Unified Organic, Inorganic, and Morphological Analysis of Forensic Samples via SEM/TES

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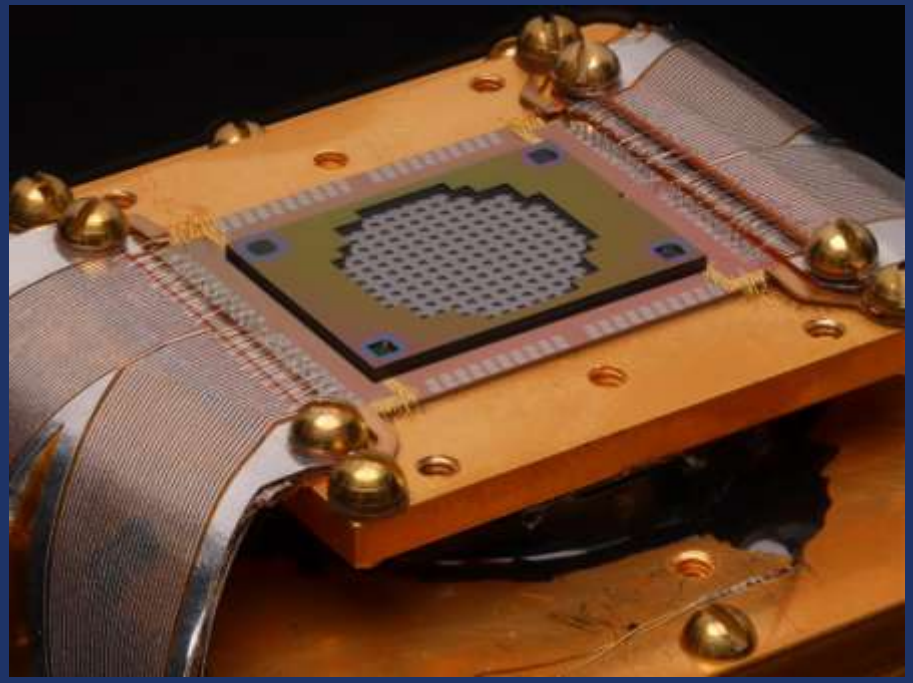
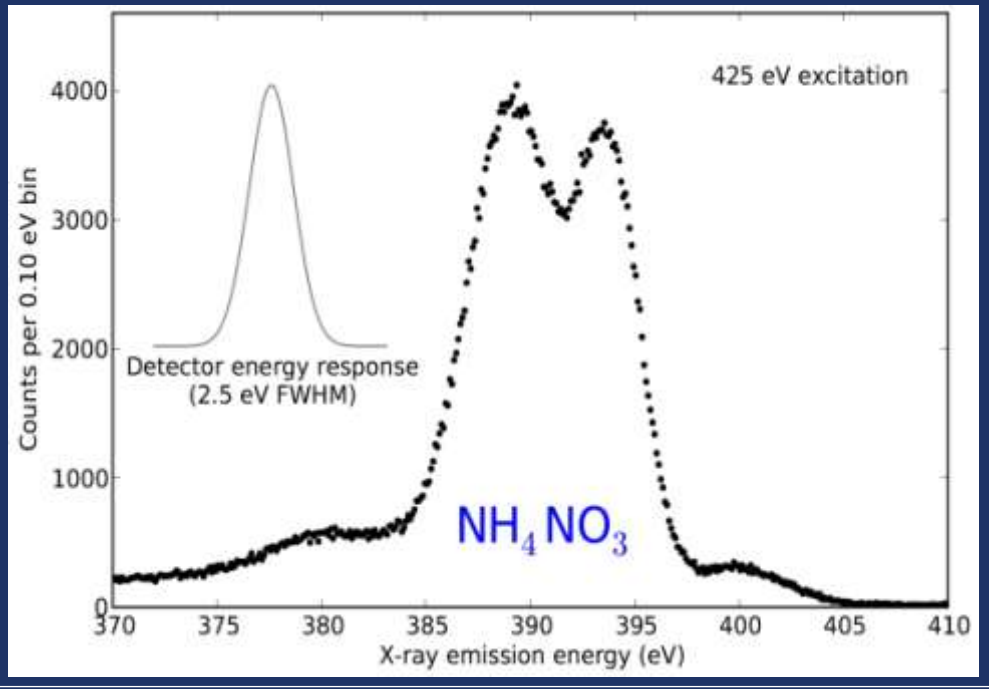
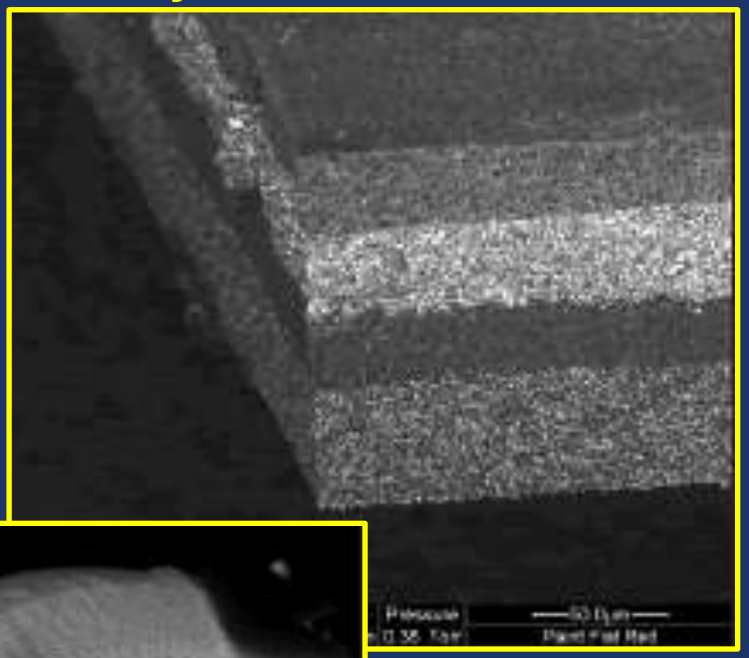
NIST (Boulder)

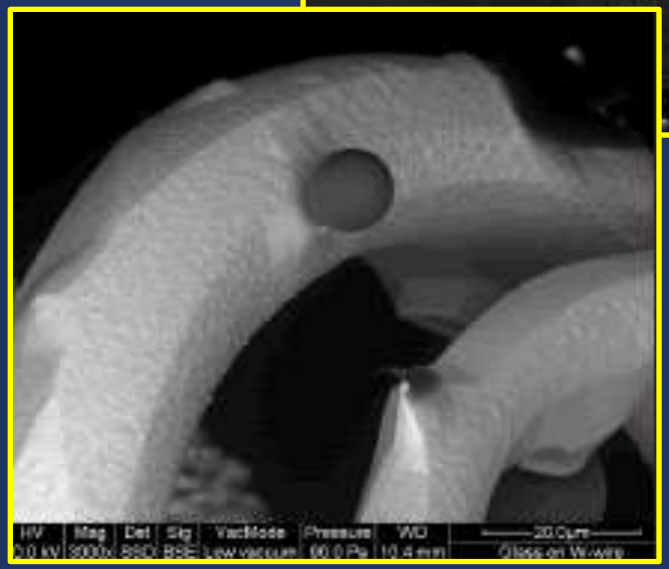




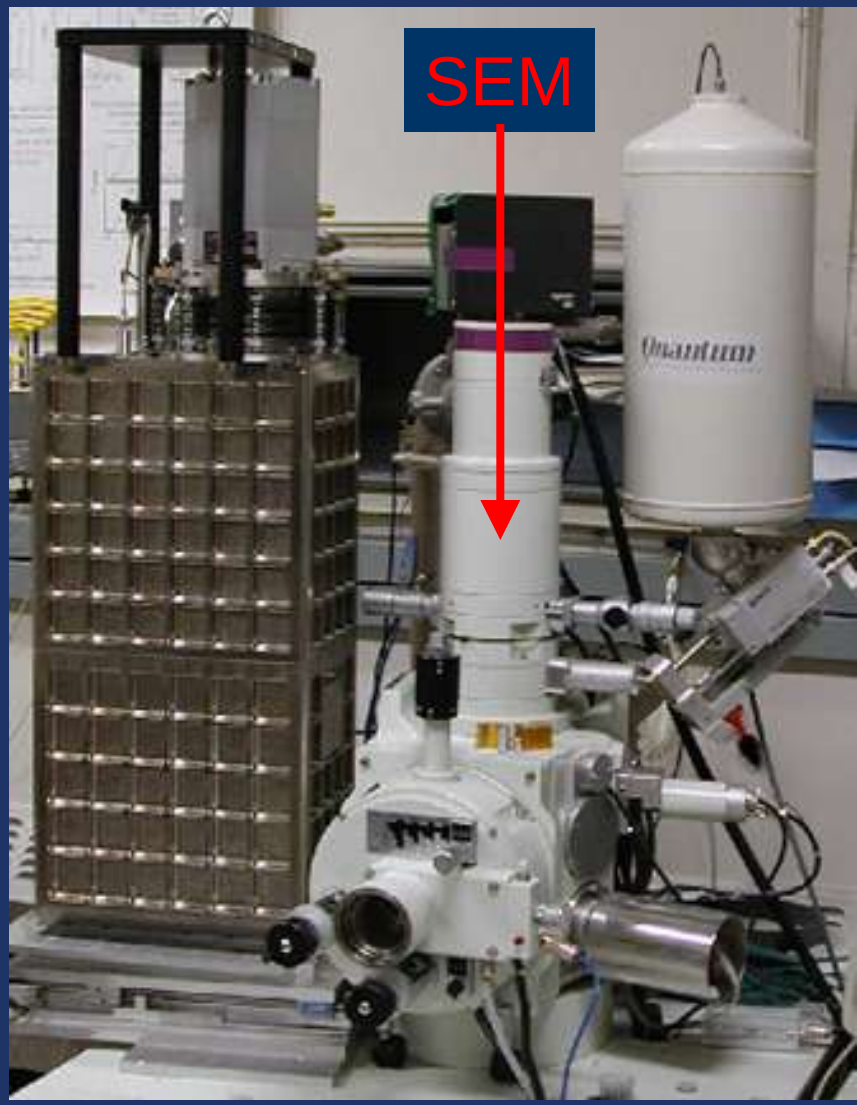
the basic idea…

SEMs are widely used in forensics.



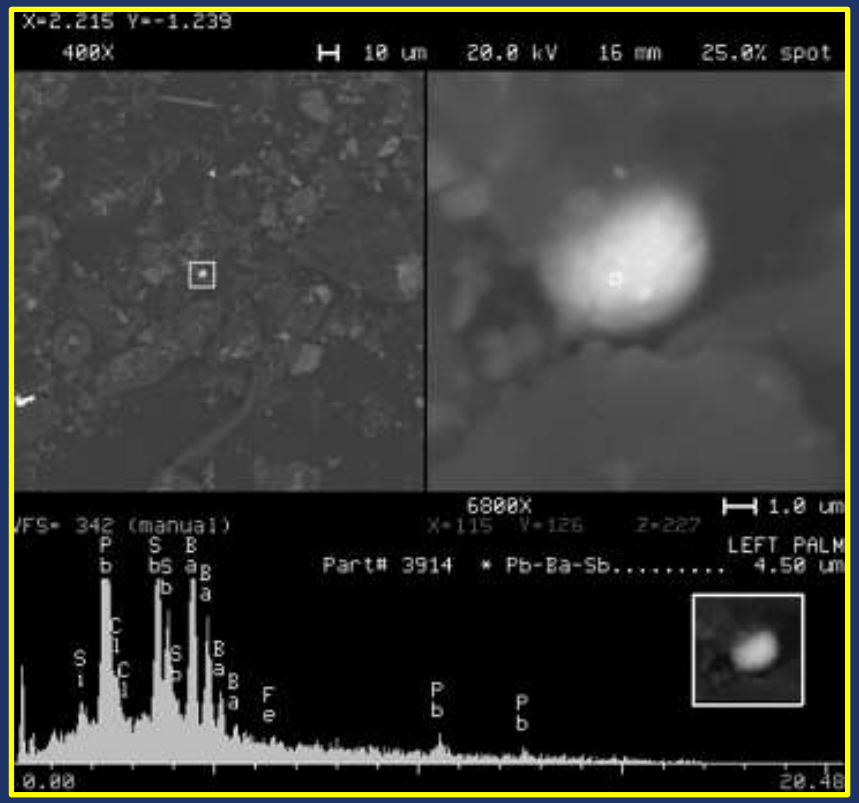


SEM images from
Forensic Magazine,
Dec., 2008
(Hans Kruesemann)

