

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

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JOWOG 28 MAIN MEETING

Y-12 National Security Complex

June 29, 2011– Oak Ridge, TN



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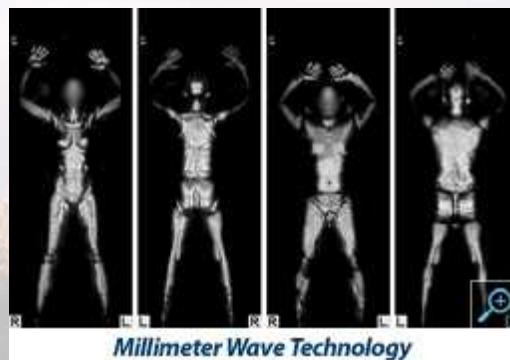


Problem to be Addressed

- 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

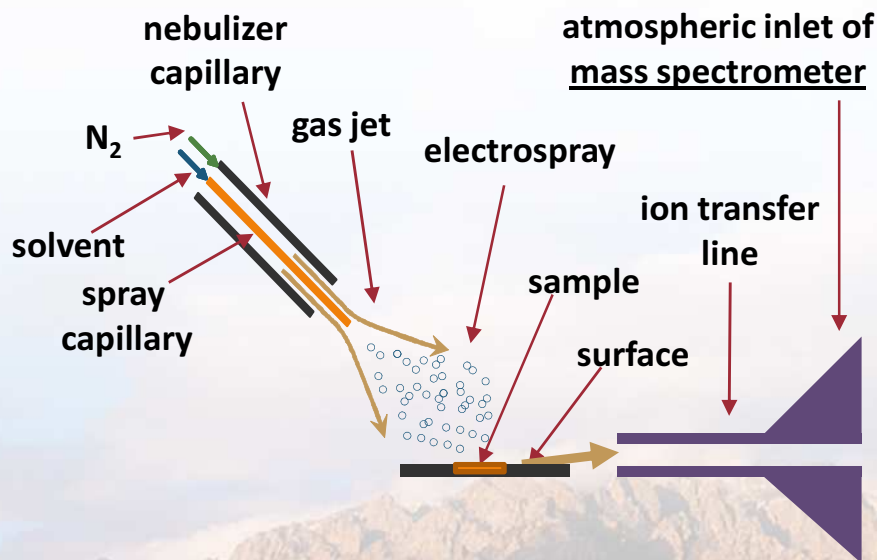


Possible Solutions for Explosives Detection

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™



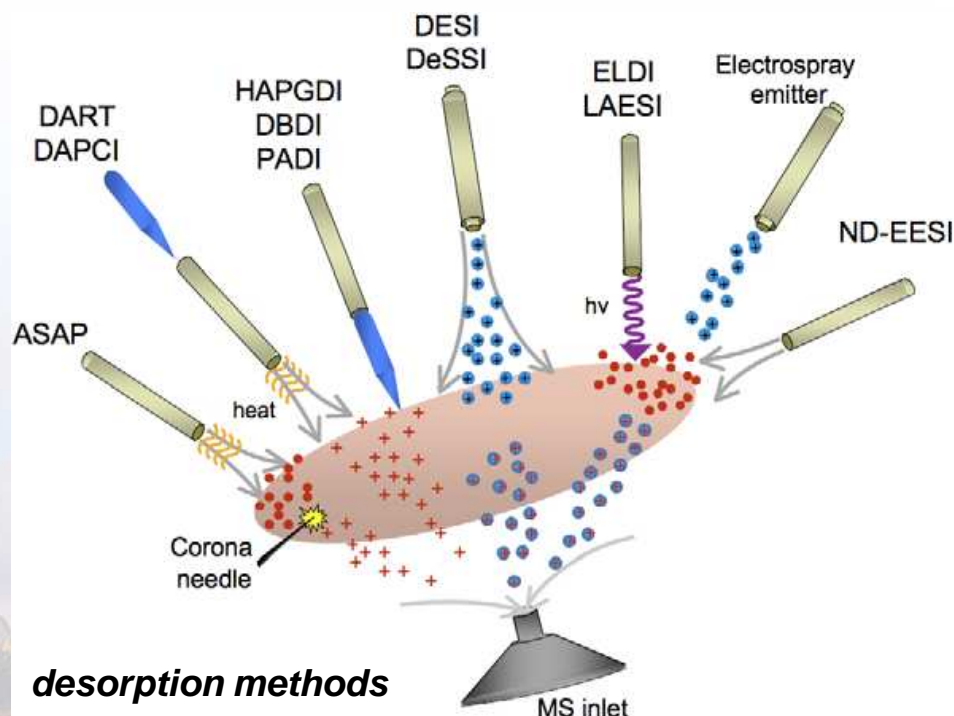
Fast, easy, and reliable detection!

