Report from Group B: Experimental Objectives of an Expert System for XPS

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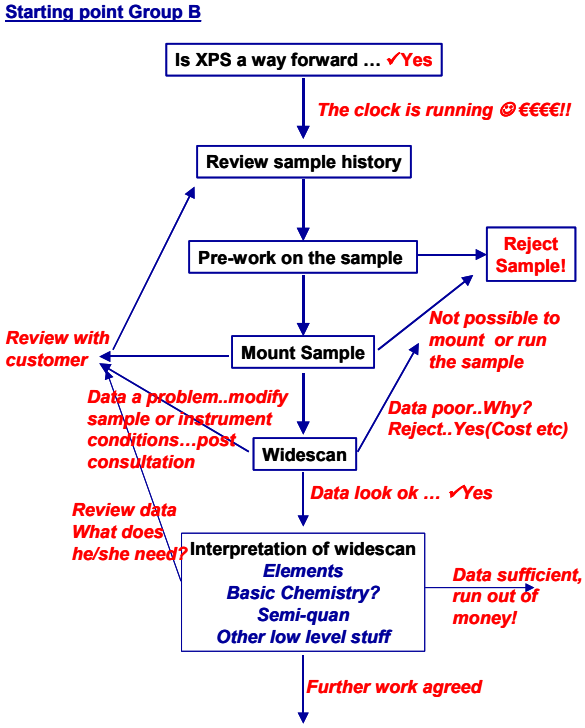
Summary:
The analyst uses XPS to examine many kinds of materials, present in many forms, to solve many types of problems, using many different experimental approaches, and with knowledge of many experimental limitations. By studying how an analyst interacts with a client about a new problem and by detailing five categories related to an XPS experiment (materials, forms, customer objectives, experimental approaches, and instrument limitations), we can begin to elucidate the dozens of 'expert rules' the analyst consciously and unconsciously employs to direct an XPS experiment.

Here is a starting point for looking at the experimental objectives for an XPS expert system. A customer brings some 'samples' to an analyst and begins to explain a problem that needs to be solved. The process the analyst uses to conduct an XPS experiment can be diagrammed with the flowchart (below).

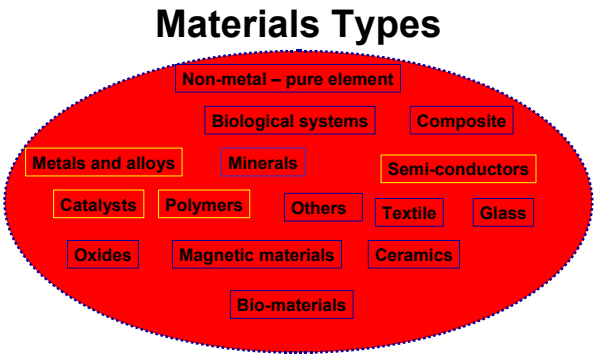
What do we do as analysts?

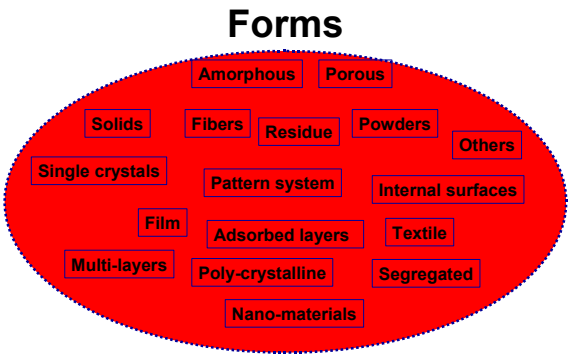


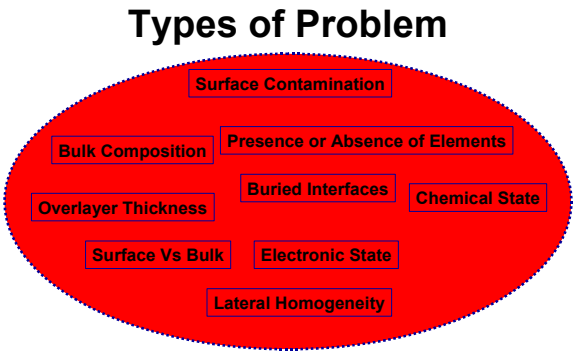
Modules from this?

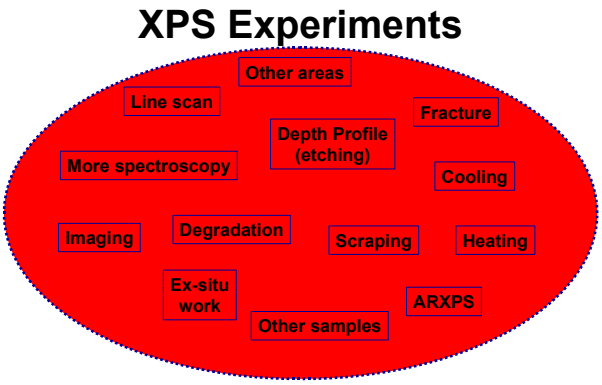
- Materials types
- Forms
- Types of problem
- Types of XPS expt
- Limitations of XPS

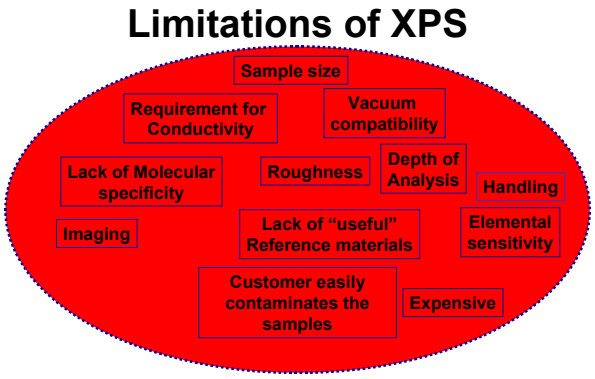
The analyst has a near-infinite number of approaches that can be taken in the course of an XPS experiment. The approach that is used will depend on (1) the kind of material to be analyzed, (2) the form of the material, (3) the problem that is required to be solved, (4) the experimental or instrumental technique that can be employed, and (5) the known limitations of the instrumental method. The 5 categories (modules) that direct the analyst's approach are detailed below.











Category 1, Material Type. For different materials, here are various consequences for an XPS experiment that can be considered for preparing 'expert rules'.

Materials	Consequences - Pre XPS	Consequences- from XPS	Proposed Actions	Post XPS issues
Metals & alloys	If possible grind front surface	Expect to see high C contamination	Solvent clean (Methanol/Isopropanol(IPA))	
	Flood gun not likely to be required		Mild heat in vacuum (~100degC)	
	Minimal surface charging		Soft - low fluence, low ion energy ion etch	
			Run all spectral regions prior to ANY ion etch	
		Expect to see oxide film	Check spectral library	
		Expect to see metal/oxide peak components	Check spectral library	
		Expect mixed valence states (e.g.,II+III)	Check spectral library	
		Expect preferential oxidation in alloys	Expect not to see all the major elements	
Polymers	May not pump down - outgassing			
	Consider isolating the sample			
	Mount using ceramic holder plate			
		Expect to see carbon	Expect adventitious C in low levels	
			Expect challenges with referencing	
			Use elemental ratios to determine approx composition	
			Consider use of second "C" ref system -spin cast	
			Other deposited references may be considered	
		Spectra dominated by C,O, and N (or F,Cl,S)		
		Expect charging	Use neutraliser	
			Take care optimising the neutraliser settings	
			Charging may be vertical or lateral	
		Expect degradation	Do virtual profile	Clean machine after work!
			Minimise exposure in any given region	Clean machine after work!
			Try to use lower X-ray flux conditions	Clean machine after work!
			Expect changes in signal intensity, poorer quantitation	Clean machine after work!
			Expect changes in chemistry with time, poorer characterization	Clean machine after work!
Semiconductors	Sample size			
		Expect low C contamination	rejoice	
		Expect relatively high signal from standard instrument settings	rejoice	
		Expect to see oxide film	Check spectral library	
		Be aware of possible channeling effects	Changes in intensity with analytical conditions	
		Expect to see preferential oxidation in some systems	Check spectral library	
		Expect band bending	Odd positions compared to lit database	
Magnetic materials	Take care on sample handling - MAKE secure			
	Degauss if possible			
	Use instrument that belongs to someone else			
	Use instrument with magnetic immersion lens			
	If possible grind front surface	Expect to see high C contamination	Solvent clean (Methanol/Isopropanol)	
	Flood gun not likely to be required		Mild heat in vacuum (~100ºC)	
	Minimal surface charging		Soft - low fluence, low ion energy ion etch	
			Run all regions prior to ANY ion etch	
		Expect to see oxide film	Check spectral library	
		Expect to see metal/oxide peak components	Check spectral library	
		Expect mixed valence states (e.g.,II+III)	Check spectral library	
		Expect preferential oxidation in alloys	Expect not to see all the major elements	
Ceramics	Consider carefully the method of sample handling			
	May not pump down - outgassing			
		Expect medium levels of C contamination		
	Probably high surface roughness	Low signal intensity	Consider changing collection conditions	
		Charging may be vertical or lateral	Extensive charge neutralization study may be required	
		Expect mixed valence states (e.g.,II+III)	Check spectral library	
		Expect complex charge states	Check spectral library	
		Expect large displacement from reference values	Charge neut is required	
		Expect possible beam damage	Adjust analytical conditions	
Catalysts	Consider carefully the method of sample handling			
	May not pump down - outgassing			
	May be air sensitive use glove box/bag			
	May be health and safety issues			
		Expect medium levels of C contamination		
	Probably high surface roughness	Low signal intensity	Consider changing collection conditions	
		Charging may be vertical or lateral	Extensive charge neutralization study may be required	
		Expect mixed valence states (e.g.,II+III)	Check spectral library	
		Expect complex charge states	Check spectral library	
		Expect large displacement from reference values	Charge neut is required	
		Expect possible beam damage	Adjust analytical conditions	
		Expect to see metal/other peak components	Check spectral library	
		Expect preferential enrichment compared to predicted composition	rejoice	

