COVALENT METROLOGY

CHEMICAL SURFACE CHARACTERIZATION

What's on my surface, and should I care?

Chris Moore, PhD

May 28, 2020 11am PDT

COVALENT ACADEMY

EPISODE 09

RSVP at:
https://bit.ly/covalent09

Covalent Metrology

- **Founded 2016**
- Testing, measurement & characterization **Platform**
- **30 team members** (13 PhDs)
- **9,500 ft^2 lab in Sunnyvale, CA**
- **1-Stop-Shop Source for Answers**
  - 30 instruments in-house
  - 6 partnerships with instrument manufacturers
  - 11 partner labs
  - 6 corporate “tool shares”
- **More than 275 customers** (80 % repeat)

Covalent Technical Groups and Organization

COVALENT METROLOGY

hello@covalentmetrology.com

Electron & Scanning Probe Microscopy

(SEM/TEM, AFM, EDS, EELS, Nanoindent, acoustic microscopy)

Surface Analysis

(XPS, Auger, ToF-SIMS, dSIMS)

Optical Microscopy & Spectroscopy

(Laser Confocal, White Light, Chromatic Aberration, Spectral Ellipsometry, UV-Vis-NIR Spectroscopy)

Materials/ PC Board FA

(Cross Sections, Inspections, Dye & Pry)

X-Ray Characterization

(XRD/XRR, XRF, μCT)

Chemical Analysis

(ICPMS, GCMS, FTIR, Raman, Solid & Solution NMR, 2D NMR)

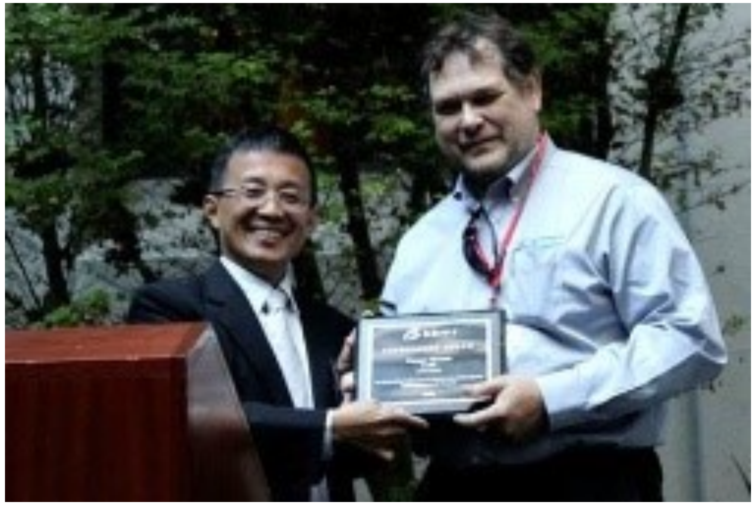
Nanoparticle Analysis

(DLS, PSA, Particle Zeta Potential)

Bulk Properties Characterization

(DSC, TGA, DMA, Rheometry, Tensile Test, Pencil Test, Surface Zeta Potential)

Dr Chris Moore, VP Technology



- PhD Solid State Physics , University of Waterloo, 1983
- Extensive experience in metrology technology and systems
  - Lead teams that designed
    - Optical tool UV to mid IR
    - High speed mapping x-ray
    - Photoluminescence
    - Non-contact electrical
    - Contact electrical tools

  worked with many other types of tools and imaging systems
- Experience in measuring or characterizing:
  - semiconductor materials and devices
  - compound materials and devices
  - Flat panel display
  - Solar cells and batteries
  - MEMS and micro-fluidics

Episode 9 Overview

- **General introduction**
  - Short Discussion on Surface Characterization
  - Why does it matter
- **How to Choose a Technique**
  - General guidelines
  - Specific Needs
  - Packaging and Sample preparation
- **An Overview of A Few Techniques**
  - Introduction
  - Plusses and minuses
- **Next Episode**
- **Question and Answer Session**

How Do You Characterize a Surface?

Here are a few examples of how you can characterize a surface:

Mechanical

- Roughness
- Flatness
- Hardness
- Scratch resistance

Chemical

- Elemental Composition
- Chemical Bonding
- Contamination

Electrical

- Spreading Resistance

Physical

- Work Function
- Carrier Lifetime

Why Care about the Surface?

Surfaces are the interfaces to the real world. Failure to understand the nature of what makes up a surface and how it will react is the single most common failure mode of devices and processes

Mechanical

- Adhesion and bonding
- Grain structure / growth
- Friction
- Wettability

Chemical

- Specular or Diffuse Reflectance
- Color
- Catalytic reaction
- Corrosion

Electrical

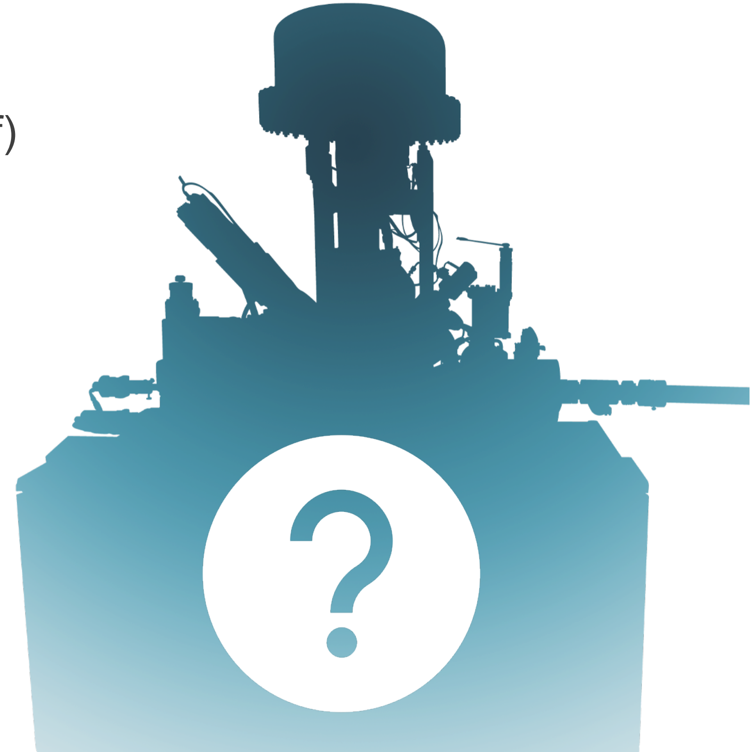
- Coupling / Resistance

Physical

- Interdiffusion / Surface area Effects

How do you Choose a Technique?

- **Three primary Considerations** (Field or Lab)
  - ***What am I looking for?*** (the one most people think of)
    - Contaminant's (not supposed to be there)
    - Uniformity of coverage
    - Unknown
  - ***Over what area do I need a measurement?*** (the one most people think of)
    - Few microns
    - Few mm
  - ***Over what depth do I need a measurement?*** (the one most people do not think of)
    - Am I truly looking at a surface effects (few Angstroms to a few nm)
    - Near surface (10's of nm to a few microns)
    - Do I even know?
- **And a host of others…**
  - *How easy is it to damage the material?*
  - *Is it sensitive to air?*
  - *Is it chemically sensitive to sample preparation?*
  - *How big is the sample?…*



Two Types of Conditions

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	In The Lab	In the Field
Restriction	• Sample or part of the sample or a swab can be brought to the lab	• Part cannot be dismantled or is too big or safety restriction on chemical swabbing
Pros	• Number of choices • Controlled environment • Higher sensitivity	• Quick turnaround
Cons	• Response time • Sample prep may affect results	• Limited number of choices

Technique Choices

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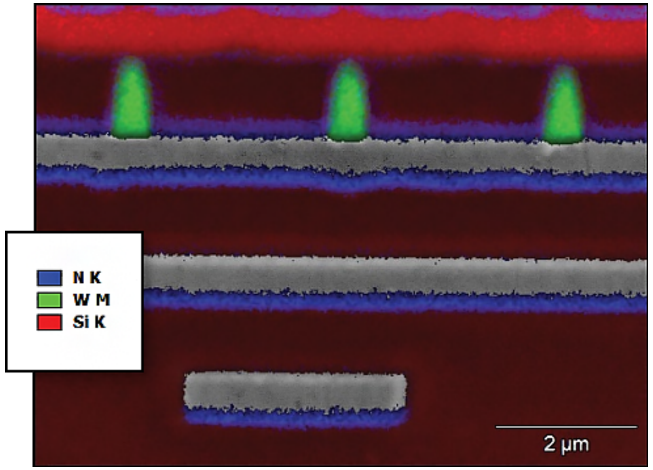
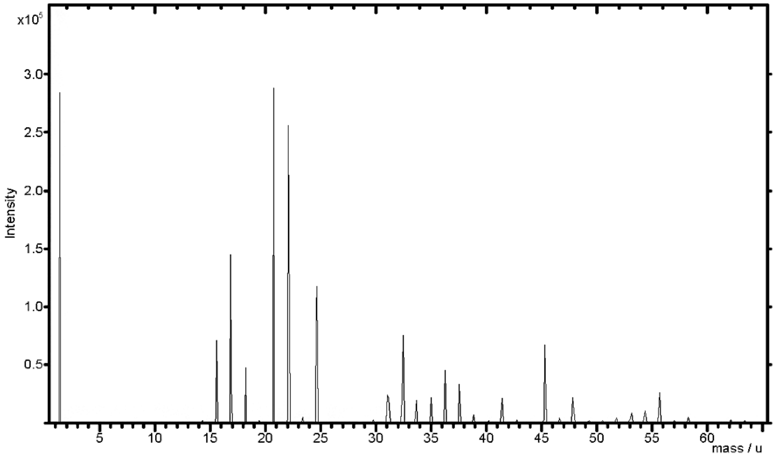
- Some basic choices
  - **Imaging techniques** (look at the uniformity of the surface chemistry)
    - SEM + EDS
    - TOF SIMS
    - Mapping XPS
    - Mapping Auger
  - **Sampling Techniques** (measure the output of a large area)
    - Glow Discharge Mass Spectroscopy (GDMS)
    - Inductively Coupled Plasma Mass Spectroscopy (ICPMS)
    - Laser Ablation Inductively Coupled Plasma Mass Spectroscopy (LA-ICPMS)
    - Thermal Desorption Analysis (TDA)
    - Gas Chromatography Mass Spectroscopy (GCMS) + many more
  - **Spectroscopic techniques** (single spot sampling techniques)
    - X-ray Photo-electron Spectroscopy (XPS or ESCA)
    - Auger
    - Secondary Ion Mass Spectroscopy (SIMS)



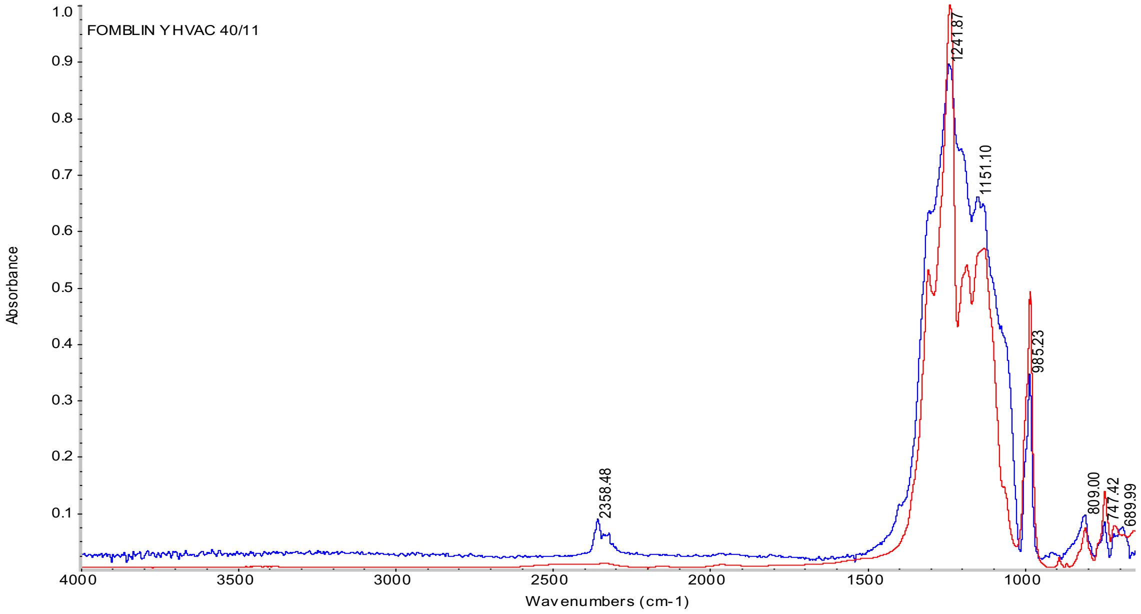
From *Thermo Fisher Scientific*. Quantitative map of a semiconductor cross section showing Si, W, and N layers.

