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 is it? – qualitative analysis
➢ How much of it is there? – quantitative analysis

Quantities We Are Going To Deal With:
Order-of-Magnitude Estimations

(1) Surface density of water molecules at the surface of a water drop:
\[
d = \left( \frac{PN_a}{M_w} \right)^{2/3} = \left( \frac{10^6 \text{ atm} \times 6 \times 10^{19} \text{ molecule atm}^{-1}}{18 \text{ g/mole}} \right)^{2/3} = 10^{4} \text{ molecule/m}^2
\]

(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 \times 10^{-6} g or 2 \times 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

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
Analytical 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 (rarely 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)**

Electron Spectroscopy for Chemical Analysis (ESCA)

Step 1: Excitation by X-rays
(Mg K$_{\alpha}$ 1253.6 eV or Al K$_{\alpha}$ 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

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.%

**Electron Microscopy with Microanalysis (SEM / EDX)**

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.

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)

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

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)

Secondary Ion Mass Spectrometry: Application Examples

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

Comparison of Various Methods (by Techniques)
Comparison of Various Methods (by Analytical Capabilities)

<table>
<thead>
<tr>
<th>Method</th>
<th>AES</th>
<th>XPS (ESCA)</th>
<th>SIMS (IBA)</th>
<th>RBS (EDS)</th>
<th>EDX (EDS)</th>
<th>GOEDS (GDAES)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detected elements</td>
<td>no/yes</td>
<td>no/yes</td>
<td>no</td>
<td>no/yes</td>
<td>no/yes</td>
<td>no</td>
</tr>
<tr>
<td>Detection limit, at.%</td>
<td>0.1 - 1</td>
<td>0.00001 - 0.01 to 1 (depending on Z)</td>
<td>0.1 - 1</td>
<td>0.0001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Resolution, nm</td>
<td>0.3 - 3</td>
<td>1 - 3 (with speckles)</td>
<td>1000 (1)</td>
<td>1000 (10)</td>
<td>1000 (100)</td>
<td></td>
</tr>
<tr>
<td>Chemical structure</td>
<td>no/yes</td>
<td>yes/no</td>
<td>yes/no</td>
<td>yes/no</td>
<td>yes/no</td>
<td>yes/no</td>
</tr>
<tr>
<td>Organic analysis</td>
<td>no/yes</td>
<td>yes/no</td>
<td>no/yes</td>
<td>yes/no</td>
<td>yes/no</td>
<td>yes/no</td>
</tr>
<tr>
<td>Commercial / in broad use</td>
<td>Academic / specific applications</td>
<td></td>
<td></td>
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</tbody>
</table>

Vibrational Spectroscopy: Surface-Specific Methods

**Vibrational Spectroscopy: What It Can and What It Cannot**

![Image of vibrational spectroscopy](image)

**Ellipsometry**

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

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)**

Applications:
- Thin film deposition onto a surface from gases or liquids (ng/cm²).
- Viscoelastic properties of adsorbed phases

\[
\Delta m = \frac{C \Delta f}{f} = \frac{\Delta m}{\rho}
\]

- \( \Delta m \) = measured frequency shift;
- \( C \) = instrument-specific constant (18 ng Hz⁻¹ cm⁻² for 5 MHz crystal);
- \( \rho \) = adsorbed layer density;
- \( n = 1, 3, 5, \ldots \) = the overtone number.

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)

**Differential Reflection FT-IR**

External Reflectance

FT-IR

0.1 to 10 um organic films on metals. Specular reflectance from metal surface

Moving diffraction signal averaging is still around 1 um, but with multiple-antenna interferometer constant on far surfaces.

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Reflectivity of Neutrons and X-Rays

Reflectivity (ratio of intensities $R/I$) changes with the incidence angle, $l = \hbar \lambda$ (where $\hbar$ is Planck's constant, $\lambda$ - 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.

Wave-particle duality says that neutrons behave as a short-wave radiation, $\lambda = \hbar/|p|$, where $p$ is the momentum, and hence the classical optical formulae can be used.

<table>
<thead>
<tr>
<th>Incident</th>
<th>Reflected</th>
<th>Transmitted</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n_1$</td>
<td>$r_1$</td>
<td>$t_1$</td>
</tr>
<tr>
<td>$n_2$</td>
<td>$r_2$</td>
<td>$t_2$</td>
</tr>
</tbody>
</table>

\[ R(q) = \frac{R_1(q) + 2R_2(q)}{1 + R_2^2(q)} \exp(-iql) \]
\[ q = \frac{4\pi}{\lambda} \sin \alpha \]

- Fresnel coefficients; $\lambda$ - wavelength

<table>
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<tr>
<th>Special Applications of Neutron Reflectivity</th>
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<td>(When NR Can What Other Methods Cannot)</td>
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</table>

Determination of the orientation of surfactant molecules at Interfaces

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)

Special Applications of Neutron Reflectivity

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Atomic Force Microscopy (AFM)

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

AFM modes:

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

As seen by AFM

When what you see is not what it is

sharper cantilever

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 mixture, 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

10 to 200 nm

oxides Cu$_2$O, CuO, Cu$_2$O, CuO carbonates: Cu$_2$(OH)$_2$$_7$ - CuCO$_3$

(ii) But the oxides can be reduced later:

CuO + H$_2$O = Cu + H$_2$O

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

Equilibrium shifts:

<table>
<thead>
<tr>
<th>(Cu^2+/Cu)</th>
<th>(Cu^3+/Cu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$^-$</td>
<td>0.55V</td>
</tr>
<tr>
<td>Cl$^-_2$</td>
<td>0.14V</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>0.35V</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>0.95V</td>
</tr>
</tbody>
</table>

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 Cu²⁺ can be differentiated by ESR)
  - Surface analysis by what? Again, it depends on what we expect to find!

\[
\text{Cu} \rightarrow \text{Cu}^{+} + e^- \quad \text{BTA} \rightarrow \text{BTA}^- + H^+ \\
\text{CuO} \rightarrow \text{Cu}^{2+} + \text{O}^2- \quad \text{H}_2 \text{O}^+ \quad \text{is much more likely}
\]

Example: Experiment Planning (cont’d)

Is there any bulk depletion of BTA?
- yes
  - Thick surface film or bulk reaction
- no
  - Thin or no surface film and no bulk reaction

GDOES 
EDX
ER-FTIR/Raman
Etching + CHN analysis or HPLC or similar

ellipsometry
SIMS
XPS
RAIRS or similar

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

Electron, ion, and vibrational spectroscopy of surfaces:


Ellipsometry:

Infrared sum-frequency generation spectroscopy:

Infrared reflection absorption spectroscopy:

Scanning probe microscopy:

Atomic force microscopy:

A student-oriented coverage of the theoretical foundations of ellipsometry and neutron reflectivity in relation to soft matter research: