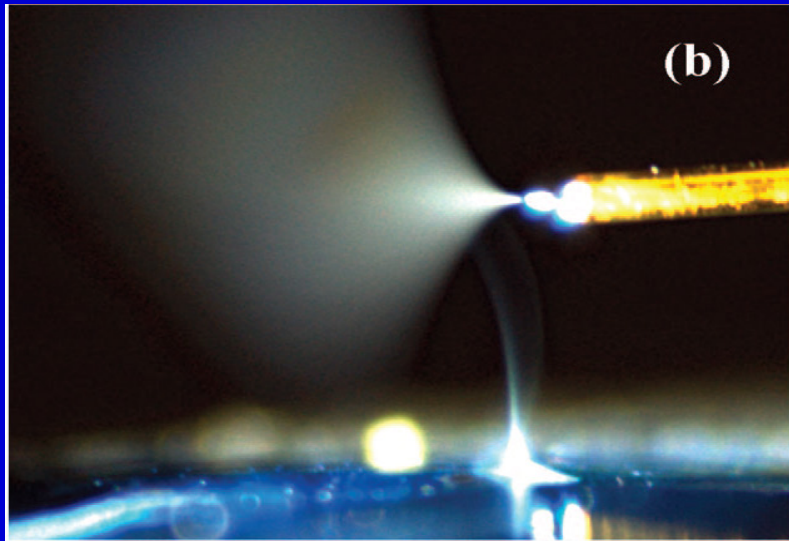
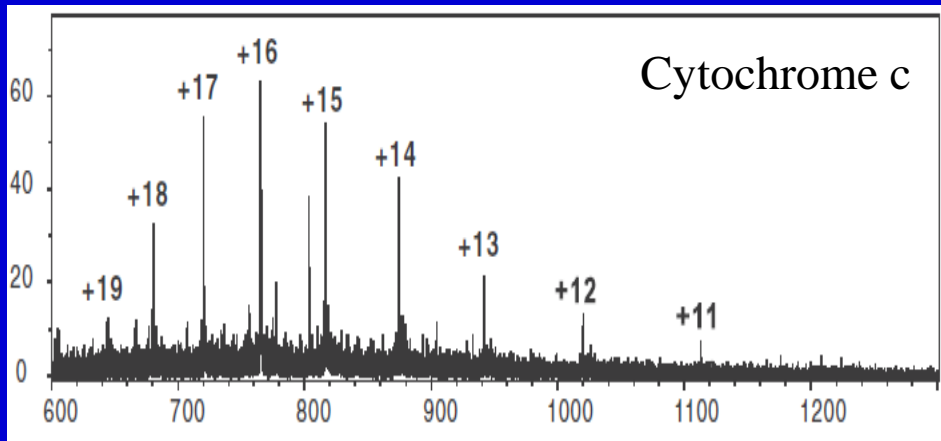
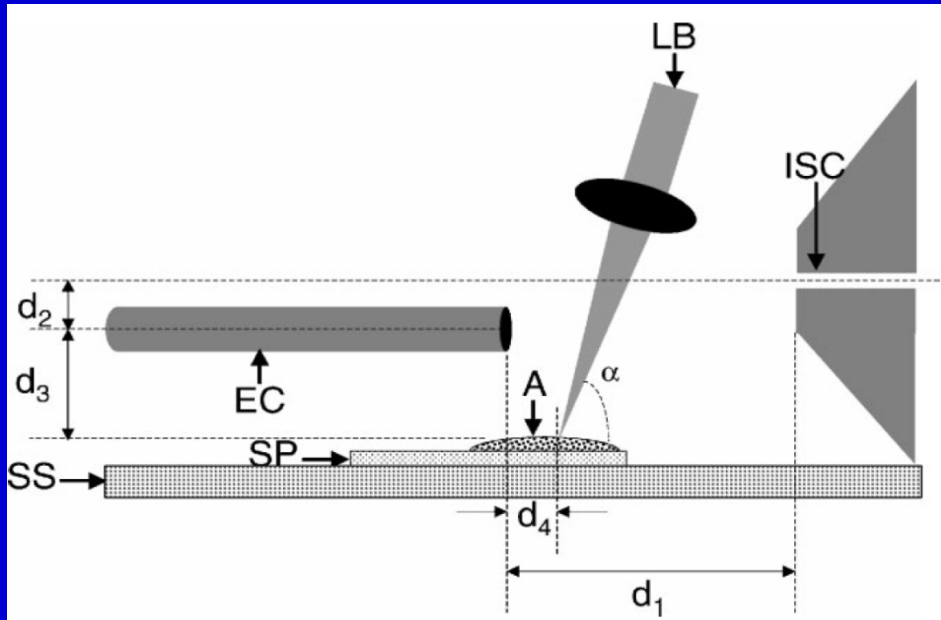
# (3) Interfaces To Connect Thin-Layer Chromatography with Electrospray Ionization Mass Spectrometry

Shiea et al. *Anal. Chem.* 2003, 75, 2493

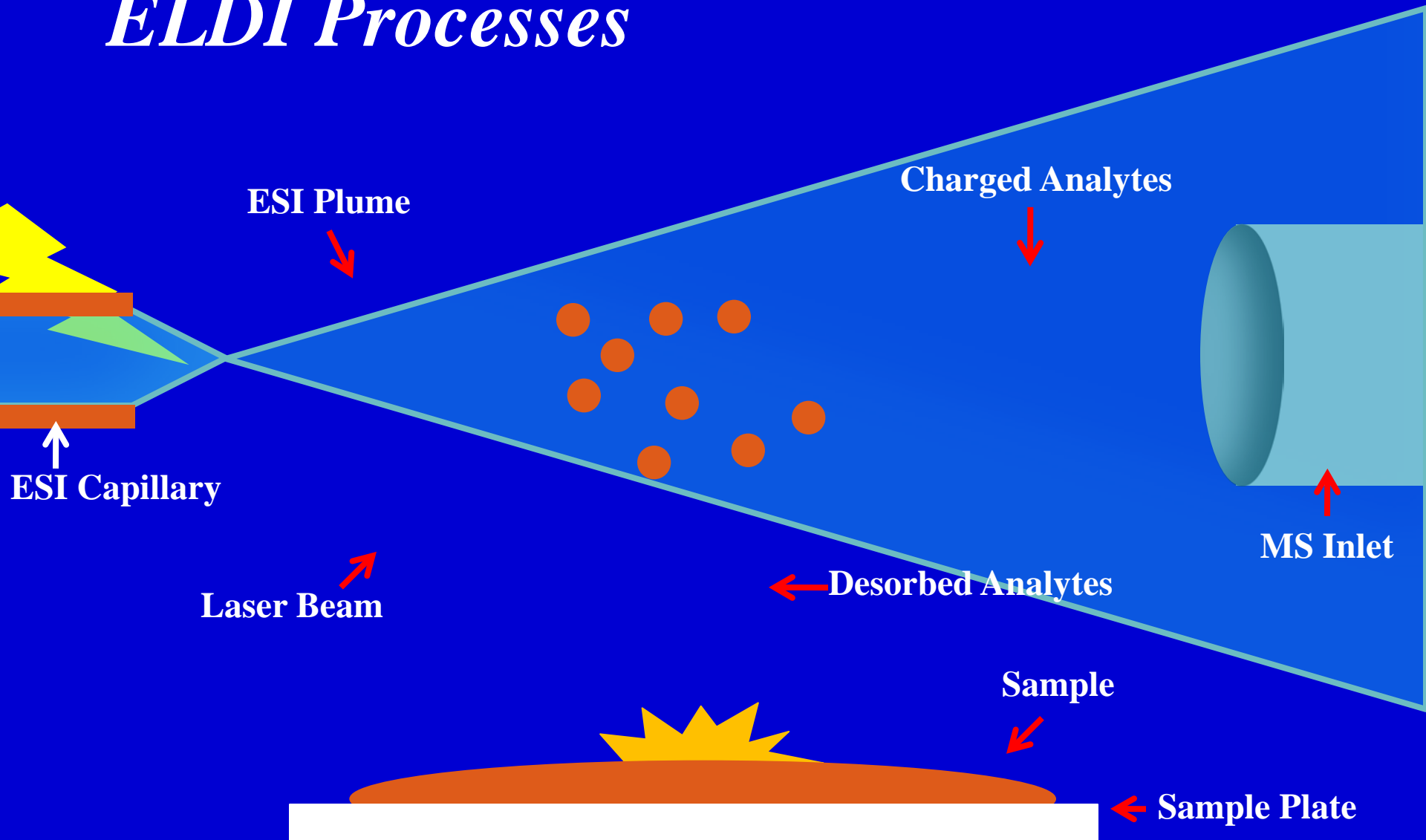


# (4) Electrospray-assisted laser desorption/ionization mass spectrometry for direct ambient analysis of solids – **ELDI/MS**