Category 2, Types of Materials Problems. From the dozen or so kinds of materials problems that XPS is commonly required to solve, an analyst-expert can list a number of consequences for the XPS experiment that the expert system needs rules to address.

Types of problems from customer:	**Consequences**
Surface contamination	• Uniform vs. patchy • Attenuation of bulk intensities • Presence of expected or unexpected material
Composition (elemental)	• Surface vs. bulk • May only need widescan • How much accuracy?
Composition (chemical state, oxidation state)	• Nearly always requires narrow scans • The chemical state result is only from the surface, not the bulk • Binding energy matches difficult for charging specimens
Overlayer thickness(es) & composition(s)	• Angle resolve if <5nm • Sputter etch if >5nm • Rough specimens very difficult
Surface vs bulk, surface segregation, enrichment	• Information depth issues
Presence or absence of something	• How many samples? • Elements, chemical states expected at what concentration?
Lateral inhomogenity	• Domain size vs. analysis area
Valence band, electronic state, band bending	• Surface may not be representative of bulk • Effect of specimen handling/transport
Evaluate a surface process (cleaning, plasma, wear, etc.)	• Many specimens possible • Sample-set selection important
Adhesion failure	• Mating surfaces • Lateral inhomogeneity
Color, haze	• May be much thicker than analysis depth, often below the surface, low probability of success
Residue	• A bulk type of analysis

Category 3, Material Form, and **Category 4, Experimental Approaches**. The form of the analysis specimen will strongly dictate the kinds of experimental approaches which can be employed. Here is a matrix which weights the utility of common experimental approaches for many material forms.

Form	ARXPS	Line Scan	Etching	Depth Profile	Imaging	Scraping	Cooling	Heating	Semiquant	Quant	Chem.State
Porous	0	0	0	0	1	0	3	1	1	0	1
Non-porous	3	2	2	2	2	1	1	2	3	3	3
Fiber	*	1	0	0	3	0	*	*	1	0	1
Powder	0	0	1	0	1	0	1	1	1	0	3
Single Crystal	3	1	*	0	3	0	1	2	1	2	3
Pattern Sample	2	3	1	*	3	0	1	1	1	2	3
Interfaces	*	*	1	3	*	1	0	0	1	0	*
Unsupported Film	3	2	*	*	2	1	0	0	1	3	3
Adsorbed Layer	3	1	0	0	3	0	2	0	1	3	3
Multi-layer	0	0	1	3	*	0	0	0	1	*	1
Others											

1 possible
0 impossible
2 useful
3 recommended
* perhaps

The experimental approaches which the analyst can employ are also dictated by the kind of materials problem that needs to be solved. Here is a second matrix which weights the utility of these combinations.