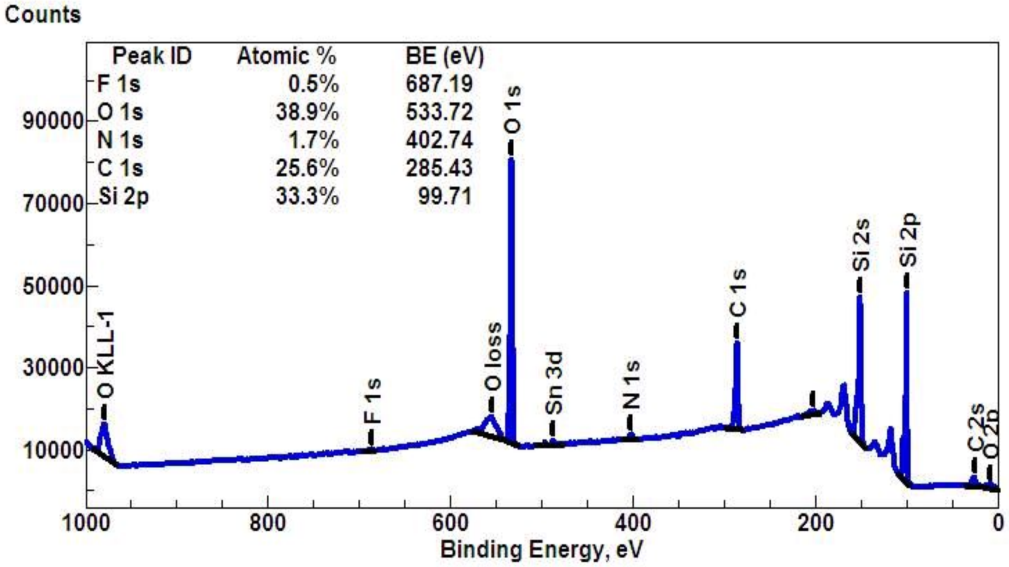


Generated on *IONTOF Model IV ToF-SIMS*. Negative secondary ion mass spectrum showing heavy surface presence of Fluorine compounds.

Technique Choices II

- What are you looking for?
  - **Organic** or **inorganic**
  - **Elemental** information or **Bonding** information

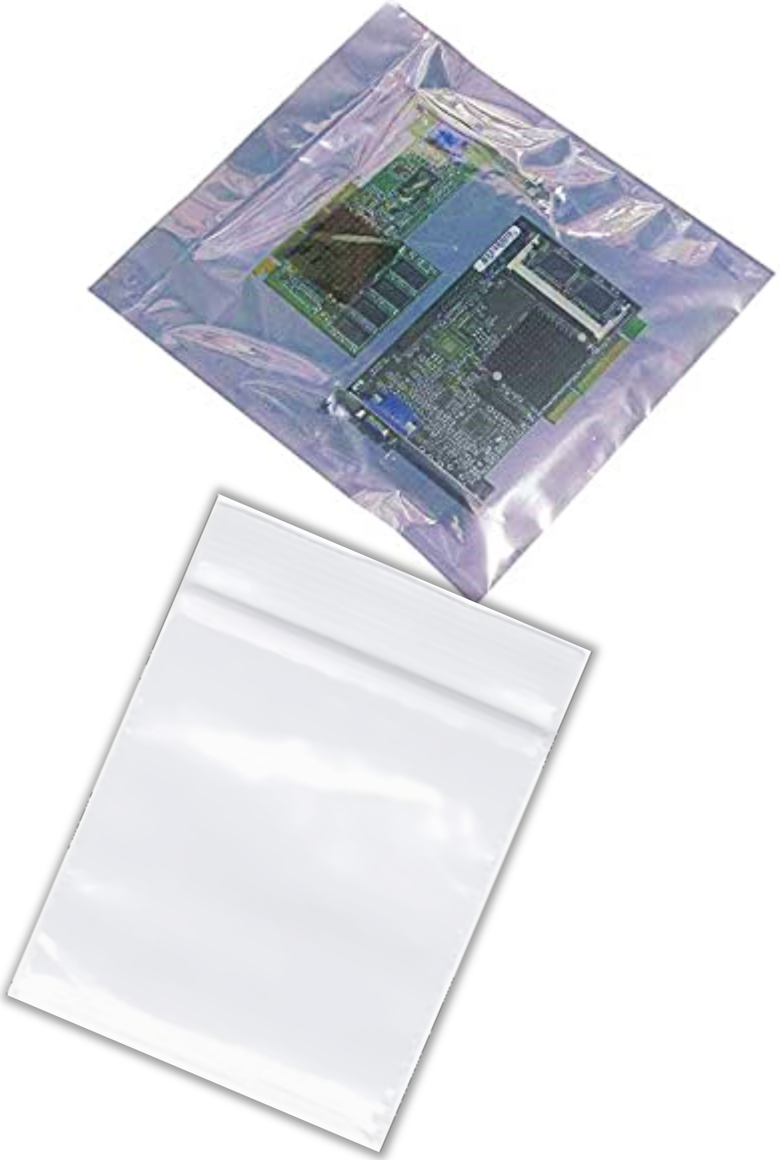




Packaging

- Environment affects the result
  - Need to understand what is environmental and what is not

- Simple example:
  - Client asks for an analysis of what is on the surface of his sample
  - Sample is shipped in a plastic bag (very common)
  - **What is the surface?**
    - Likely contaminated with plastomer from the bag
      - If you can smell the bag, then it is contaminating things you put in it
    - Could see Na and Cl (handling)
    - Could see organics (real or from handling)



Packaging II

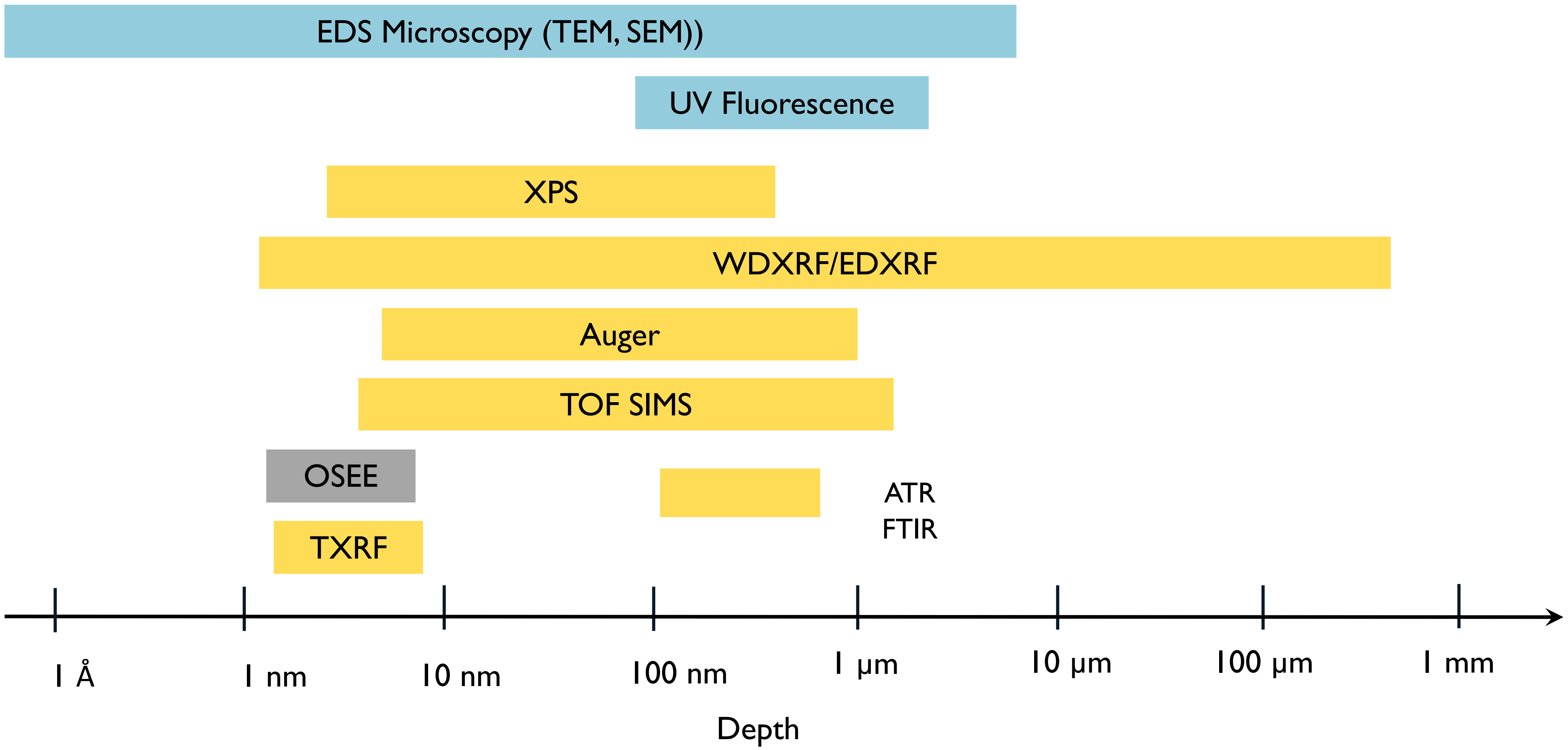
- What about using foil for packaging?
  - Depends on the foil
    - UHV foil (already cleaned) makes a great package if not looking for metal
    - Normal foil is already contaminated with oils from manufacturing process

Techniques

- Further seminars in the series will concentrate on Specific Techniques and Examples:
  - XPS, UPS and ISS
  - TOF-SIMS and D-SIMS
  - ICPMS and related techniques
- The above will be lightly covered in this talk.

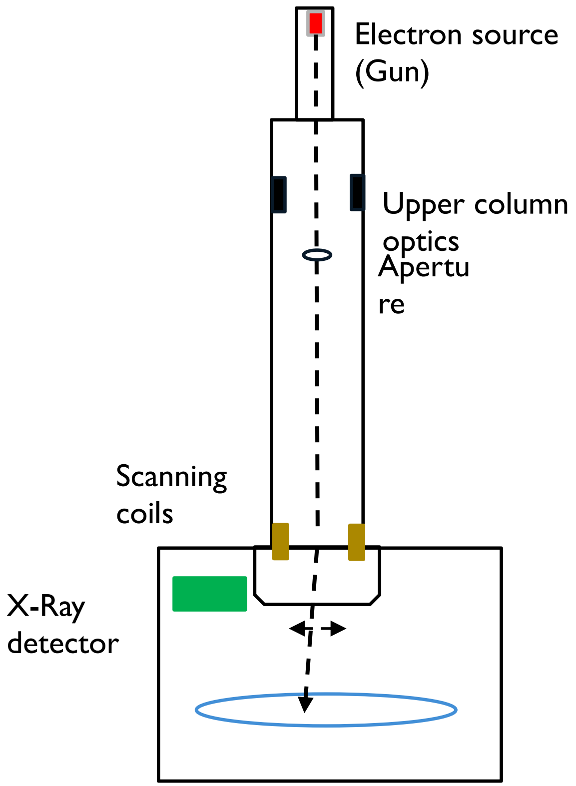
From *PHI Technologies*, and *Thermo Fisher Scientific*. Photos of some Surface Chemical Analysis Instruments we use.

