

Desorption Electrospray Ionization (DESI) Mass Spectrometry: An Overview and Future Directions

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Problem to be Addressed

- Rapid detection, identification, and quantification of *home-made explosives* and precursors in **complex matrices**
 - Current techniques used for explosives detection and other contraband have limited capabilities

Concealment

- shipping restrictions
- baggage scans
- remove shoes, coats, etc.
- liquids restrictions
- aggressive pat downs
- whole body imaging



Trace Explosives Detection

- canine teams
- swab technology
- air monitoring
 - *For example*, government buildings



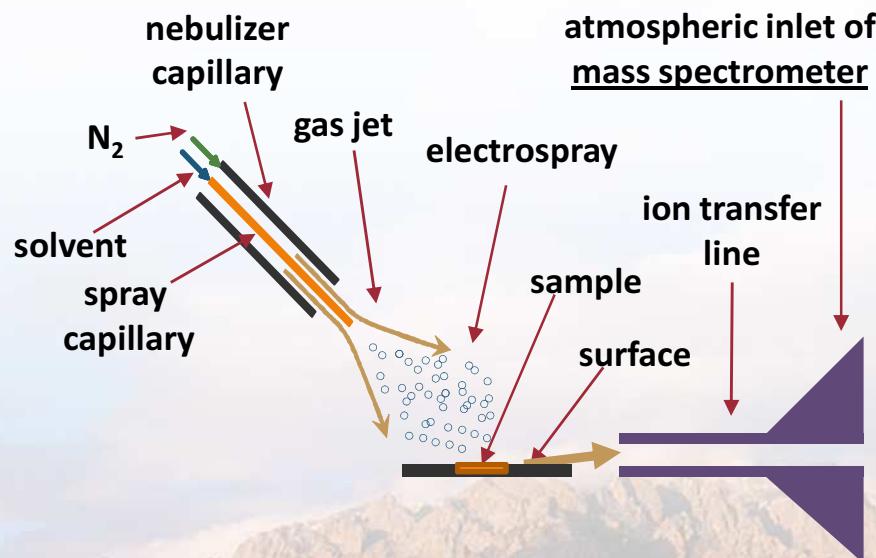
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Possible Solutions for Explosives Detection

Emerging Technology:

- Chemical detection using ambient ionization of untreated surfaces coupled with **high-resolution mass spectrometry**
 - Diverse range of detectable compounds, high throughput and sensitivity, little to no sample preparation, low false positive rates, and imaging capabilities

Desorption Electrospray Ionization (DESI)



Waters Synapt™
G2 HDMS™



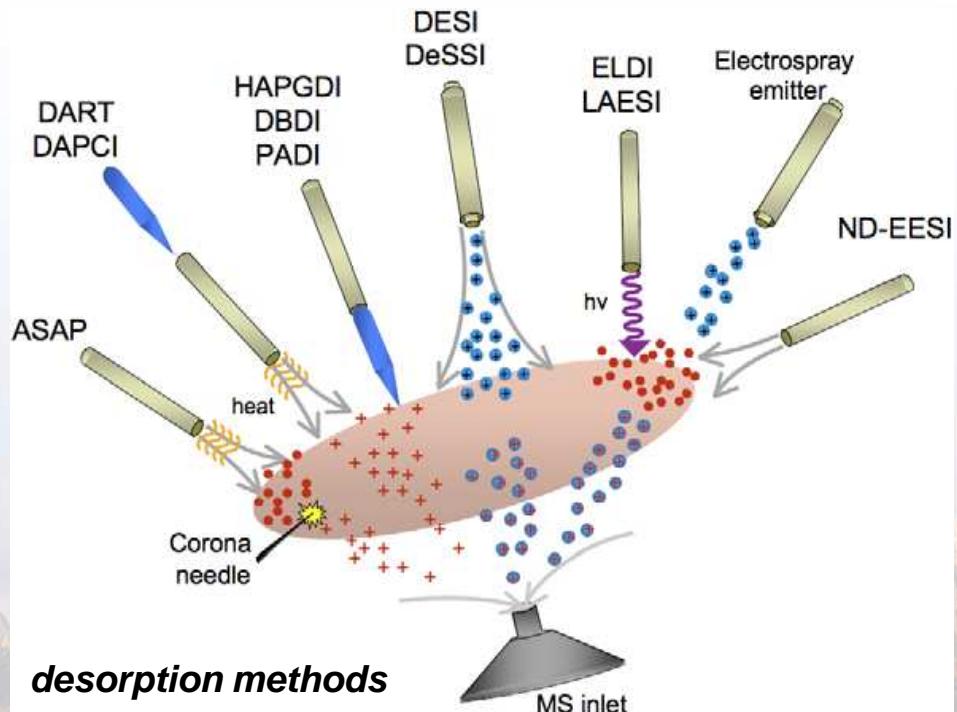
Fast, easy, and reliable detection!



