CHAPTER 11

Methodology for Chemical Analysis of Surfaces

11.1 OBJECTIVES OF ANALYSIS

1) Determine how the surface chemistry (and, therefore, properties) differs from the bulk (relative to the function of the material in the device, effects on the body, and response to effects on the body).

2) Identify contaminants (viz., with respect to effects of the material on the body).

3) Identify chemical bonding possibilities for interactions with molecules in the biological milieu with respect to the effects of the material on the body (viz., bioadhesion) and the body on the material.

11.2 OVERVIEW OF METHODOLOGY

11.3   MICROSCOPY

11.3.1 Light Microscopy

The resolution (lateral) of the light microscope is:

$$D = \frac{0.61\lambda}{N \sin \alpha}$$

Where   D = Smallest lateral dimension that can be resolved

N = Refractive index of medium surrounding the specimen (i.e., air, 1.0, or oil, 1.5)

α = Angular aperture = 1/2 angle of cone of light entering the objective lens from the specimen (depends on the width of the objective lens and distance from the specimen) -- increased by moving lens close to the specimen

N sin α = Numerical aperture

For specimens in air viewed by visible light:

   N = 1.0
   λ = 450 nm
   D = 292 (0.3 μm)

For specimens in oil

   D = 200 nm (0.2 μm)

For ultraviolet light λ = 200 nm

D is approximately 1/2 λ

Another important parameter is depth of focus

Magnification	Depth of Focus
10X	0.1 mm
100X	1 μm

11.3.2 Comparison Of Light And Electron Microscopy Methods

Microscope	Incident Radiation	λ	Resolution (nm)	Depth of Penetration	Depth of Focus
Visible light	Light	450 nm	200	-	1 μm @ 100X
Ultraviolet light	UV	200 nm	100	-	
Electron	e⁻	0.005 (at 50 kV)			
Scanning			2	1 μm	1 mm @ 100X
Transmission			0.2	0.1 μm (thickness of section)	

11.4 DIFFRACTION METHODS

Based on the principle that a monochromatic wave impinging on a <u>regularly arrayed structure</u> (e.g., a crystal) will be diffracted at specific angles only, related to the spacing between the features in the array (e.g., molecules). The wavelength of radiation needs to be on the order of (or less than) the spacing to be detected.

Bragg's Law

$$n\lambda = 2d \sin \theta$$

n = integer indicating which multiple of the diffracted wave is being considered
λ = wavelength of radiation
d = spacing between features in the structure (e.g., spacing between molecules in a crystal)
θ = the angle between incident and diffracted waves.

$$d = \frac{n\lambda}{2 \sin \theta}$$

Type of Diffraction	Radiation	λ
Optical	Laser light	400 nm
X- ray	X-ray	0.154 nm (for copper)
Electron	e⁻	0.005 nm at 50 kV

Depth analyzed for x-ray diffraction (i.e., depth of penetration of the x-ray beam) is 1-10 μm.

11.5 CONTACT ANGLE

11.5.1 Method

$$\theta \text{ (included angle)} = 0: \text{complete wetting}$$
$$0 < \theta < 90°: \text{partial wetting}$$
$$\theta > 90°: \text{nonwetting}$$

At Equilibrium, ? surface tensions $= 0$

$$\gamma_{SG} - \gamma_{LS} - \gamma_{GL} \cos \theta = 0$$
$$\gamma_{SG} - \gamma_{SL} = \gamma_{LG} \cos \theta \qquad \text{Young's equation}$$

Cannot solve for γ_{SG} because
      in equation $\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos \theta$
      There are 2 unknowns, γ_{SL} and γ_{SG}

     The experimental method employed to approximate γ_{SG} involves asking the question: what is the surface tension of a liquid that would completely wet the solid surface? This value is referred to as the critical surface tension of the solid.

11.5.2 Assumptions

Equilibrium between the liquid droplet and solid surface has been reached (i.e., no absorption of liquid by the solid and no leaking of substances from the solid). If this assumption cannot be met then the "advancing angle" can be measured to determine the contact angle of the liquid with the dry surface and "receding angle" measured to determine the contact angle with the water absorbed surface.

An alternative method is to measure the underwater (captive-air-bubble) contact angle that an air bubble makes with the immersed surface. This is particularly valuable for measuring surface that can switch from hydrophobic to hydrophilic depending on the environment.

11.5.3 Potential Problems

1) Contamination of the solid surface

2) Contamination of liquids

11.6 SPECTROSCOPY