Types	ARXPS	Line Scan	Etching	Depth Profile	Imaging	Scraping	Cooling	Heating
Surface Contamination	3	0	3	1	2	0	1	0
Bulk Composition	2	0	3	3	3	3	1	1
Presence of Absence of Elements	1	0	1	1	0	0	0	0
Overlayer thickness	3	0	2	3	0	0	0	0
Buried Interfaces	*	*	1	3	*	0	0	0
Surface vs Bulk	3	0	2	3	0	0	0	0
Electronic State	0	0	0	0	0	1	0	0
Lateral Homogeneity	0	3	*	0	3	0	0	0
Other Problem								

1 possible
0 impossible
2 useful
3 recommended
* perhaps

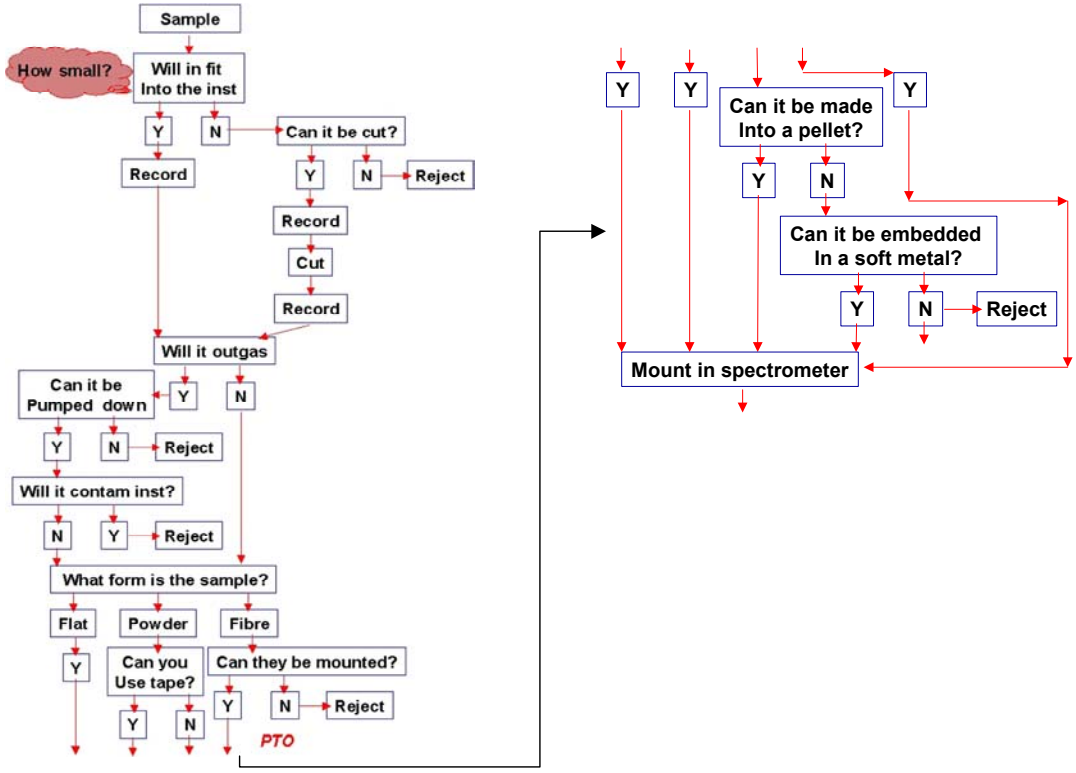
Category 5, Experimental Restrictions/Limitations. There are many limitations to the sample, the instrument, and the experiment that the analyst needs to be concerned with and address. Here are 40 limitations that will require 'expert rules'.

Input needed for analysis

Size of Sample	Temperature Limits
Size of Analysis Beam	Desired Lateral Resolution
Sample surface state	Sample Volatility
Conductivity	Signal / Noise
Health restrictions	Energy Resolution
Charging	Detection Limits
Outgassing	Step Size
Degradation due to UHV	Data Quality
Degradation due to X-rays	Smoothing
Degradation due to Flood Gun	Deconvolution
Degradation due to Ion Beam	Source FWHM
Differential sputtering	Beam Shape
Depth of Information	Beam Alignment
Analysis Volume	Surface Migration
Depth of Material	Diffusion
Final Depth of Analysis	Physical Rearrangement
Roughness	# of Samples per Mount
Lifetime of Surface	Data Transfer
Available Money Optimization	Fracture
Available Time Optimization	Grain Boundary

Every portion of the XPS experiment can be diagrammed as a flowchart and these flowcharts can be useful in developing rules for the expert system. Here is a flowchart for the handling and mounting of specimens.