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Ambient Ionization Methods

- Direct analysis
- No sample preparation
- Ionization in open environment
- Real time
- High throughput
- Imaging

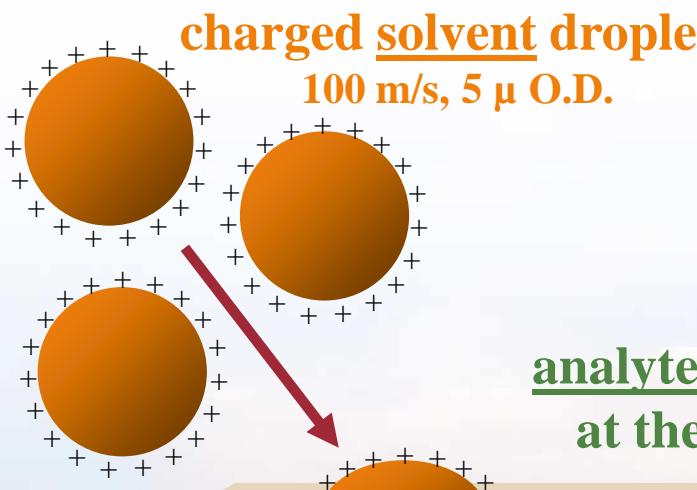


Technology explosion!

DESI	IR-LAESI
SSP	DAPPI
DART	APGDDI
ASAP	EASI
ELDI	RASTIR
FD-ESI	PESI
DAPCI	FA-APGD
AP-IR-MALDI	LTP
MALDESI	DEMI
JeDI	LM
EESI	SSP/ESI
DeSSI	SACI
APTDI	SPAMS
LAFAPA	LTP
PADI	DICE
DBDI	LAMICI
ND-ESSI	EASI
LDTD	
LAESI	<i>and more...</i>

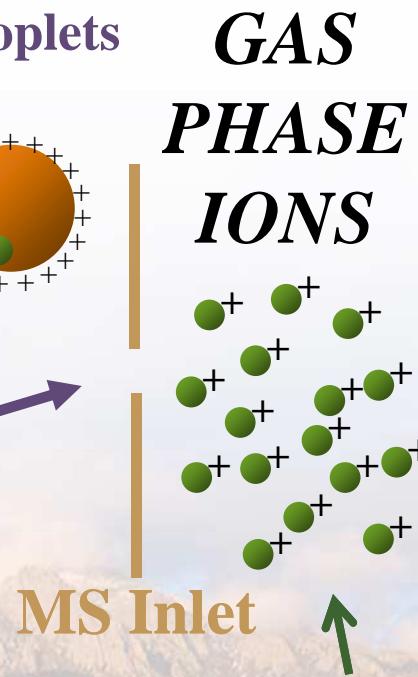
Desorption Electrospray Ionization (DESI)

- Simple, sensitive, gentle, and versatile
- Rapid and direct sample analysis
- Little to no sample preparation
- Ambient temperature and pressure
- Can be optimized for a wide range of applications



analyte extracted
at the surface

droplet pick-up mechanism

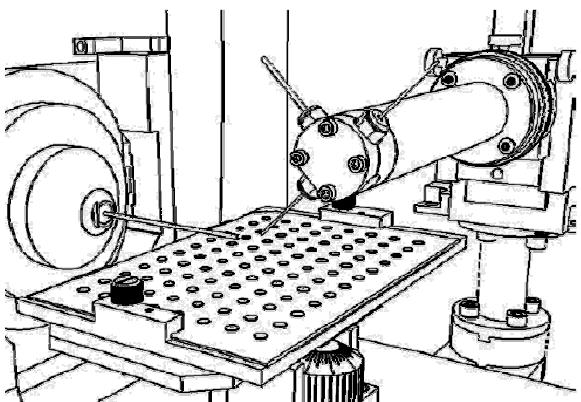


- Positive ions traditionally analyzed
- Negative ions not well understood

Example DESI Applications

High-Throughput Quantitative Analysis

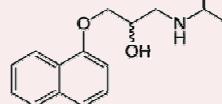
96-sample array



Analysis time = 1.5 s/sample

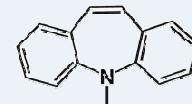
N. Manicke *et al.*, *J. Am. Soc. Mass Spectrom.* 20, 321 (2009)