Shiea et al. *Rapid Commun. Mass Spectrom.* 2005; 19: 3701



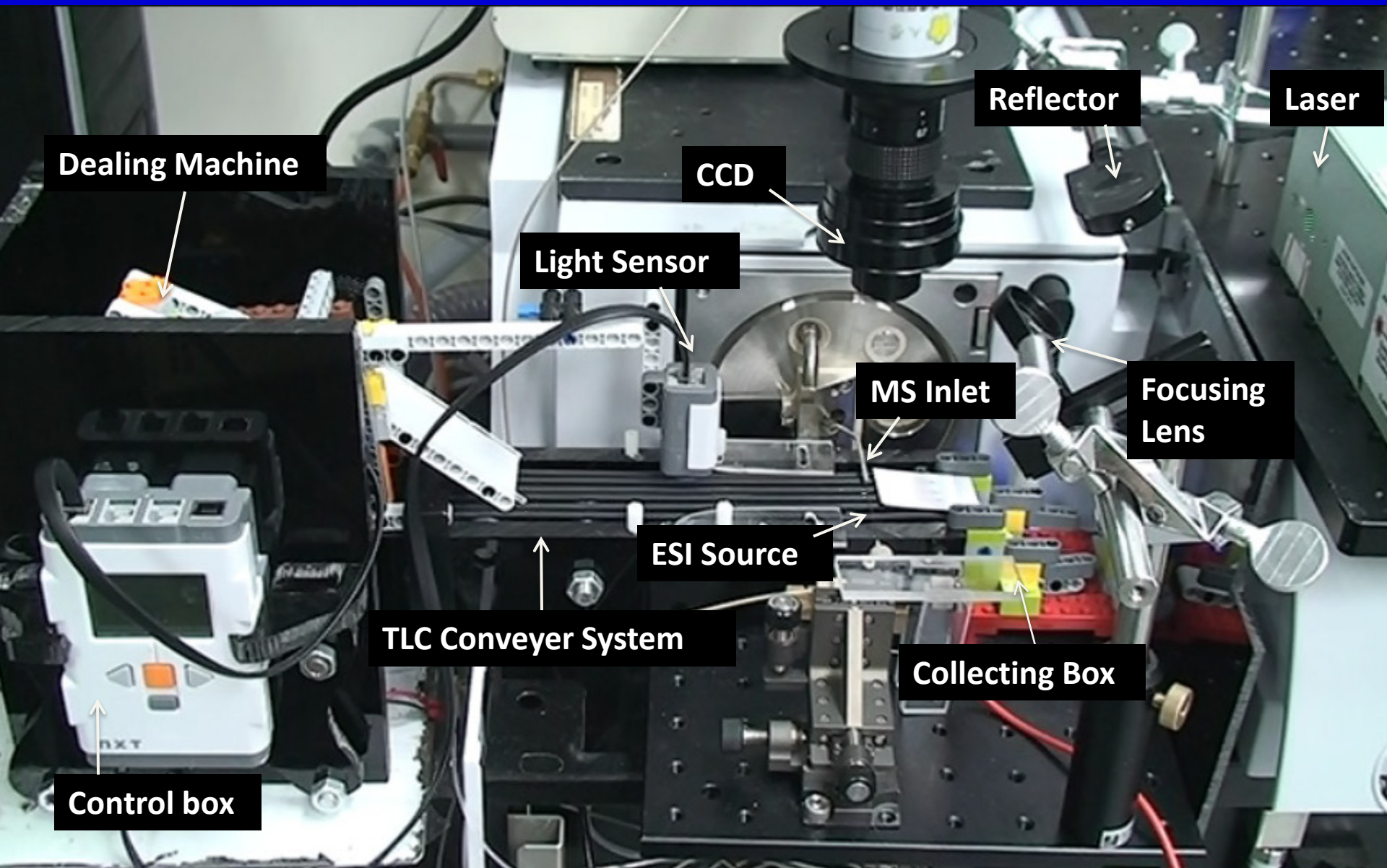
# *ELDI Processes*





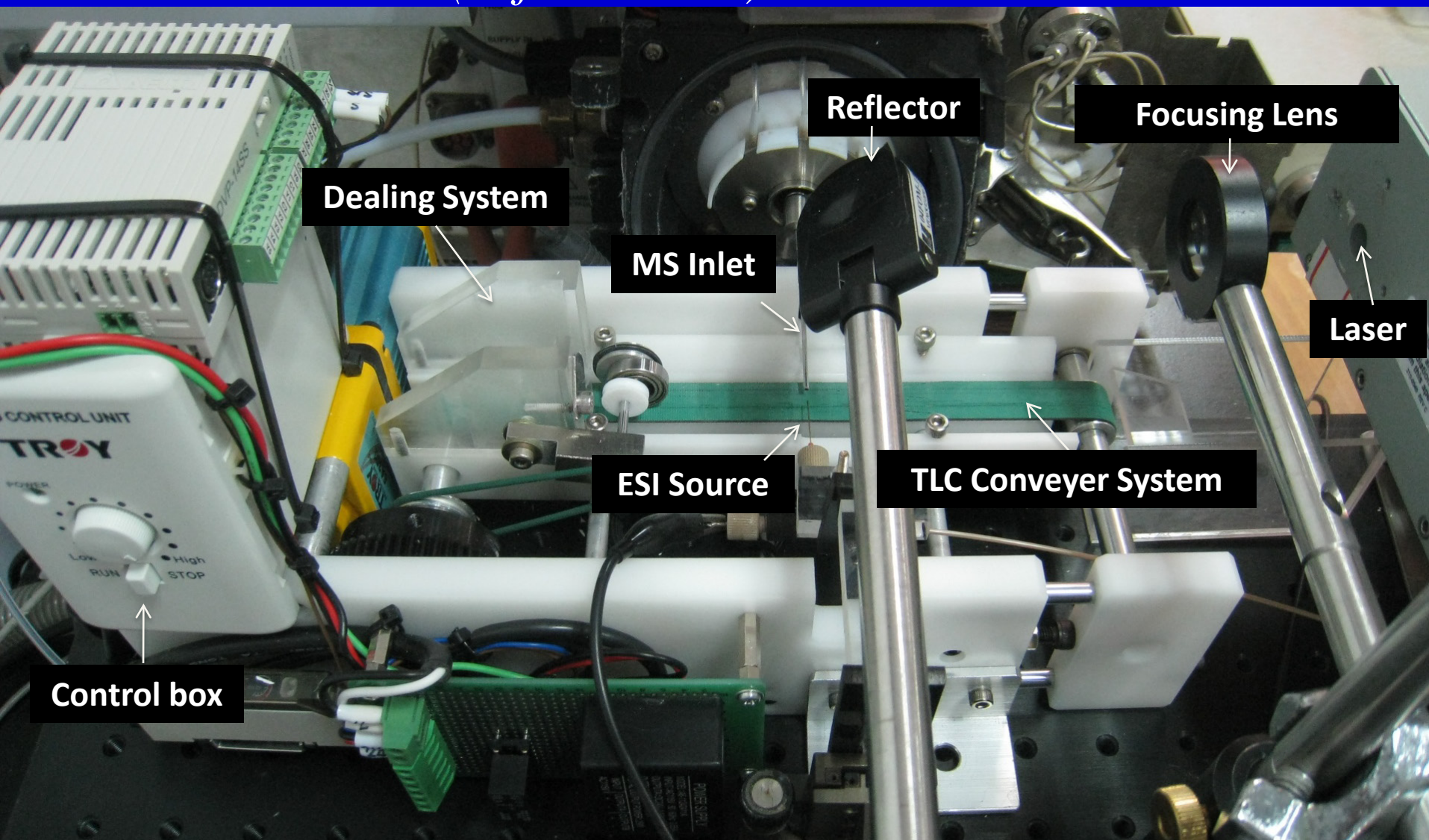
# High Throughput TLC-ELDI/MS System

*First Generation (Lego-made)* Shiea et al., *Anal Chem.* 2012, 84, 5864-8



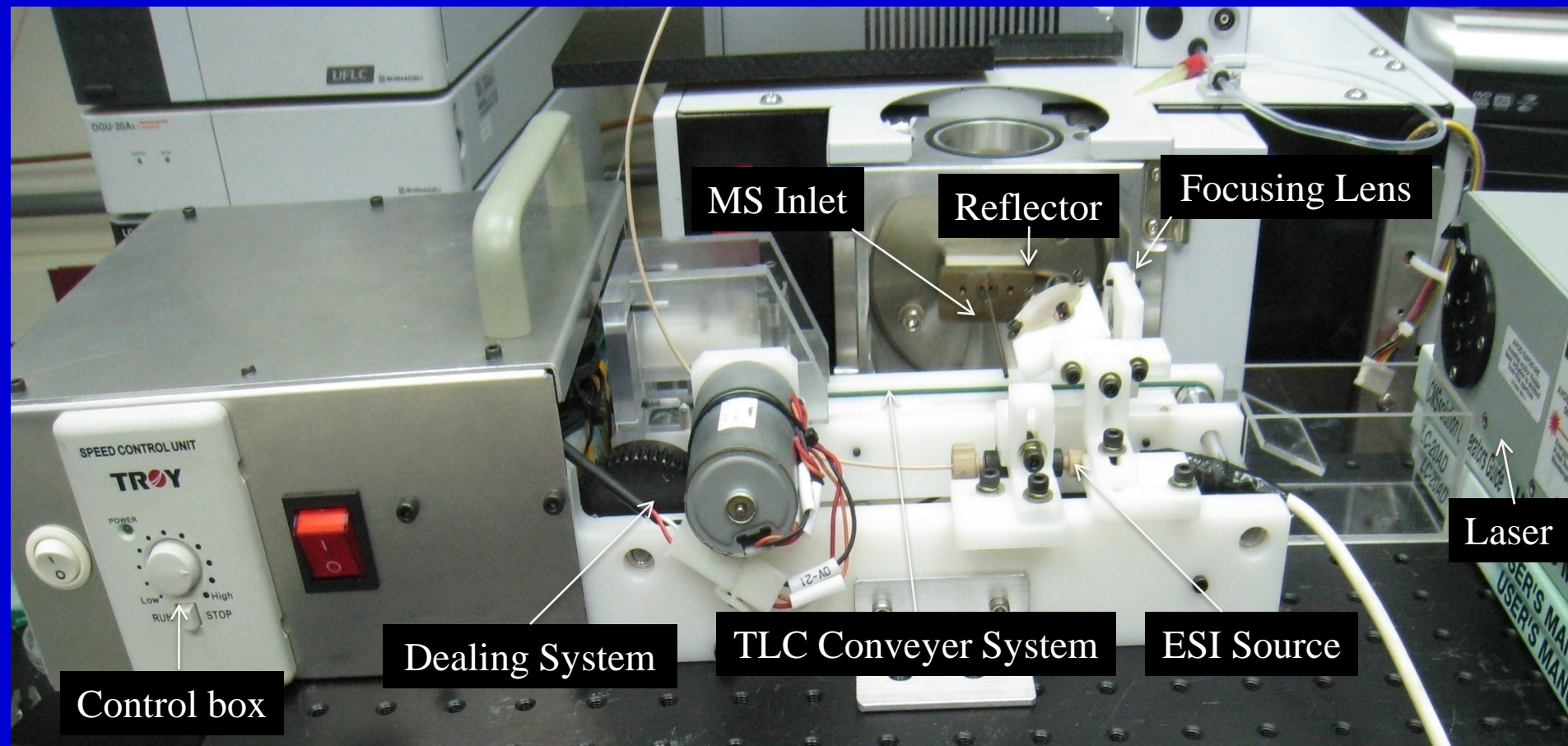
# High Throughput TLC-ELDI/MS System

*Second Generation (Teflon-made)*

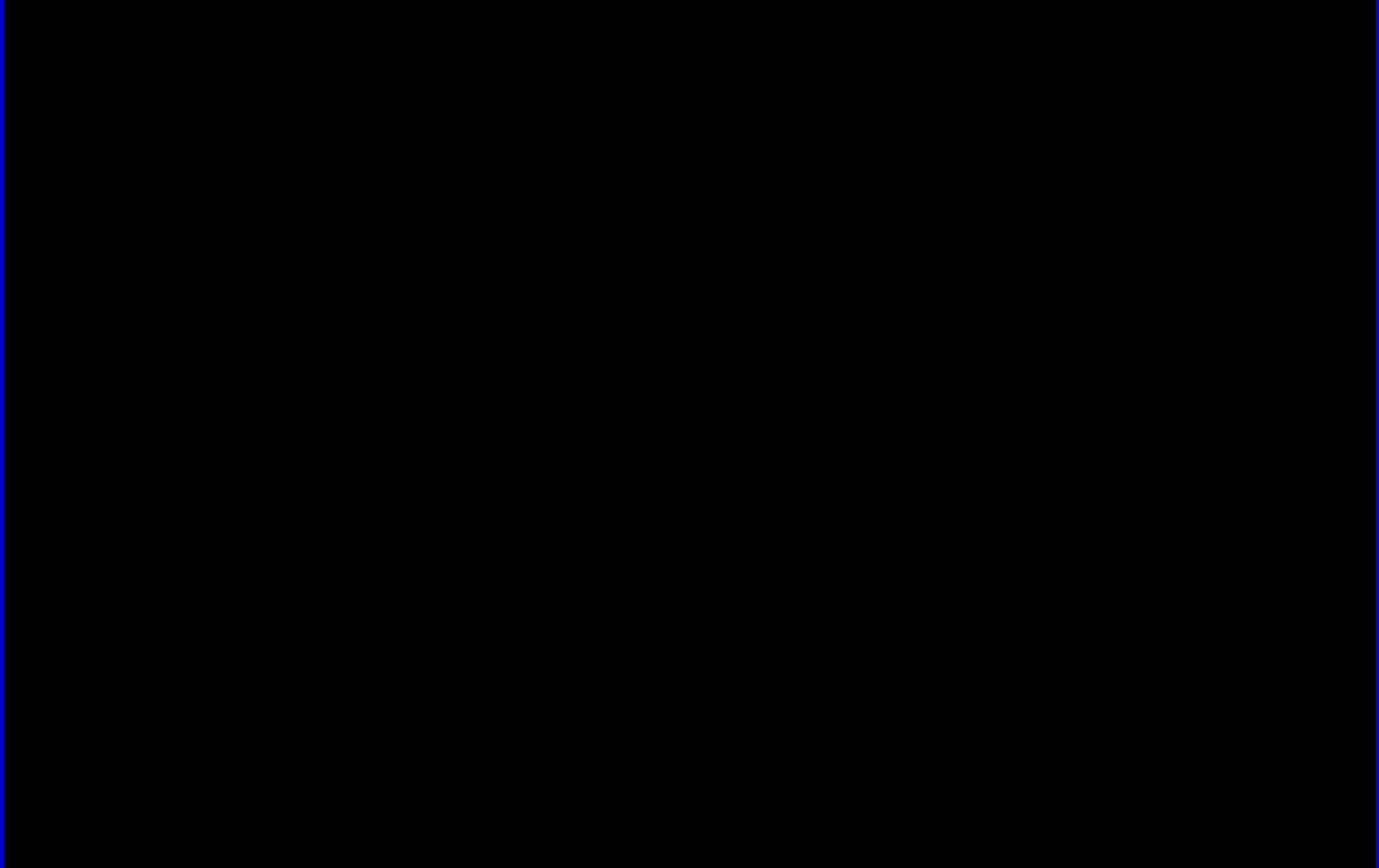


# High Throughput TLC-ELDI/MS System

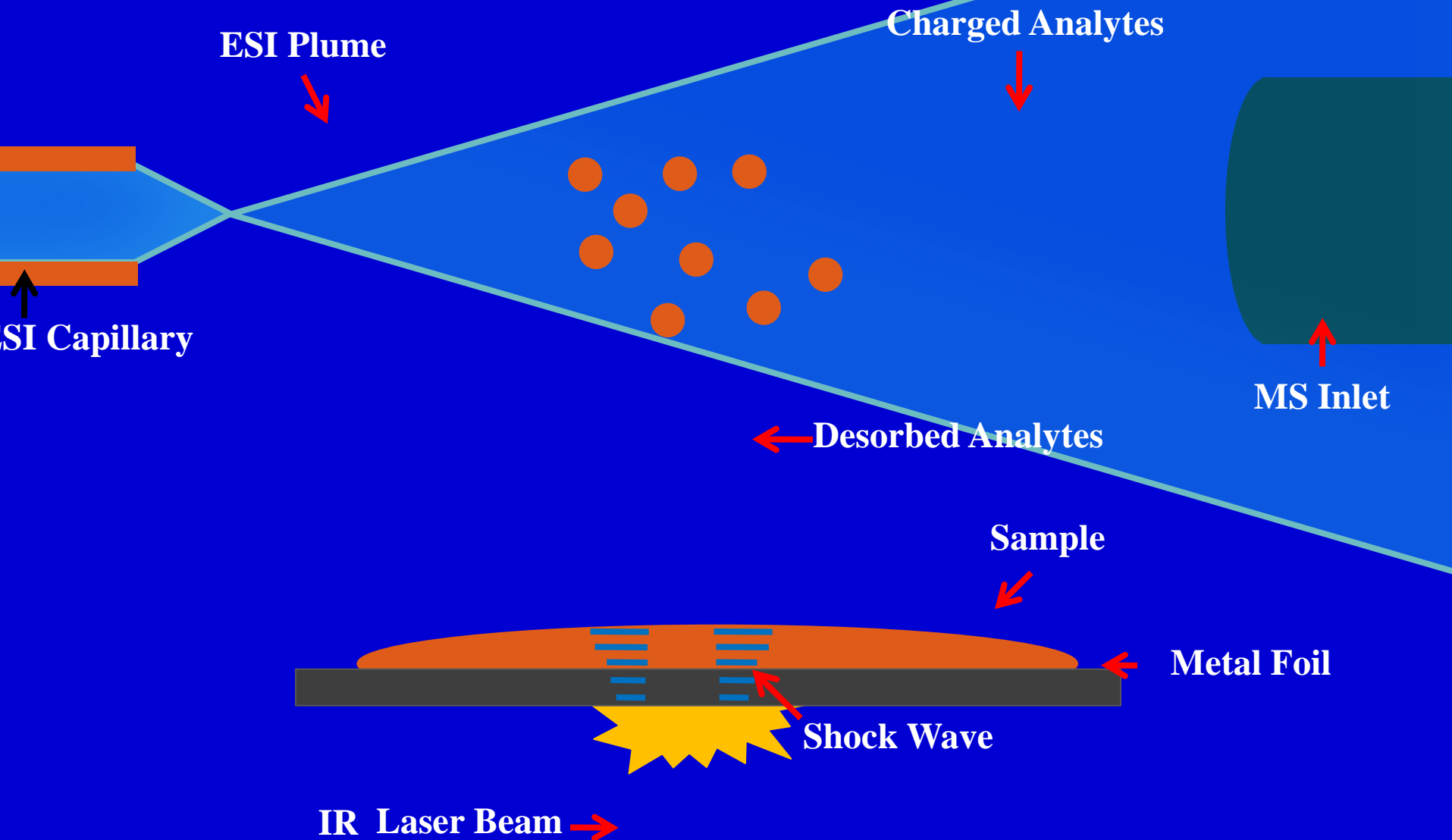
*Third Generation (Stainless Steel and Teflon made)*



# High Throughput TLC-ELDI/MS System

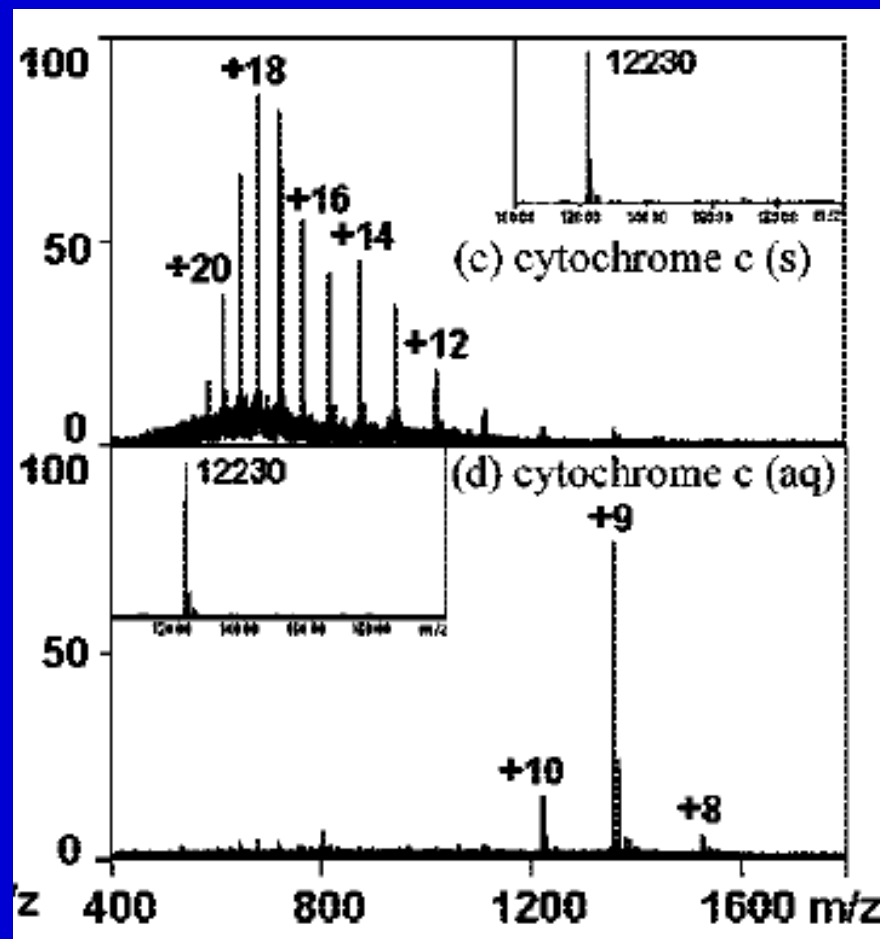
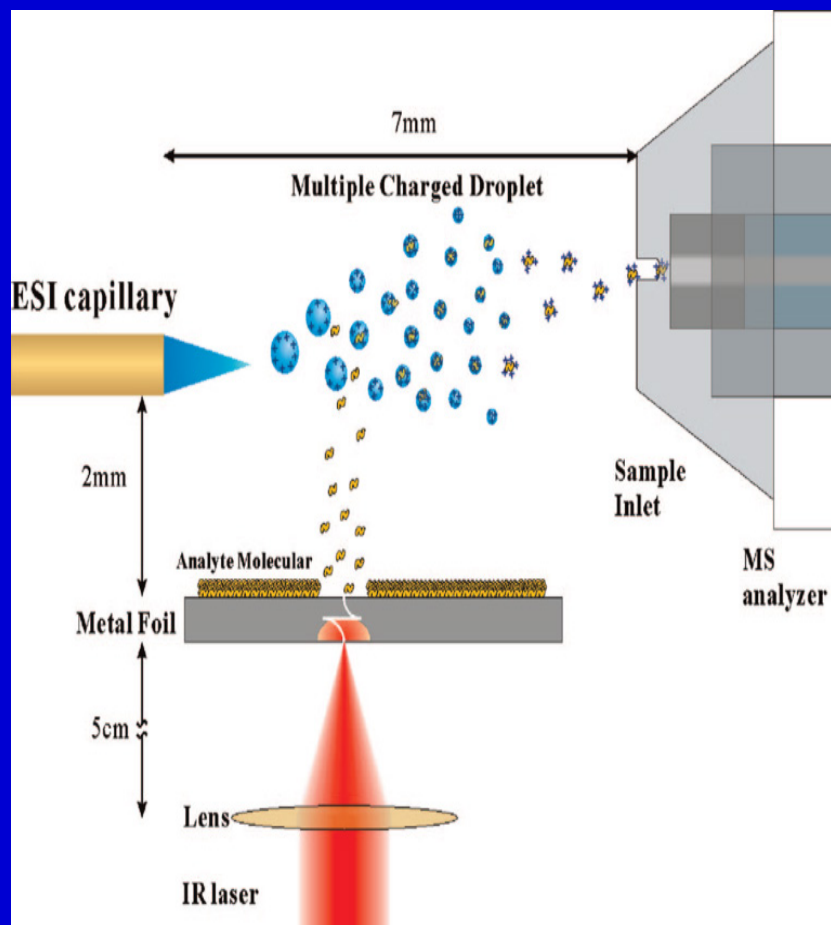