Ambient Ionization Methods

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

Technology explosion!

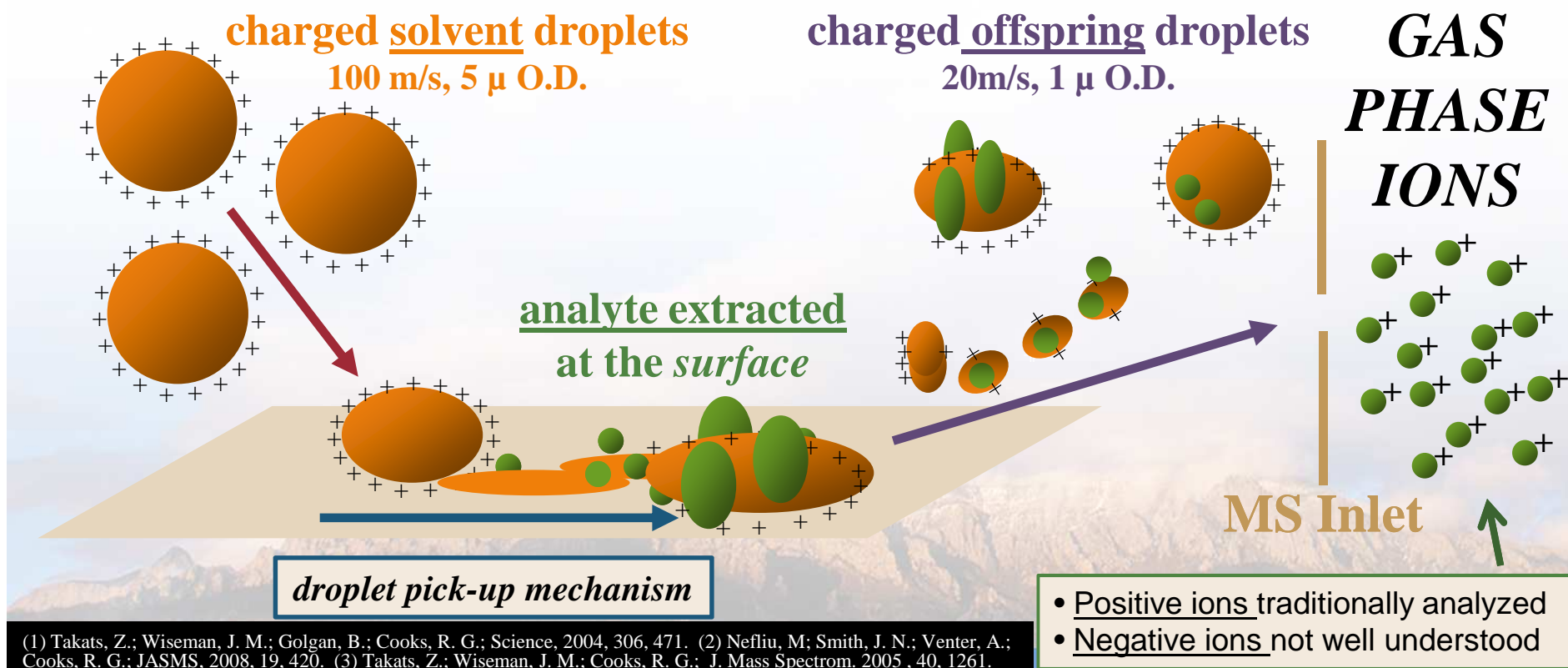
DESI	IR-LAESI
SSP	DAPPI
DART	APGDDI
ASAP	EASI
ELDI	RASTIR
FD-ESI	PESI
DAPCI	FA-APGD
AP-IR-MALDI	LTP
MALDESI	DEMI
JeDI	LM
EESI	SSP/ESI
DeSSI	SACI
APTDI	SPAMS
LAFAPA	LTP
PADI	DICE
DBDI	LAMICI
ND-ESSI	EASI
LDTD	
LAESI	and more...