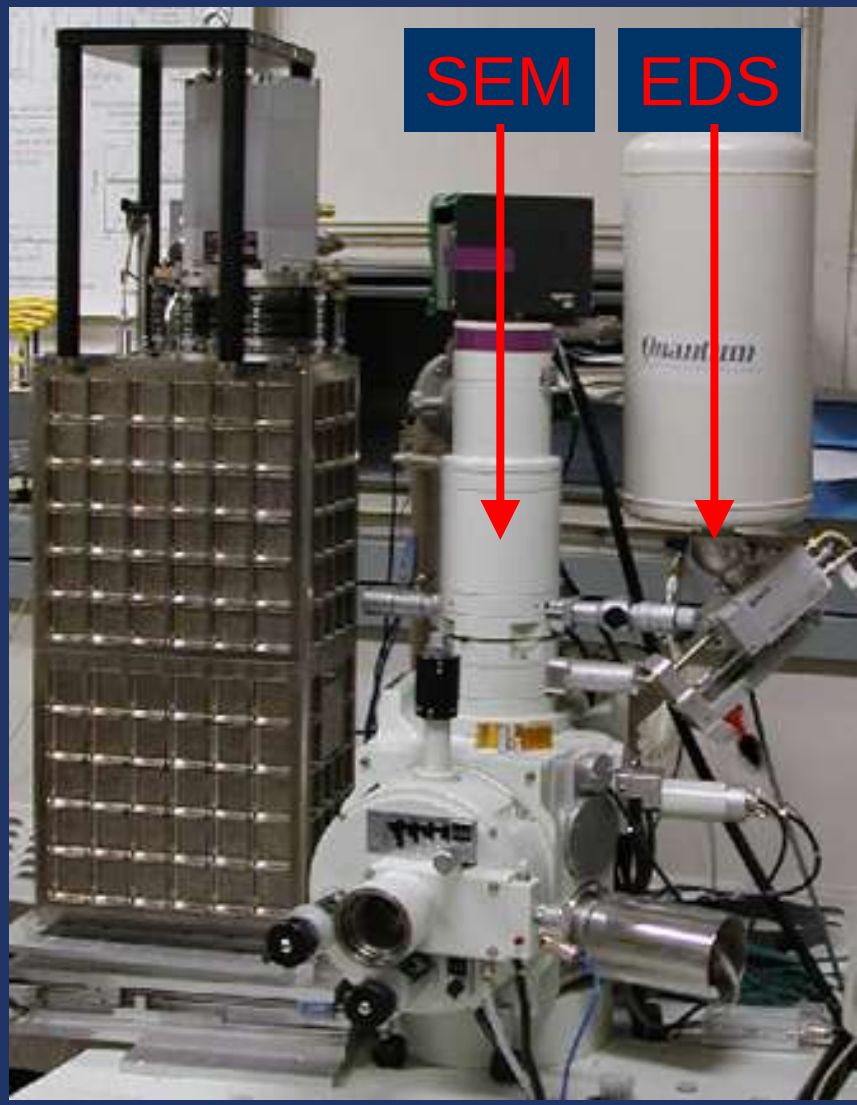


the basic idea…

A very common technique: energy dispersive X-ray spectroscopy (SEM/EDS) to analyze elemental composition.



data from Forensic Magazine, Sept., 2012
(Allison C. Murtha and Linxian Wu)



the basic idea…

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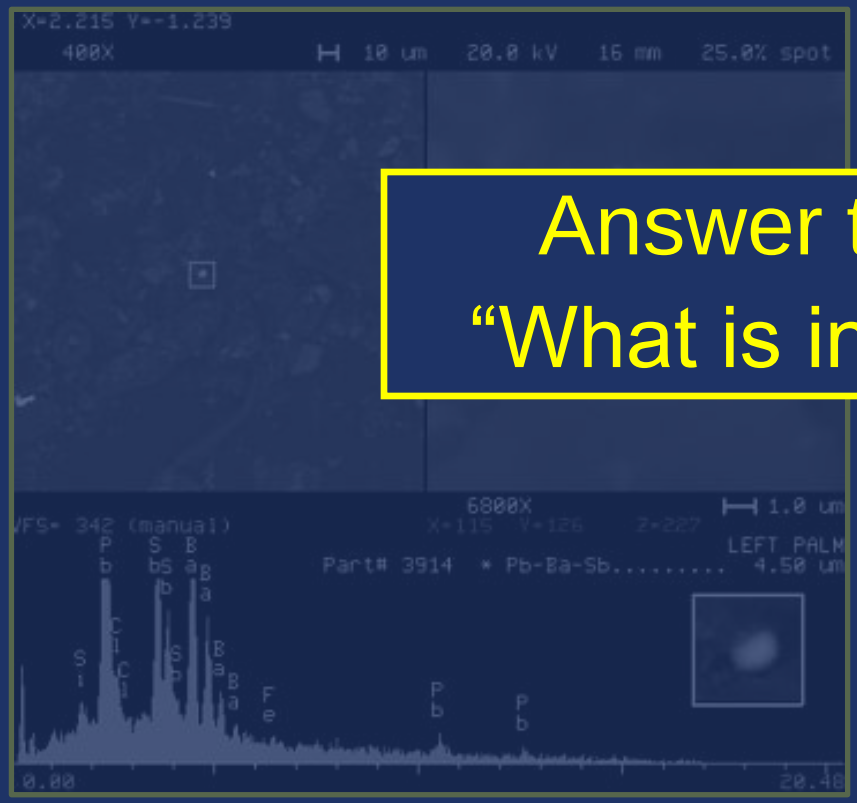


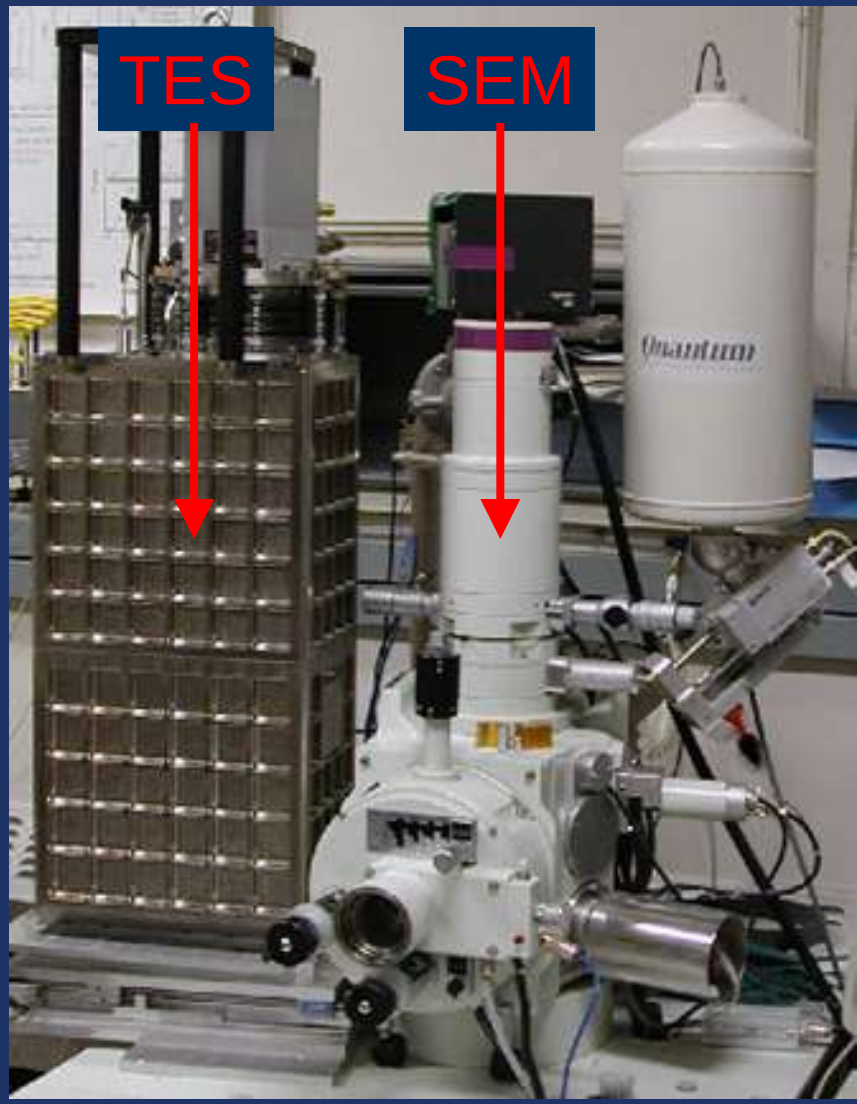
data from Forensic Magazine, Sept., 2012
(Allison C. Murtha and Linxian Wu)

Answer the question:
"What is in this sample?"

the basic idea…

Our proposal: replace standard EDS with NIST high-resolution TES X-ray spectrometer (SEM/TES)

- improved X-ray elemental analysis of inorganics.
- entirely new X-ray chemical-analysis method for organics
- retain imaging capability of SEM (small spots in context of whole sample)

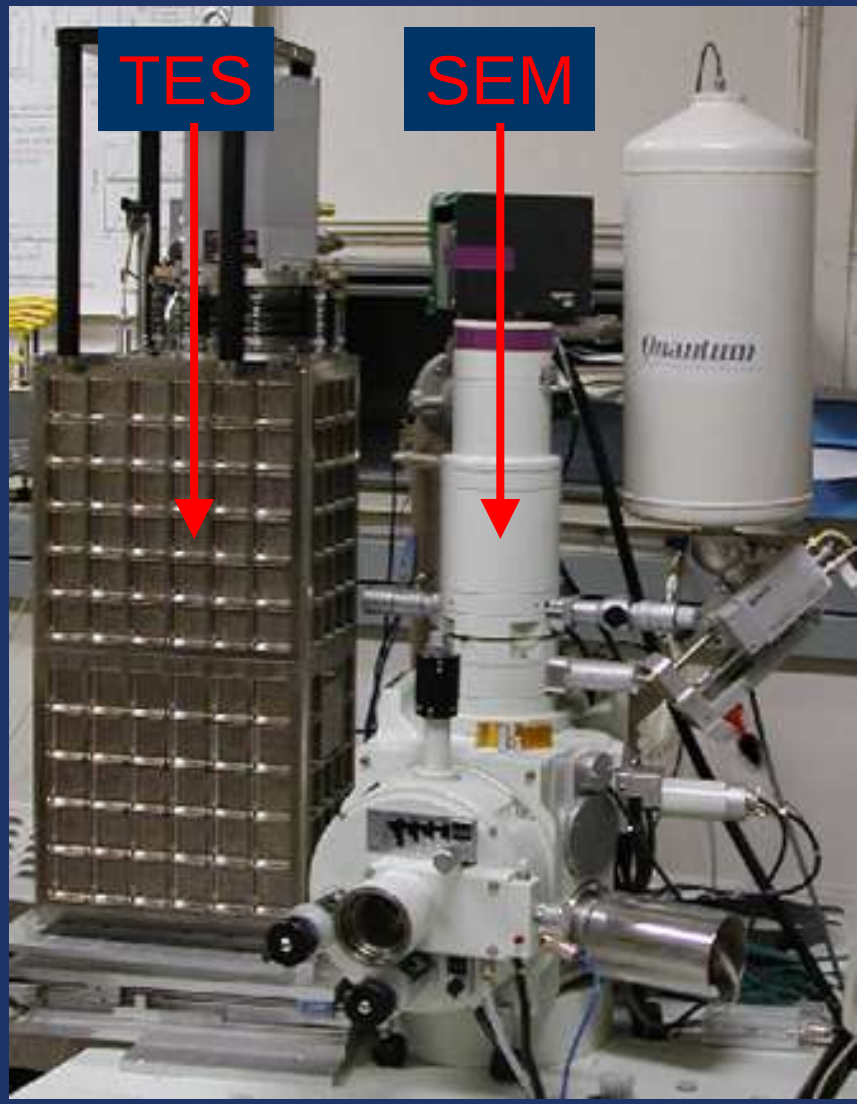


the basic idea…

Crime labs are almost always operated in a resource-starved condition (time; labor).

SEM/TES benefits:

- use same technique on many different kinds of samples/problems
- as a “first-look” method for mixed/unknown samples, may eliminate time-consuming, serial analysis steps



acknowledgements

Co-champions (NIST):

Kent Irwin, Joel Ullom (Quantum Electronics and Photonics Div., PML)

Terry Jach (Surface and Microanalysis Science Div., MML)

Forensics collaborators:

Robin Cantor, Ad Hall (Star Cryoelectronics, Santa Fe, NM)

John Rehr (University of Washington Physics Dept., Seattle, WA)

NIST TES team (Boulder, CO):

Brad Alpert	Jim Beall	Doug Bennett	Colin Fitzgerald
Joe Fowler	Gene Hilton	Rob Horansky	Vince Kotsubo
Luis Miaja-Avila	Carl Reintsema	Frank Schima	Dan Schmidt
Dan Swetz	Jens Uhlig	Leila Vale	

Synchrotron team (NIST / NSLS) (Brookhaven, NY):

Daniel Fischer	Cherno Jaye	Bruce Ravel	Joe Woicik

acknowledgements

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Bill MacCrehan, Greg Gillen, Matt Staymates,

Tom Bruno, Brian Brass (NIST)

outline

1. SEM/EDS vs. SEM/TES.
2. Elemental analysis of inorganics.
3. Chemical analysis of organics.
4. Identification of unknown threat powders.
5. Detection of gunshot residue (GSR).

silicon-drift detector

The silicon drift detector (SDD) is a semiconductor X-ray spectrometer.

- impinging X-ray creates electron-hole pairs
- size of resulting signal pulse proportional to X-ray energy.

(image from Amptek website)

silicon-drift detector

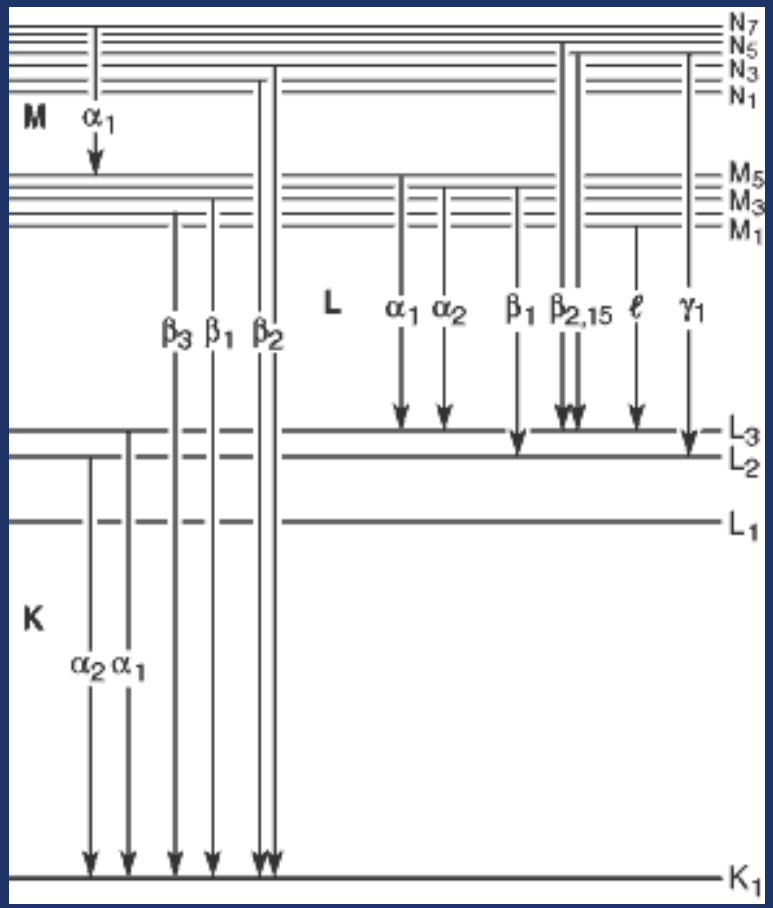
The silicon drift detector (SDD) is a semiconductor X-ray spectrometer.

- is called an “energy dispersive spectrometer” (EDS) because it uses no λ-dispersive elements (gratings, crystals)

(image from Amptek website)

SEM/EDS

SEM/EDS uses characteristic X-ray lines to identify / quantify elements in sample.



(from “X-ray Data Booklet”)

(image from Amptek website)

SEM/EDS

SEM/EDS advantages:

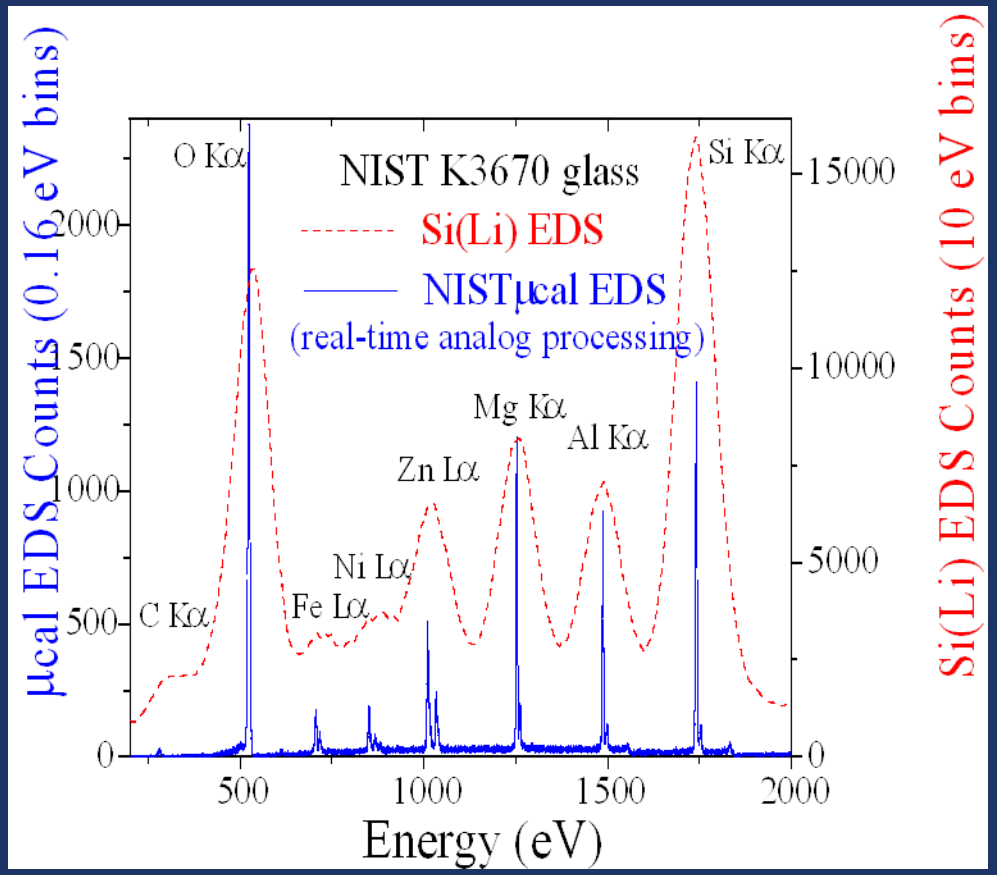
- large collecting area
- high QE
- acquire entire spectral ROI at once
- fast electronic response
- ubiquitous commercial avail.
- large body of literature on spectral interpretation
- little sample prep required
- non-destructive of sample.

(image from Amptek website)

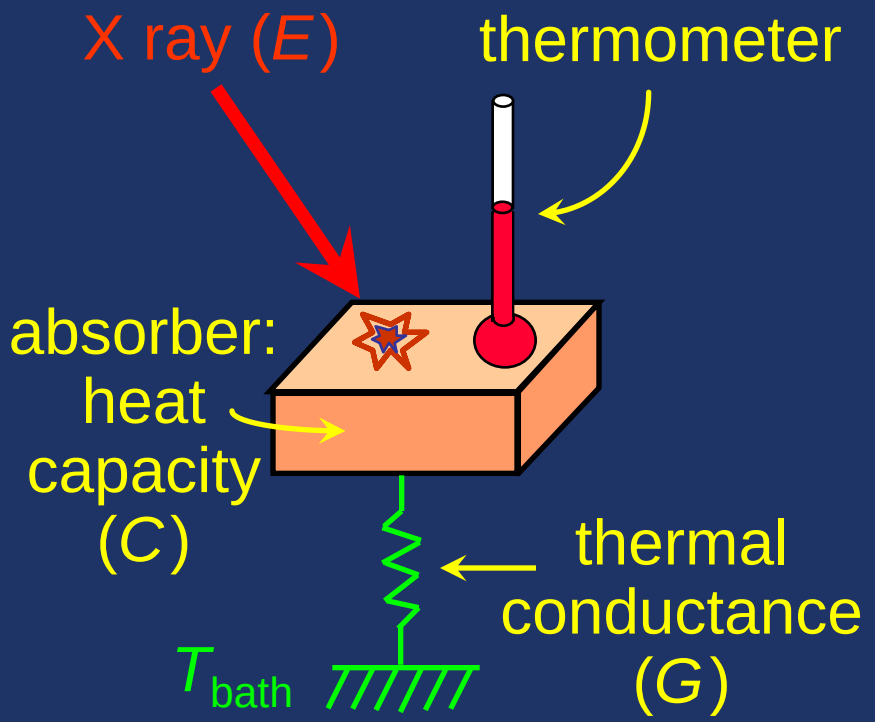
SEM/EDS vs. SEM/TES

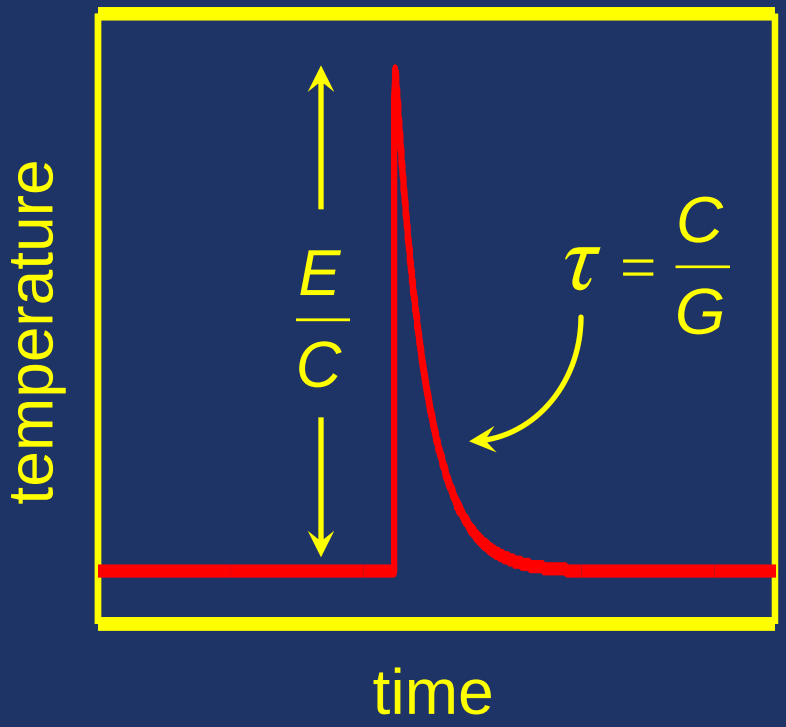
SEM/EDS main disadvantage:

- energy resolution limited to ~125 eV (FWHM, @ 6 keV)
- by contrast, NIST's TES spectrometer achieves ΔE ~ a few eV.

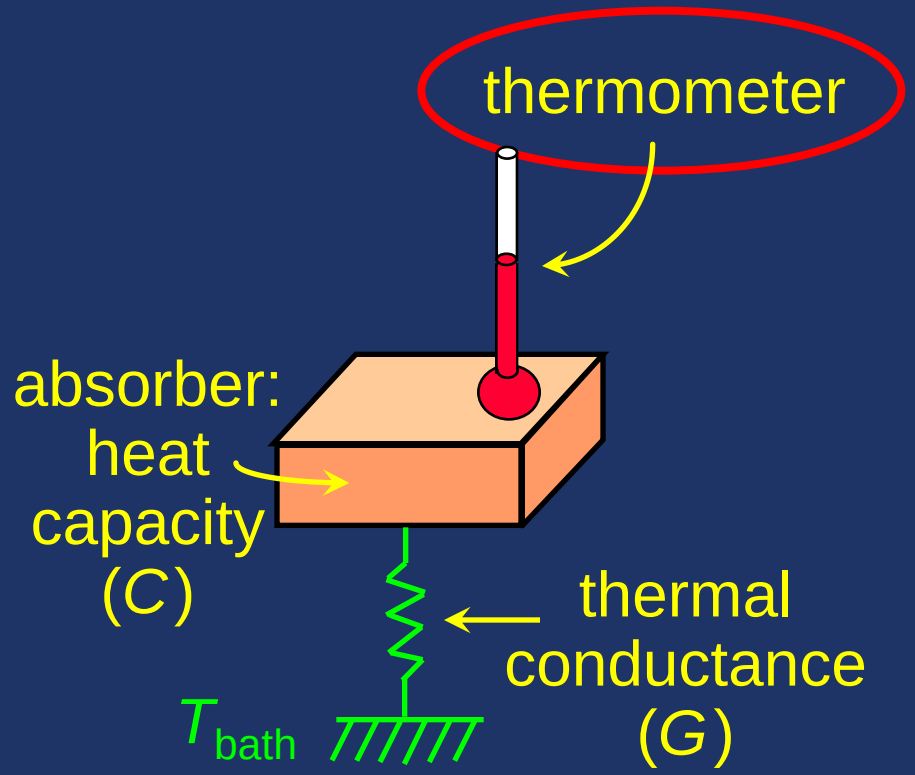


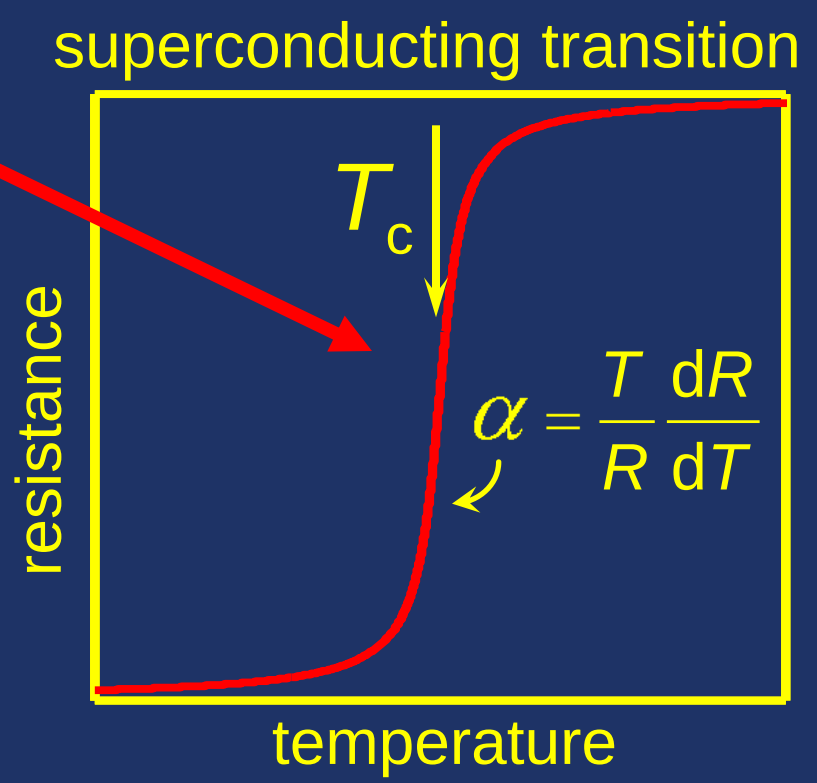
microcalorimeter basics





transition-edge sensor (TES)



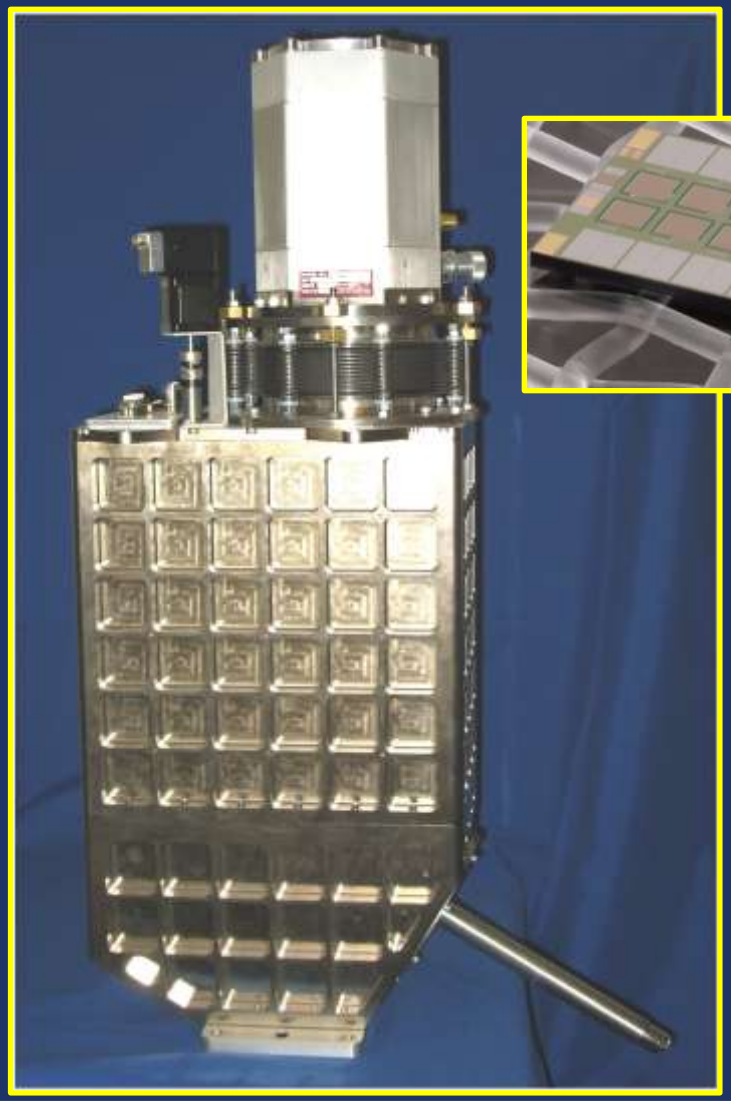


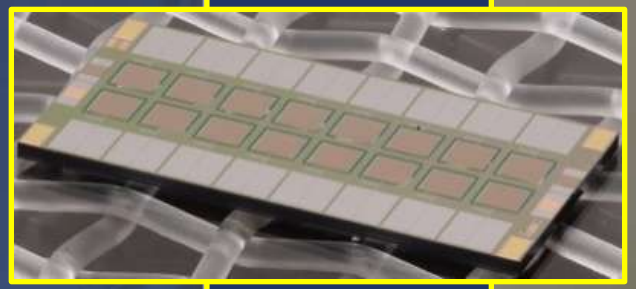
Energy resolution (Johnson & thermal fluctuation noise):

$$\Delta E_{FWHM} \sim 2.355\sqrt{\frac{4k_B T_c^2 C}{\alpha}}$$

Best ΔE → low T_c (~ 100 mK)
high α (~ 75)
low C (< 1 pJ/K)

SEM/TES commercialization





Star Cryoelectronics TES array on a Hitachi SEM

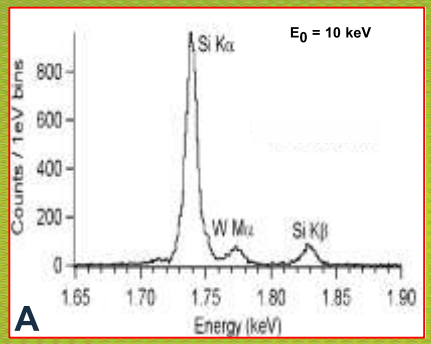
SEM/TES commercialization

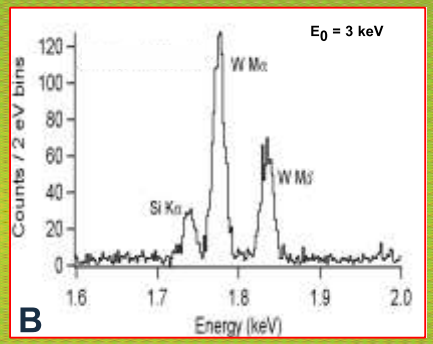
New! The MICA-1600 Microcal EDS

- **Provides Energy Resolution Better than 10 eV at 1.74 keV**
- **Performs at Count Rate of approximately 10 kcps**

The new MICA-1600 X-Ray Spectrometer from STAR Cryoelectronics is a next-generation EDS that combines conventional EDS with WDS resolution into a single instrument to provide the high resolution, throughput, uptime and ease-of-use required for materials characterization and analysis. Its unique microcalorimeter easily resolves line overlaps, detects light elements and characterizes the thinnest, smallest features at very low beam voltages.

NANOSCALE MATERIAL ANALYSIS SERIES





W, 20 NM ON SI SUBSTRATE

THE SPECTRA A AND B DEMONSTRATE CLEAR SI AND W PEAK SEPARATION. THE W/SI PEAK INTENSITY RATIO DEPENDENCE ON BEAM VOLTAGE DEMONSTRATES THE POWER OF MICA-1600 TO ANALYZE EVEN 20 NM FEATURES.

SEND US YOUR SAMPLES
TRY OUR NEW MICA-1600 DATA SERVICE WHERE WE TAKE YOUR SAMPLES, PROCESS IT AND GET YOU THE DATA YOU NEED...FAST!
CALL 408-722-8478 FOR DETAILS.

FOR MORE INFORMATION, CONTACT HIDEO NAITO, MARKETING DIRECTOR, STAR CRYOELECTRONICS TODAY AT 408-722-8478 OR MICROCAL@STARCRYO.COM

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• info@starcryo.com • www.starcryo.com

