Practical Introduction

to the Methods of Surface Analysis

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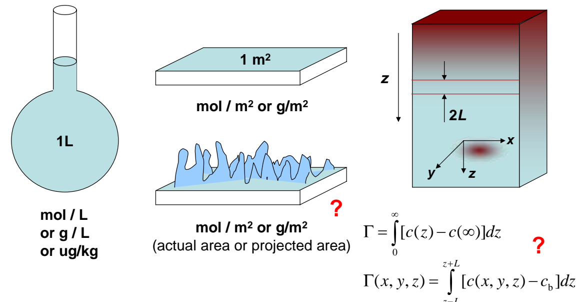
Quantitative Surface Analysis vs Bulk Analysis

Two questions that puzzle the analyst:
- ***What it is*? – qualitative analysis**
- ***How much of it is there*? – quantitative analysis**



$$\Gamma = \int_0^\infty [c(z) - c(\infty)]dz$$

$$\Gamma(x,y,z) = \int_{z-L}^{z+L} [c(x,y,z) - c_b]dz$$

Quantities We Are Going To Deal With:

Order-of-Magnitude Estimations

(1) ***Surface density of water molecules at the surface of a water drop:***

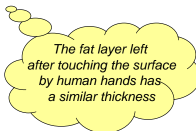
$$d = \left(\frac{\rho N_A}{M_W}\right)^{2/3} = \left(\frac{10^6 \frac{grams}{m^3} \times 6 \cdot 10^{23} \frac{molecules}{mole}}{18 \frac{grams}{mole}}\right)^{2/3} = 10^{19} molecule / m^2$$

(2) ***Thickness of TTA film produced by drying 1 drop of 100 ppm solution on the surface of a 50 öre coin (~2 cm²):***

1 drop ~ 0.02 ml ~ 0.02 g has $2 \cdot 10^{-6}$ g or $2 \cdot 10^{-8}$ mol TTA
1 monolayer ~ 10^{-10} mol/cm², so we have ~ 100 monolayers

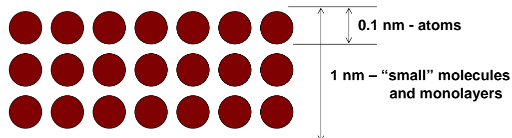
Experiment planning:
- Appropriate method is used
- Concentrations are within the detection range
- Sample is handled properly

The fat layer left after touching the surface by human hands has a similar thickness



What Is a Surface or How Thin Is Thin?

- **Earth crust (50 km) is thin as compared to the Earth diameter (12,700 km).**
- **Paint layer or a galvanic coating (100 um) are thin as compared to substrate dimensions.**

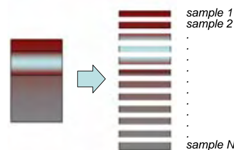


As the Chemistry Is Concerned, "Nano" and Below is Surface; "Micro" and Above is Bulk

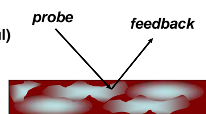
Classification of the Methods for Surface Analysis

Analysical methods can be:

Destructive (sampling followed by the analysis of samples)
- **- slicing,**
- **- etching,**
- **- scrubbing,**
- **- laser ablation,**
- **- ion beam,**
- **- plasma sputtering;**



Nondestructive (in-situ probing)
Probes: human receptors (raraly useful)
- **- electrons**
- **- light (IR, UV, X-rays)**
- **- neutrons**
- **- alpha particles**



Classification of the Methods for Surface Analysis (cont'd)

Chemical ⇒ information about chemical composition:
- **- Extraction followed by HPLC or GC-MS of extracts;**
- **- Dissolution or selective etching followed by solution analysis;**
- **- Surface "titration" by appropriate coupling agents.**

Physical ⇒ information about physical properties:
- **- Optical properties of thin films by reflectivity or ellipsometry;**
- **- Surface structure by electron microscopy;**
- **- Surface roughness by interferometry or stylus profiling;**
- **- Work function of metals and semiconductors;**