# *LIAD-ESI Processes*



# (4) Using Laser-Induced Acoustic Desorption/ Electropray Ionization Mass Spectrometry To Characterize Small Organic and Large Biological Compounds in the Solid State and in Solution Under Ambient Conditions – **TLC-LIAD/MS**

Shiea et al., *Anal. Chem.* 2009, 81, 868–874

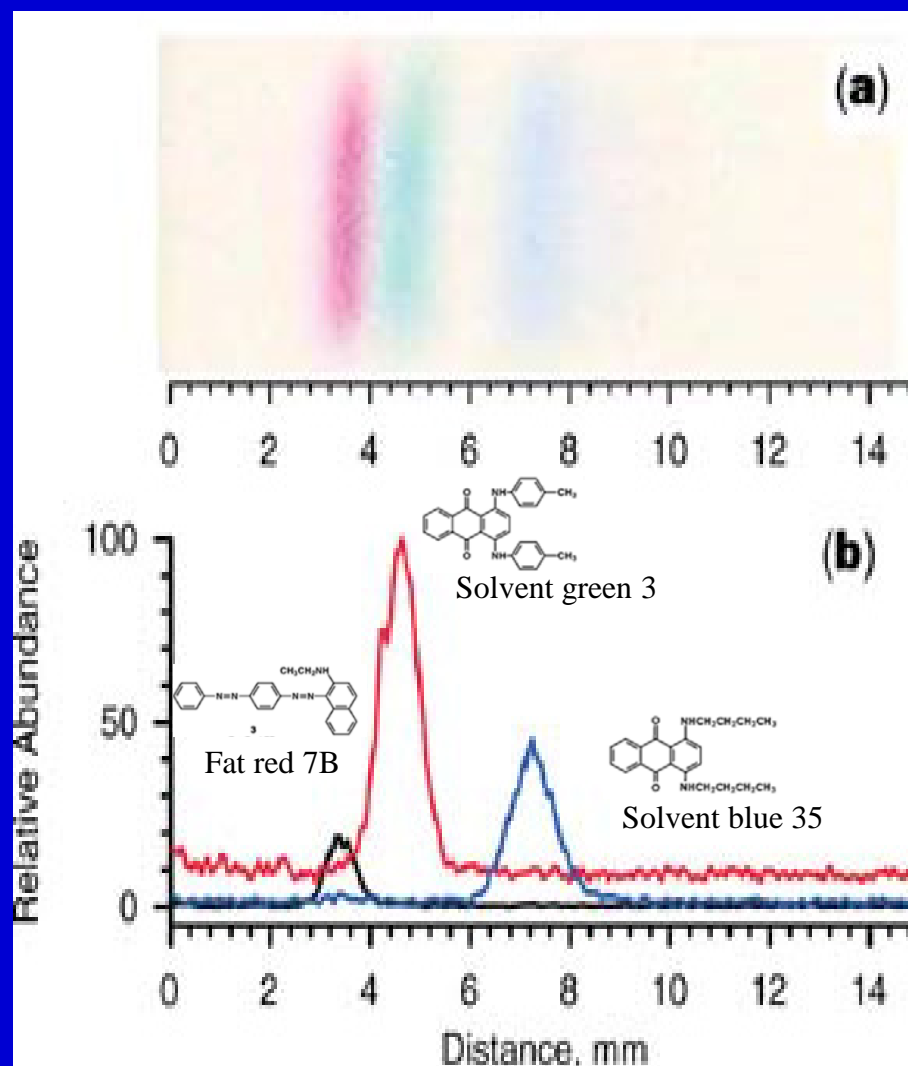
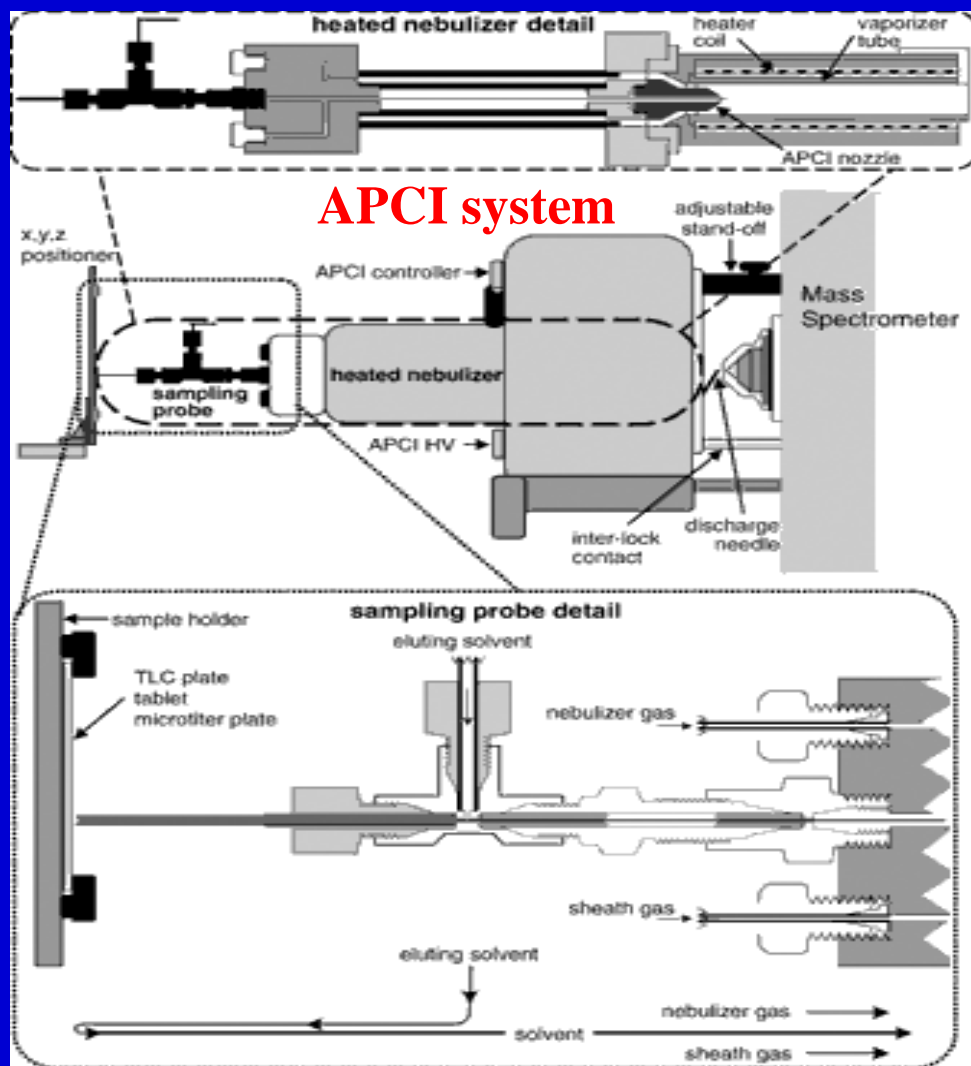


# **APCI-based TLC/MS:**

- 1. Solvent elution followed by APCI**
- 2. Desorption/Ionization by charged APCI species impact (DART)**
- 3. Over-run TLC followed by APCI/MS**
- 4. Two-Step ionization: pulsed laser for sampling and APCI for ionization**
- 5. Thermal desorption followed by APCI/MS**

# (1) Self-aspirating atmospheric pressure chemical ionization source for direct sampling of analytes on surfaces and in liquid solutions

Van Berkel et al. *Rapid Commun. Mass Spectrom.* 2012, 19, 2305





## (2) New coupling of planar chromatography with direct analysis in real time mass spectrometry

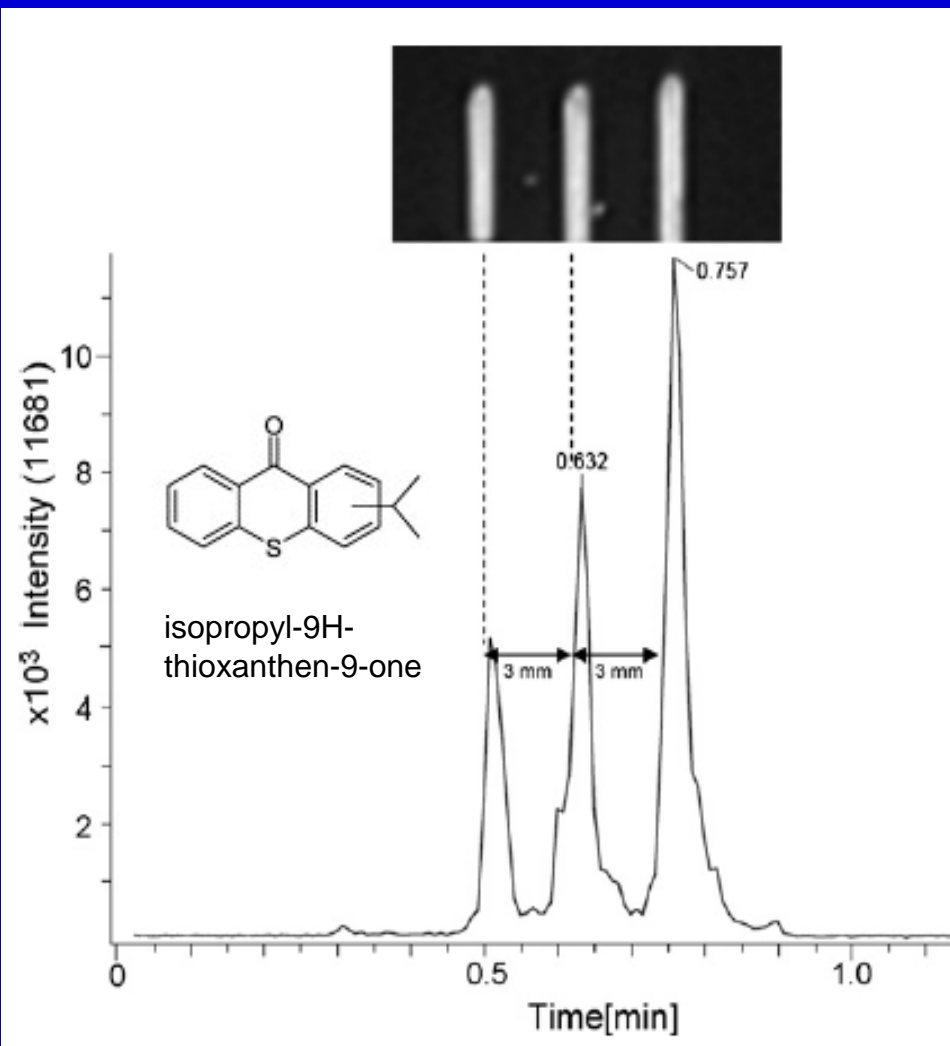
Morlock and Ueda *J. Chromatogr. A* 2007, 1143, 243