Propranolol



RSD = 3%
LOD = 10 fmol

Carbamazepine

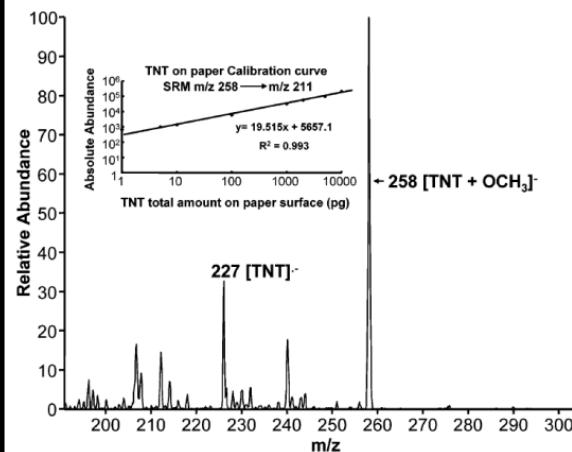


RSD = 5%
LOD = 30 fmol

- High-throughput tablet analysis
- Metabolites and drugs of abuse from urine
- Liquid profiling of bacteria
- Natural products in plants
- Trace detection of agrochemicals in food

In Situ Trace Detection of Explosives

TNT detection



LOD: sub-picogram for TNT

I. Cotte-Rodriguez *et al.*, *Anal. Chem.* 77, 6755 (2005)



- Non-proximate large-area of pharmaceuticals
- Rapid screening of anabolic steroids in urine by reactive DESI-MS
- DESI-MS for solid-phase analysis of polymers
- Post blast bomb fragment analysis



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Taking DESI to the Next Level

■ Existing Knowledge

- Neat samples are commonly used in publications
- Ideal conditions (laboratory, etc.)
- Limited applicability to the real-world
- Ideal substrates with enhanced ionization efficiency used in publications
- Survey understanding

■ New Frontiers

- High-resolution mass spectrometry with exact mass and no mass overlap
- Multiple modes of mass separation
- Enhanced sensitivity
- Identification of new markers
- Complex matrices
- Applicable to real-world samples
- Identify solvent systems and substrates to identify home-made explosive (HME) precursors and residues that are currently unknown for this technique



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Applications for DESI at Sandia

- **Early detection and characterization of home-made explosives (HME)**
 - Extremely important to the Department of Homeland Security (DHS)
 - Safety and security reasons make this an ideal research area for national labs
- **Possible areas of interest**
 - Materials aging and degradation studies, possible leak detector for FC-72, monitor weapon state of health for enhanced surveillance, SFIs, etc.
- **Our Objectives:**
 1. **Demonstration of HME detection and identification in *complex matrices***
 2. **Identification of new *chemical signatures* for HMEs**
- **Technology at Sandia**
 - DESI coupled with a cutting edge mass spectrometer
 - Waters Synapt™ G2 HDMS™
 - **High resolution**
 - **Exact mass MS/MS**
 - **Differentiation by size, shape, charge, and mass**
 - **Multiple ionization options**
 - **DESI imaging capabilities**