desorption methods

Desorption Electrospray Ionization (DESI)

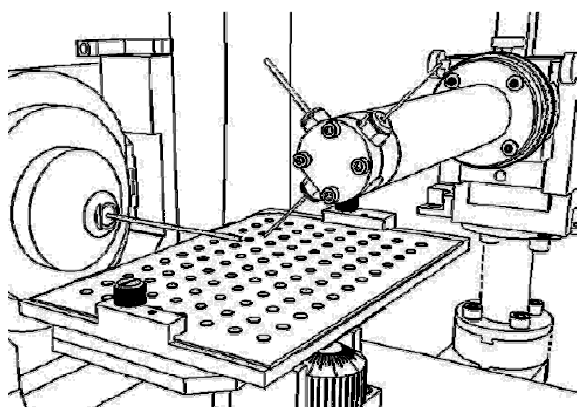
- Simple, sensitive, gentle, and versatile
- Rapid and direct sample analysis
- Little to no sample preparation
- Ambient temperature and pressure
- Can be optimized for a wide range of applications



Example DESI Applications

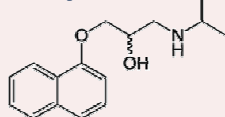
High-Throughput Quantitative Analysis

96-sample array



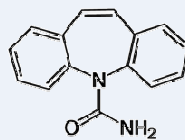
Analysis time = 1.5 s/sample

Propranolol



RSD = 3%
LOD = 10 fmol

Carbamazepine



RSD = 5%
LOD = 30 fmol

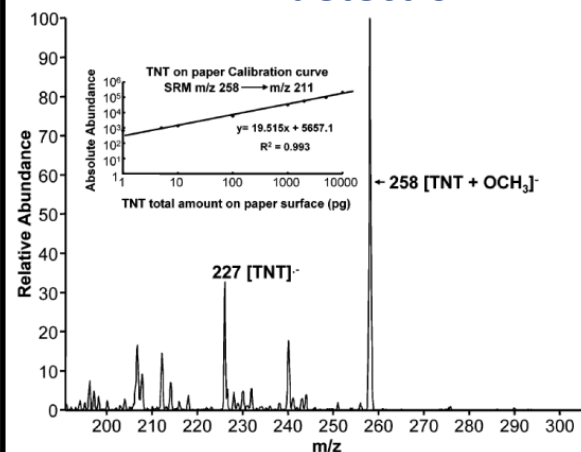
N. Manicke *et al.*, *J. Am. Soc. Mass Spectrom.* 20, 321 (2009)

- 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

- 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

In Situ Trace Detection of Explosives

TNT detection



LOD: sub-picogram for TNT

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





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

Applications for DESI at Sandia

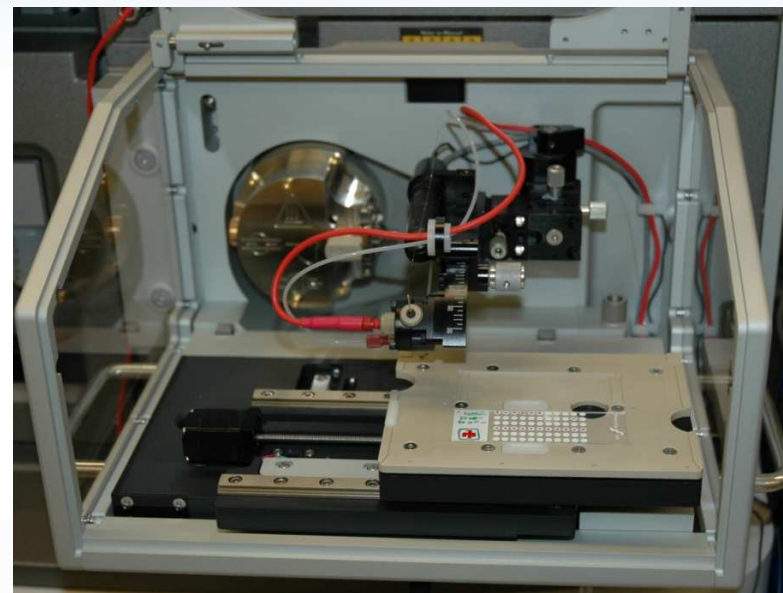
- **Early detection and characterization of home-made explosives (HME)**
 - Extremely important to the Department of Homeland Security (DHS)
 - Safety and security reasons make this an ideal research area for national labs
- **Possible areas of interest**
 - Materials aging and degradation studies, possible 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**



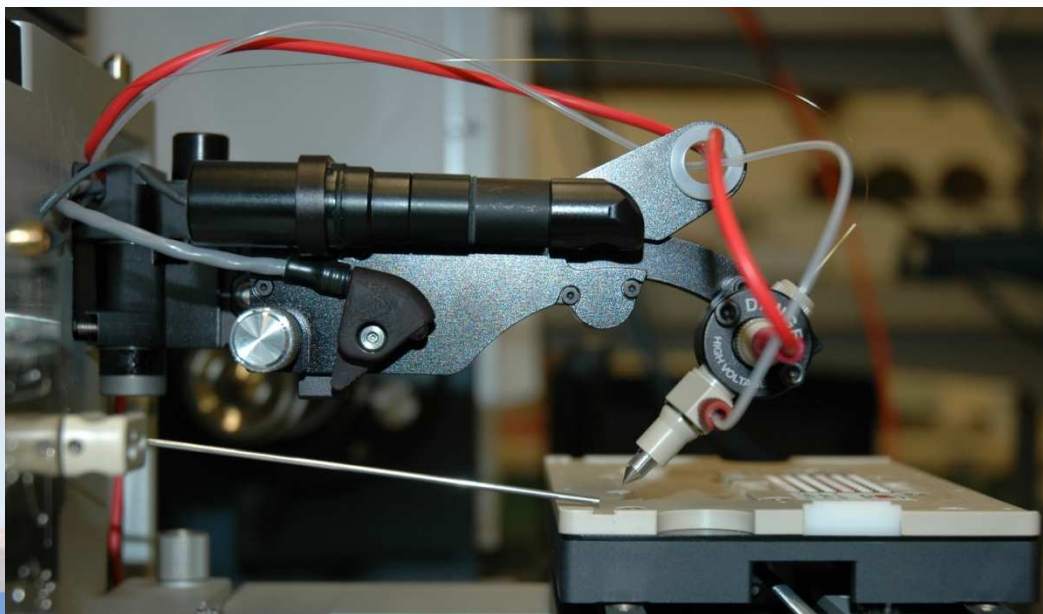
DESI Imaging Equipment

■ 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



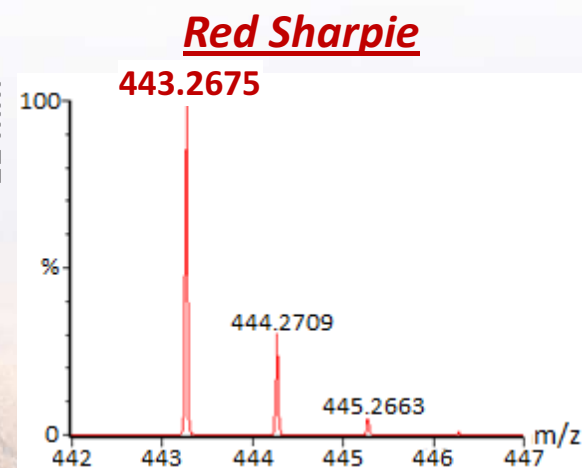
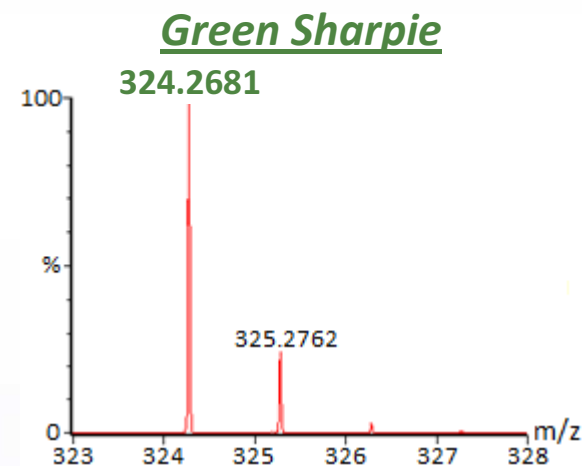
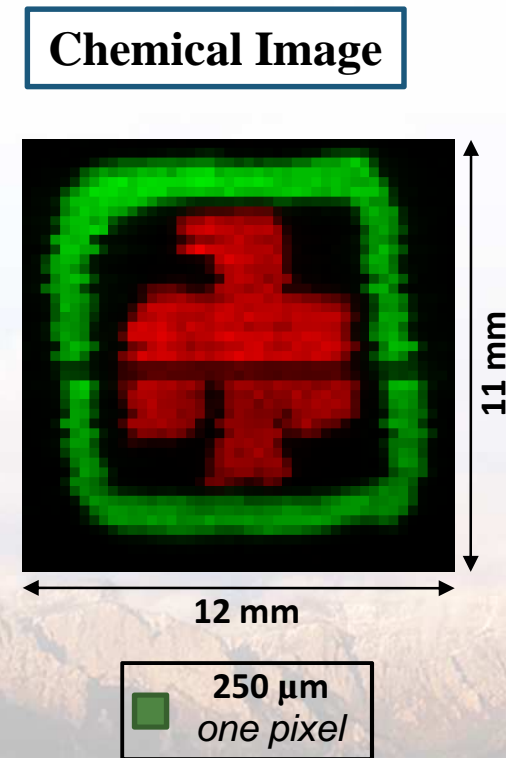
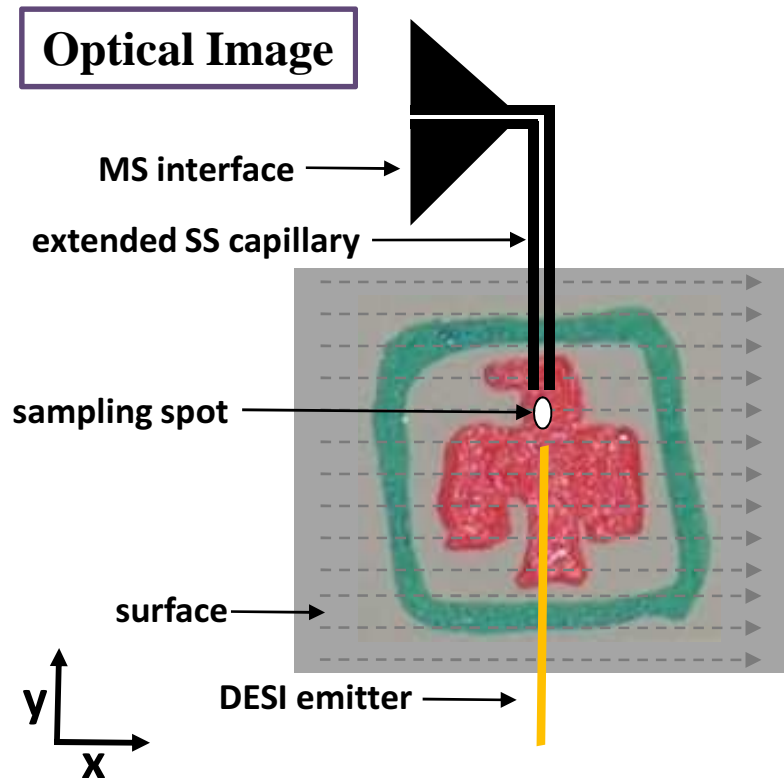
DESI Source