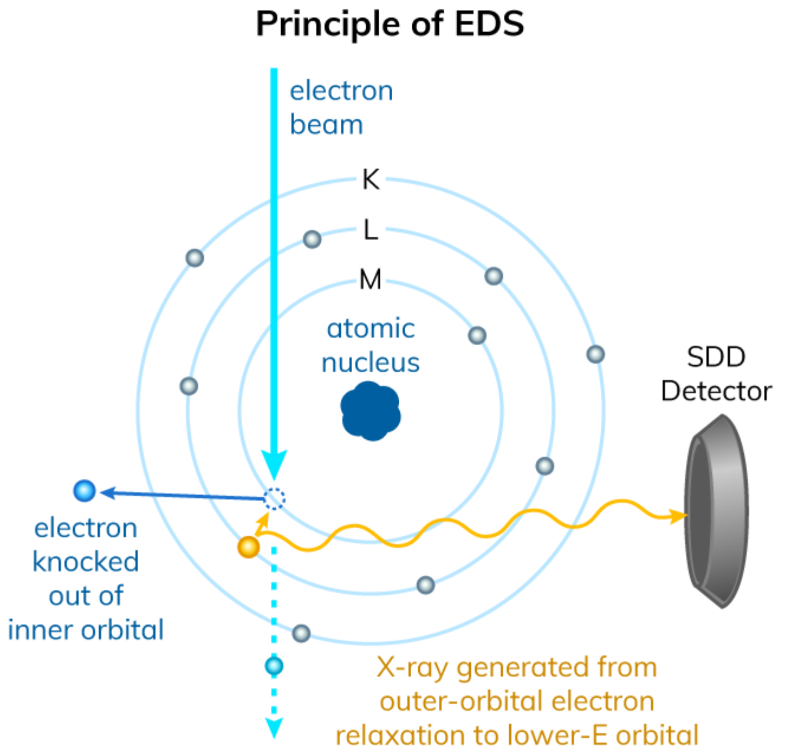
Information Depth (and why it matters)

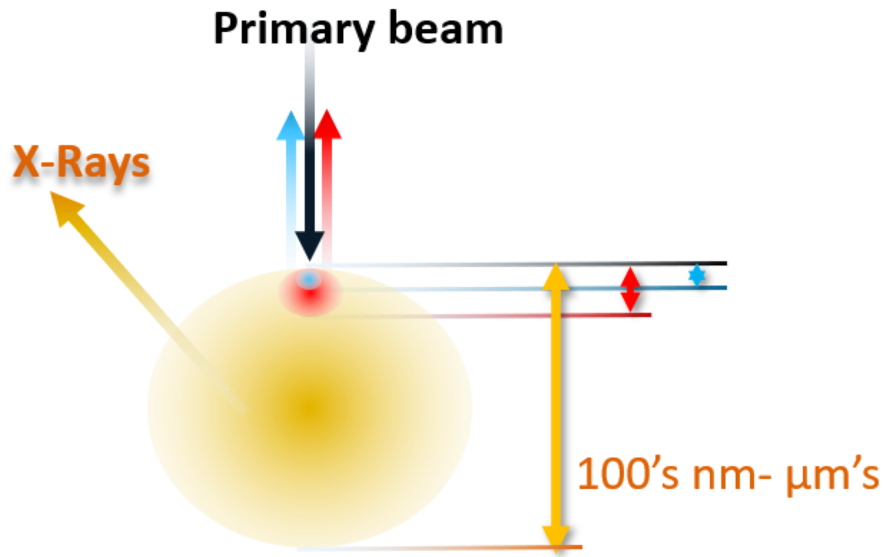


Energy Dispersive X-ray (EDX/EDS)

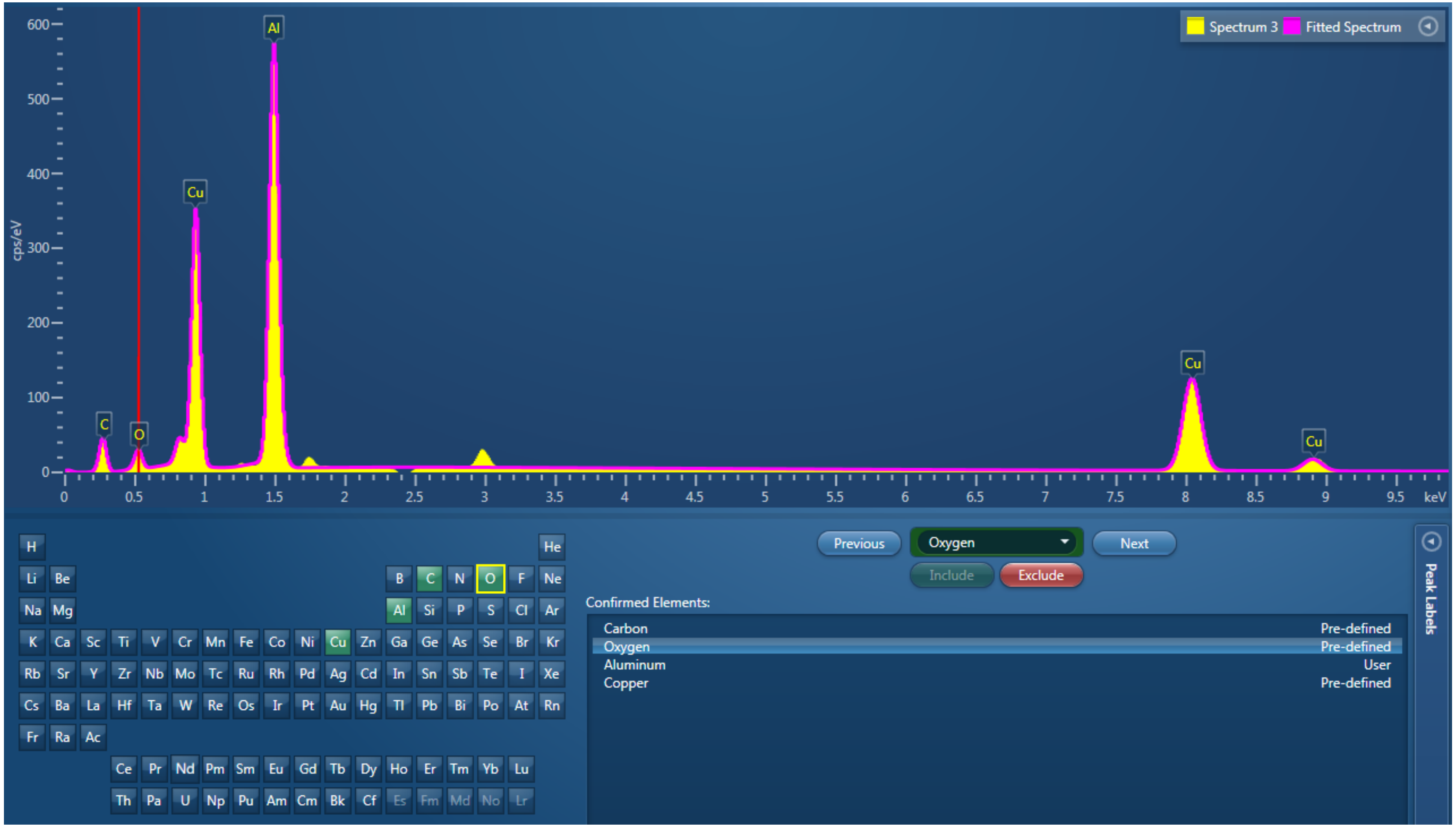
- Electron beam (SEM or TEM) used to excite characteristic electrons
- X-ray energy used to determine composition information







EDX/EDS

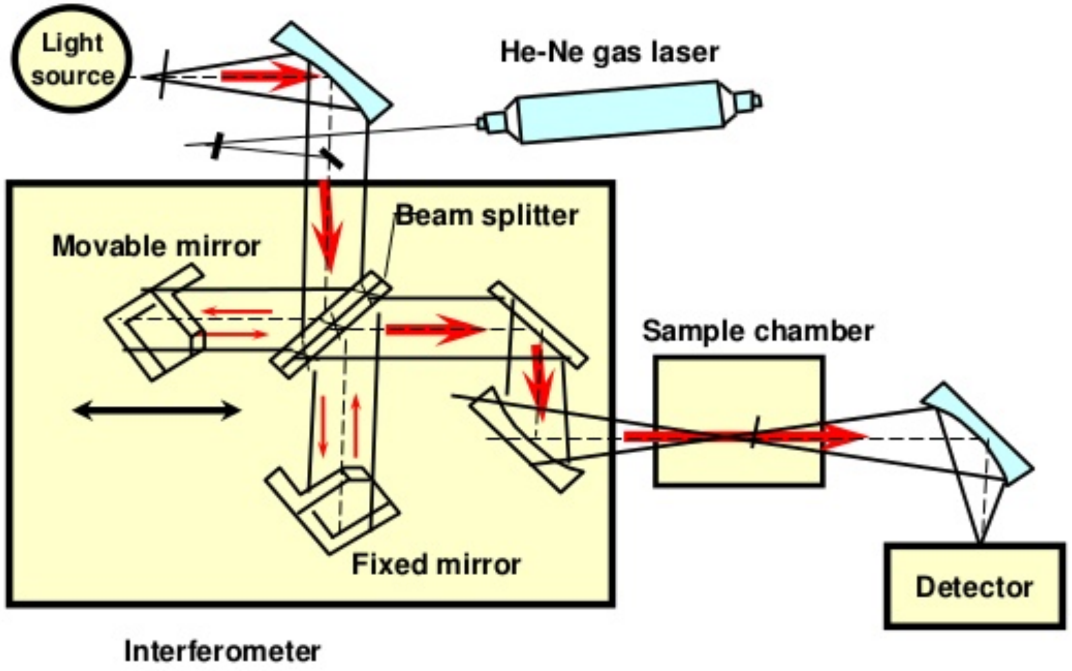

Spectrum 3
Fitted Spectrum
cps/eV
600
500
400
300
200
100
0
Al
Cu
C
O
Cu
Cu
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
5.5
6
6.5
7
7.5
8
8.5
9
9.5
keV
Previous
Oxygen
Next
Include
Exclude
Confirmed Elements:
Carbon Pre-defined
Oxygen Pre-defined
Aluminum User
Copper Pre-defined
Peak Labels

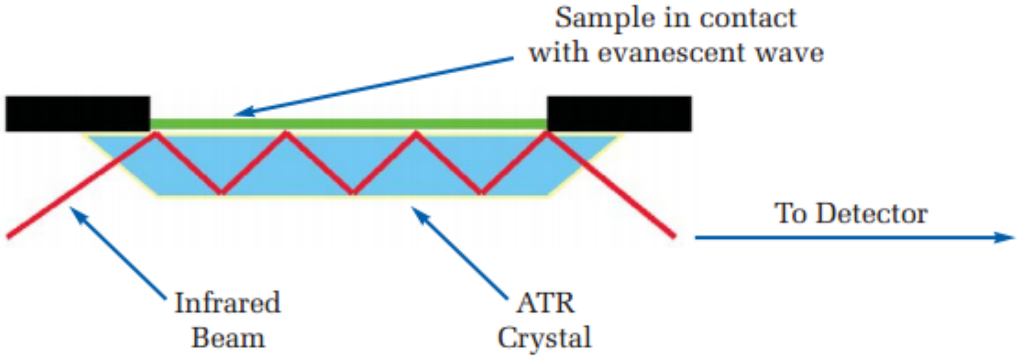
EDX/EDS

Pros	Cons
• *Well-known technique*	• *No light element capability*
• *Can use e-beam energy to look at near surface versus depth*	• *Can be difficult to interpret* • *Al or Br*
• *Can have very high spatial resolution (TEM)*	• *Low sensitivity 0.1%*
• *Readily available*	• *May need extensive sample prep (TEM)*