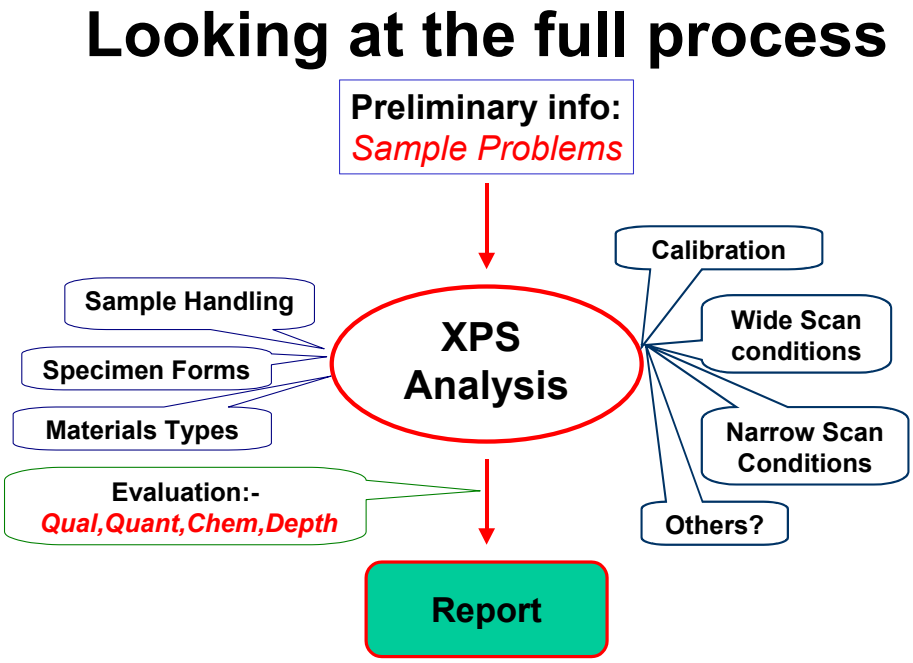
Handling and Mounting Specimens



There are a number of international or other standards which can guide the analyst regarding handling and mounting of specimens, also regarding charge-control of specimens:

ISO 18117 (draft)	Surface chemical analysis – Handling of specimens prior to analysis
ASTM E1829	Guide for Handling Specimens Prior to Surface Analysis
ASTM E1078	Guide for Procedures for Specimen Preparation and Mounting in Surface Analysis
ISO 19318 (draft)	Surface chemical analysis – X-ray photoelectron spectroscopy – Reporting of methods used for charge control and charge correction
ASTM E1523	Guide for Charge Control and Charge Referencing Techniques in X-Ray Photoelectron Spectroscopy

Most of the expert system rules regarding Experimental Objects for XPS are considered before the XPS spectral data are even acquired. But one step at the end of the experiment, **Report Generation**, may also require a set of expert system rules.



Here is a listing of common reporting requirements for XPS results. The items on this list will be useful for developing expert system rules.

Report

1. Report number, purchase order number, etc.
2. Description of the problem; objective
3. Experimental
   - 3.1. Sample description
   - 3.2. XPS system
4. Results
   - 4.1. Composition – Default information: no H, surface sensitivity, sensitivity limits for elements requested, effect of adventitious carbon, etc.
   - 4.2. Composition based on identified elements
     Precision and accuracy statements
   - 4.3. Picture of sample before and after analysis
   - 4.4. Near surface composition (ARXPS)
     Mostly qualitative
     Interpretation is model dependent
     Topographical effects
   - 4.5. Depth distribution (depth profiling)
     Estimate of depth
     Estimate of depth resolution
     Detection limits for impurities
     Topographical effects
   - 4.6. Imaging
     Spatial resolution dominated by counting statistics
     Registration issues
     Long exposure time issues (drift, damage, etc)
   - 4.7. Chemical state
     Level 1: more than one chemical state detected
     Level 2: Identification of chemical states
     Limits on interpretation depends on elements involved
     Curve fitting issues