How DESI Imaging Works

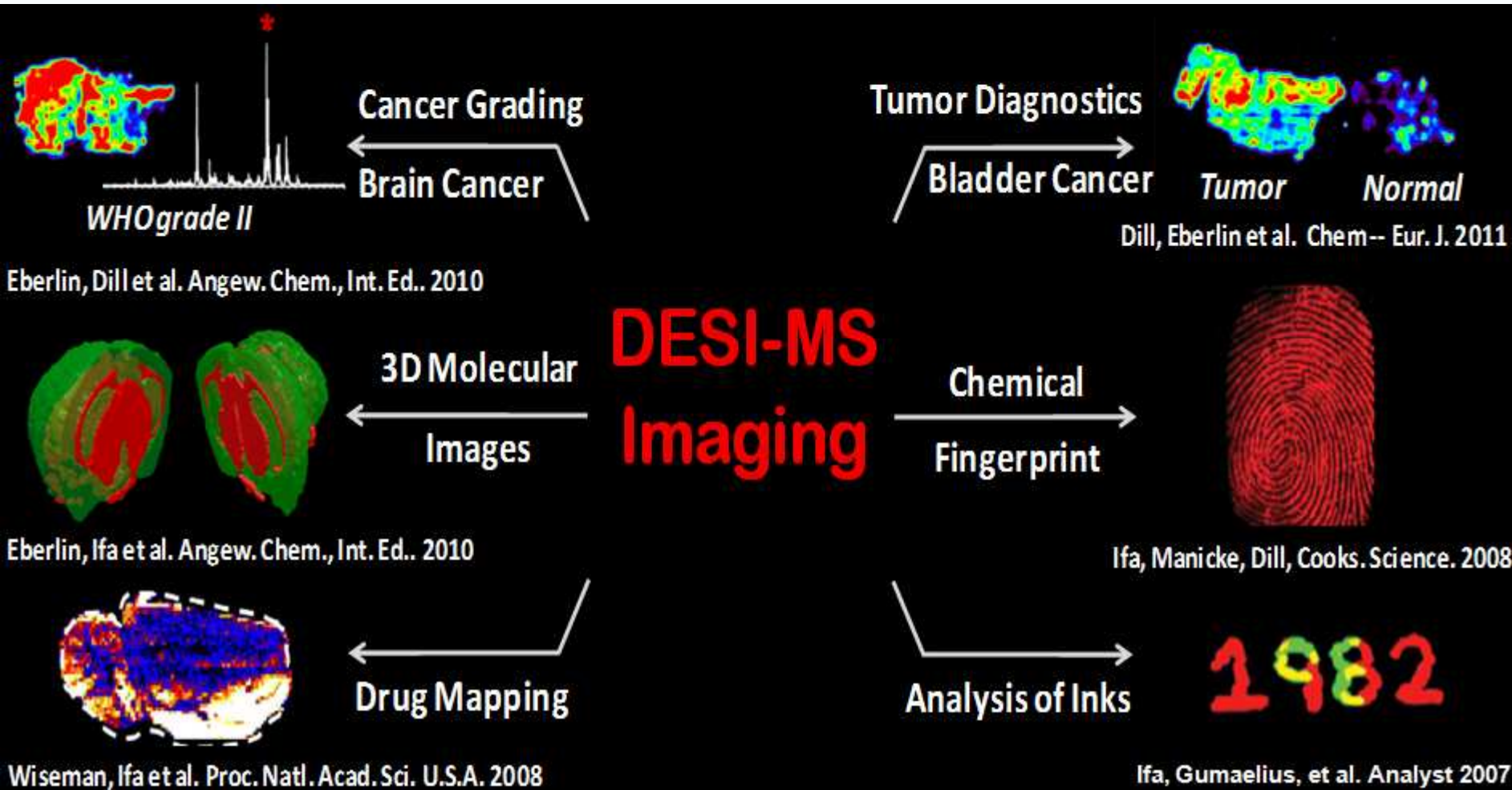
- Raster across the image from left to right then downward

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

- Visually map individual ions of interest



DESI Imaging Applications





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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