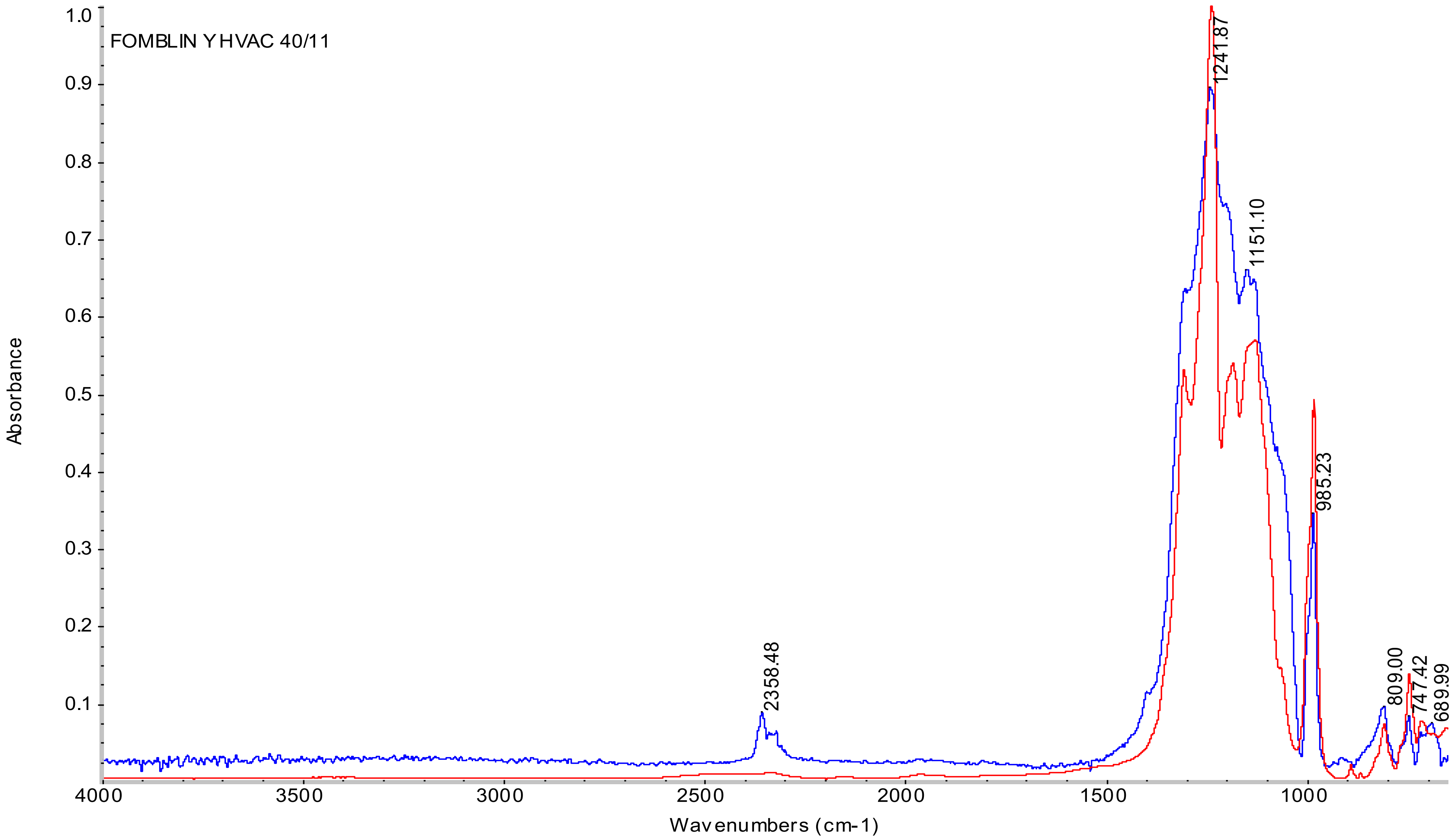
ATR-FTIR (Attenuated Total Reflection – FTIR)

- FTIR (Fourier transform infrared spectroscopy) provides information on the bonding of the elements
- IR wavelength of absorption provides information of the chemical bond
- Often used as a non-destructive fingerprinting method
- ATR-FTIR is a variation used to measure thin films (typically 100 nm and up)





ATR-FTIR Data



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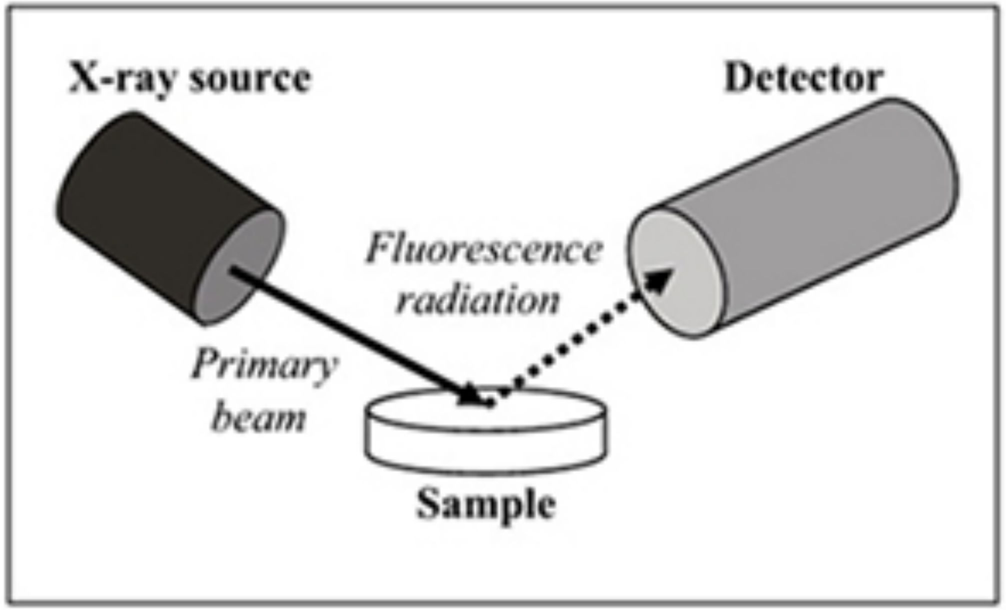
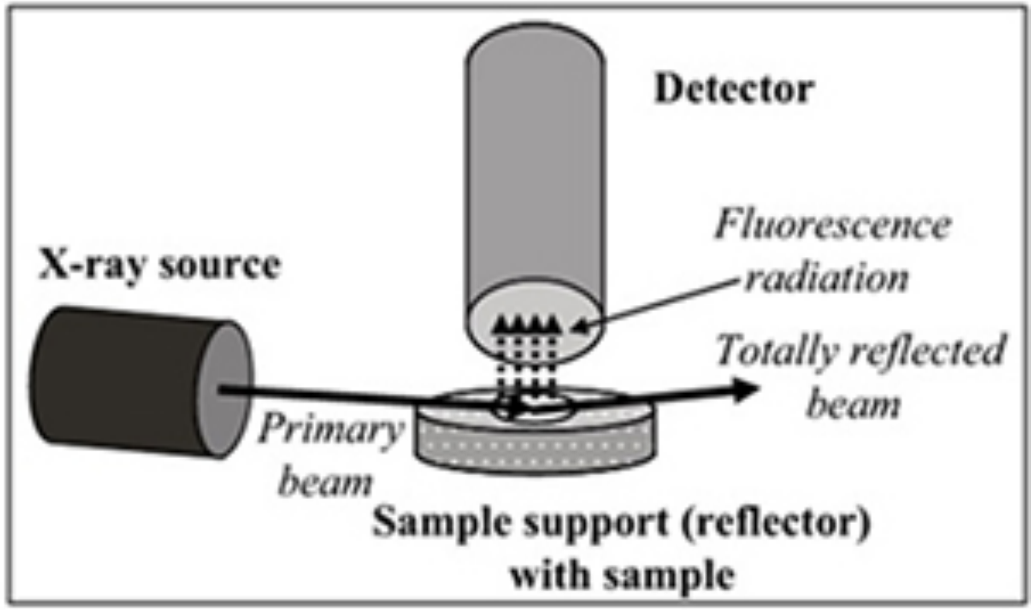
Pros	Cons
• *Well-known technique* • *Fast* • *Done in air* • *Good sensitivity for organic materials* • *Easy to fingerprint and identify* • *Does not affect the surface*	• *Requires a thicker film (>100 nm)* • *Signatures can get very complex* • *Large area (typically mm^2) sampled*

TXRF (Total Reflection X-Ray Fluorescence)

- Collects information from about 5 nm depth unlike conventional XRF
- Used for elemental identification
- Sample must be flat and smooth due to beam geometry

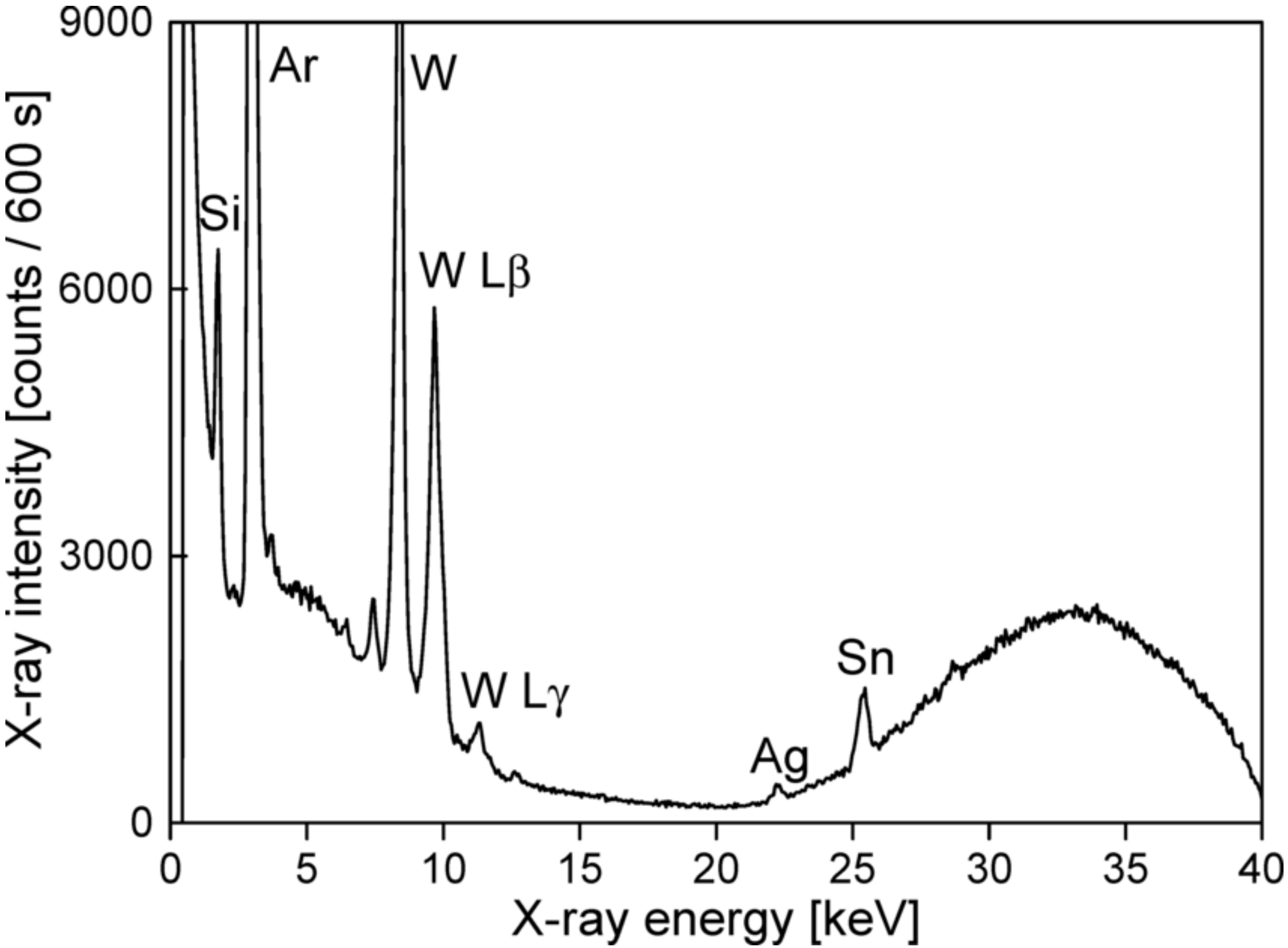


Standard XRF



TXRF

TXRF Data



9000
6000
3000
0
X-ray intensity [counts / 600 s]
Ar
W
Si
W Lβ
W Lγ
Sn
Ag
0
5
10
15
20
25
30
35
40
X-ray energy [keV]