STAR Cryoelectronics

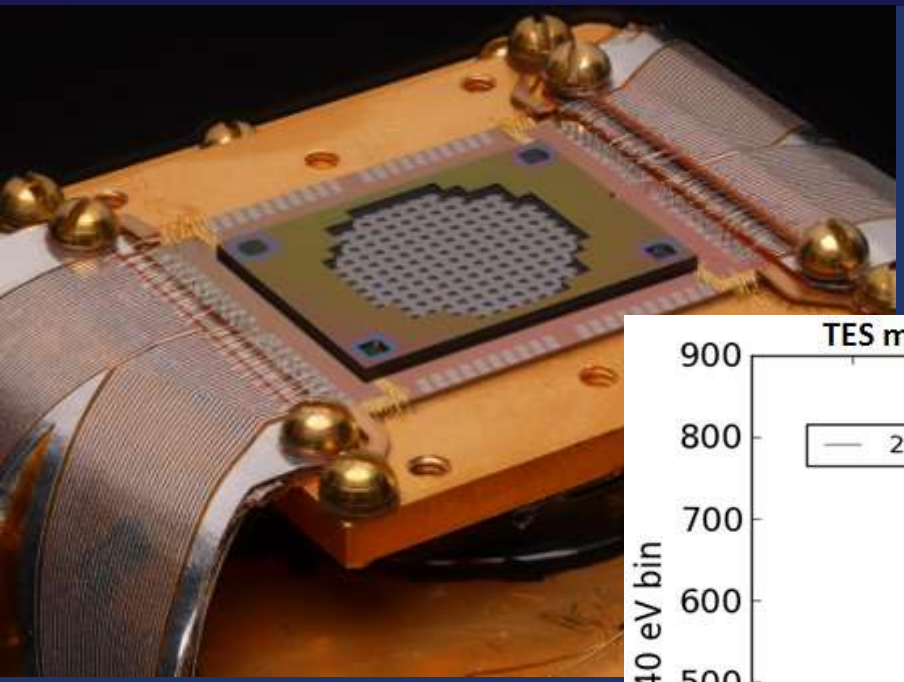
← recent ad in *Microscopy Today*

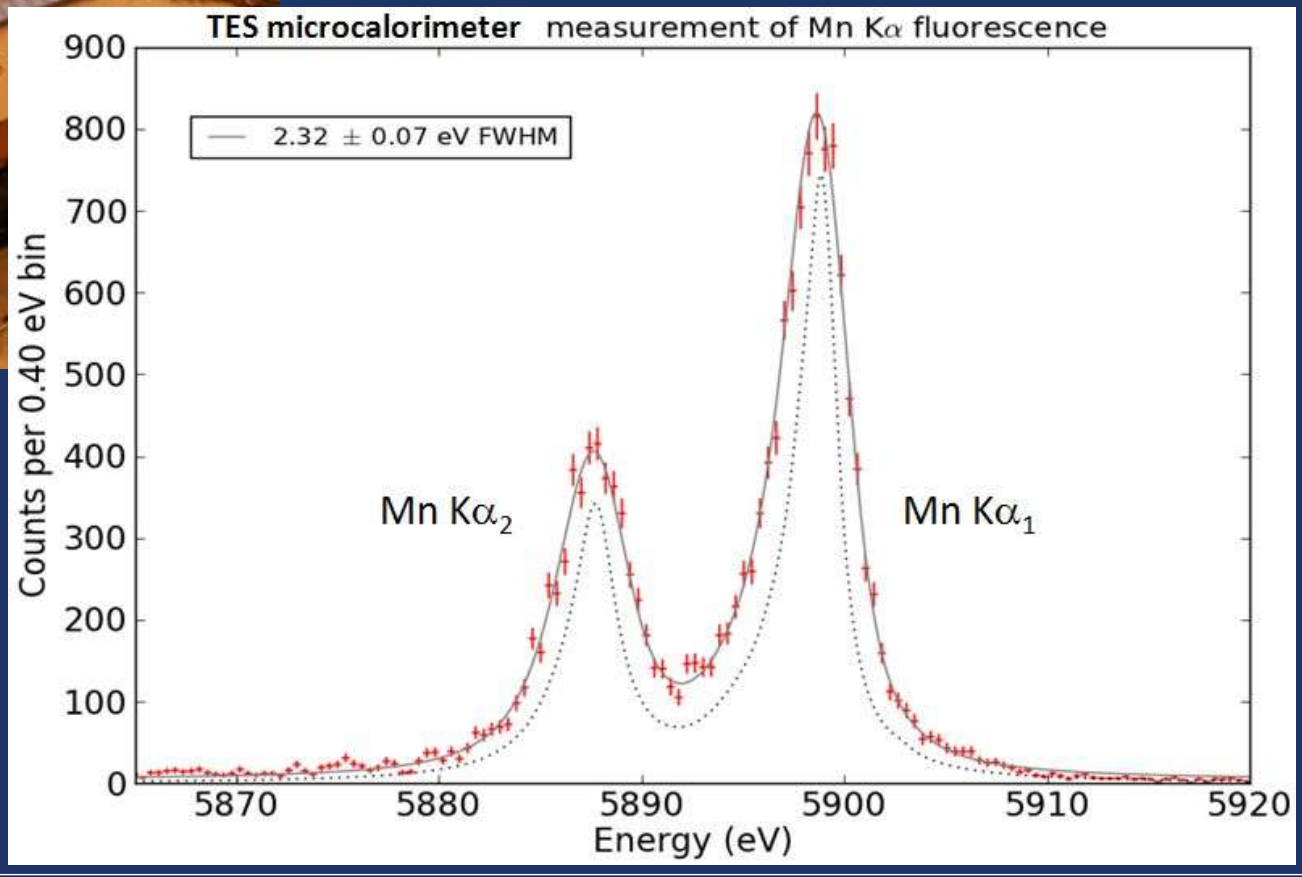
Star-Cryo TES specs:

- 16-element spectrometer
- ΔE ~ 10–15 eV (FWHM)
- count rates ~ 10 kc/s

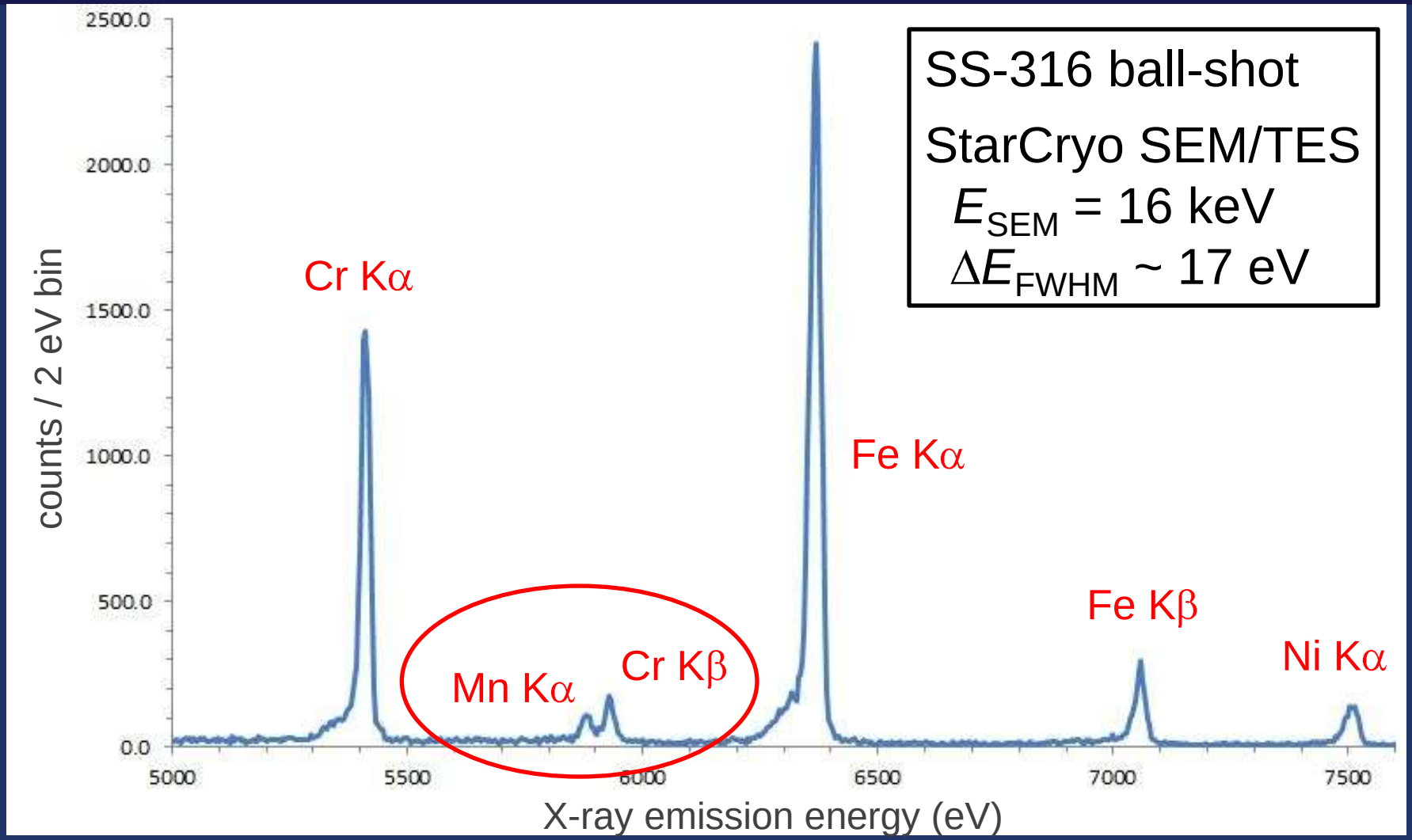
Possibly appropriate for mobile forensics labs!

continued NIST TES development



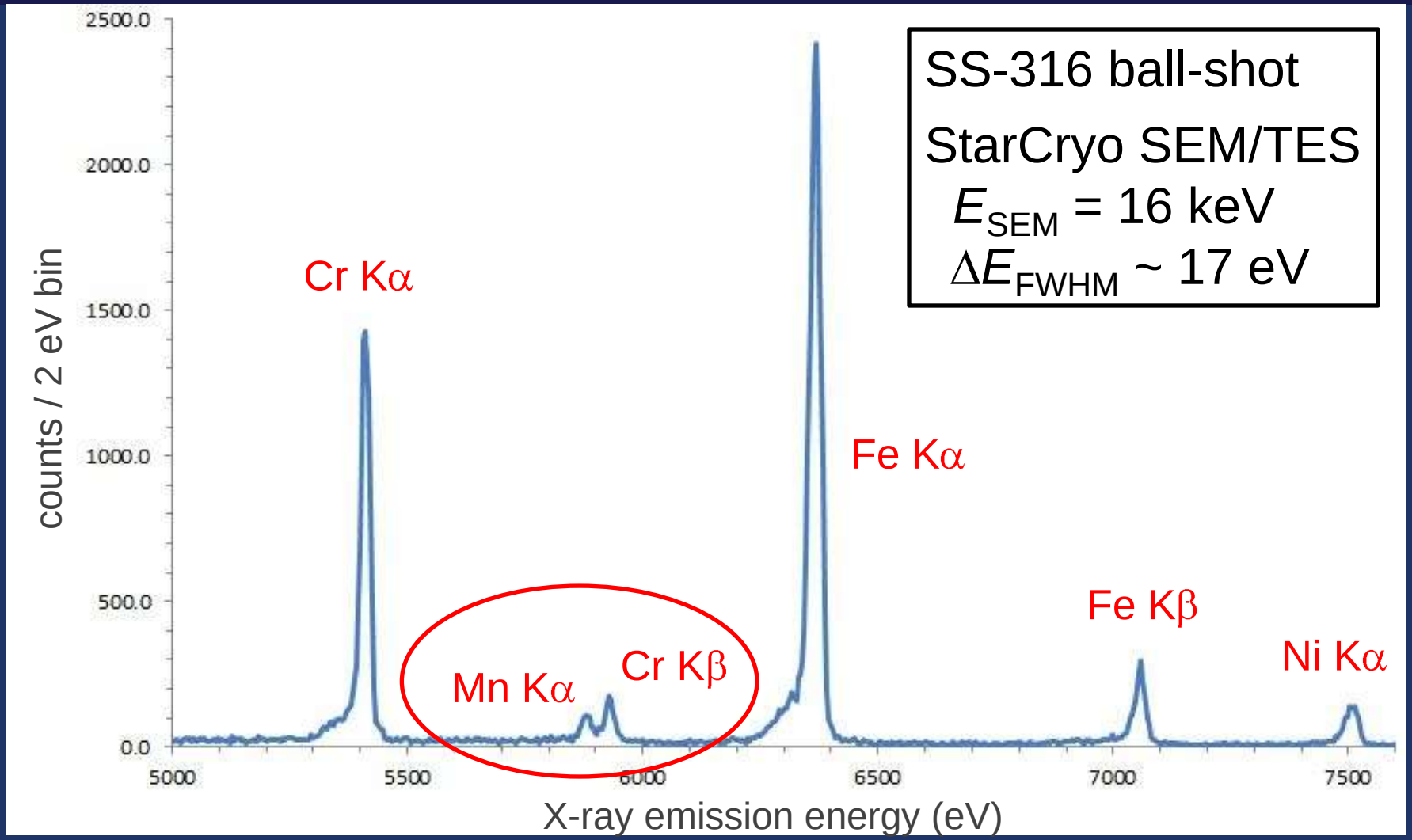


inorganic example #1: stainless-steel



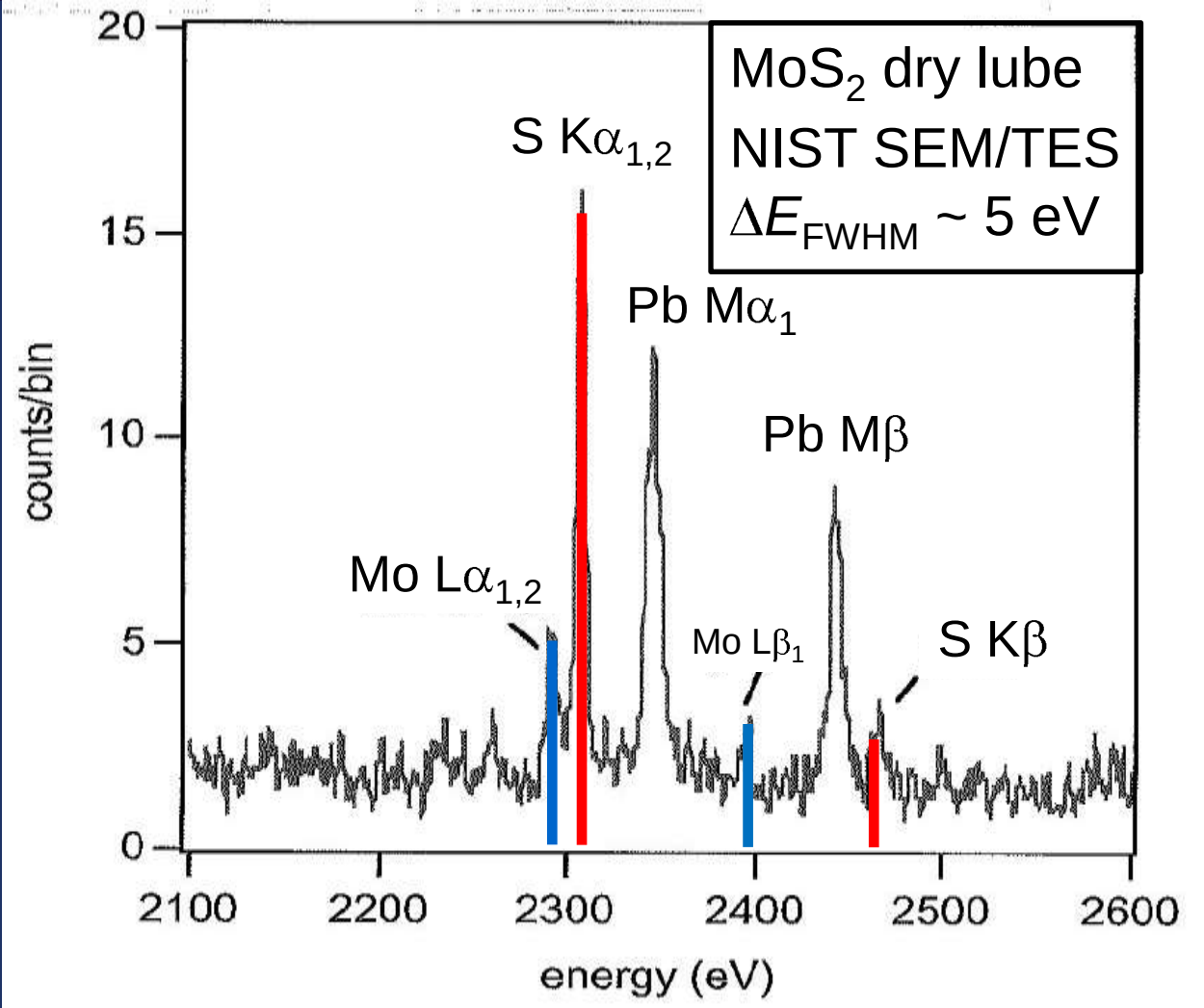
ID/quantify Mn in the presence of Cr?