Physicochemical ⇒ information about chemical composition based on measurements of specific physical properties
- **- Spectroscopic techniques (IR, AES, XPS, EDX, SIMS, RBS, GDOES)**

X-Ray Photoelectron Spectroscopy (XPS)
a.k.a.
Electron Spectroscopy for Chemical Analysis (ESCA)

(Siegbahn, 1967)

Step 1: Excitation by X-rays
(Mg K_α 1253.6 eV or Al K_α 1486.6 eV radiation)

Step 2: Relaxation by emitting a photoelectron

XPS Applications

1. **Broad spectrum (element identification)**
2. **Detailed spectrum (element quantification)**
3. **High-resolution spectra (valent state differentiation)**

ESCA as an Analytical Tool

In-situ Element Identification

$E = h\nu - E_b - e\varphi$

Things to keep in mind:

(1) Elemental analysis is not the same as "chemical" analysis of compounds;
(2) Depth of analysis is determined by electron free path (1 to 10 nm);
(3) Indirect in-depth profiling via angle-dependent measurements;
(4) Sensitivity limit 0.1 to 1 at.%

XPS Applications: Examples

Chemical analysis

Depth profiling by angle-dependent measurement

Depth profiling by etching (sputtering)

Elemental composition mapping

Electron Microscopy with Microanalysis (SEM / EDX) and Electron Probe Microanalysis (EPMA)

Secondary and backscattered electrons and X-rays

Incident electron beam (10-20 keV)

Information provided:

- Surface appearance (in black and white, up to 1,000,000x)
- Elemental composition if an EDX (EDS) module installed (atomic no. ≥ Na, surface layer ca 1 um in depth)
- Element distribution over the surface (surface mapping)

The ideal sample should be:

- Solid
- Non-volatile (non-gassing at 10^{-6} to 10 mbar)
- High melting point
- Electrically conductive (or rendered so by Au deposition)

Electron Microscopy with Microanalysis (TEM / EELS)

Features:

- Imaging of internal structure, inclusions and defects in thin films with an atomic resolution (~ 0.1 nm)
- EELS (electron energy loss spectroscopy) or EDS (energy dispersive X-ray spectroscopy) modules for detecting low-Z elements and transition metals.

HREELS – high resolution EELS also provides information on molecular vibrations

Sample limitations:

- Thin films (<0.1 um) are required.
- Non-volatile solids or frozen liquids (cryo-TEM)

Energy Dispersive X-Ray Spectroscopy (EDX, EDS) and Auger Electron Spectroscopy (AES)

Step 1: Ionization (2 to 10 keV electrons or X-rays)

once electrons are used only conductive samples can be analysed

Step 2: Relaxation by emitting an Auger electron (used by AES) or X-ray quantum

X-ray — hv (used by EDX)

Auger — Auger electron (used by AES)

Secondary Ion Mass Spectrometry (SIMS, ToF SIMS)

Features:
- Very high sensitivity (below ppm level)
- Identification of all elements and molecular fragments
- In-depth profiling, erosion speed ~ 0.001 to 10 um per hour
- Surface mapping (sub-um) and 3D mapping (surface + in-depth)

In ToF SIMS m/z is determined from time of flight of ions

Secondary Ion Mass Spectrometry: Application Examples

Compound identification

Mass spectrum of Metoprolol showing molecular and fragment peaks

Integration of specific ion currents by time provides means for accurate quantification of chemical species

Surface mapping

In-depth profiling

Rutherford Backscattering (RBS) and Particle Induced X-Ray Emission (PIXE)

incident He^{2+} (1 – 3 MeV)

backscatterd He^{2+} (RBS)

X-rays (PIXE)

Glow Discharge Optical Emission Spectroscopy (GDOES) or Mass Spectrometry (GDMS)

Glow discharge (Ar^+) (material atomization and atom excitation) ⇨ **Optical emission by excited atoms** ⇨ **Spectrometer (element identification based on atomic spectra or *m/z* ratio)**

it's rather bulk than surface analysis

Comparison of Various Methods (by Techniques)