TXRF

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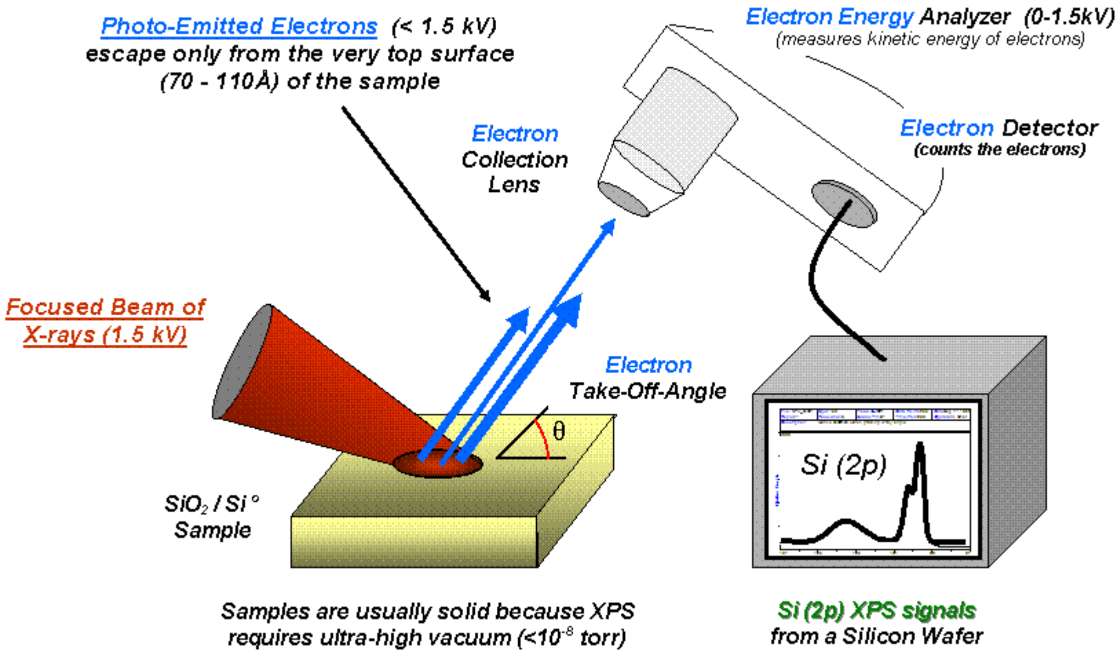
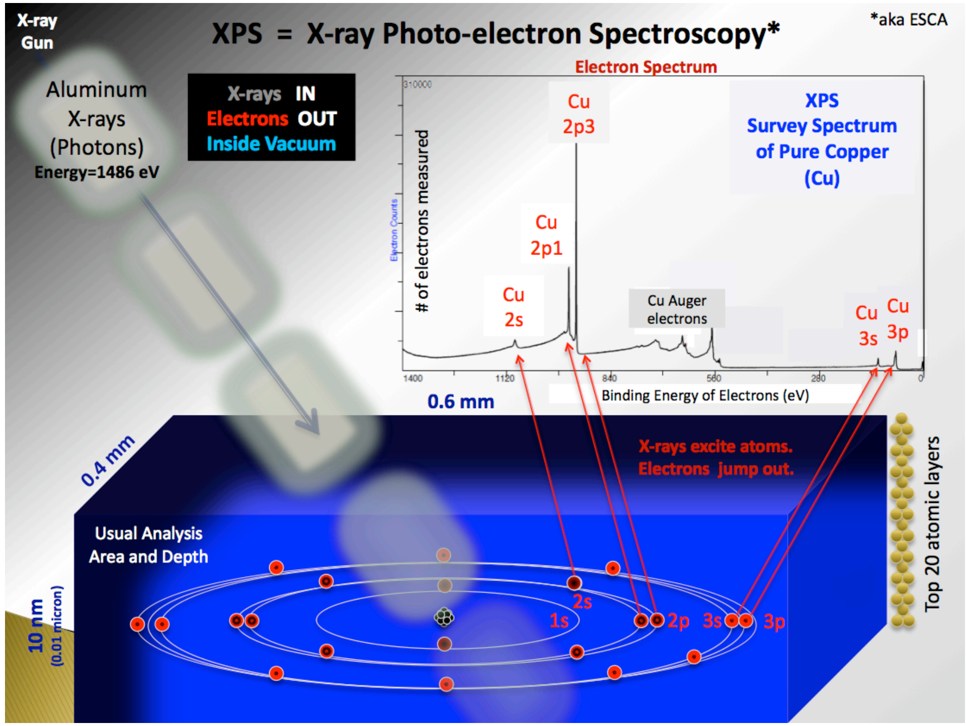
Pros	Cons
High sensitivity	*Measured in vacuum*
Can map (at a large scale)	*Sample must be flat and smooth*
Can be enhanced using VPD	*Limited availability*

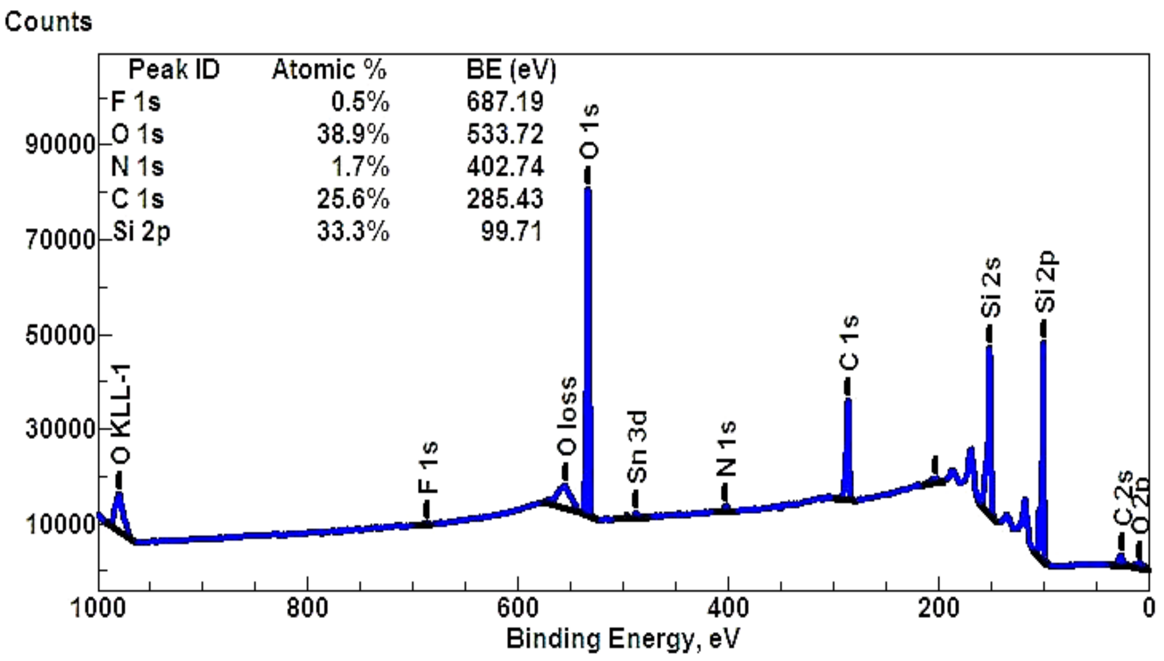
XPS (X-ray Photo-Electron Spectroscopy)

- Information depth 3.0 to 10.0 nm
- Provides elemental composition in parts per thousand and chemical state
- Often used as a fingerprint especially with non-conducting surfaces
- Signal mainly comes from top few nanometers of surface





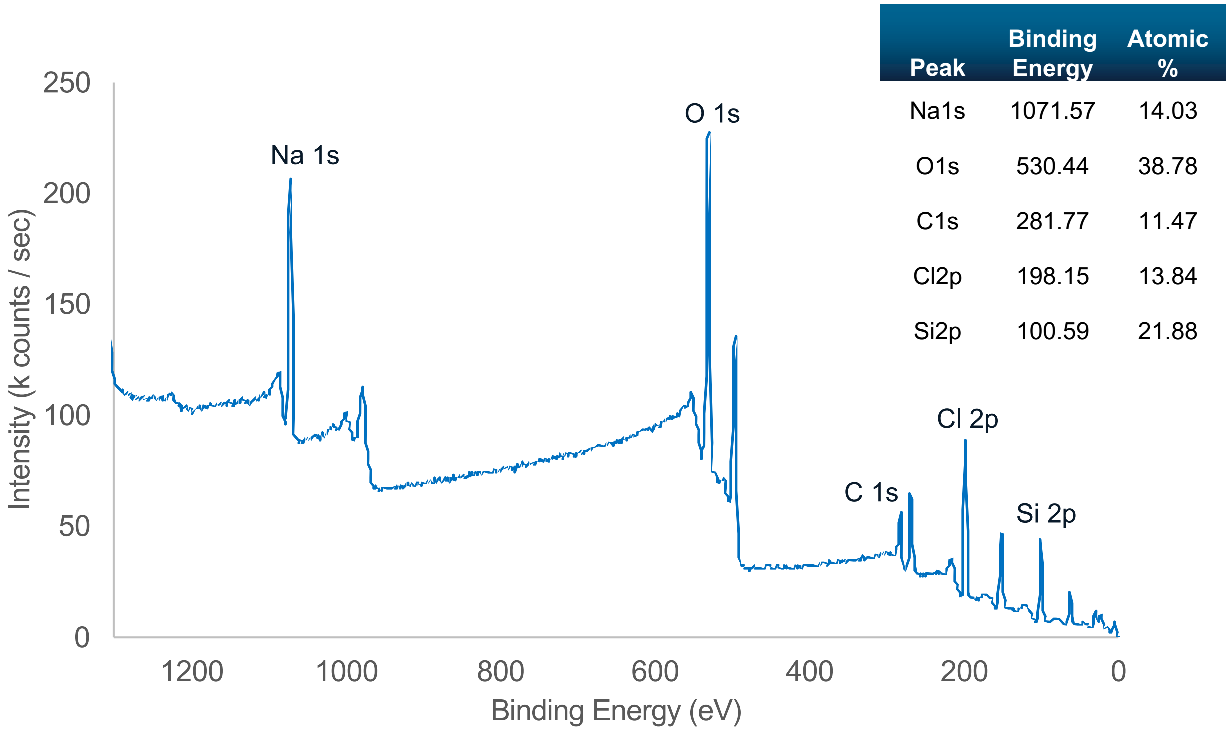
XPS Data



Peak ID	Atomic %	BE (eV)
F 1s	0.5%	687.19
O 1s	38.9%	533.72
N 1s	1.7%	402.74
C 1s	25.6%	285.43
Si 2p	33.3%	99.71

From *Wikimedia Commons*; contributor: *Bvcrist*

XPS Survey Scan on Si Wafer with Surface Contaminants

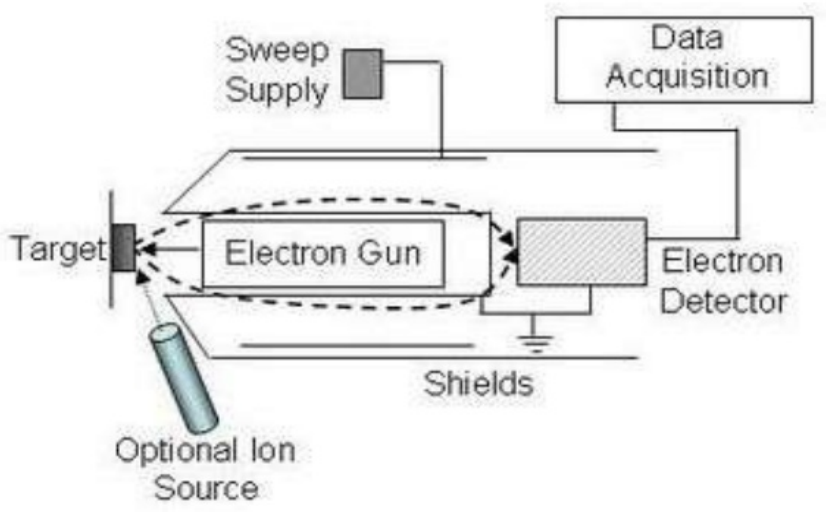


Peak	Binding Energy	Atomic %
Na1s	1071.57	14.03
O1s	530.44	38.78
C1s	281.77	11.47
Cl2p	198.15	13.84
Si2p	100.59	21.88