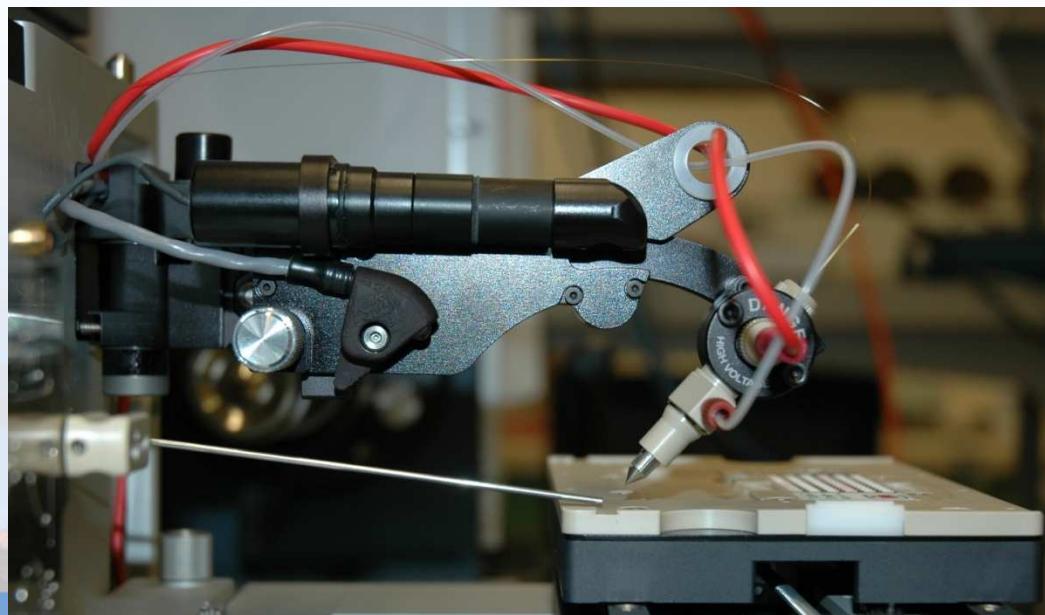
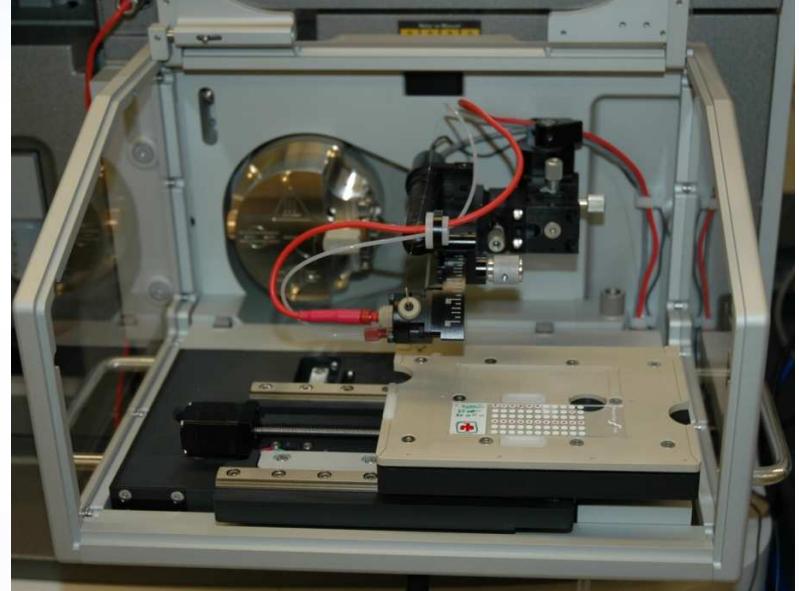
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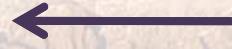
DESI Imaging Equipment

- **2-D Automated Sampling Stage**

- Runs independent of MS instrument
- Software control
- Easy to use
- On-screen video camera display
- Automated motion profiles
- Fully automated in the x and y direction
 - 5 x 3.5 inch sampling area