Probe	Method	Emission
Photons	XRFS	Photons
Photons	XPS	Electrons
Electrons	EDX	Photons
Electrons	AES, EELS	Electrons
Ions	PIXE	Photons
Ions	SIMS, RBS	Ions

Comparison of Various Methods (by Analytical Capabilities)

Method	AES	XPS (ESCA)	SIMS	RBS (IBA)	EDX (EDS)	GDOES (GDAES)
Detected elements	>Li	>He	>H	>C	>Na	>H
Detection limit, at.%	0.1	1	0.0001	0.01 to 1 (depend on Z)	0.1	0.0001
Max. depth (resolution), nm	0.3-3 (no)	1-3 (with sputter)	1000 (1)	1000 (10)	1000 (no)	100000 (10)
Lateral resolution, um	0.1	10	0.1	1000	0.1	no
Chemical structure	no	yes, limited	yes	no	no	no
Organic analysis	no	yes	yes	no	no/yes (elemental)	no/yes (elemental)

Commercial / in broad use — Academic / specific applications

Vibrational Spectroscopy: Surface-Specific Methods

Method	Full Name	Based on	Application Notes
DRIFT	Diffuse Reflectance Infrared Fourier Transform	Diffuse reflectance from powders	Used in catalyst and adsorbent research; monolayer sensitivity for disperse systems with high specific surface areas.
ER FT-IR	External Reflectance	Specular reflectance from metal surface	0.1 to 10 um organic films on metals.
ATR / MIR FT-IR	Attenuated Total / Multiple Internal Reflectance	Multiple reflectance and multiple light passes through adsorbate film	Penetration depth (signal averaging) is still around 1 um; but both methods achieve monolayer sensitivity on flat surfaces.
IRRAS RAIRS	Infra-Red Reflection Absorption	Different absorption of s- and p- polarized light	Monolayer sensitivity on flat metal surfaces
VSFS	Vibrational Sum Frequency Spectroscopy	Nonlinear polarization and sum frequency generation	Truly surface-specific. By symmetry rules, only surface molecules can give SF signal. Distinguish surface groups from bulk groups.
SERS	Surface Enhanced Raman Spectroscopy	Enhanced inelastic scattering by adsorbed molecules due to surface plasmons	Molecules adsorbed on special (molecularly rough) metal substrates (Ag, Au, Cu).

ATR-FTIR — RAIRS (FTIR beam, PEM, Lens, Detector, Polarizer, Sample)

Vibrational Spectroscopy:
What It Can and What It Cannot

N≡C—CH$_3$ on Ag: ν(CN) 2270 cm^{-1} (σ-bonding)

N≡C—CH$_3$ — Free state: ν(CN) 2250 cm^{-1}

N≡C—CH$_3$ on Ag: ν(CN) 2150 cm^{-1} (π-bonding)

N=C—CH$_3$ on Ag: ν(CN) 1600 cm^{-1} (chemisorption)

Line assignment is very easy for small molecules but it's getting increasingly difficult with increasing molecular size. Shifts are *not known* a priori.

Thin Film Analysis

An Overview of the Physical Methods for Determination of Surface Morphology and Thickness of Adsorbed Films (1 to 100 nm)

- **Ellipsometry**
- **Quartz crystal microbalance**
- **Reflectivity of neutrons and X-rays**
- **Atomic force microscopy (AFM)**

Ellipsometry

Ellipsometry is based on the measurement of the light polarization change upon reflection from a surface or interface.

Ambient (n_0, k_0); Film 1 (n_1, k_1, d_1); Film 2 (n_2, k_2, d_2); Film (n, k, d); Substrate (n_s, k_s)

Application notes:

- **Transparent and smooth dielectric films from 0.1 to 100 nm.**
- **No chemical information; film thickness and refractive index only.**
- **Ellipsometry data are a model-dependent:**
  Measurement ⇒ Model ⇒ Best Fit Parameters

Quartz Crystal Microbalance (QCM)

cell

Applications:
- thin film deposition onto a surface from gases or liquids (ng/cm^2);
- viscoelastic properties of adsorbed phases

$$\Delta m = -\frac{C\Delta f}{n}$$

$$h = \Delta m / \rho$$

f – measured frequency shift;
C – instrument-specific constant (18 ng Hz^{-1} cm^{-2} for 5 MHz crystal);
ρ – adsorbed layer density;
n = 1,3,5,... – the overtone number.