**DART**  
(APCI-based)

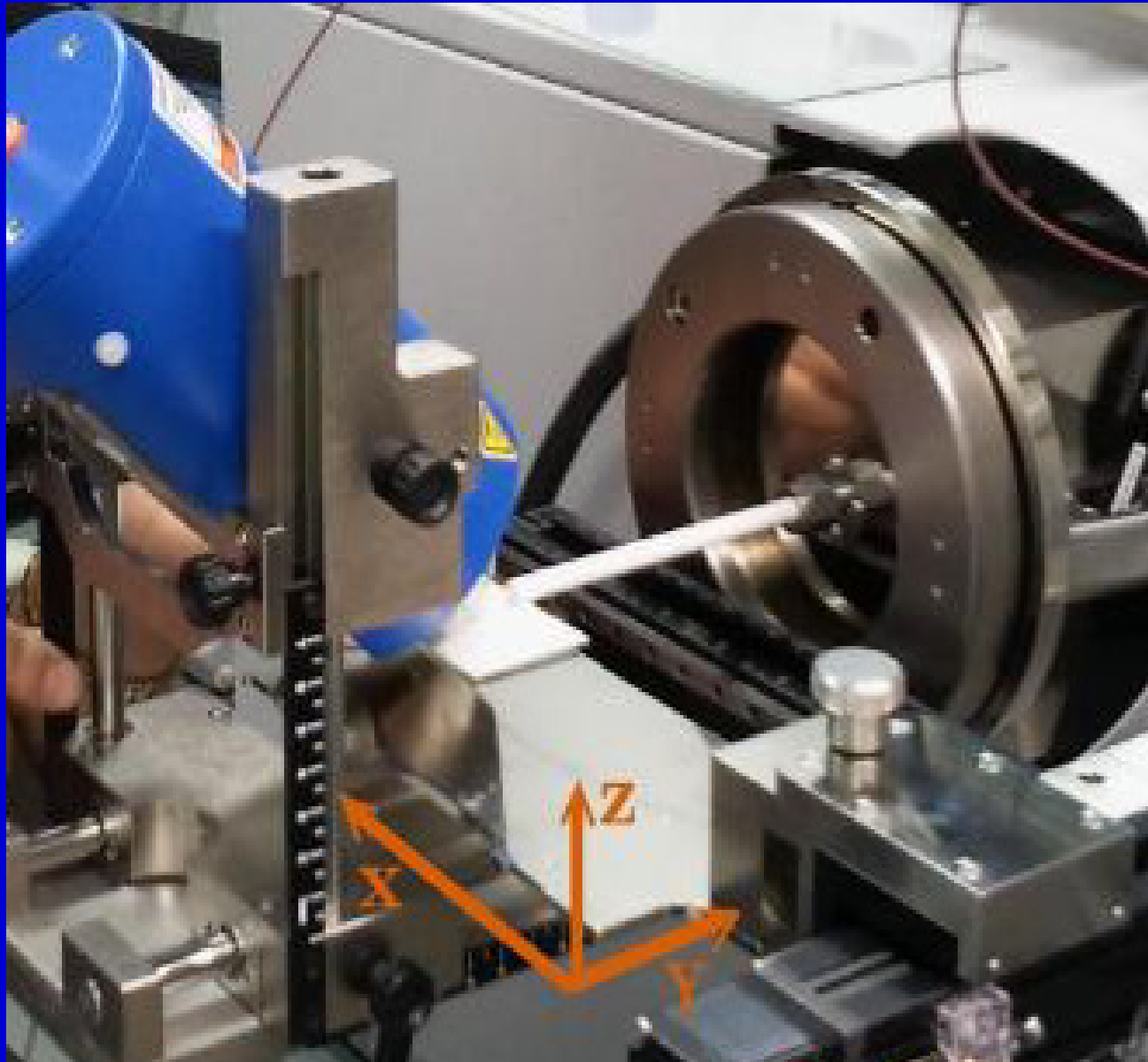
MS

TLC plate

DART  
source

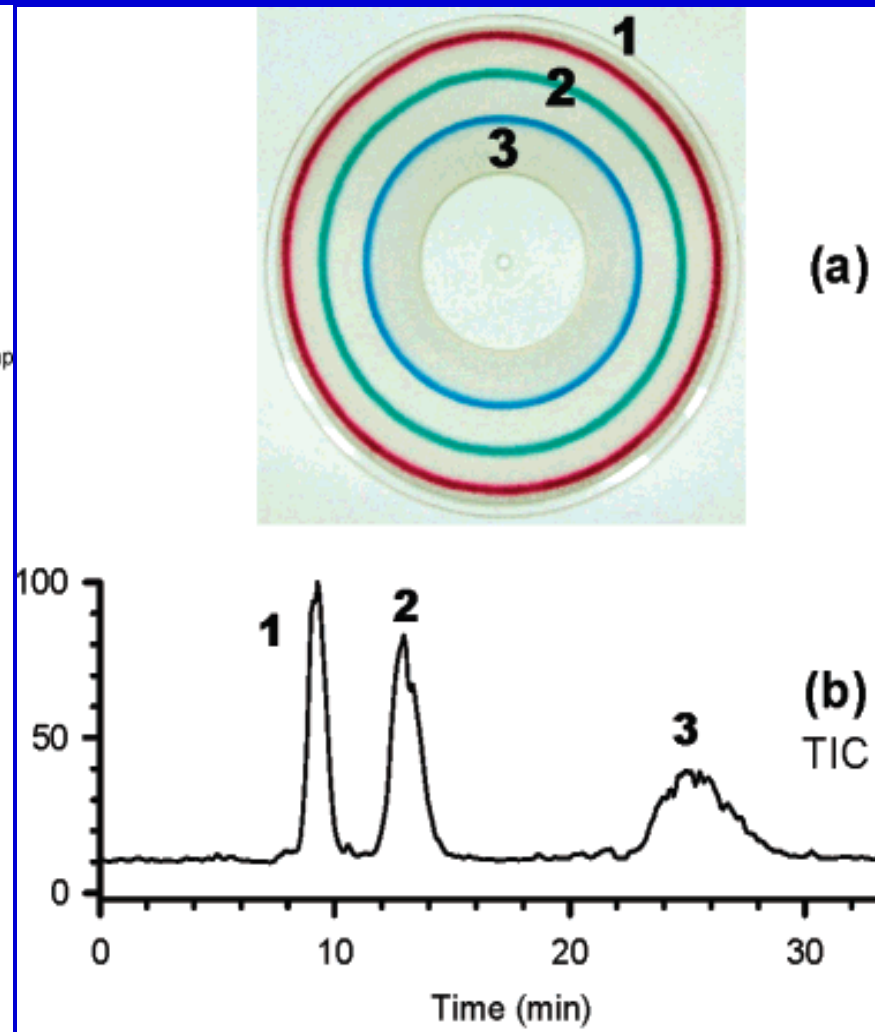
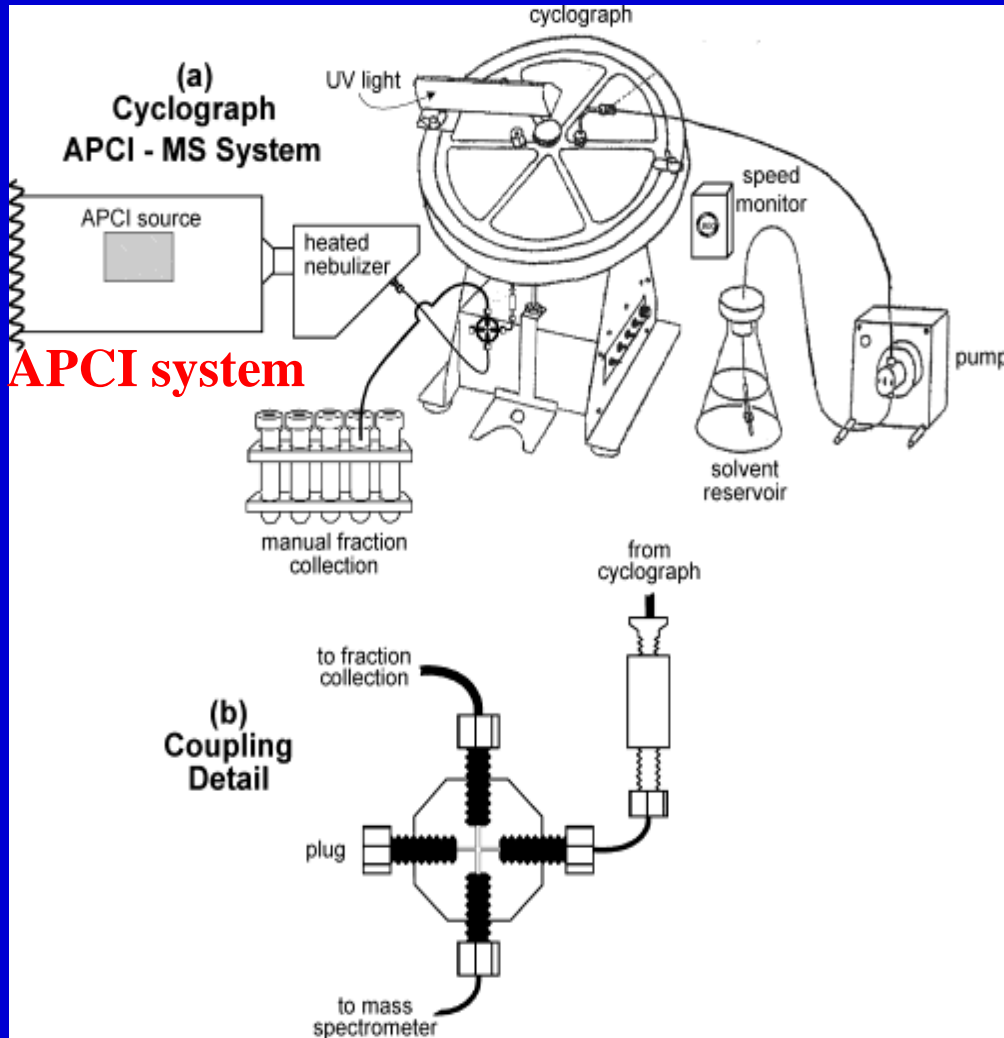


## (2) TLC-DART/MS



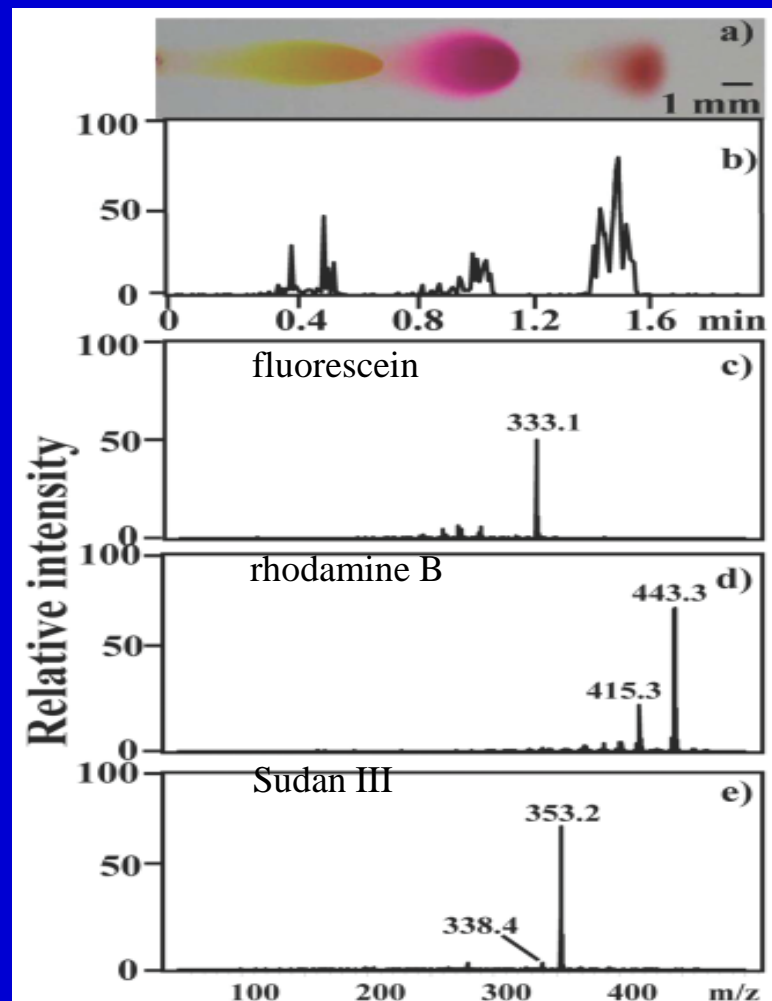
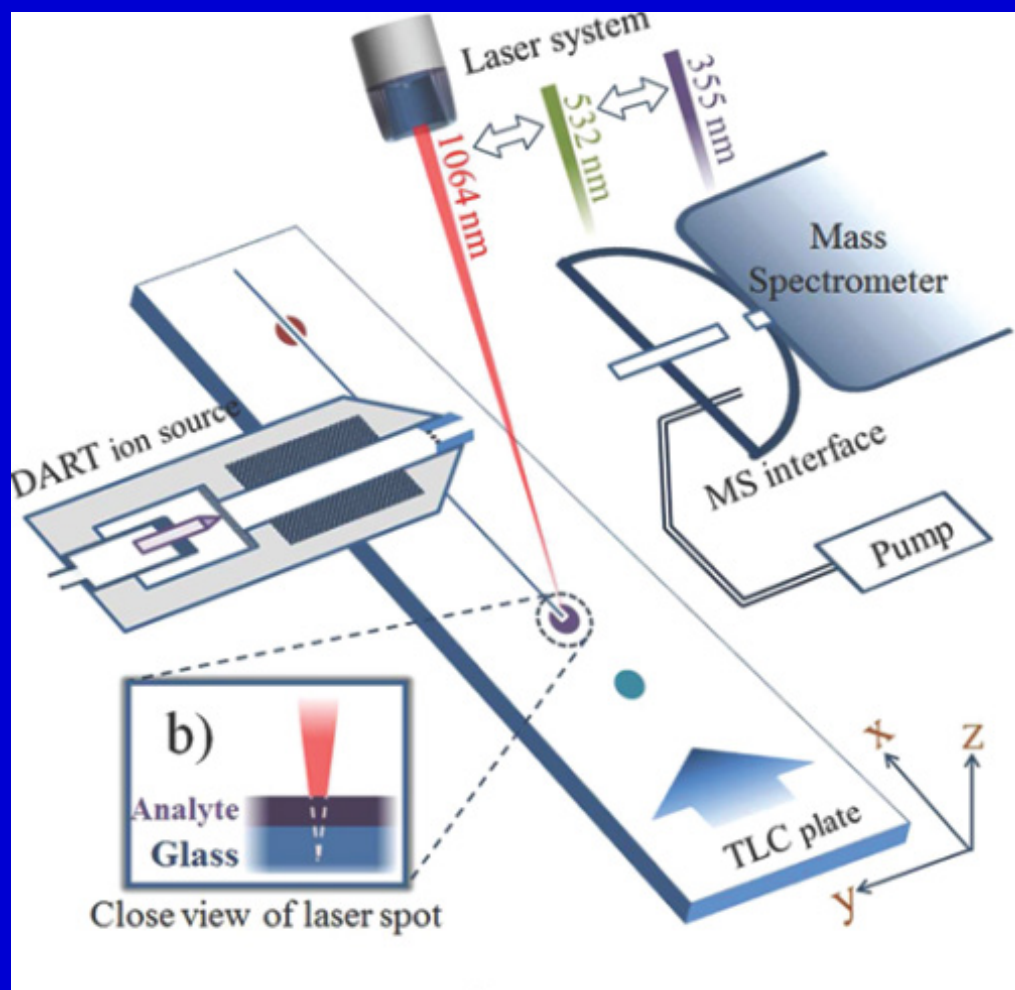
# (3) Rotation Planar Chromatography Coupled On-Line with Atmospheric Pressure Chemical Ionization Mass Spectrometry

Van Berkel et al. *Anal. Chem.* 2004, 76, 479



# (4) Thin Layer Chromatography/Plasma Assisted Multiwavelength Laser Desorption Ionization Mass Spectrometry for Facile Separation and Selective Identification of Low Molecular Weight Compounds (PAMLDI or LD-DART/MS)