2-D Automated Stage



DESI Source



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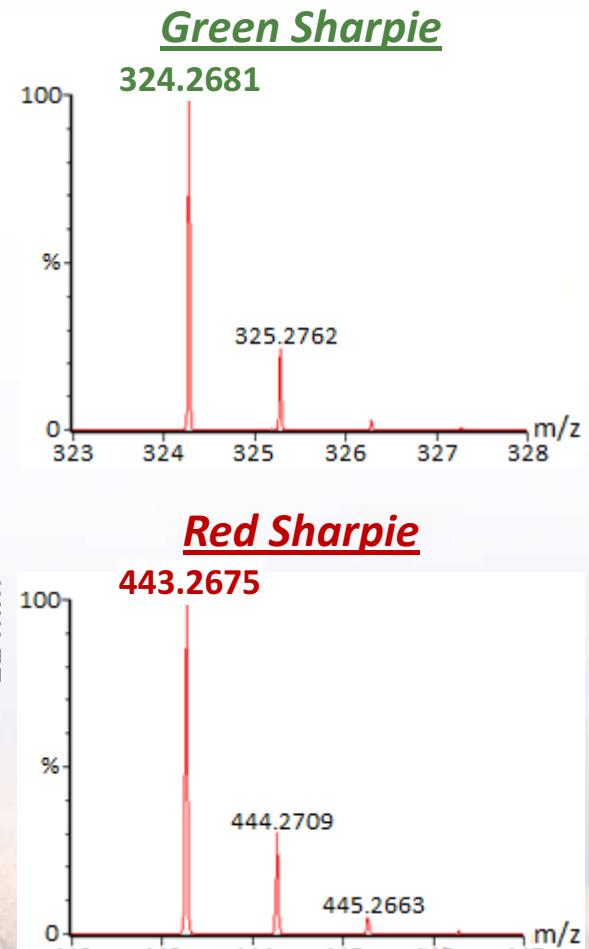
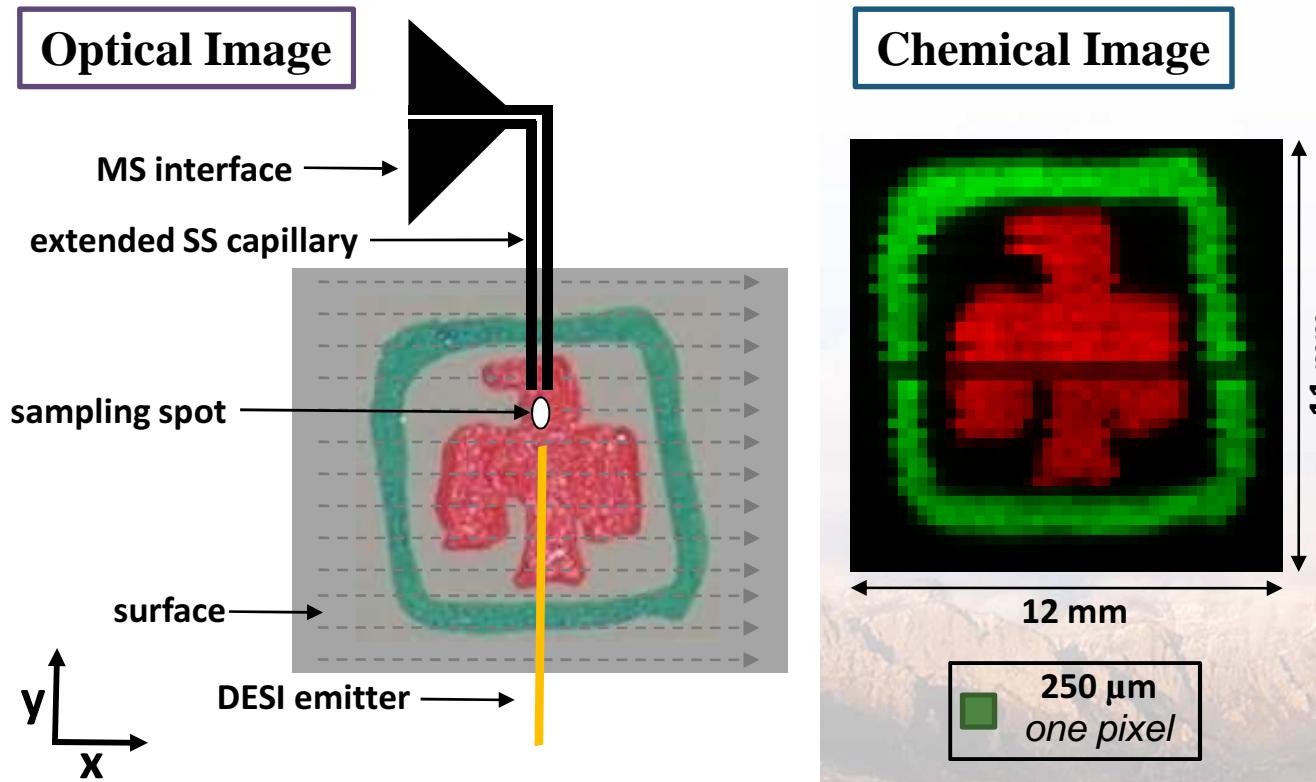