Rigid / Viscoelastic — Amplitude vs. Time

Reflectivity of Neutrons and X-Rays

Incident
Reflected
n_1
α
n_2
l
n_3
Transmitted

Reflectivity (ratio of intensities R^2/I^2) changes with the incidence angle,

$$\mathscr{R}(q) = \frac{R_{12}^2 + R_{23}^2 + 2R_{12}R_{23}\exp(-iql)}{1 + R_{12}^2 R_{23}^2 + 2R_{12}R_{23}\exp(-iql)}$$

$$q = \frac{4\pi}{\lambda}\sin\alpha$$

R_{ij} – Fresnel coefficients;
λ – wavelength

Wave-particle dualism says that neutrons behave as a short-wave radiation,
$\lambda = h/m_n v$ (h – Planck's constant, m_n – neutron mass and v – velocity)
and hence the classical optical formulae can be used.

- **Neutrons are scattered by nuclei, whereas X-rays are scattered by electron clouds.**
- **When neutron probe is used, the refractive index can be changed by H/D isotopic substitution.**

Special Applications of Neutron Reflectivity

(When NR Can What Other Methods Cannot)

Determination of the orientation of surfactant molecules at Interfaces

NMe_3Br NMe_3Br NMe_3Br NMe_3Br

null water

NR isn't a routine method!
(1) Time-consuming;
(2) Require knowledge and synthetic effort;
(3) Require neutron source.

Deuterated surfactant: average density of molecules per unit area can be measured (do you really need NR for that!)

Many component system with one compound deuterated: density of deuterated compound can be found in the presence of other compounds

Alkyl chain deuterated; (borders of the region where alkyl chains are localized can be determined)

Atomic Force Microscopy (AFM)

Photodetector
Laser Beam
Cantilever
Tip
Line Scan
Surface

as seen by AFM
actual surface

When what you see is not what it is

sharper cantilever

AFM modes:
- Contact mode (profiling & friction measurements)
- Tapping mode (profiling of sensitive samples)
- Phase imaging (local nanorheology of sample)
- Force measurements

Remarks on Experiment Planning

The choice of technique is task-specific and should be based on the following considerations:

(1) Type of the sample (solid, liquid, organic, inorganic, volatile, metal, dielectric, transparent, opaque, single component or mixure, etc.);

(2) Type of information you need (surface appearance, layer thickness, composition, elemental analysis, quantitative analysis, depth profiling, surface mapping, molecular structure, etc.)

(3) Depth of surface layer of interest (nm, um, mm);

(4) Availability of appropriate technique;

(5) Analysis time and your budget.

No technique is perfect, none is universal! Work with your head!

Example: Experiment Planning

Task: Adsorption of a metal passivator from oil onto copper
Questions to ask yourself first:
- Is in-situ study possible? (YES)
- Is the copper surface in mineral oil under reducing conditions pure? (NO)
- Is mineral oil absolutely inert? (NO)

(i) The surface cannot be pure from the beginning because the exposure to air during manufacturing causes oxidation

Cu
10 to 200 nm
oxides $Cu_{64}O, Cu_8O, Cu_2O, CuO$
carbonates: $Cu(OH)_2 \cdot CuCO_3$

(ii) But the oxides can be reduced later:

$CuO + H_2 = Cu + H_2O$ (200ºC)

(iii) Is this the case? Does any oxygen remain? Are there other reactive compounds present? Is oil acidity growing? Is it possible without oxygen?

Example: Experiment Planning (cont'd)

Feasibility analysis (helps to skip re-inventing the wheel)

⇨ What do you expect to find: oxidation state: +2 or +1?