inorganic example #1: stainless-steel



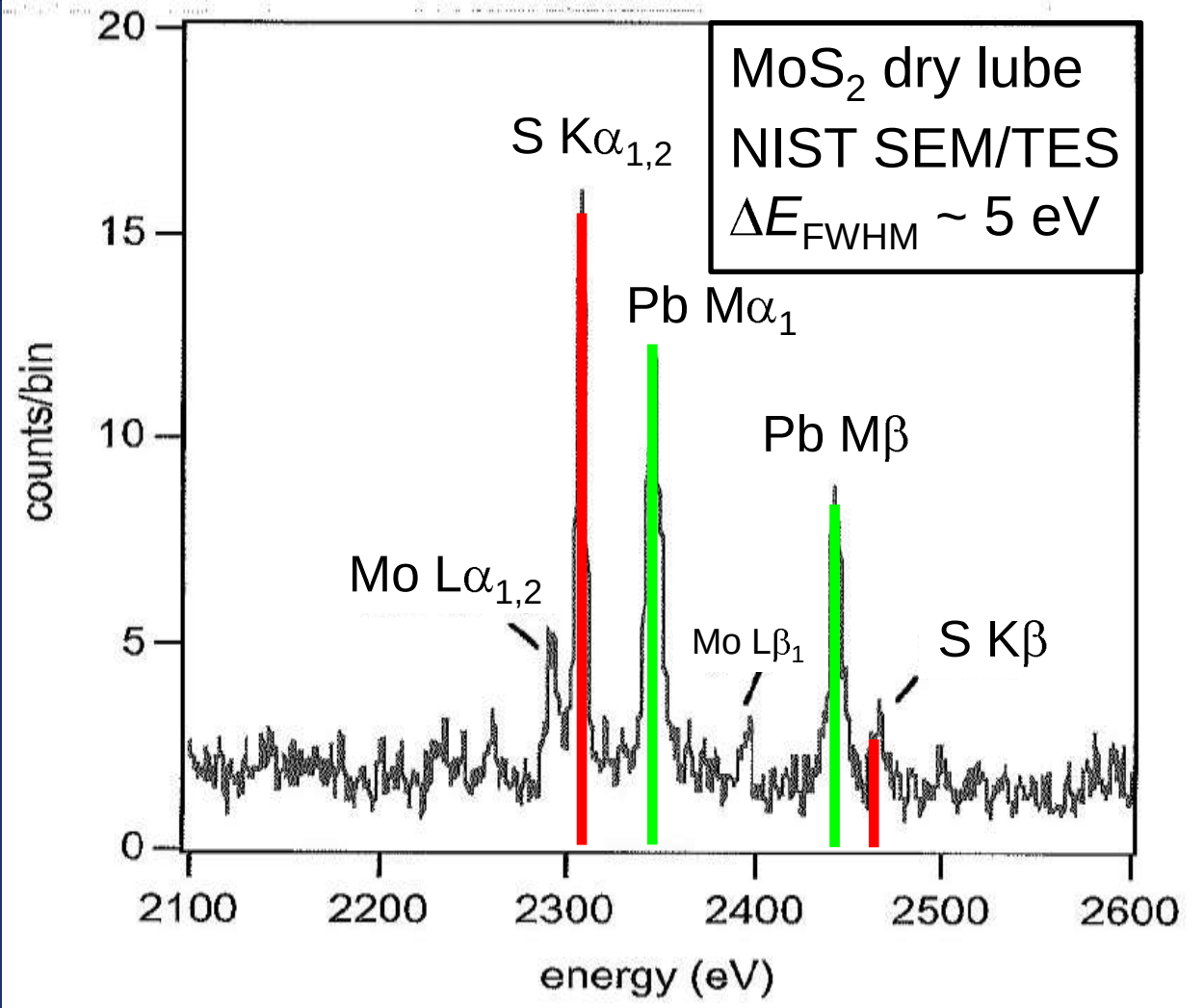
Forensics: SS-420 (knife blades).

inorganic example #2: S / Mo / Pb overlaps



ID/quantify S in presence of Mo (forensics: carbon steels)

inorganic example #2: S / Mo / Pb overlaps



co-ID/quantify S and Pb (forensics: copper alloys)

inorganic example #3: As content in Pb

In analysis of Pb bullet fragments, As content (typically 1–5 %) can ID the Pb alloy.

Crucial line overlap:

- As $K\alpha_1$ (10.544 keV)
- Pb $L\alpha_1$ (10.552 keV)

image from website of National Park Service

NIST SEM/TES should be able to resolve (no data yet).

organic chemical analysis

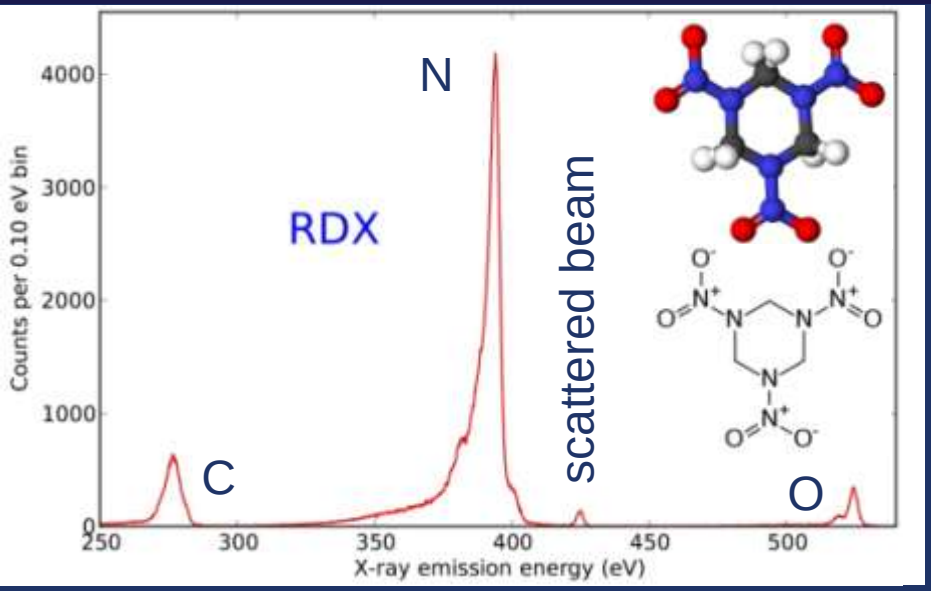
Organic chemicals all contain basically the same elements: C, N, O, and then S and some other stuff.

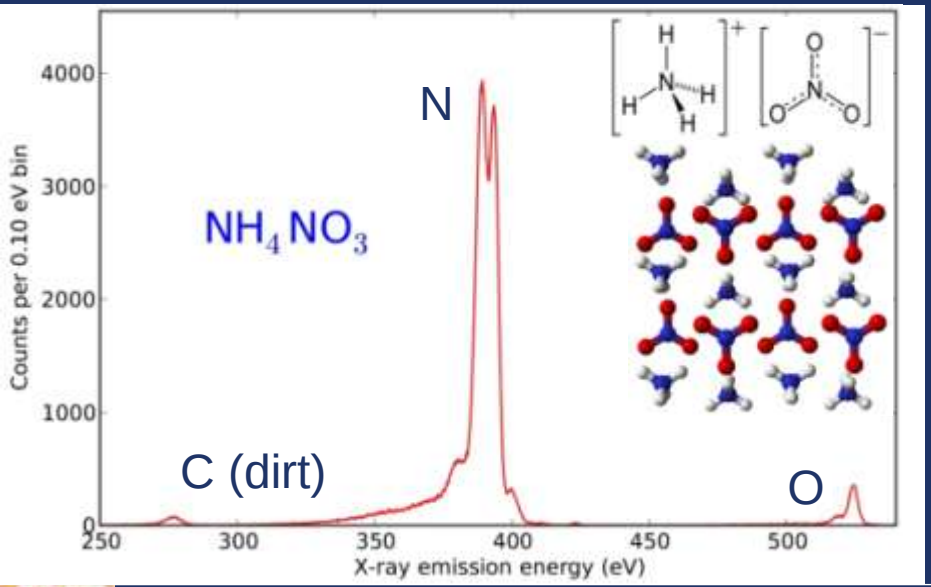
To ID them, you need to know the chemistry.

X-rays: need to measure few-eV shifts in line positions/shapes. THIS IS HARD!

Recently demonstrated with NIST TES spectrometer installed at the NSLS (synchrotron).

chemical-shifts in TES spectra



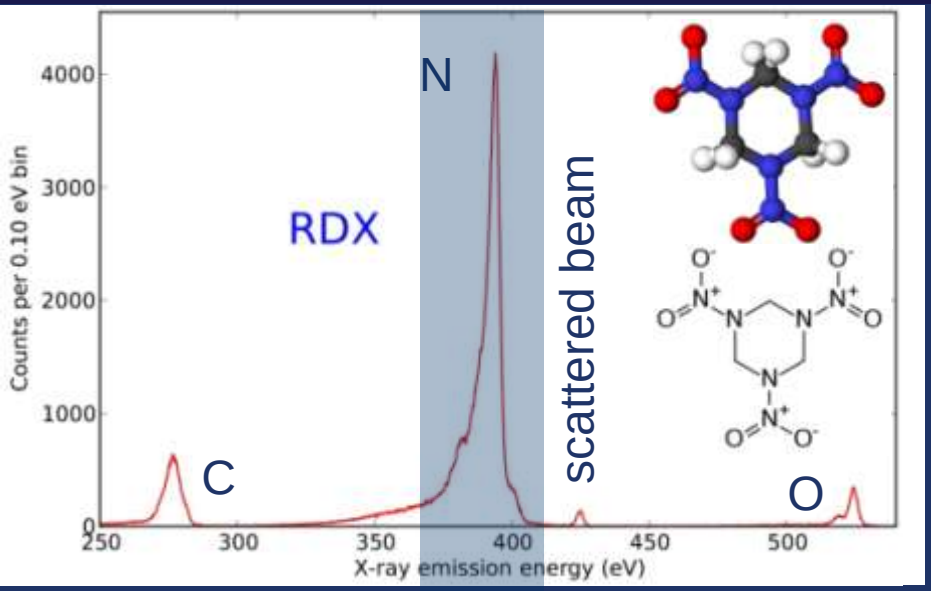


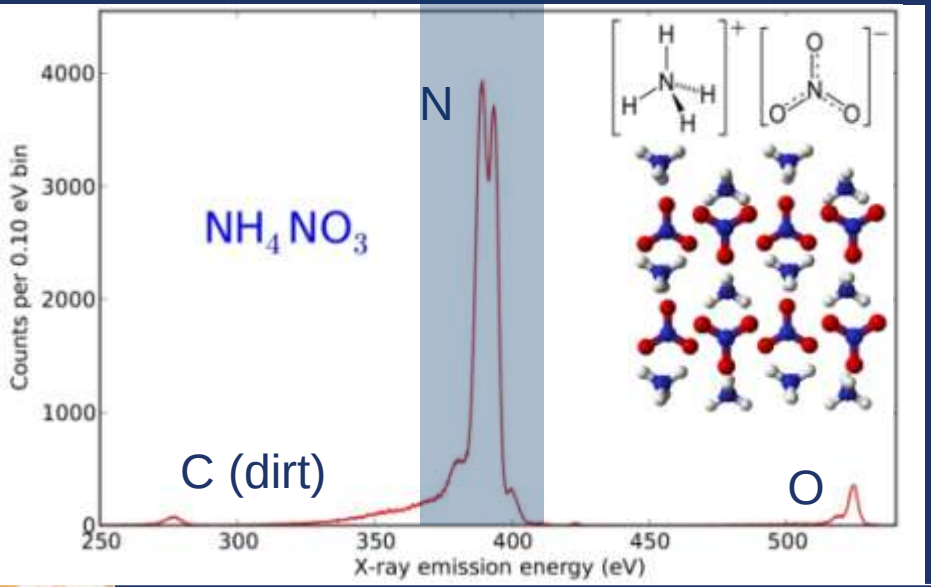
Observe two explosives at the NSLS synchrotron with TES:

- RDX: major component of C4 plastic explosive
- ammonium nitrate (fertilizer; can be used to build fertilizer bombs)

excite @ 425 eV
(well above N edge) to simulate excitation by SEM.