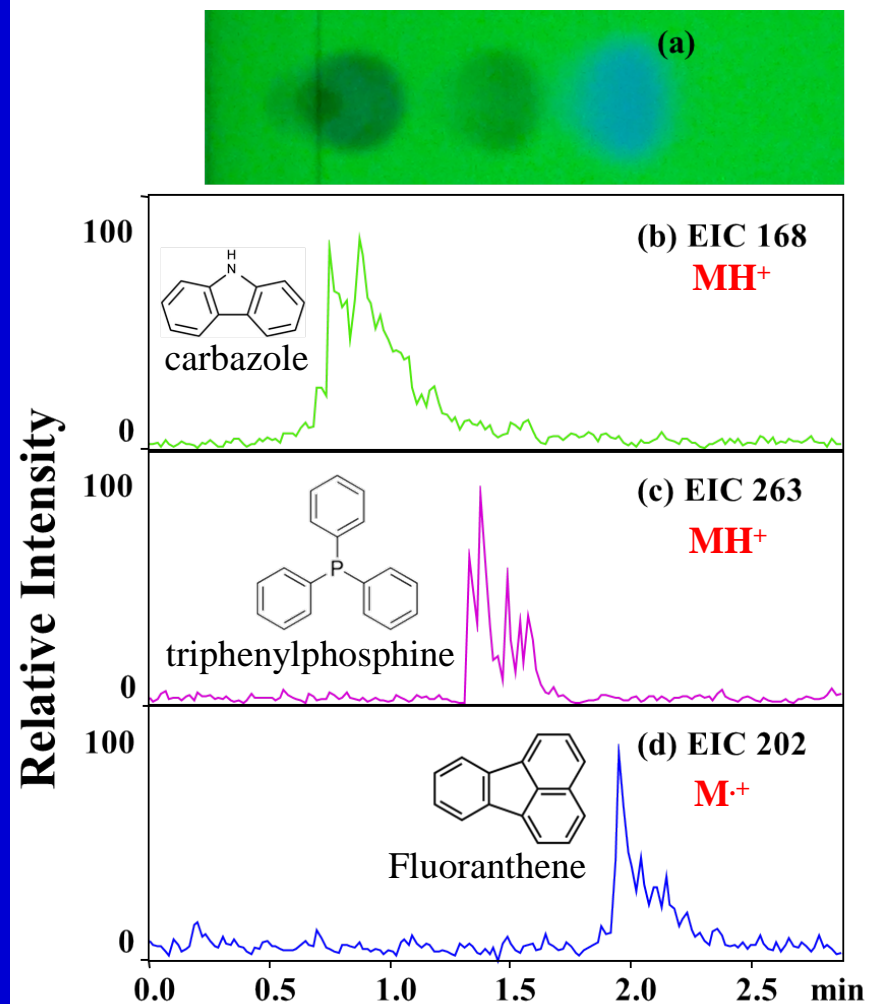
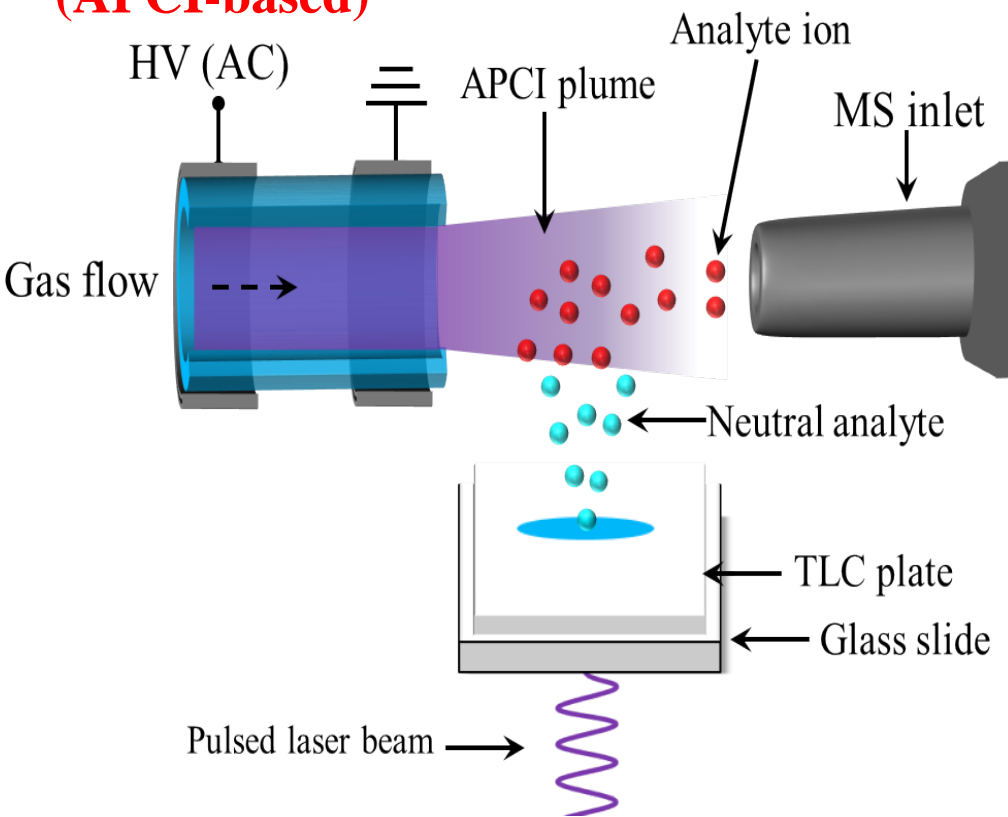
Liu et. al. Anal. Chem., 2012, 84, 1496



# (4) TLC combined with laser-induced acoustic desorption/dielectric barrier discharge ionization mass spectrometry (LIAD-DBDI/MS)

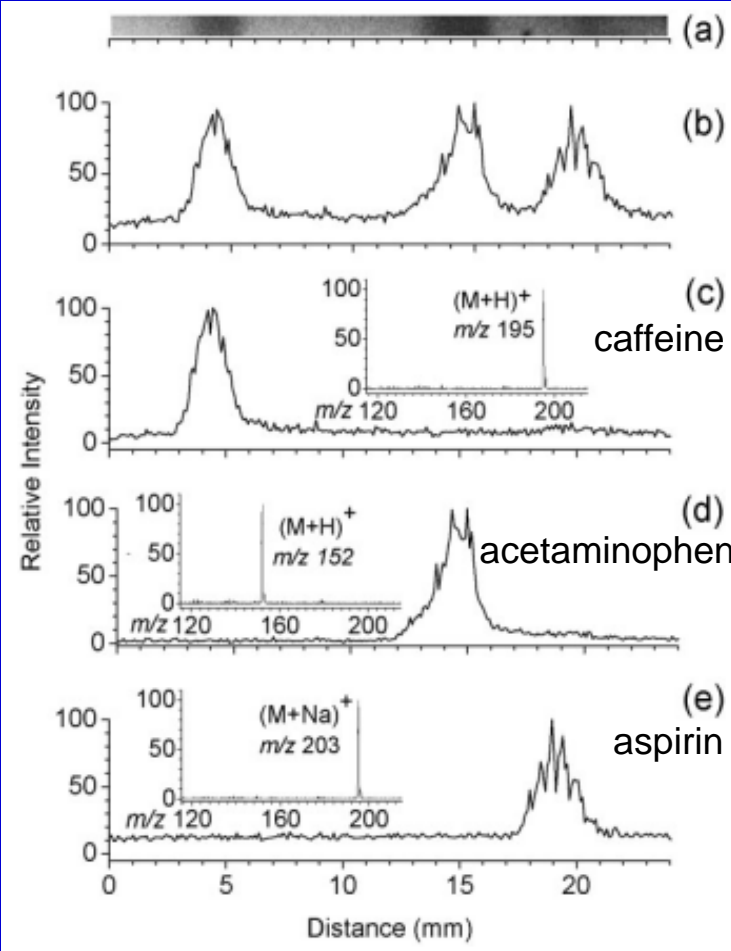
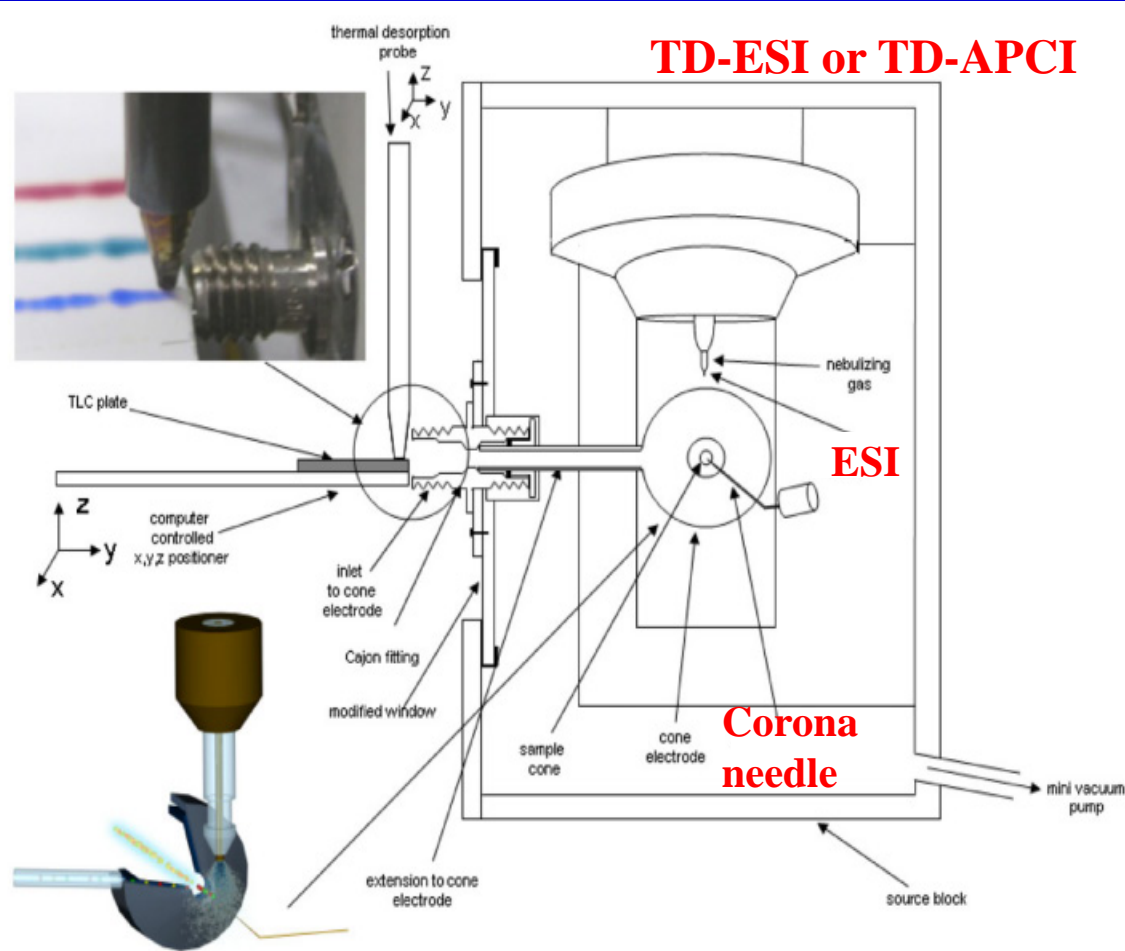
Shiea et. Al. (poster #28 in this symposium)

## LIAD-DBDI (APCI-based)



# (5) Thin-layer chromatography and mass spectrometry coupled using proximal probe thermal desorption with electrospray or atmospheric pressure chemical Ionization

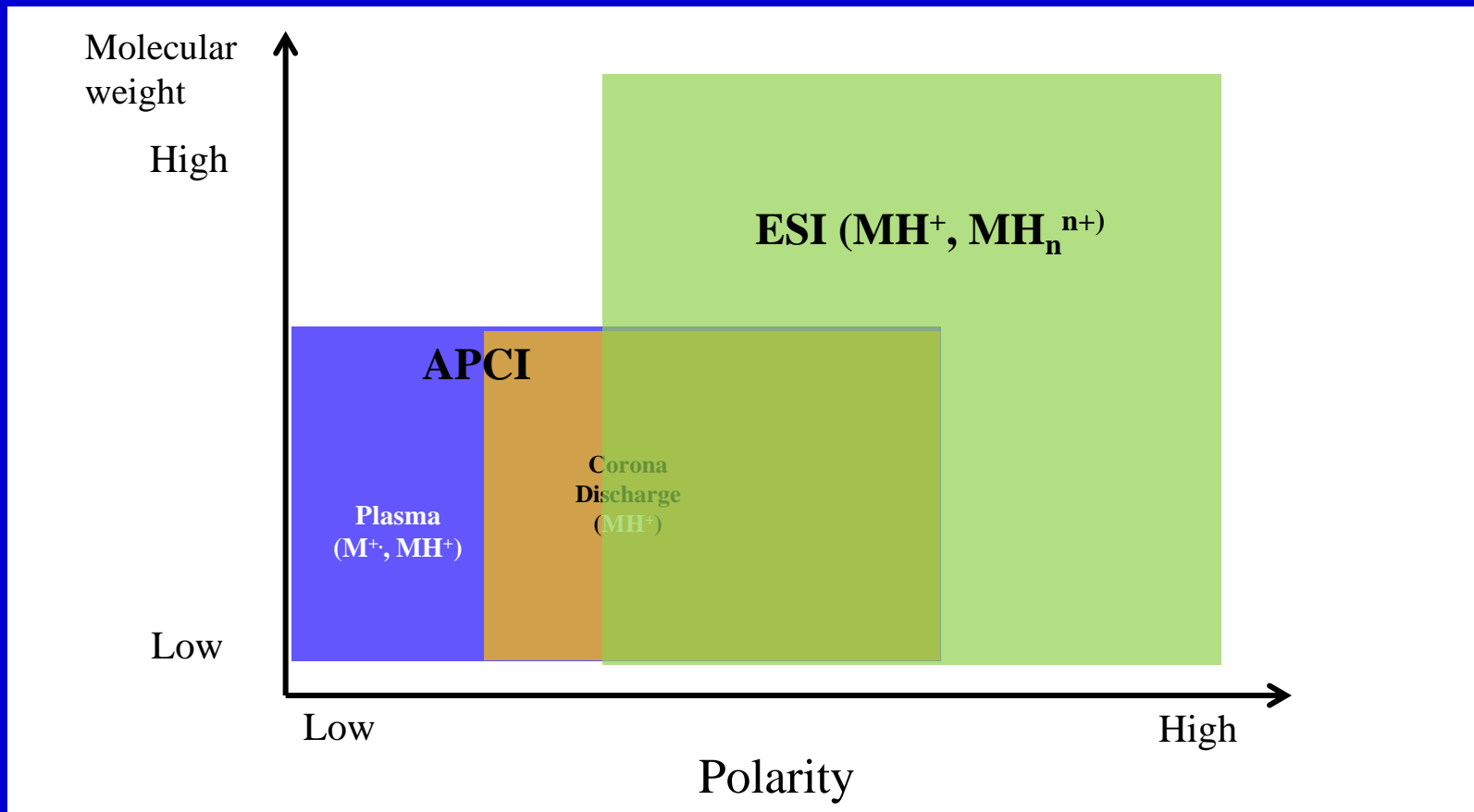
Van Berkel et al. *Rapid Commun. Mass Spectrom.* 2010, 24, 1721



**Due to limitations in ionization capabilities, each of current ambient ionization technique can only ionize analytes with limited mass ranges and polarities:**

**ESI: nonvolatile and polar compounds,**

**APCI: small and less or non-polar compounds.**



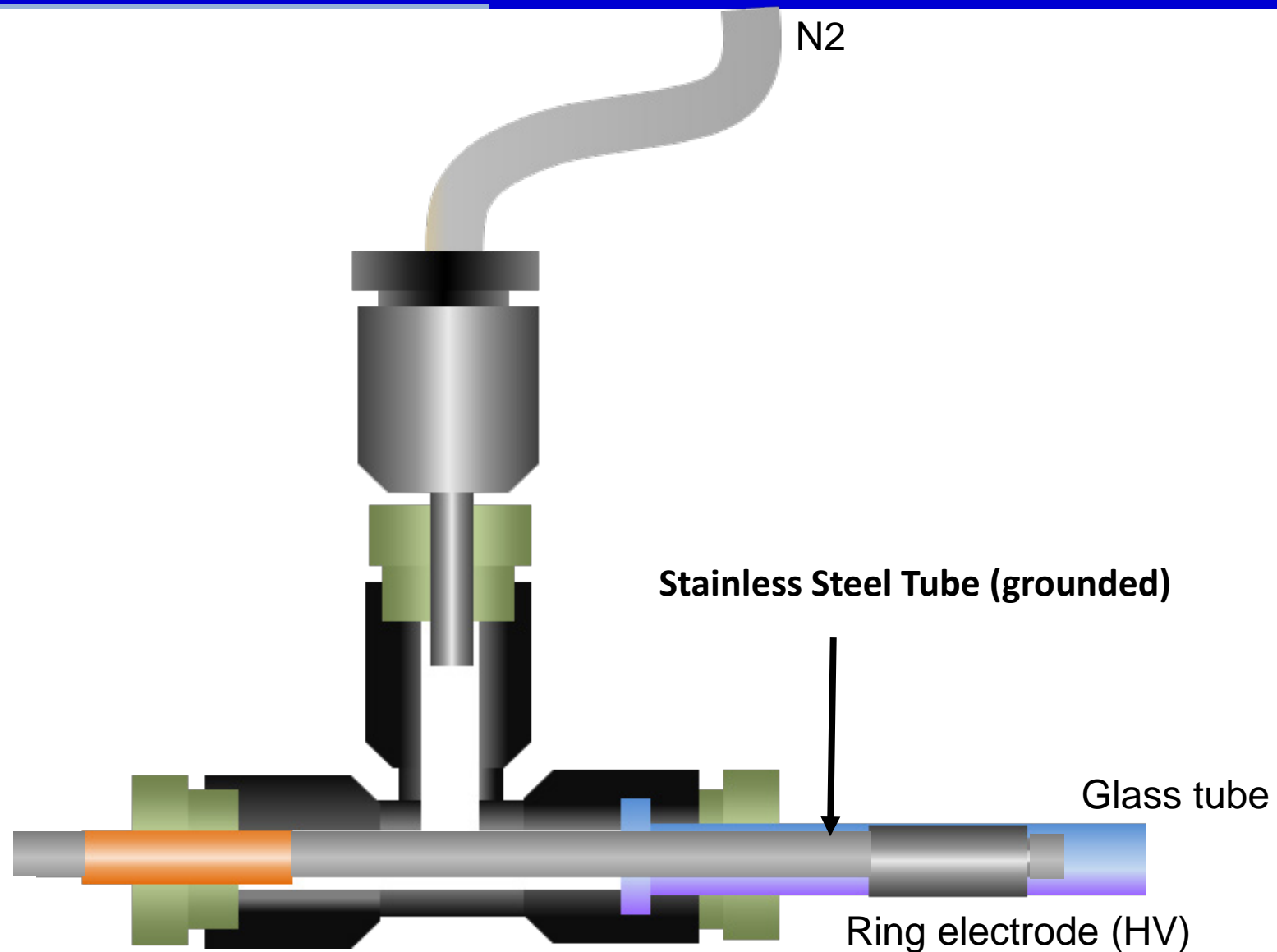
**TLC combined with laser desorption and  
ESI+APCI/MS**



# TLC/LD-ESI+APCI/MS

- (1) An ambient ionization source capable to generate primary ions (reacting species) from both **ESI and plasma-APCI** was developed.
- (2) The analytes on the TLC plate were desorbed using a pulsed laser beam (LD).
- (3) The desorbed analytes (polar, nonpolar, volatile, and nonvolatile) were simultaneously interacted with the primary ions to form analyte ions. The analyte ions were subsequently detected by an ion trap mass analyzer attached to the ESI+APCI source.