How DESI Imaging Works

- Raster across the image from left to right then downward

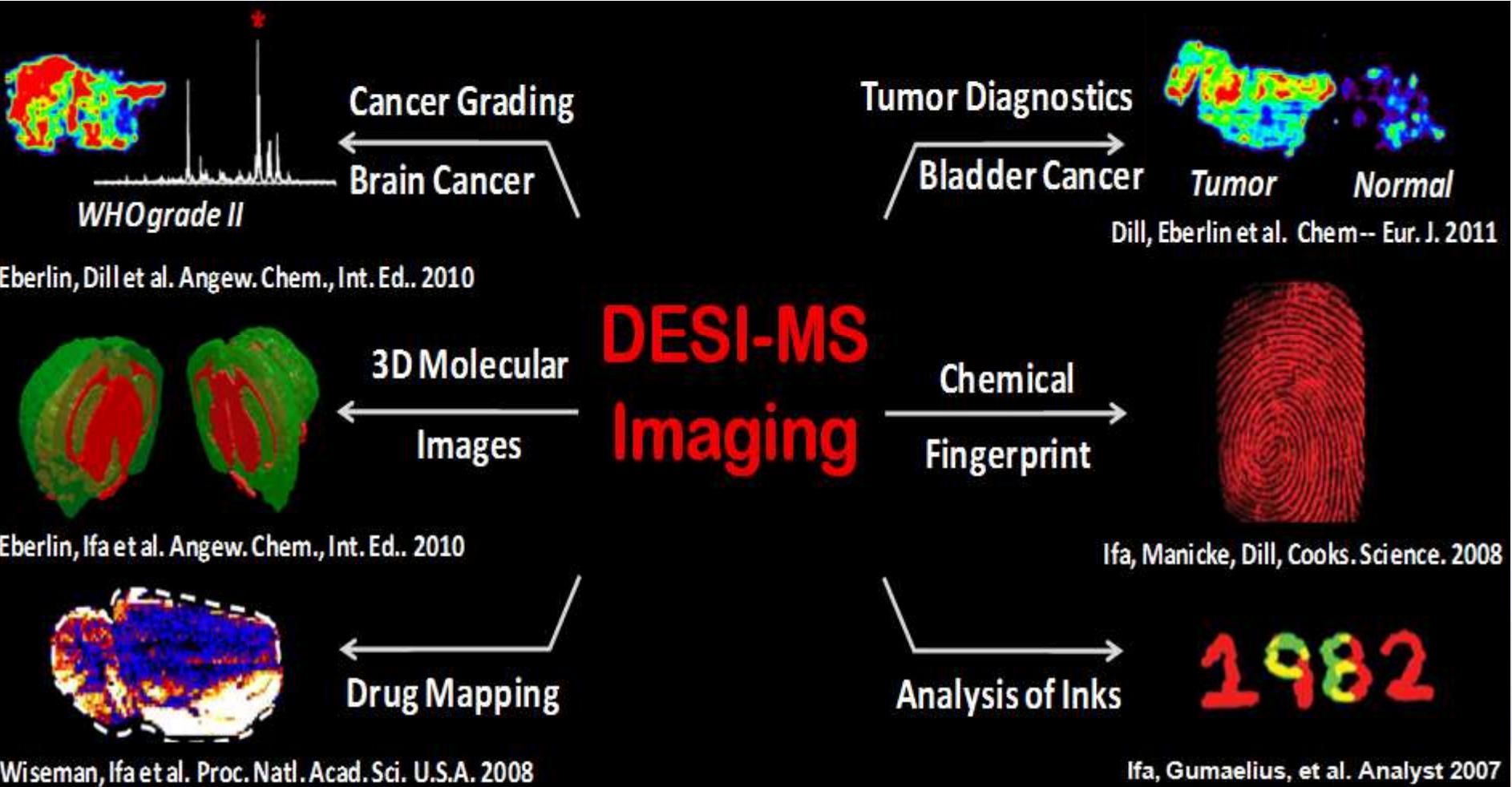
- Rows lengths across are identical
- Each row downward is equally spaced
 - Ensures a square pixel size

- Visually map individual ions of interest



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DESI Imaging Applications



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Closing

■ Summary

- **Identification, detection, and quantification of chemicals **on untreated surfaces** is possible and of extreme importance to national security**
 - Further exploration of DESI technology with HME detection at Sandia
 - **New frontiers: negative ion detection, complex matrices, new chemical signatures, real-world substrates, and imaging capabilities**

■ Future Directions

- Advancements in how ambient ionization and cutting edge mass spectrometry techniques are used
- Further establishing DESI-MS as a tool for gathering forensic evidence for both chemical and biological materials
- Using imaging capabilities to add visual information to the detected residues
- Designing a new miniature DESI source and coupling it with emerging miniature mass spectrometry instrumentation for *in situ* use

Fast, easy, and reliable detection!



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