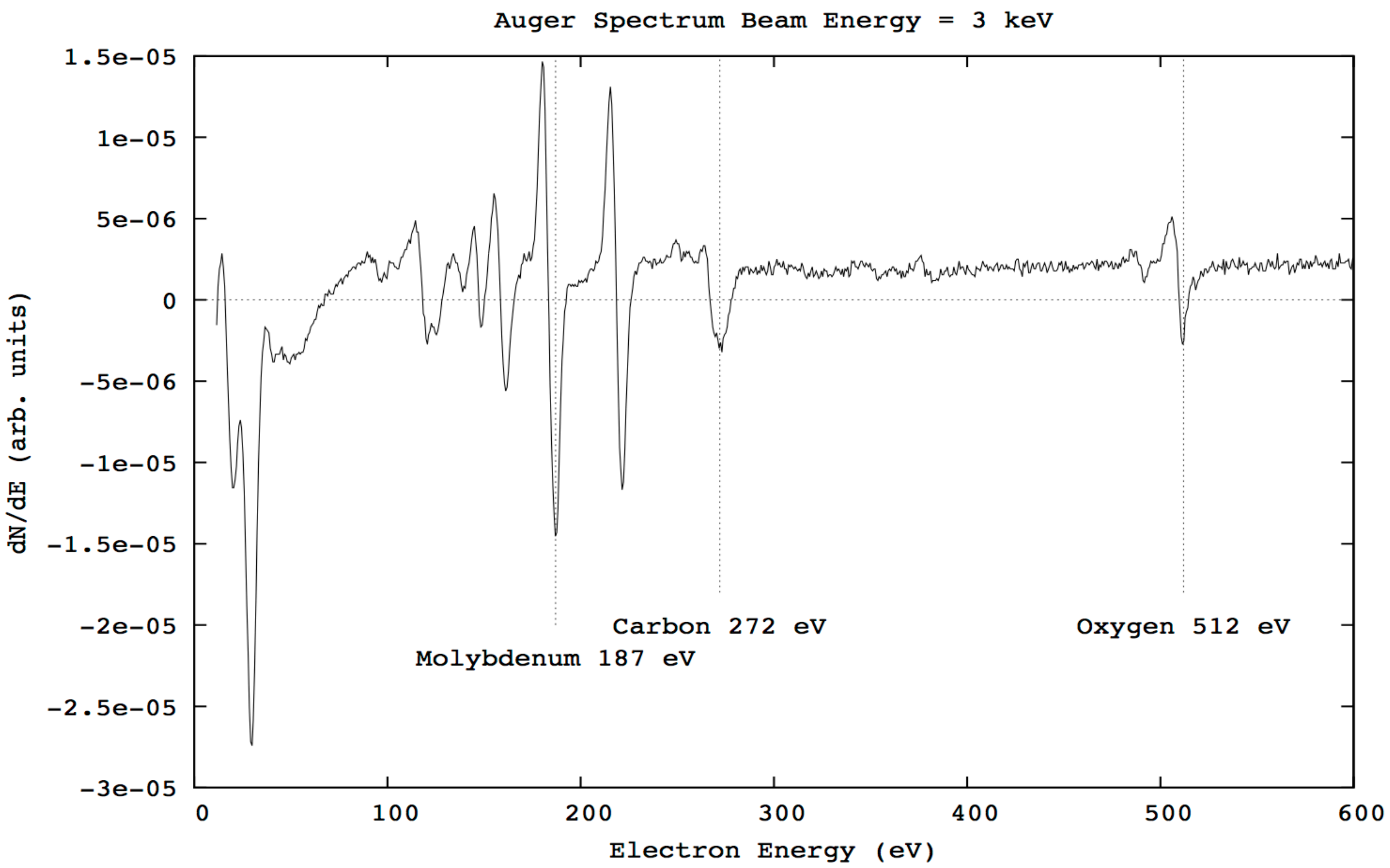
Pros	Cons
• *Chemical bonding Information* • *Well known technique* • *Less effects of charging on analysis* • *Mapping available on newer systems*	• *Measured in vacuum* • *Surface roughness can affect measurement* • *Mid level sensitivity*

Auger

- Usually top 2 to 5 nm
- Electron beam excitation (high resolution for small areas)
- Analyze electrons emitted by Auger process which are related to the element involved



Auger Data

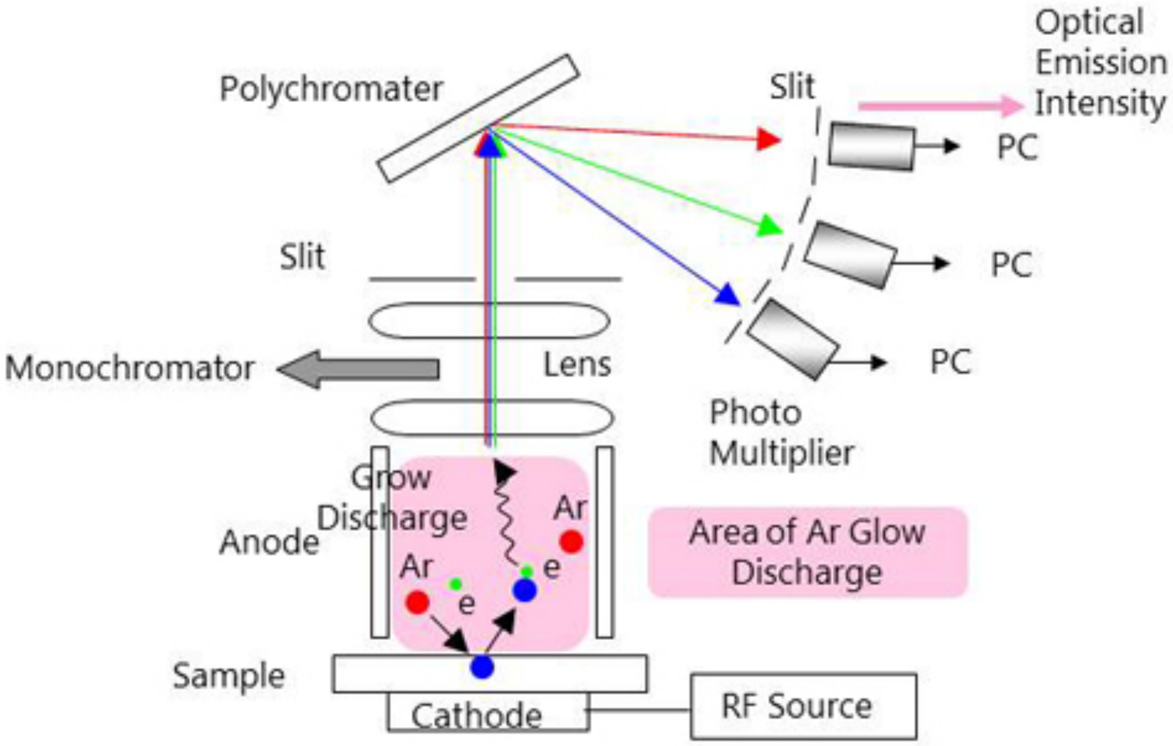

Auger Spectrum Beam Energy = 3 keV
1.5e-05
1e-05
5e-06
0
-5e-06
-1e-05
-1.5e-05
-2e-05
-2.5e-05
-3e-05
dN/dE (arb. units)
0
100
200
300
400
500
600
Electron Energy (eV)
Carbon 272 eV
Oxygen 512 eV
Molybdenum 187 eV

Auger

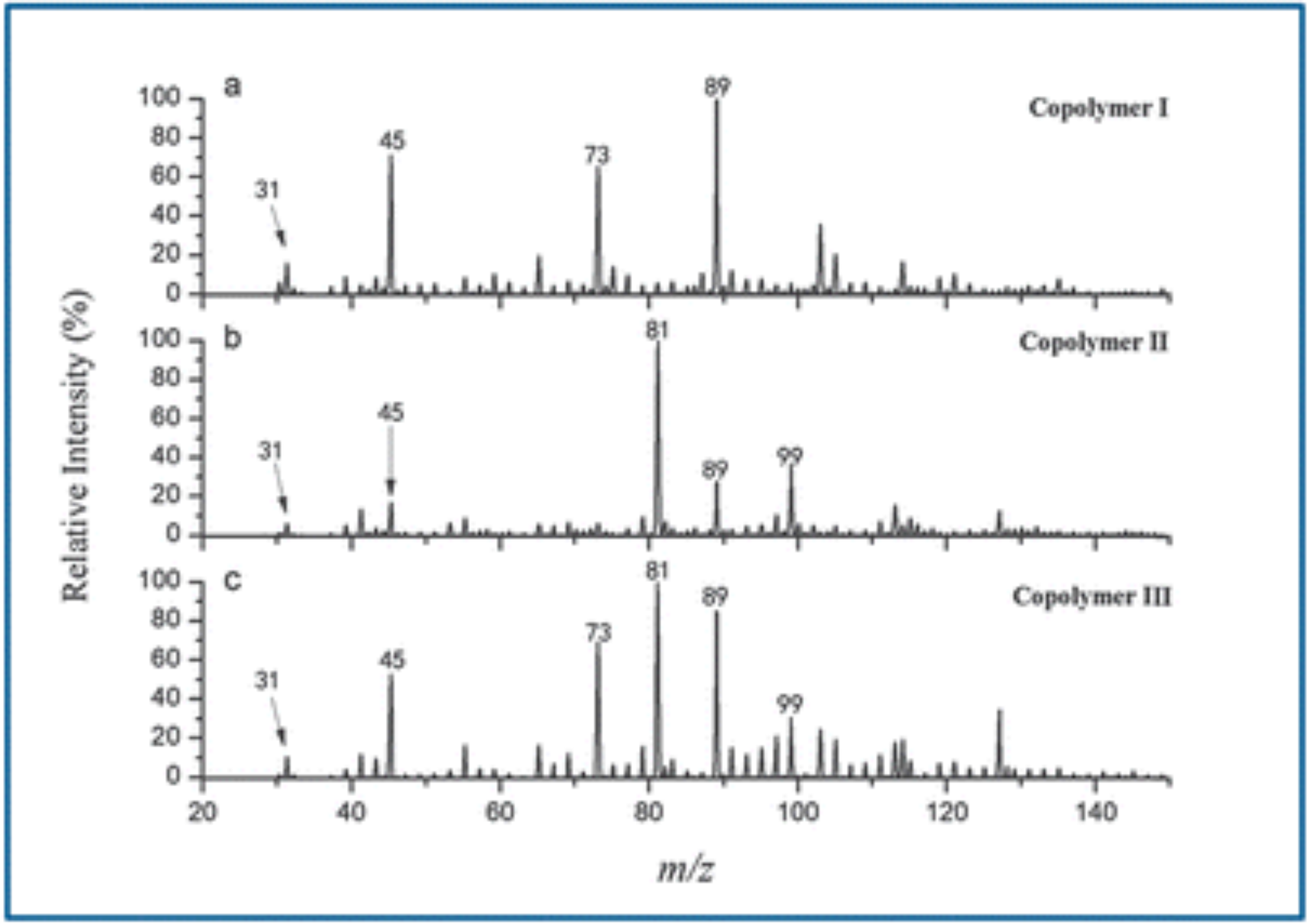
Pros	Cons
High spatial resolution (10 nm)	*Measured in vacuum*
Limited chemical bonding Information	*Charging causes analysis problems*
Well known technique	*Mid level sensitivity*
Mapping available on newer systems	

GDMS/GDOES (Glow Discharge Mass Spectroscopy)

- Typical of several chemical analysis techniques
  - Sample is broken down in a number of ways (in this case, plasma eroding the sample)
  - Resultant material is analyzed using a mass spectrometer, or, in the case of plasma, the optical emission spectra
  - For liquids/aerosols have ICPMS