Cu^{2+}/Cu = +0.34 V
Cu^{+}/Cu = +0.52 V

Will the reaction $2Cu^{+} \rightarrow Cu^{2+} + Cu$ *occur?*

Yes, of course, $\Delta G = -zF\Delta E_0 = -2F\cdot(0.52) + 2F\cdot(0.34) < 0$,
but it only applies to aqueous solutions.

Cu^+/Cu^0 potential

CuL⁺ stability

ClO_4^-	+0.52V
Cl^-	+0.14V
CN^-	-0.43V
Me_2S	-0.93V

Equilibrium shifts:

$2CuCl + 2en \rightarrow [Cuen_2]^{2+} + 2Cl^- + Cu^0$
but
$[Cu(NH_3)_4]^{2+} + Cu^0 \rightarrow 2[Cu(NH_3)_2]^+$

Unless specifically stabilized (e.g. by porphyrin), Cu^{2+} is very strong oxidant in organic solvents. Cu^+ is the preferred state (also stabilized by olefins).

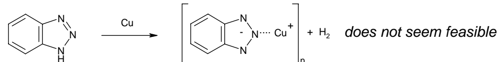
Example: Experiment Planning (cont'd)

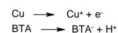
Feasibility analysis

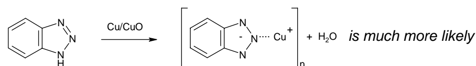
- How much of it is there:

Total = Bulk + Surface

- Which techniques will be needed:
  - Bulk analysis by ICP-AES (Cu^+ vs Cu^{2+} can be differentiated by ESR)
  - Surface analysis by what? Again, it depends on what we expect to find!







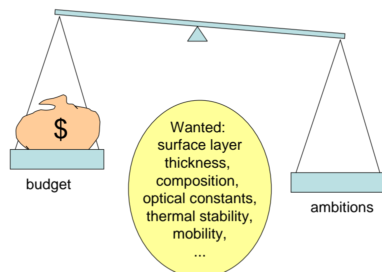
Example: Experiment Planning (cont'd)

Is there any bulk depletion of BTA?

- **yes** → Thick surface film or bulk reaction → GDOES, SIMS, EDX, ER-FTIR/Raman, Etching + CHN analysis or HPLC or similar
- **no** → Thin or no surface film and no bulk reaction → ellipsometry, SIMS, XPS, RAIRS or similar

Experiment Planning

(Comprehensiveness and Quality Do Cost Money)



Avoid mismatch between your budget and your ambitions.

A Little Understanding Is Better Than a Lot of Misunderstanding

(Part I)

Task 1: *Protein film is deposited from aqueous solution on a Ti surface. Film thickness and softness in-situ are of interest. You contacted a commercial lab "Superficial Science for Innovation Engineering" and got their offer:*

- ❑ **ESCA**
- ❑ **ToF-SIMS**
- ❑ **GDOES**
- ❑ **ATR-FTIR**
- ❑ **Ellipsometry**
- ❑ **QCM**
- ❑ **AFM**

Task 2: *Galvanized steel undergoes limited corrosion after one year atmospheric exposure in an industrial area. You want to determine the depth of corrosion penetration and primary corrosion products formed:*

- ❑ **ESCA**
- ❑ **Electron microscopy / EDX**
- ❑ **ToF-SIMS**
- ❑ **GDOES**
- ❑ **ER-FTIR**
- ❑ **Ellipsometry**
- ❑ **AFM**

A Little Understanding Is Better Than a Lot of Misunderstanding

(Part II)

After exposing a copper substrate to dodecylmercaptan solution, student X suspecting that there might be some interaction between Cu and sulphur, carried out ESCA and EDX, but got apparently conflicting results:

- ESCA: Cu: 20 at%; C: 65 at.%; S: 5 at%; O: 10%;

- EDX: Cu: 80%; O: 19%; C and S < 1%.

What is the reason? What would happen if ESCA sample were sputtered with Ar^+ ions?

Further, he/she decided to determine *molecular composition* of sulphur-containing layer by using:

- ❑ **ToF-SIMS**
- ❑ **IRRAS**
- ❑ **QCM**

Is it an appropriate choice of techniques?

Some Useful References

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