# Configuration of ESI+APCI Source (patent pending)

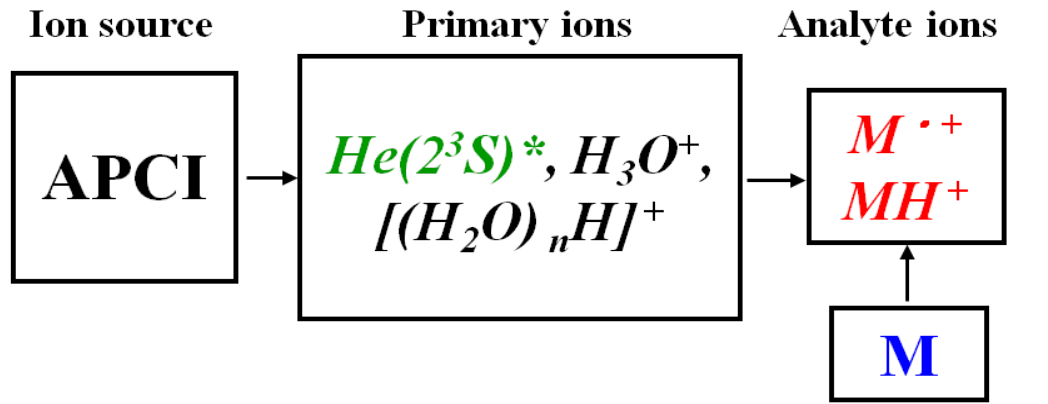
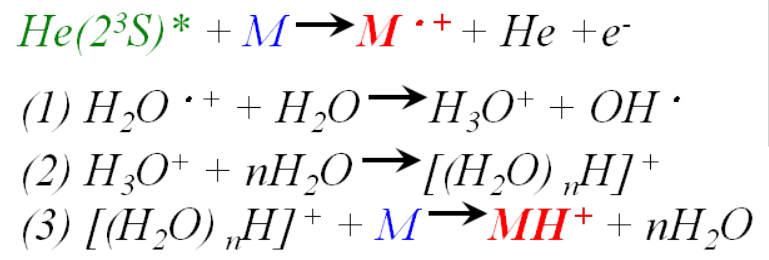




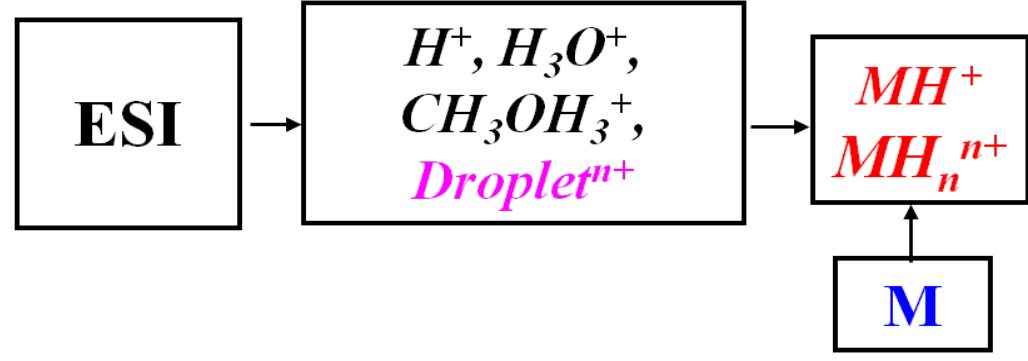
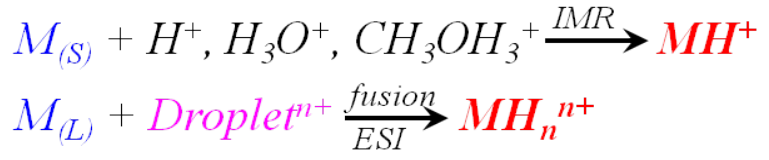
# Ionization Mechanisms Involved in ESI+APCI Ion Source

## Penning Ionization, Ion-Molecule Reactions, Electrospray Ionization

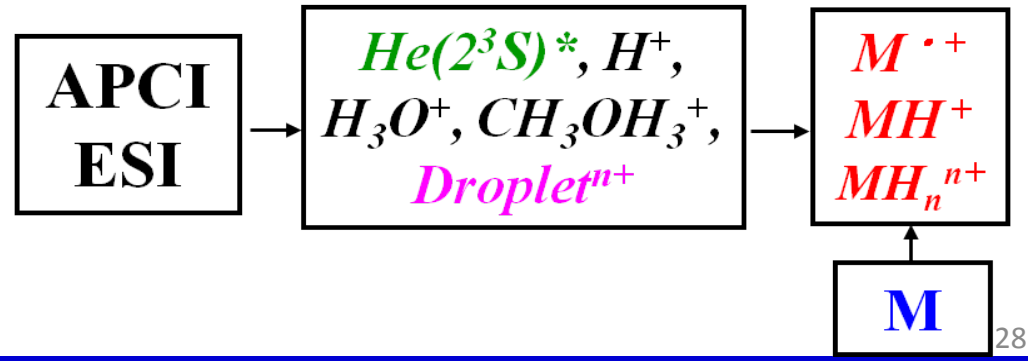
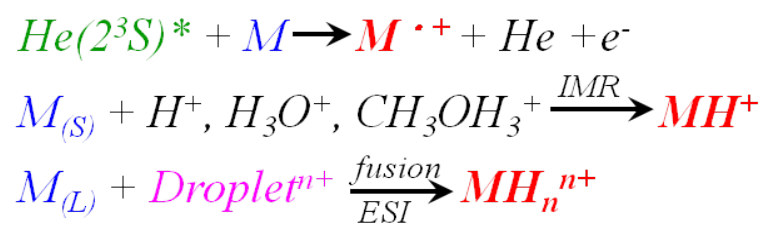
### APCI only:



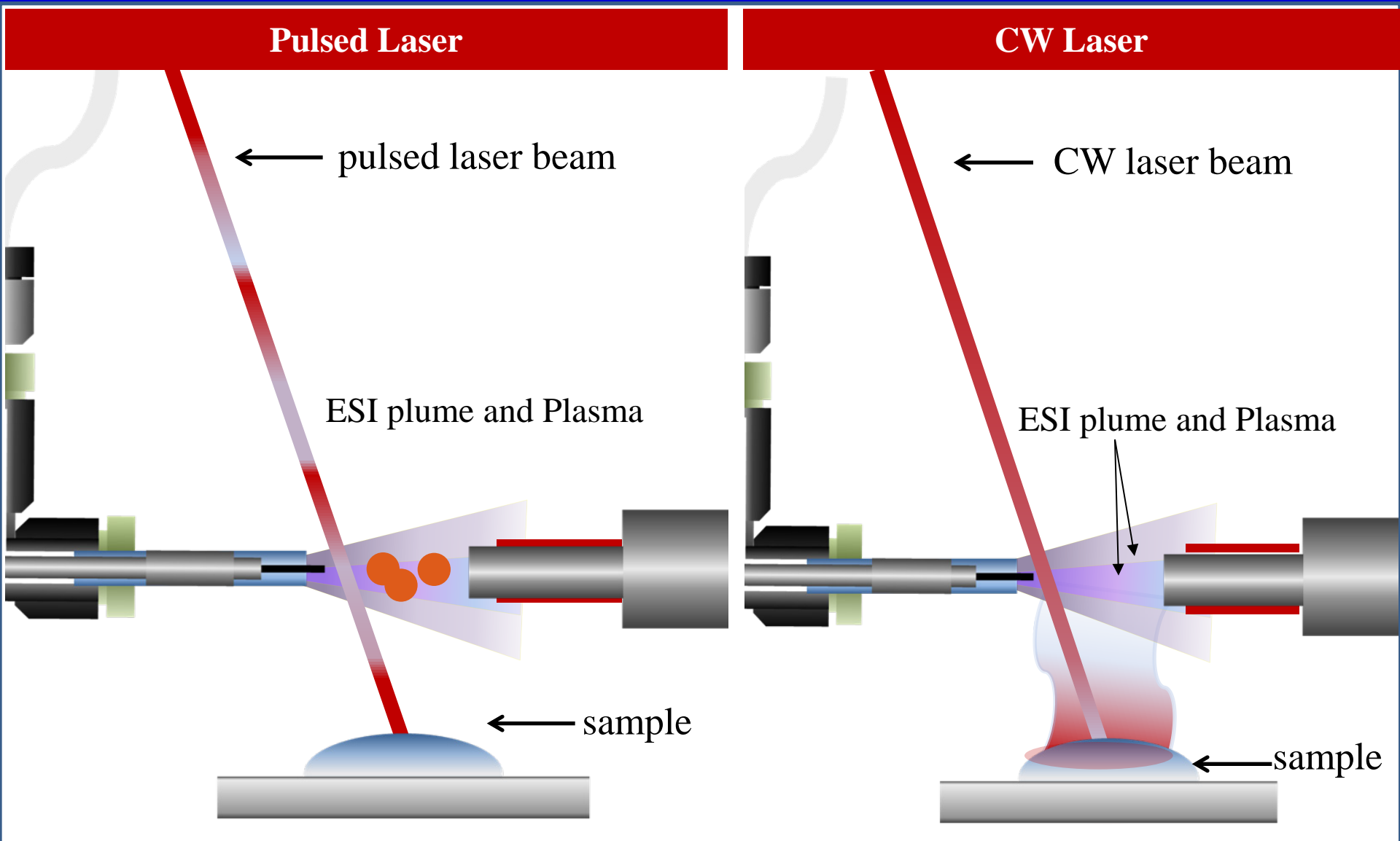
### ESI only:



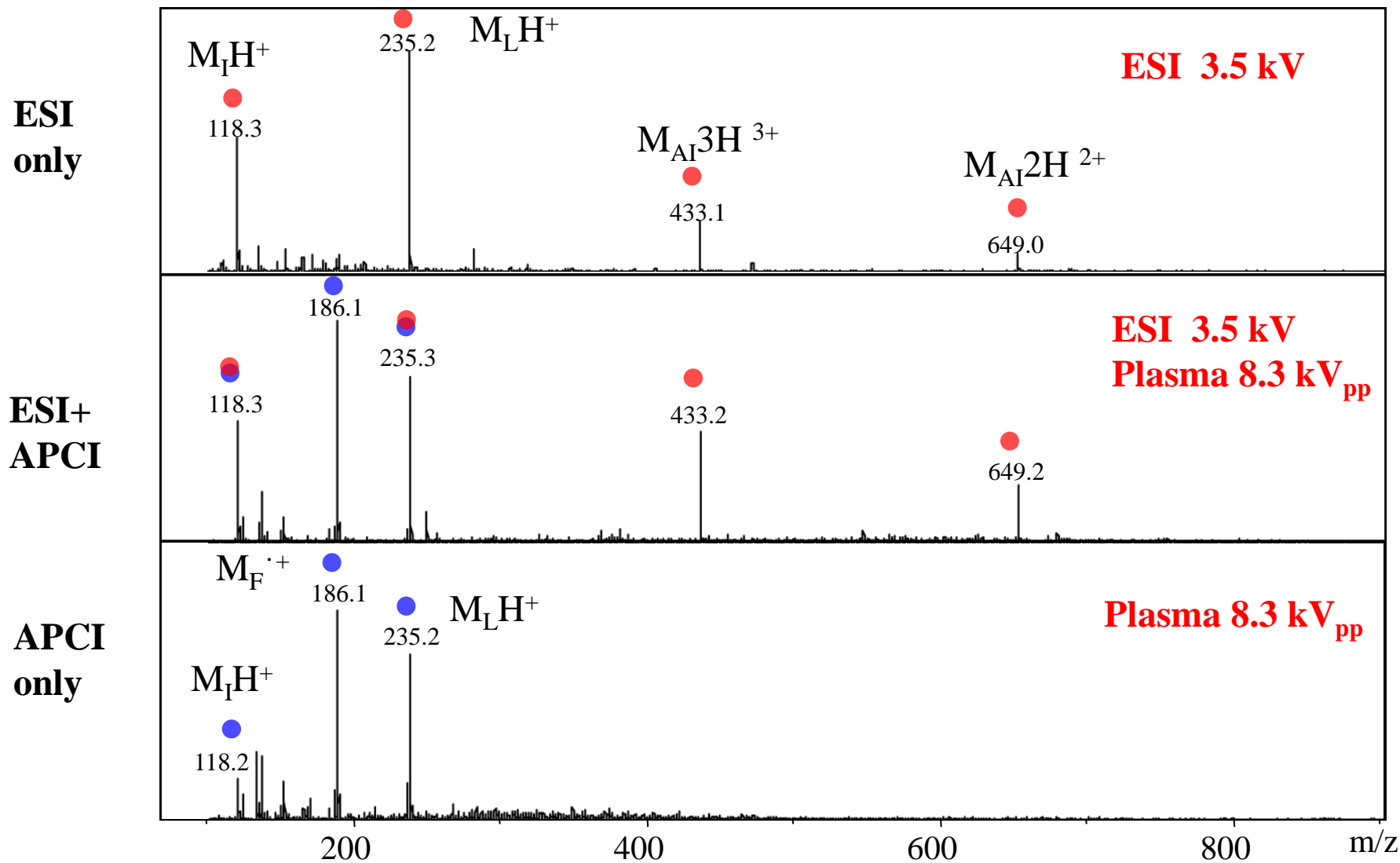
### APCI + ESI:



# TLC-LD/ESI+APCI/MS

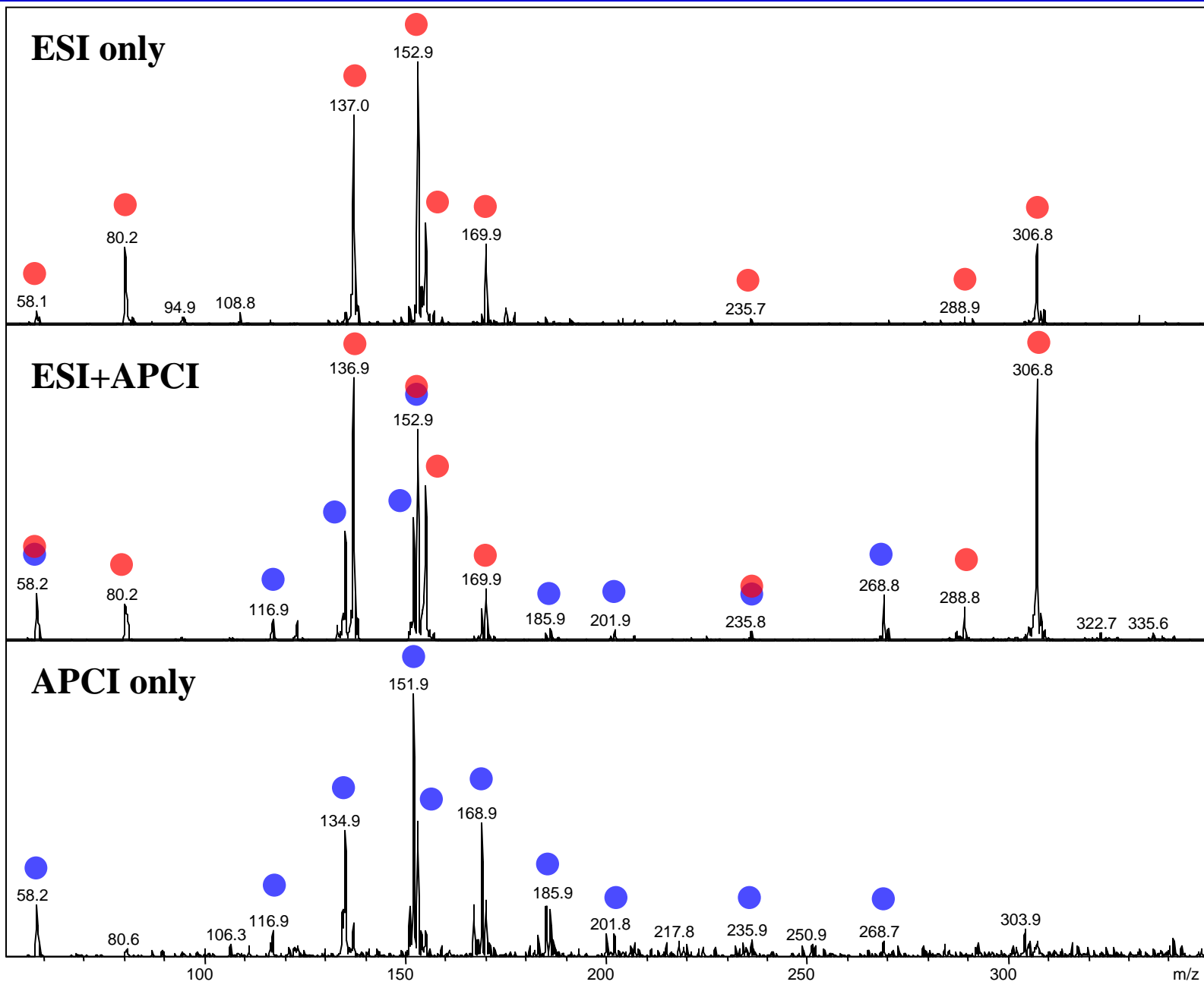


# Pulse laser desorption/ESI+APCI/MS to simultaneously characterize Indole, Ferrocene, Lidocaine, and Angiotensin I

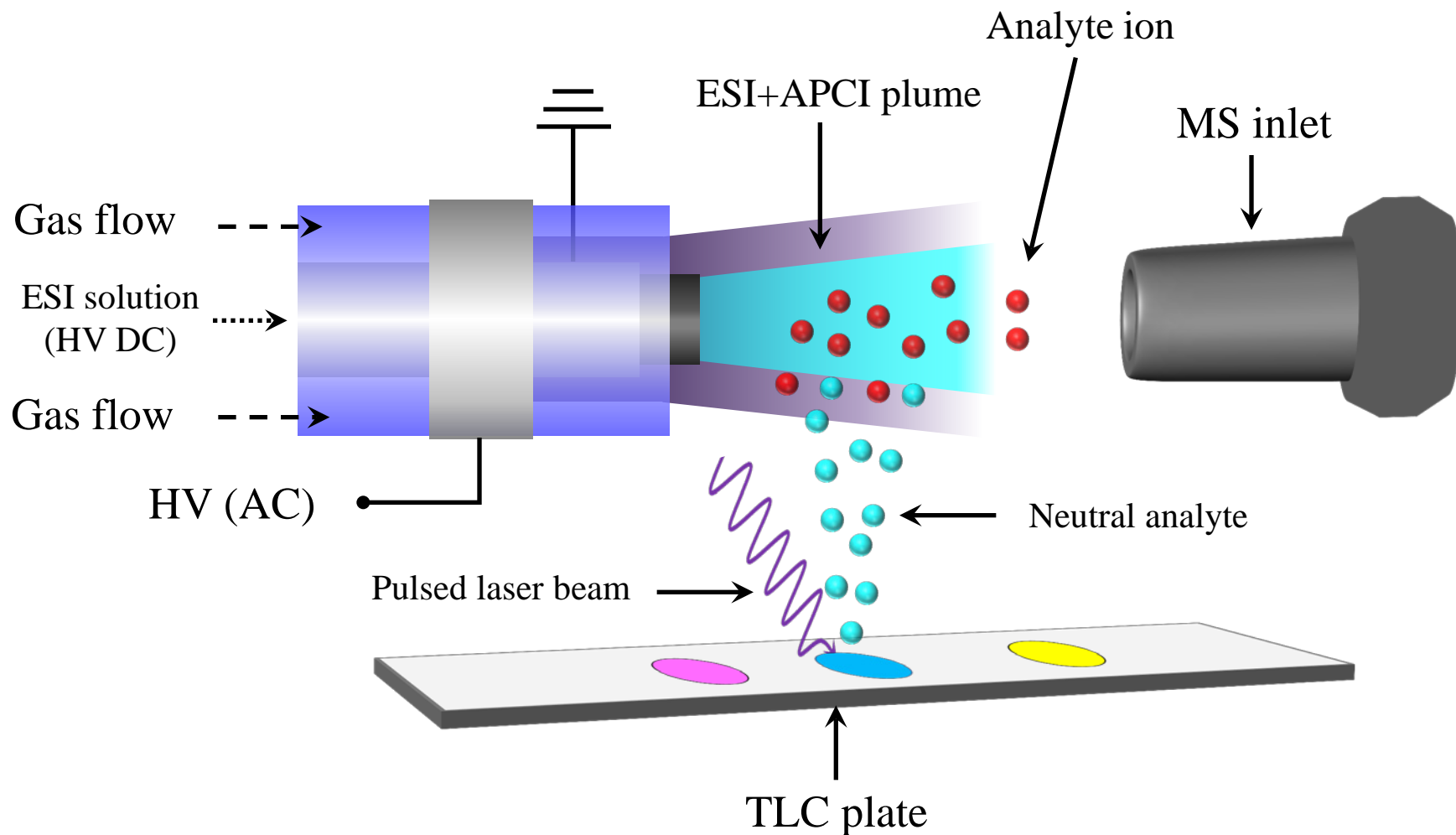


# Rosemary Essential Oil – CW LD-ESI+APCI/MS

Relative intensity

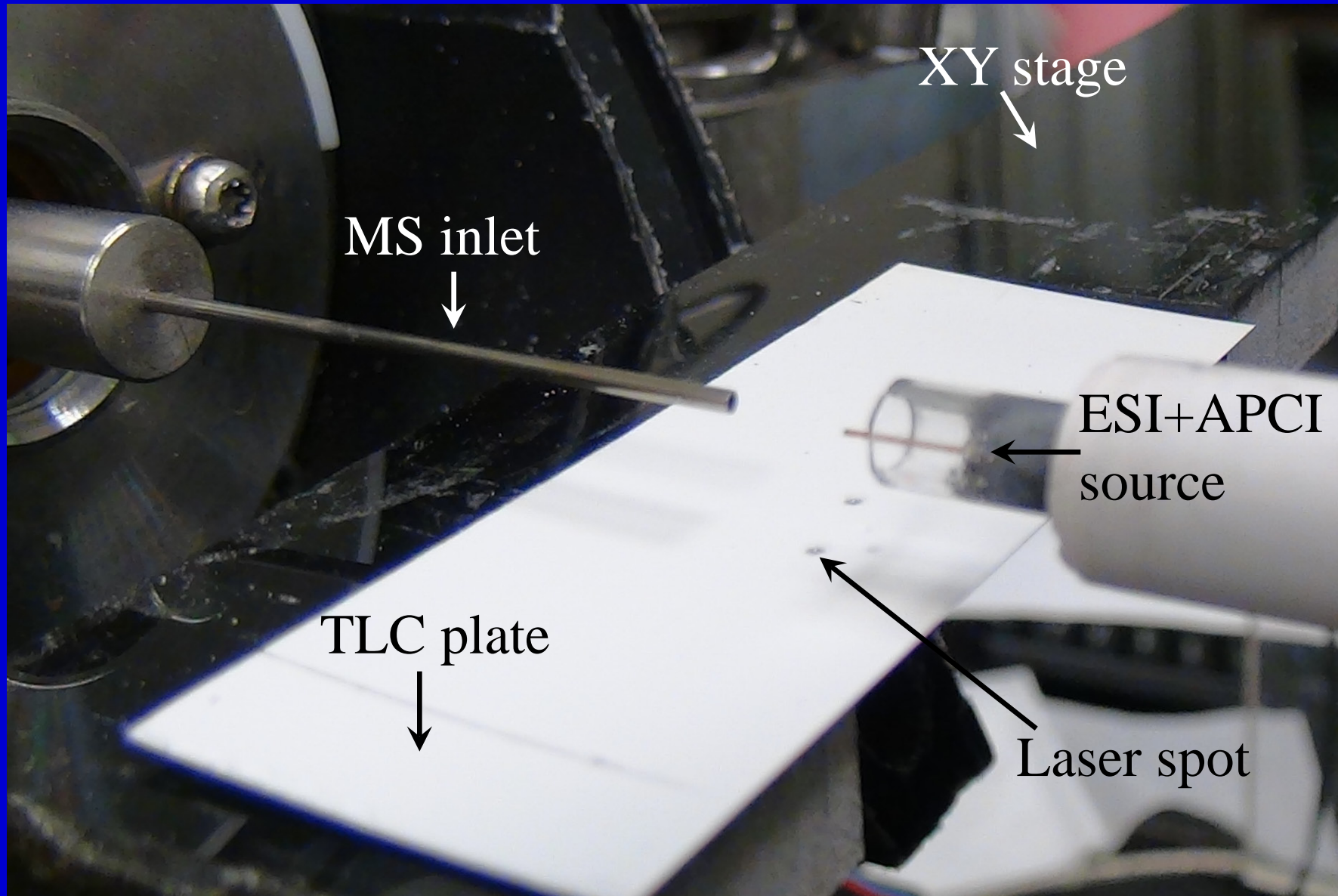


# TLC combined with LD/ESI+APCI/MS for sample analysis



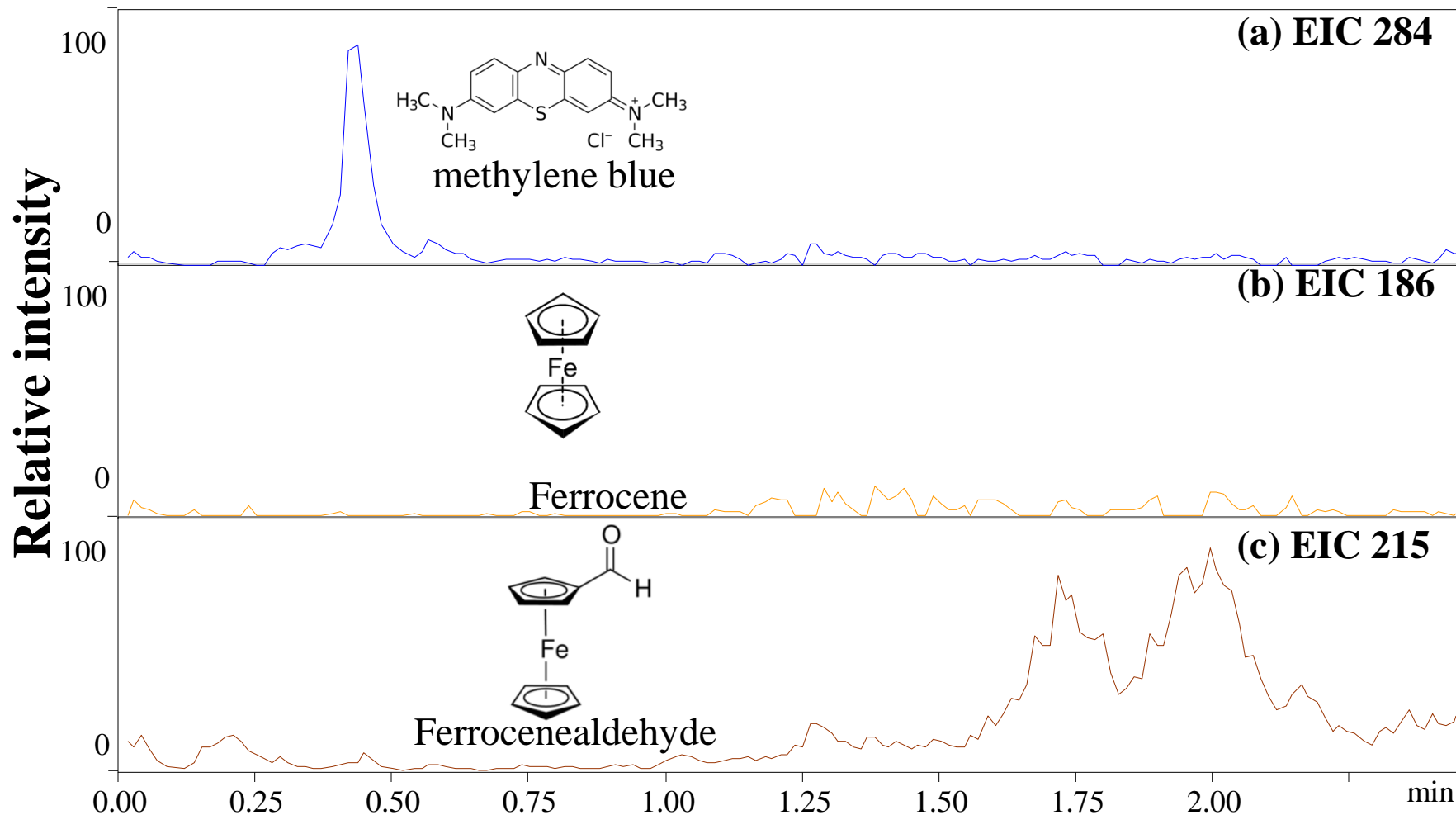


# Photograph of TLC-LD/ESI+APCI/MS system



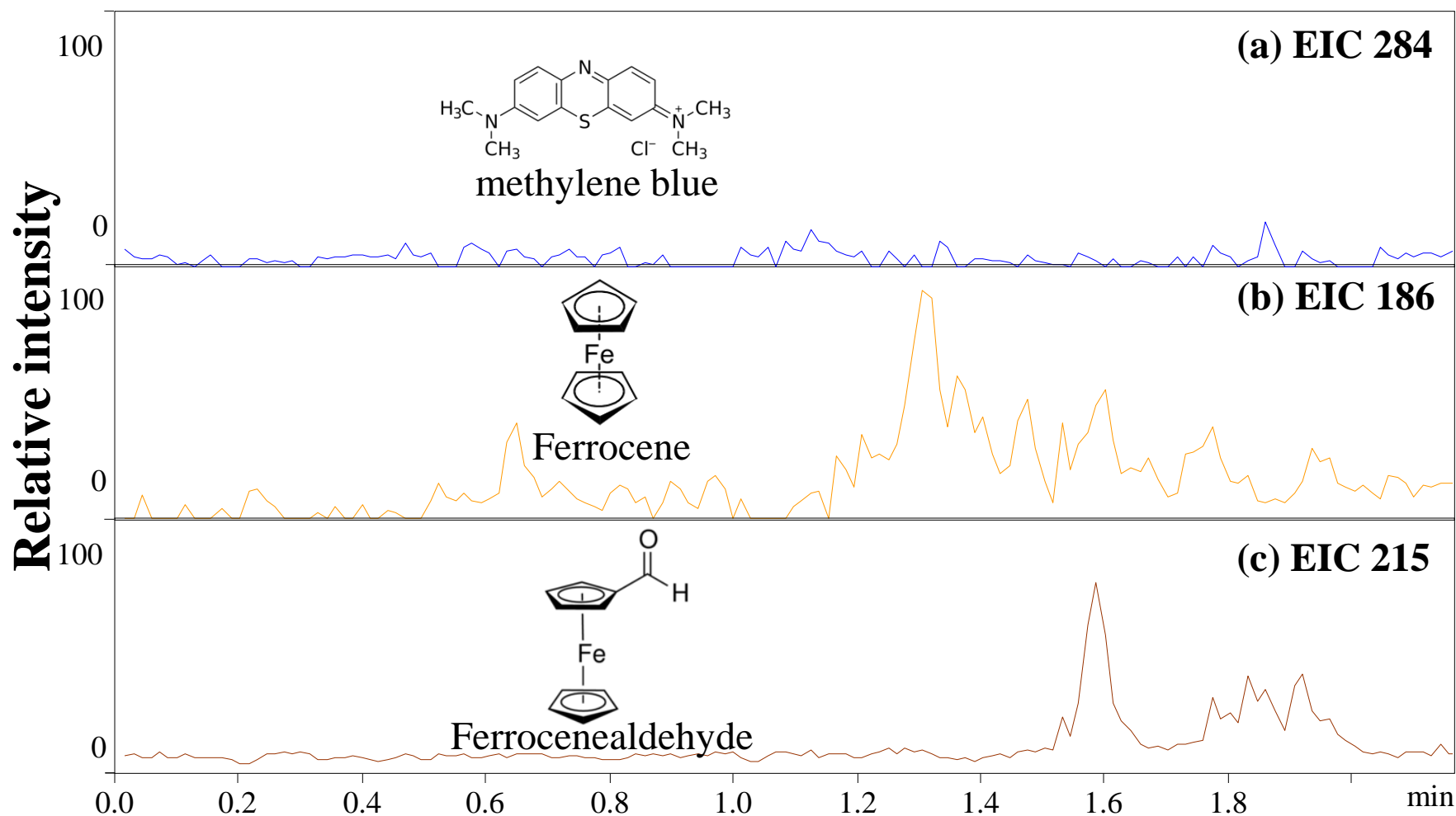
# TLC-LD/ESI+APCI/MS to characterize standard mixture

**ESI  
only**



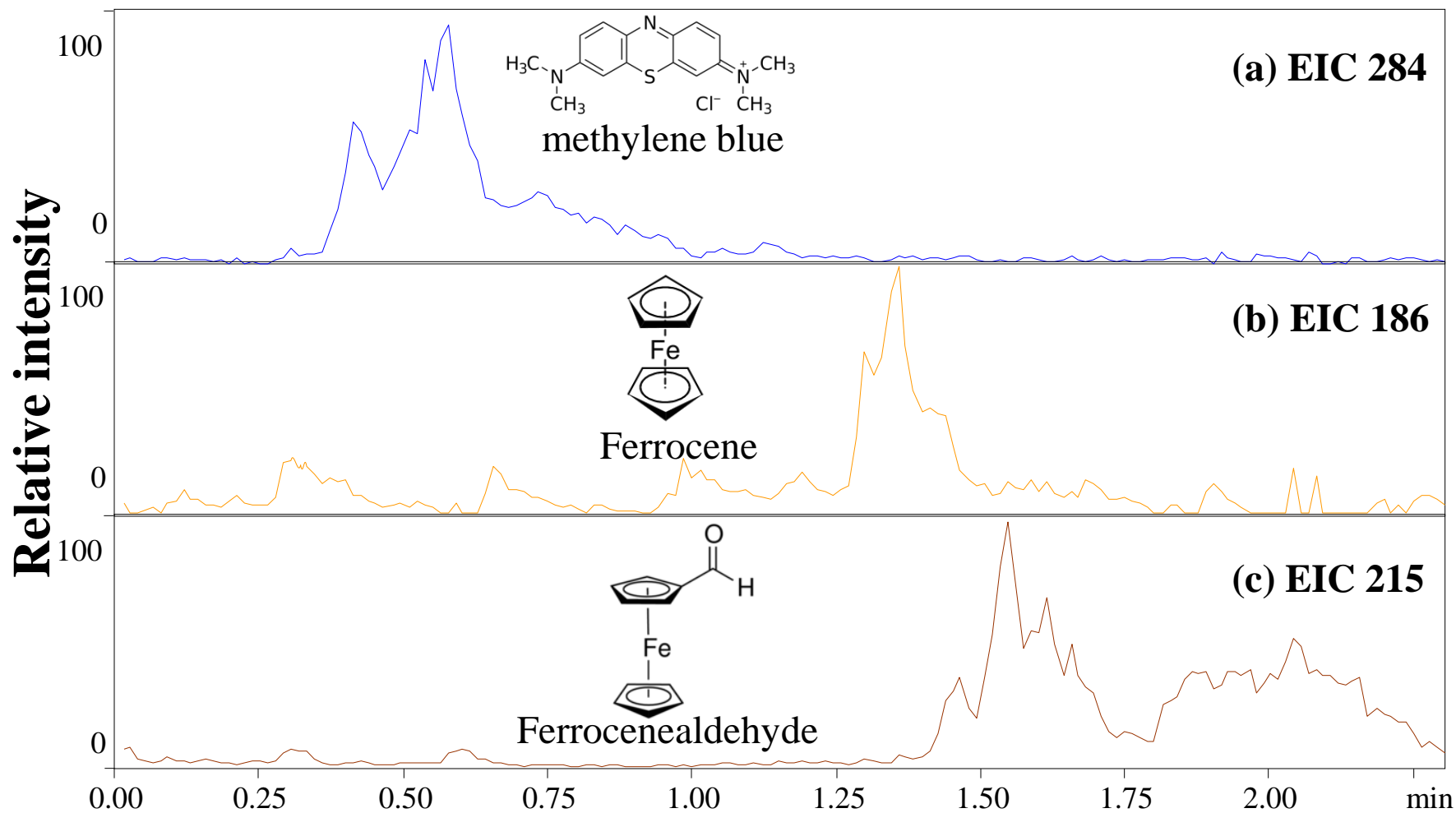
# TLC-LD/ESI+APCI/MS to characterize standard mixture

**APCI  
only**

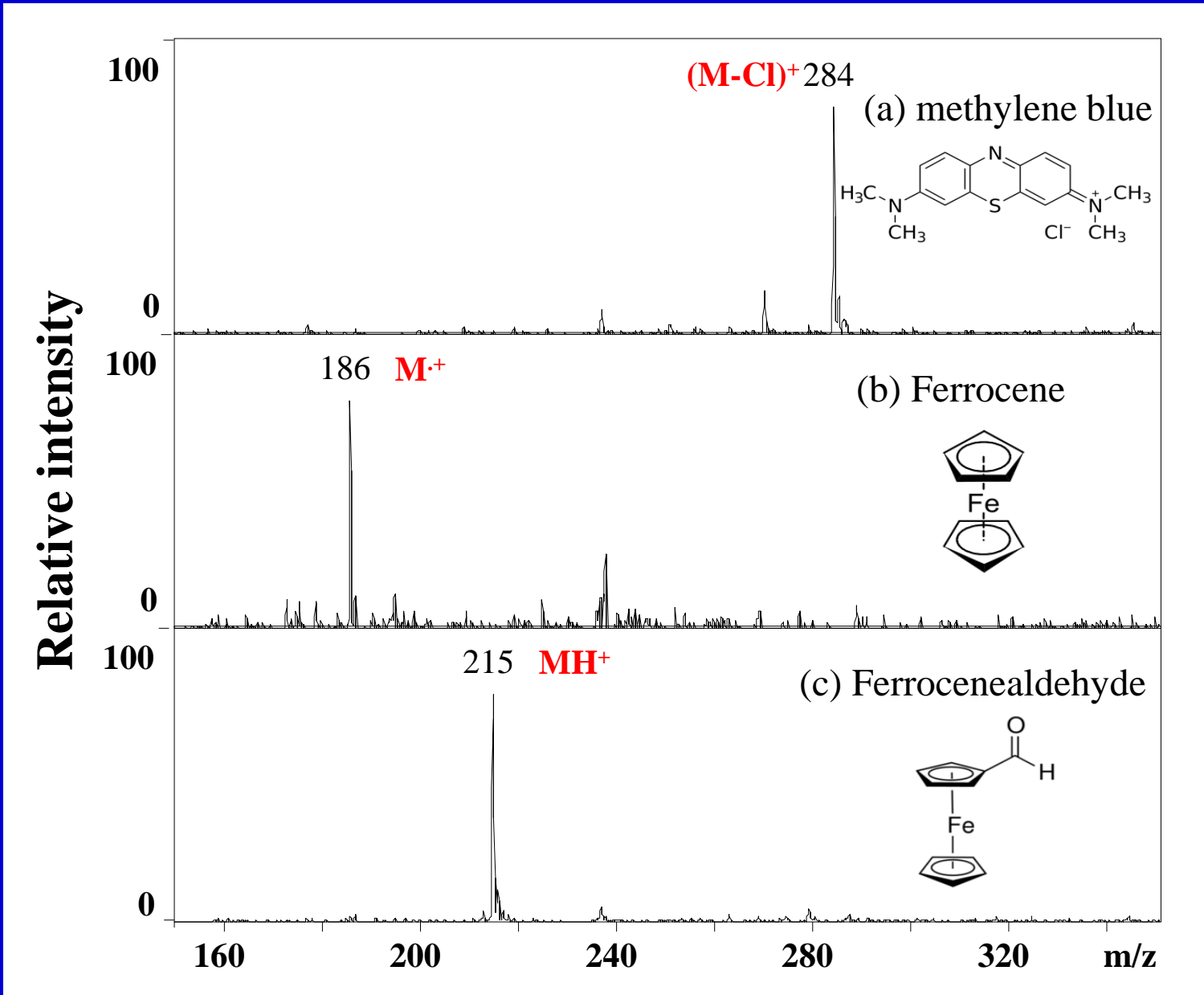


# TLC-LD/ESI+APCI/MS to characterize standard mixture

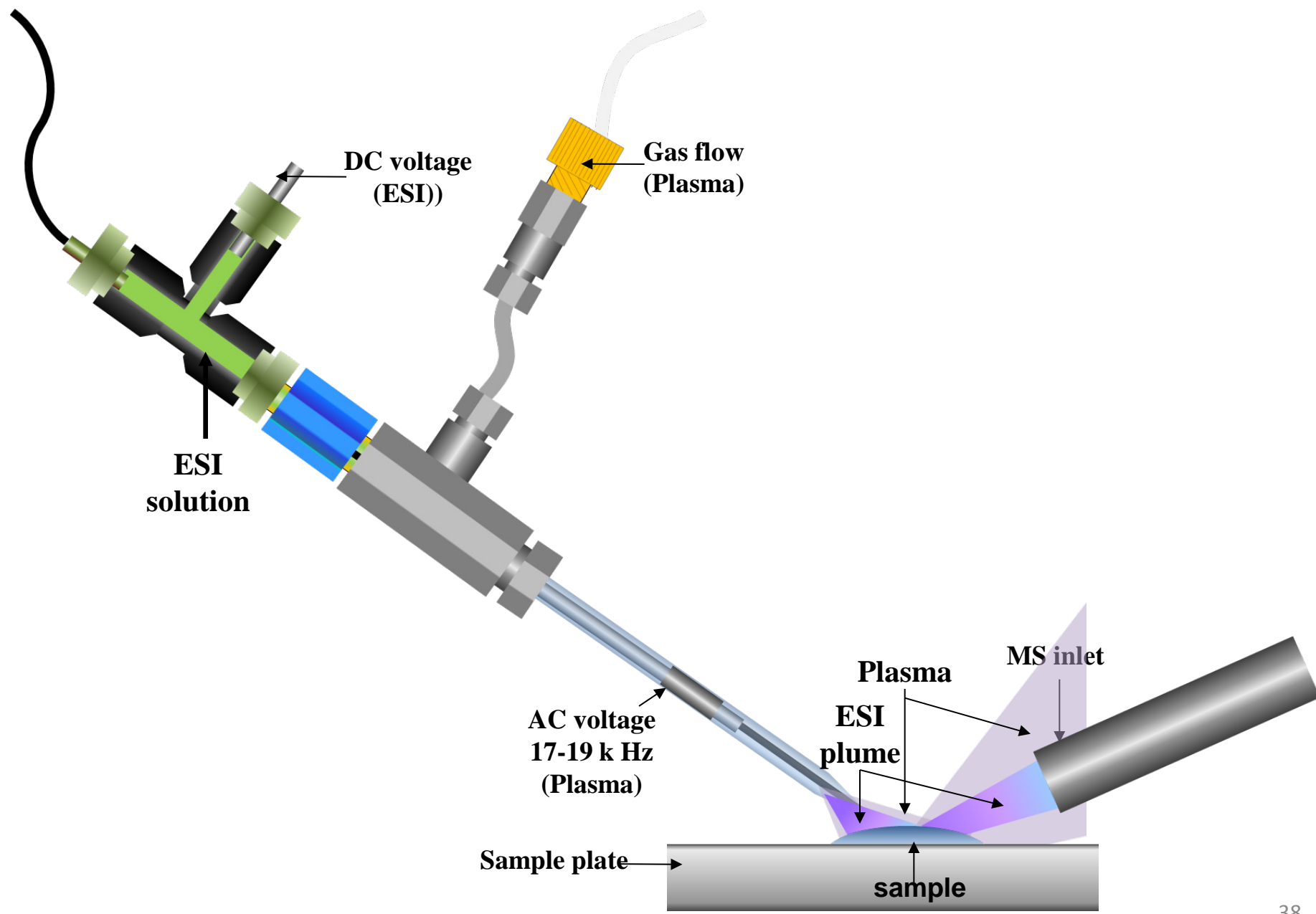
**ESI+  
APCI**



# LD/ESI+APCI mass spectra of methylene blue, ferrocene, and ferrocenealdehyde



# ESI+APCI/MS for desorption/ionization of analytes on TLC plate



# Summary

An ambient source coupling ESI with APCI was developed to simultaneously generate primary ions by ESI and APCI.

This ambient ESI+APCI source was successfully used to characterize polar and nonpolar compounds on surfaces (e.g., TLC plate) through direct desorption/ionization and two-step ionization processes. Both radical and protonated analytes ions (including singly and doubly charged ions) were detected in the ESI+APCI mode.

# Acknowledgement

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Mr. Zuei-Hung Hung

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National Science Council, Taiwan

Ministry of Education, Taiwan





# National Sun-Yat Sen University





# 95 Unleaded Gasoline - CW LD-ESI+APCI/MS