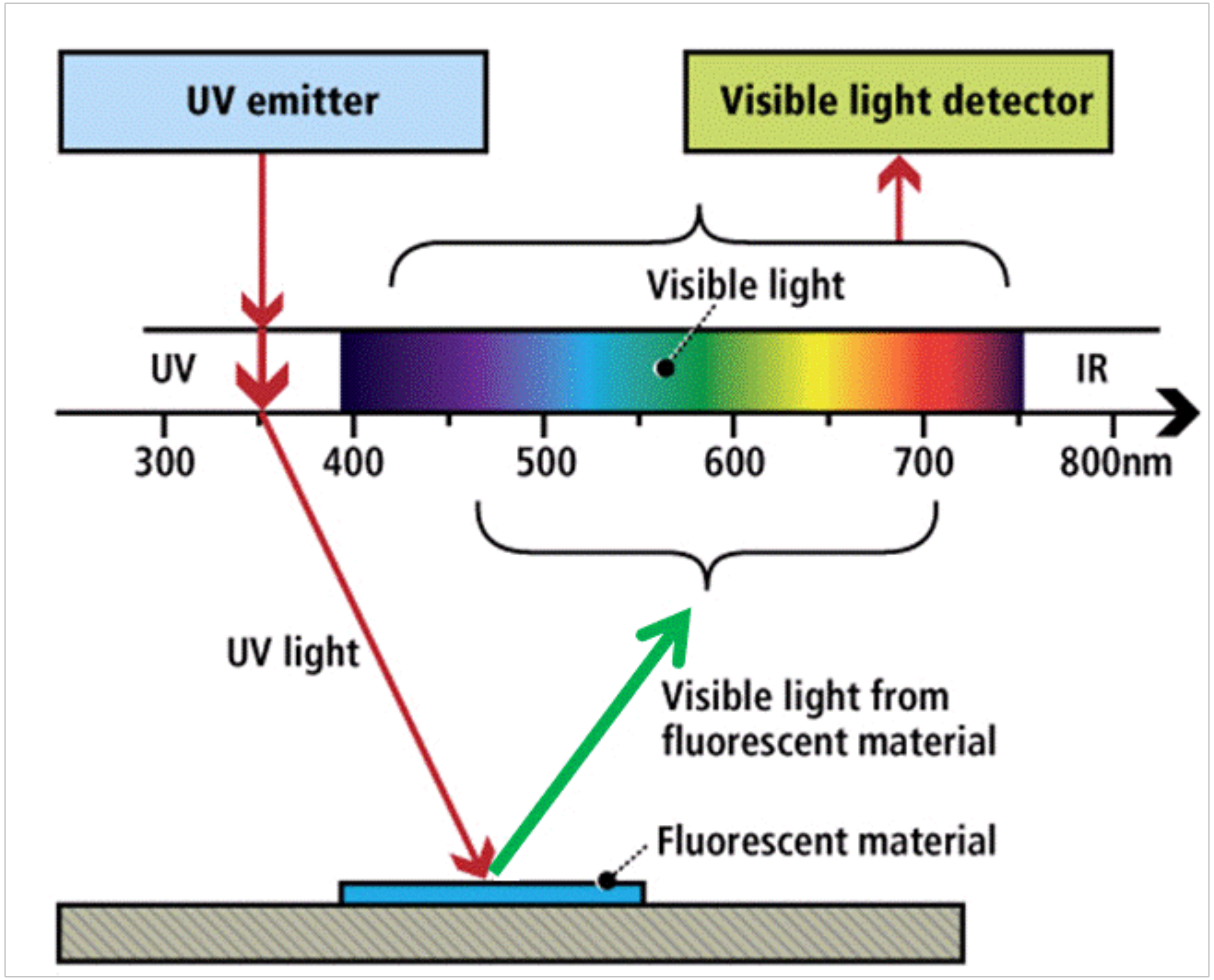
GDMS Data from a Polymer



GDMS

Pros	Cons
• *Well-known technique* • *Fast depth profiling*	• *Not particularly surface sensitive* • *Plasma can alter surface chemistry* • *Etch rate material dependent*

UV Fluorescence Spectroscopy



Uses UV light to excite fluorescence transitions
Spectral response measured and fingerprinted
Field versions of this exist

UV Fluorescnece

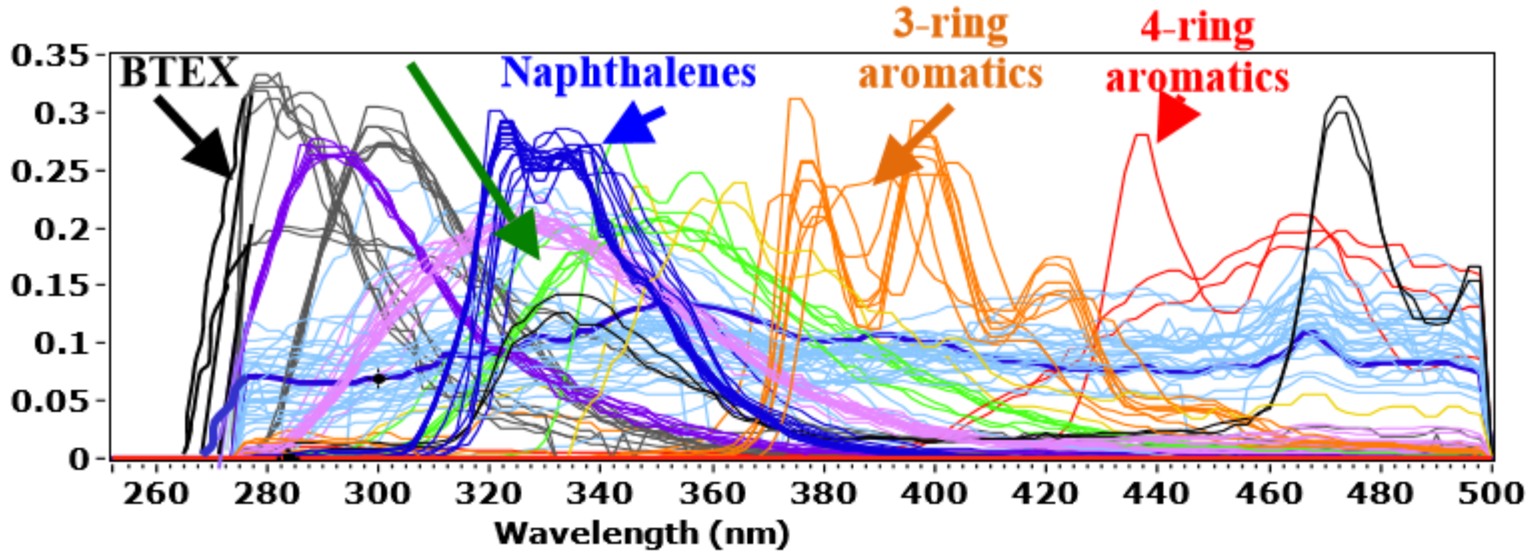
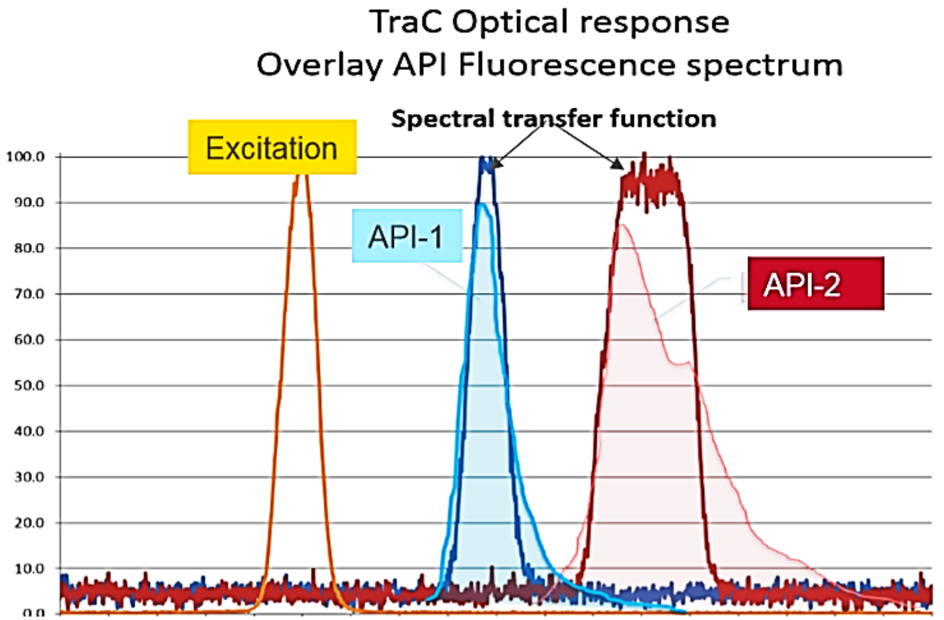


Figure 1. Emission spectra for most organics is limited to wavelengths above 260nm. Illustration of the range of autofluorescence emission spectra for a wide range of materials. The arrows show fluorescence data for compounds and groups of interest. Excitation below 270 nm and especially below 240 nm improves sensitivity & specificity.

A Field-Portable Example

- Portable UV Fluorescence System
- Uses solid state UV source
- Originally developed for the food industry



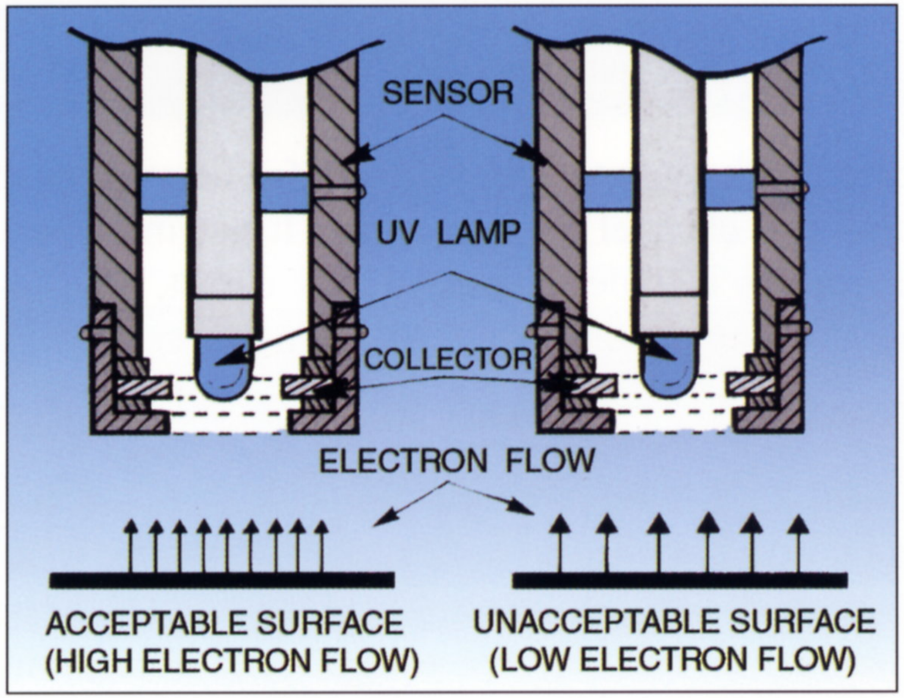
UV Fluorescence Spectroscopy

Pros	Cons
• *Operable in air* • *No solvents or extra sample-prep necessary* • *Very simple instrument operation* • *Useful to detect chemicals with aromatic or conjugated chemical structures.* ○ *Examples: crude oil & quinine (found in tonic water)*	• *Non-specific identification of organic contaminant* • *Possibility of damaging / changing organics (contaminant can break down)*

Optically Stimulated Electron Emission

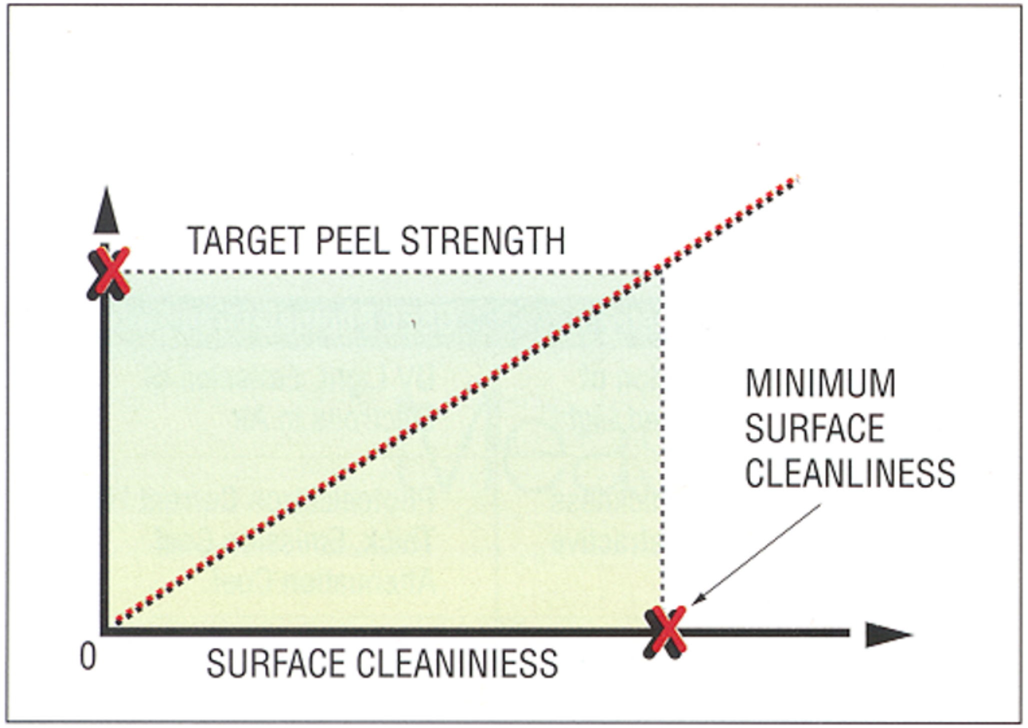
- UV light excites surface and low energy electrons emitted
- For a metal the condition of the surface determines the number of electrons emitted
- Electron current used as a measure of surface cleanliness