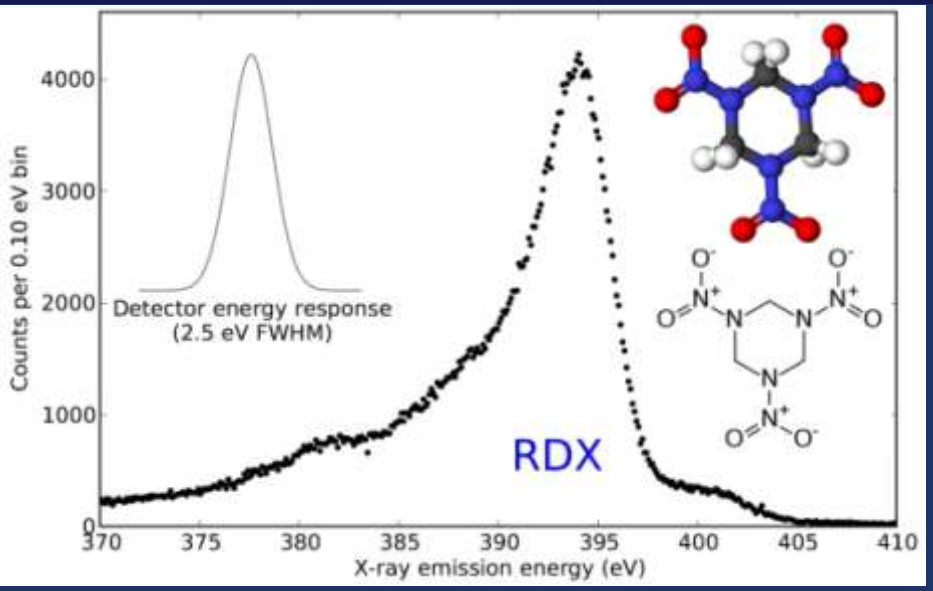
chemical-shifts in TES spectra

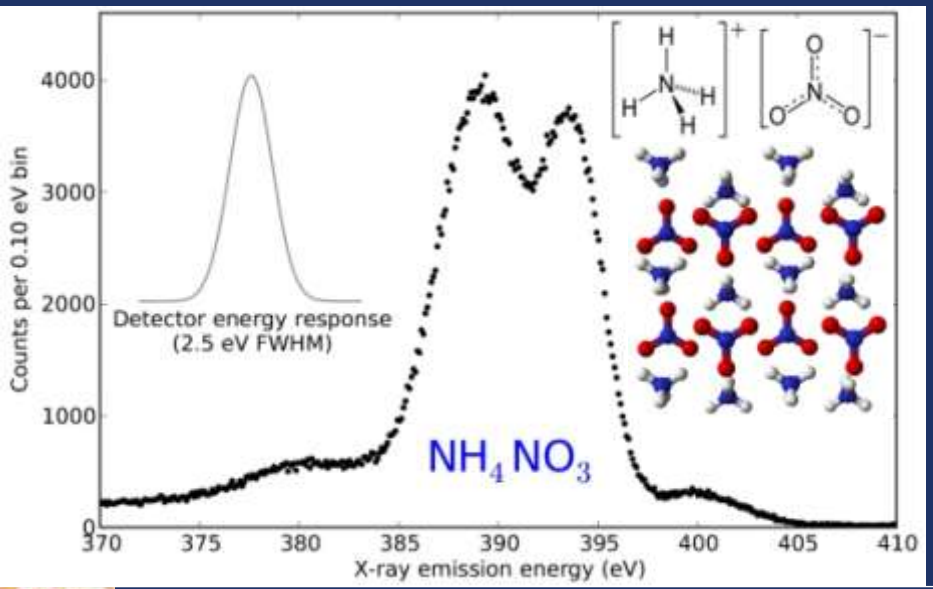




zoom in on nitrogen peak in each spectrum:

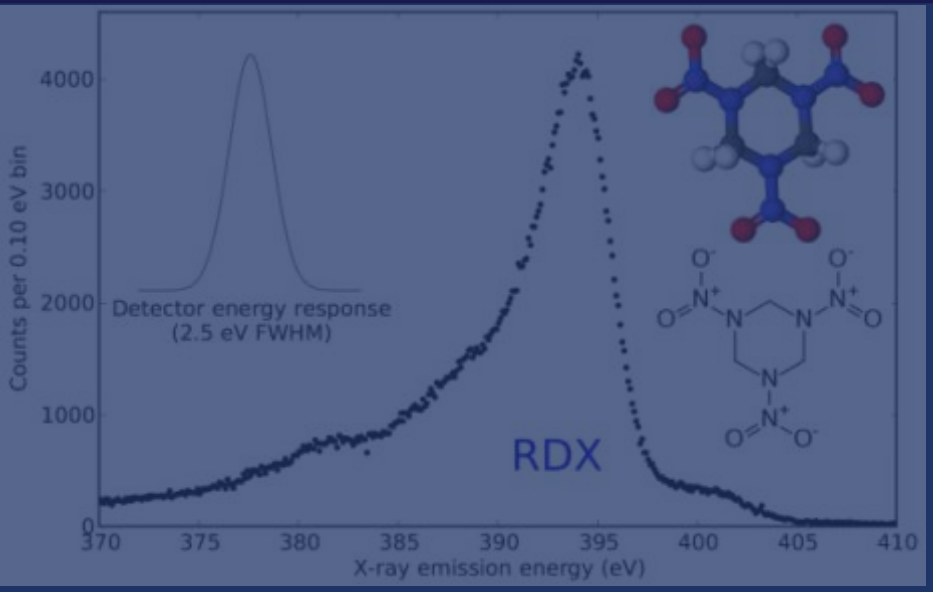
chemical-shifts in TES spectra

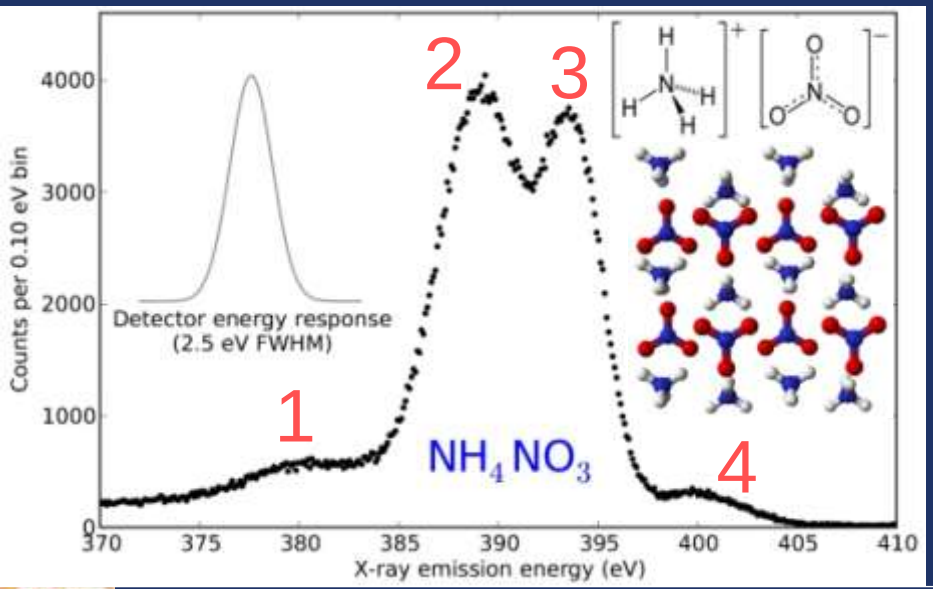




RDX is clearly distinguishable from NH_4NO_3.

chemical-shifts in TES spectra



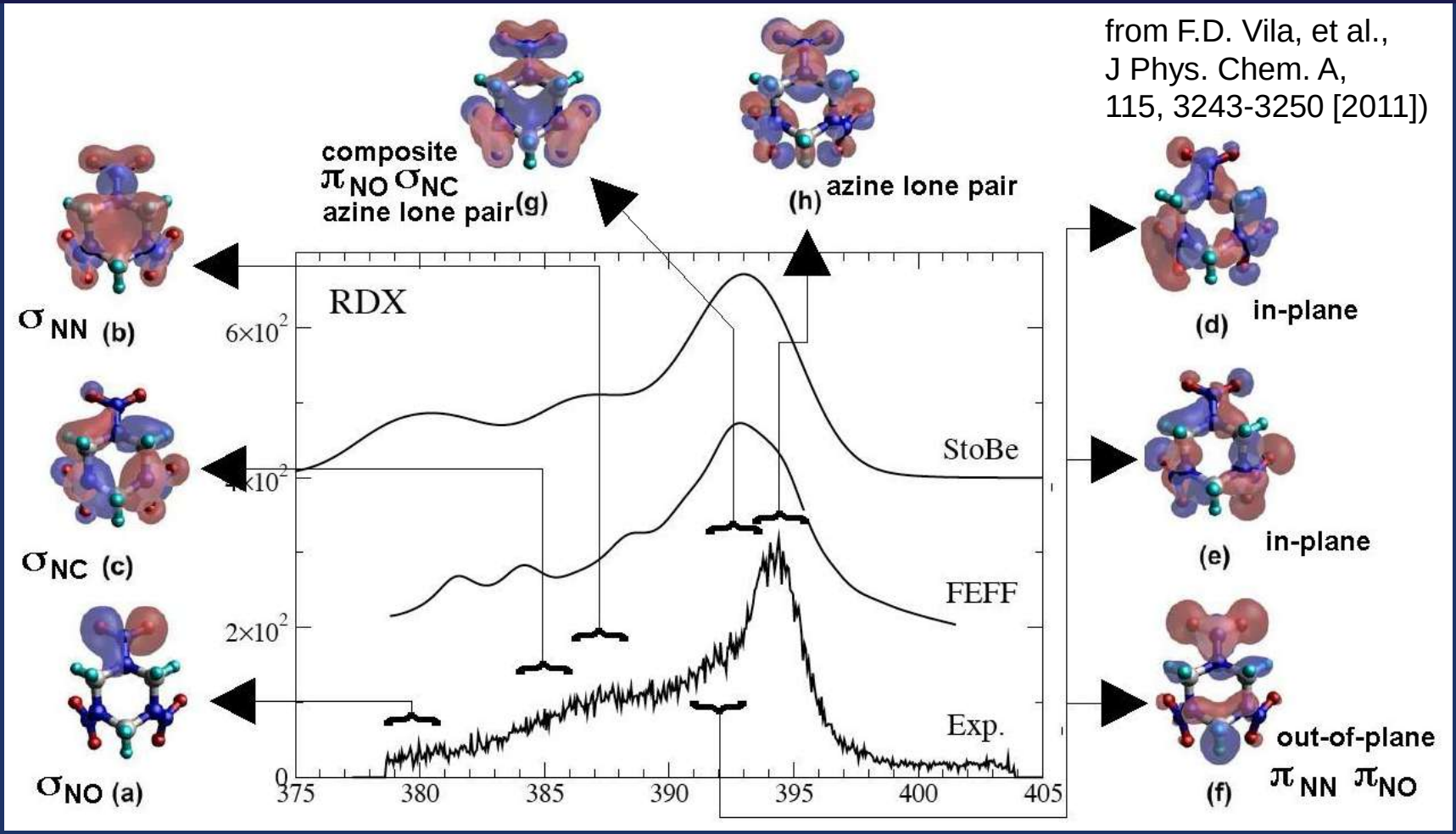


NH_4NO_3 has four resolved features that are associated with:

- NH_4^+ (highly reduced N)
  (2)
- NO_3^- (highly oxidized N)
  (1, 3, 4)

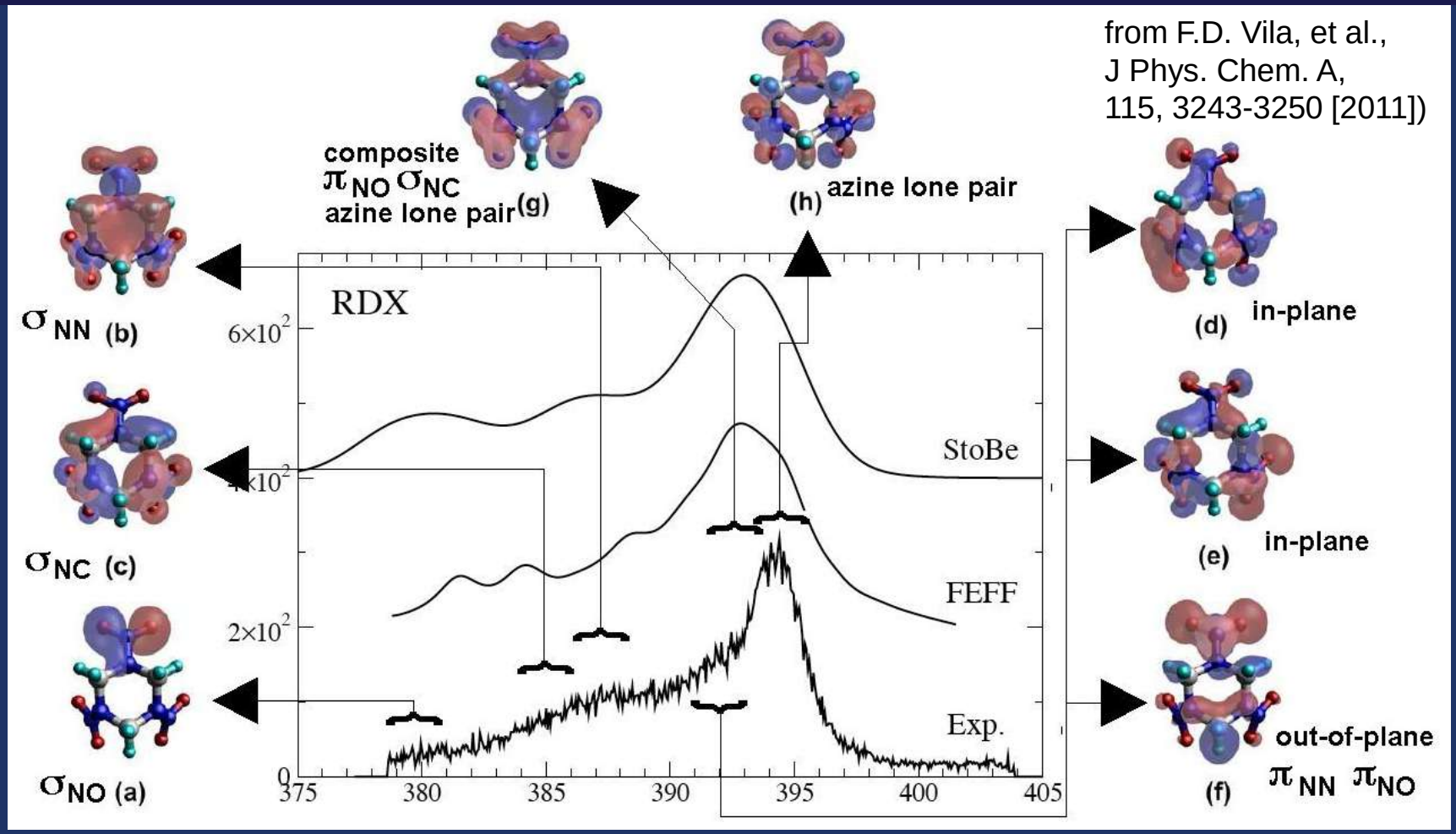
(feature ID's from F.D. Vila, et al., *J Phys. Chem. A*, 115, 3243-3250 [2011])

NIST X-ray chemical database



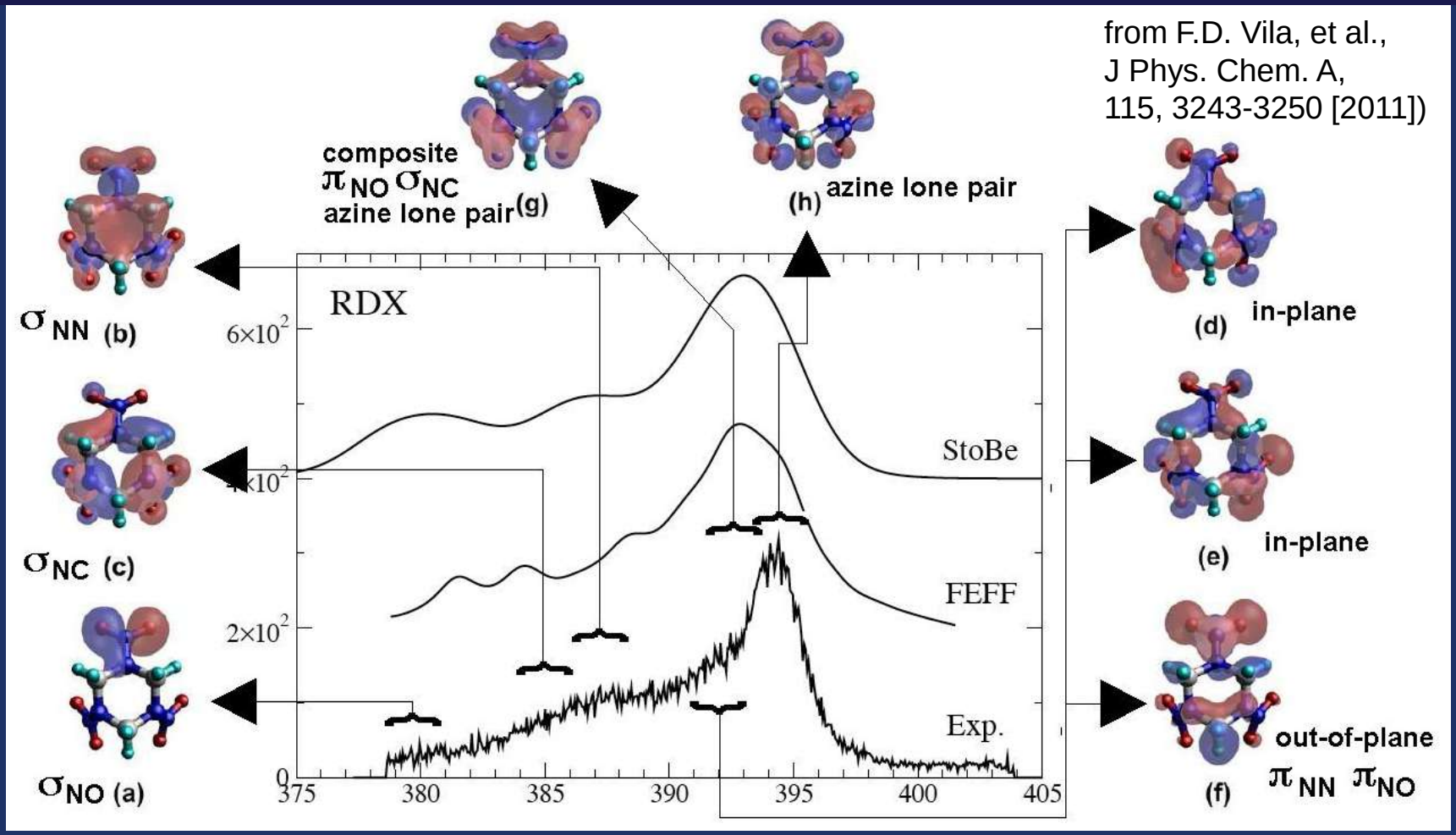
Generalization of this method will require NIST database of C, N, O spectral-emission features.

NIST X-ray chemical database



Terry Jach (Div. 637) and collaborator John Rehr (UW) have begun a pilot program to build such a database.

NIST X-ray chemical database



Will combine high-res. spectra from a synchrotron grating spectrometer with StoBe and FEFF8 theoretical models.

mixed/unknown threat powders

If not anthrax, what is it?

- Explosive?
- Toxin?
- Baby powder?
- Table salt?
- Wheat flour?
- Several of these together?

mixed/unknown threat powders

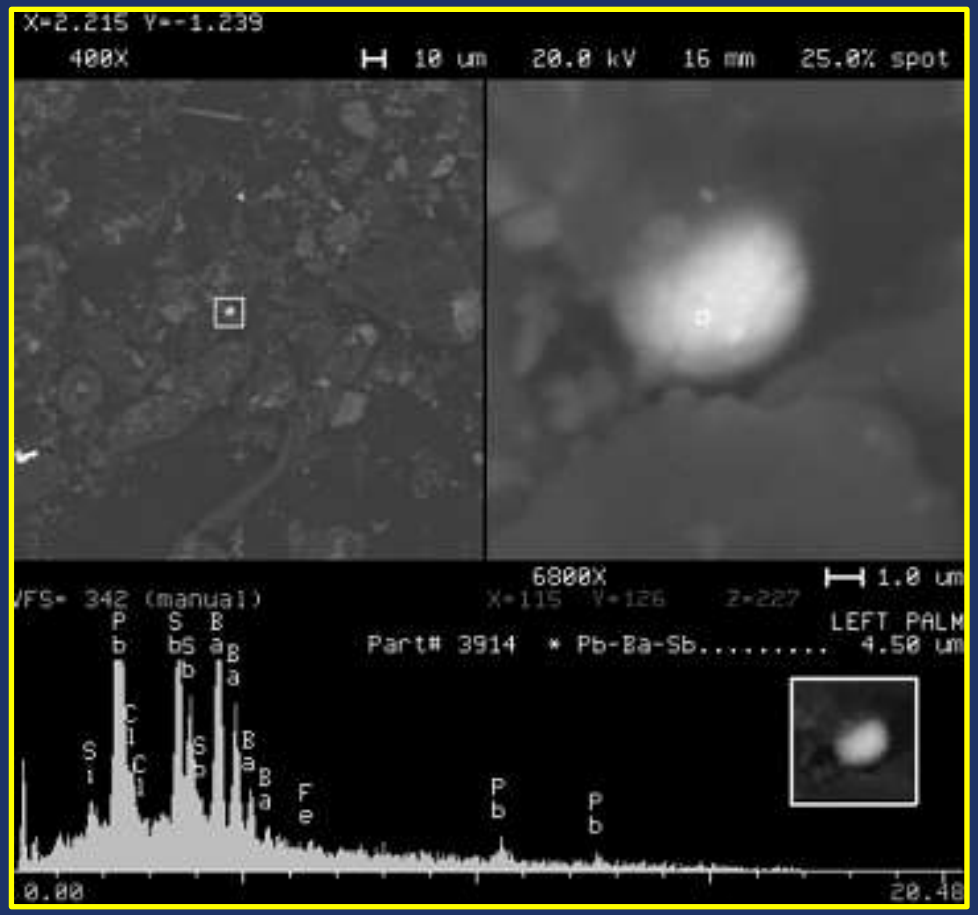
If not anthrax, what is it?

Presently, methods include:

- FTIR spectroscopy
- PL microscopy
- GC-MS
- LC-MS
- SEM X-ray microanalysis
- Raman spectroscopy
- XRD crystallography

SEM/TES for mixed GSR detection?

SEM/EDS is presently used to detect primer gunshot residue.



data from Forensic Magazine, Sept., 2012
(Allison C. Murtha and Linxian Wu)

Key primer materials:

- lead styphnate (initiator)
- barium nitrate (oxidizer)
- antimony sulfide (fuel)

SEM/TES for mixed GSR detection?

Organic residue of unburned propellant can be detected by LC-MS / GC-MS:

- nitrocellulose
- nitroglycerin
- nitroguanidine
- dinitrotoluene (DNT)
- diphenylamine (DPA)
- ethyl centralite
- resorcinol

conclusions

- SEM/TES is available commercially, but is also being further developed and improved by NIST.
- Can provide instant improvement to X-ray microanalysis of inorganics.
- Have begun a program to assess X-ray microanalysis of organics.
- Mixed organic/inorganic capability could save a lot of time and effort.