Surface Quality Monitor model SQM200W

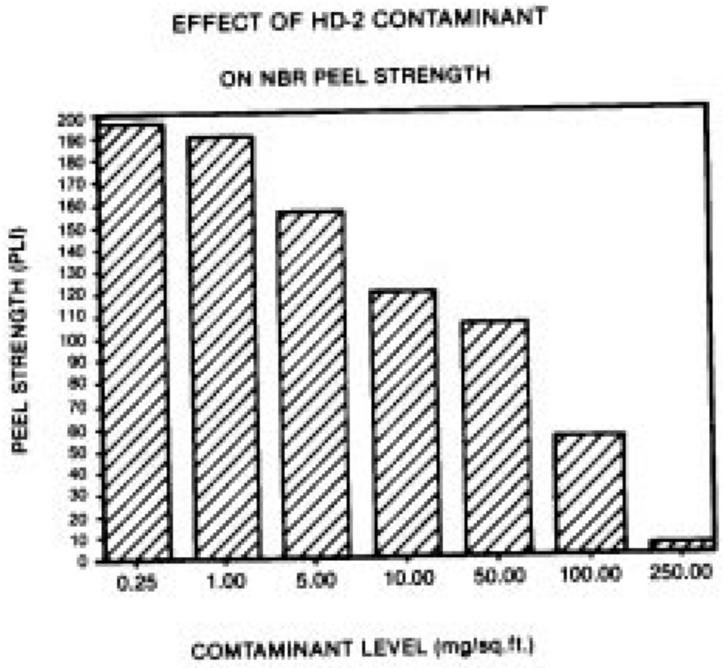


Case Study

- How Clean is Clean? Defining Acceptable Cleanliness Levels.
- Mantosh K. Chawla Photo Emission Tech., Inc. 3255 Grande Vista Drive, Newbury Park, CA 91320



Surface Cleanliness vs. Peel Strength
Figure 1



"A Noncontacting Scanning Photoelectron Emission Technique For Bonding Surface Cleanliness Inspection"
by Dr. Raymond L. Gause. NASA Marshall Space Flight Center. Presented to the Fifth Annual NASA NDE Workshop Cocoa Beach, Florida.

Optically Stimulated Electron Emission

Pros	Cons
• *Very surface sensitive* • *Field use capable* • *Used as a screening technique*	• *No chemical information* • *Possibility of damaging organics (contaminant can break down)* • *Highly recommend follow-up is with another technique for non-ambiguous contaminant identification.*

Pricing for Chemical Surface Characterization by techniques

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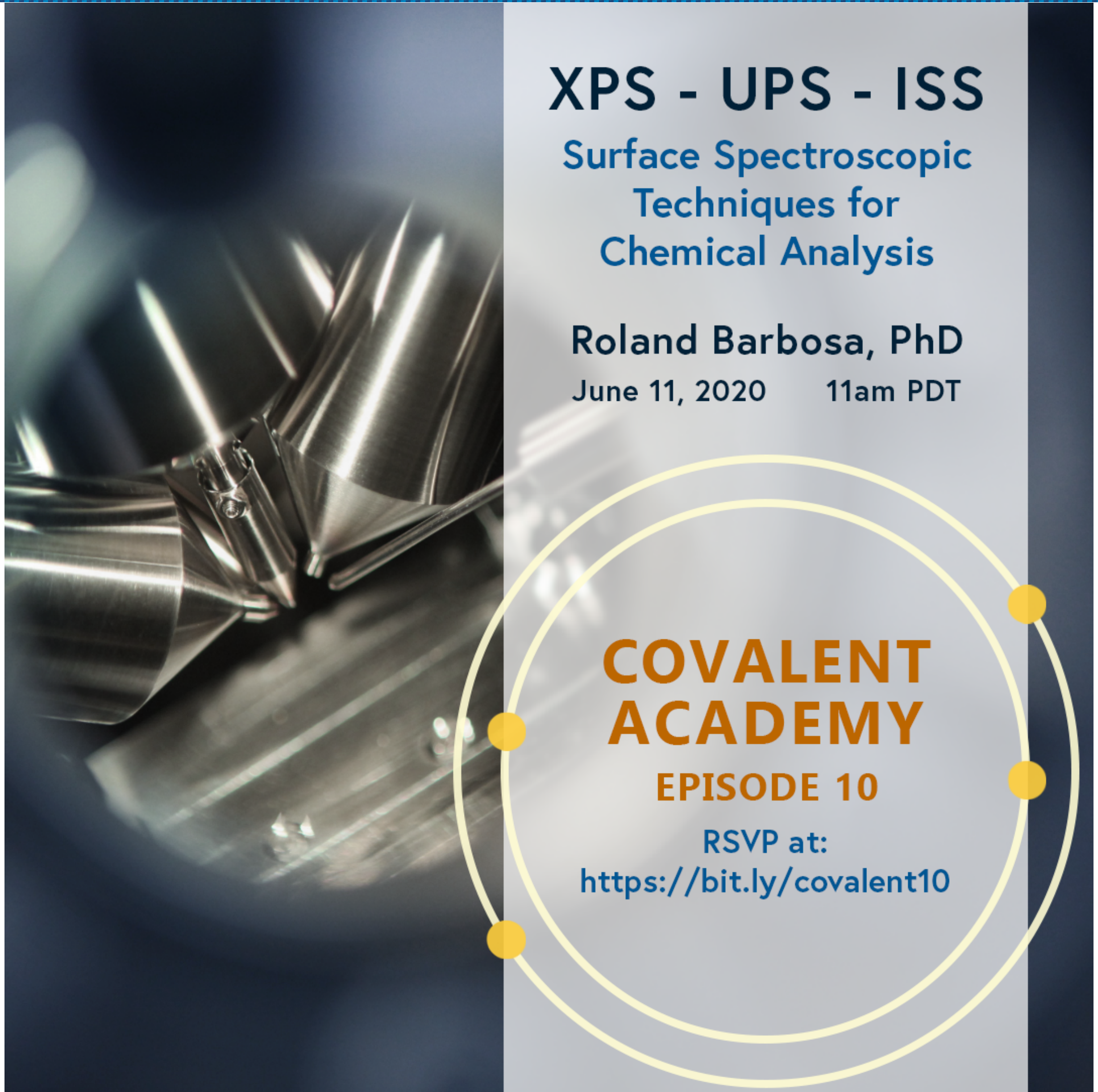
	XPS	LA-ICPMS	ATR-FTIR	Scanning Electron Microscopy	Transmission Electron Microscopy	Auger
You May Hear This Referred to As	ESCA	Laser Ablation ICPMS	ATR	SEM or HRSEM	TEM	AES
Key Manufacturers	**ThermoFisher**	**ThermoFisher**	**ThermoFisher** Agilent Bruker Shimadzu Jasco	**ThermoFisher** JEOL Zeiss Hitachi Tescan Nikon	**ThermoFisher** JEOL Hitachi	**Physical Electronics (Phi)**
Substrate Size Limitations	cm sized	Not applicable	< 6 inch	Most analytical Services < 200mm	Coupons	cm sized
Field of View /spot size	10 to 400 microns	500 microns	mm beam	1µm to 2mm	2nm to 10µm	10 nm to 1 mm
Particular challenges	Charging of samples	Cannot be highly reflective	Needs layer > 100 nm	Non-conductive samples charging	Very small field of view	Charging of samples
Cost @ Covalent	**$365/sample (survey) $730/sample (survey+hi-res)**	**$700/sample**	**$175-$225/sample**	**$325 / hr (standard res) $400 / hr (hi-res)**	**$1200 / sample (standard sample including prep)**	**$335/hr $650/hr (higher-end scanning)**

Wrapup

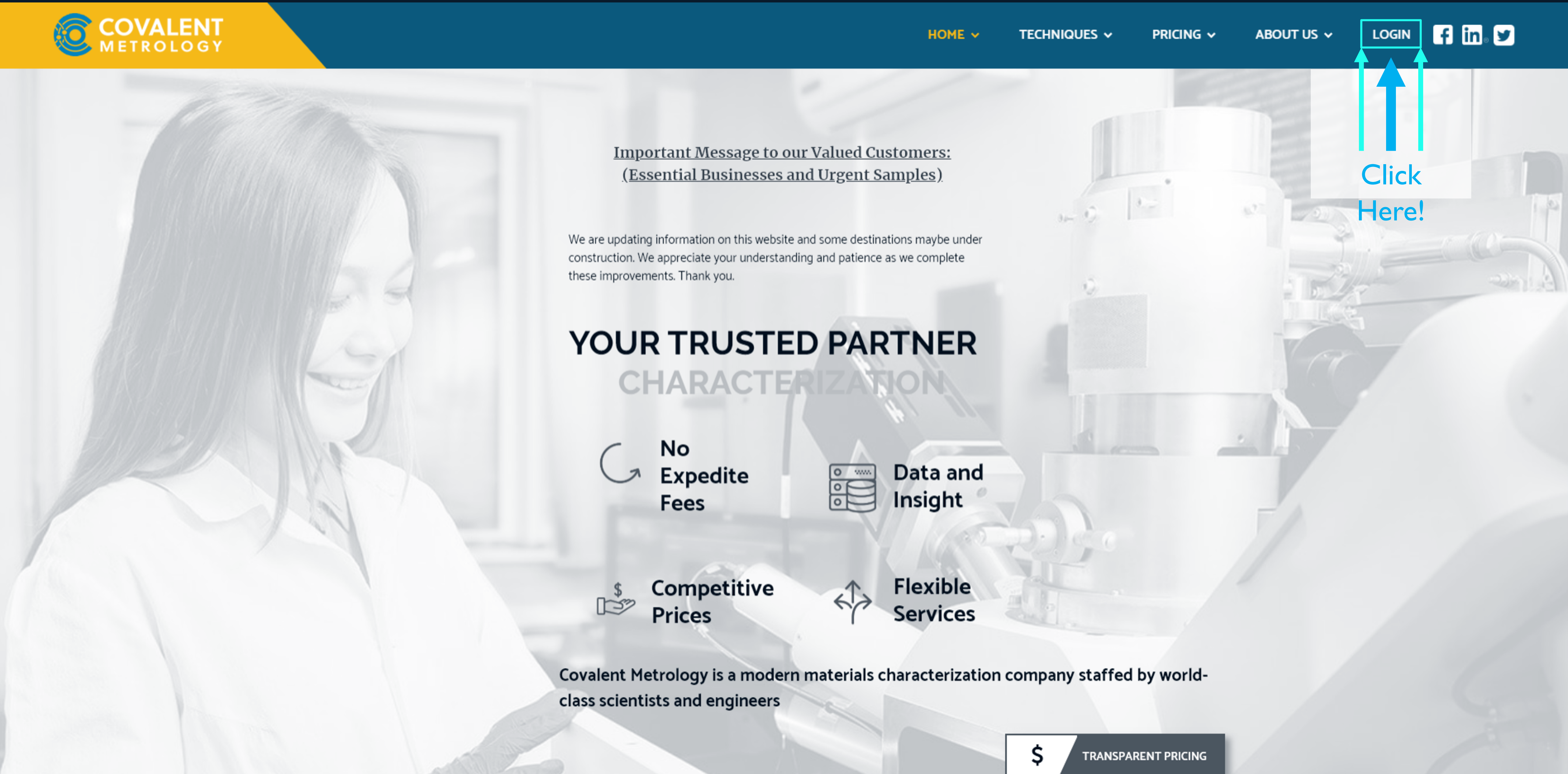
- Myriad of metrology techniques available
- New technologies and/or new versions of older technologies being released all the time
- Choosing the optimum technique can make a difference

- **Remember:**
  – It is easy to generate data. It is difficult to generate relevant data.

Next episode



Covalent Community



Covalent Community

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Data Portal

Customer Access to Data & Community Content

The DATA PORTAL is used by Customers and Lab Partners for uploading and downloading data. It requires two-factor authentication and advanced password protection. Data Portal users have complete access through their home page on the portal to all Community content, and do not require a separate Community account.

Covalent Community

All Other Users

The COVALENT COMMUNITY PORTAL requires password entry. It contains webinar and other metrology and characterization-related content that we believe would be useful and educational for the materials science innovation community. It does not provide access to any customer data and should only be used by individuals that are not Covalent customers or lab partners.

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Thank You

covalentmetrology.com