B. MEASUREMENT, ANALYSIS, CHARACTERIZATION

1. "CHEMICAL" PROPERTIES

a. ~~BULK~~ CHEMICAL COMPOSITION

(i) ATOMIC ABSORPTION (AA) SPECTROMETRY (AAS)

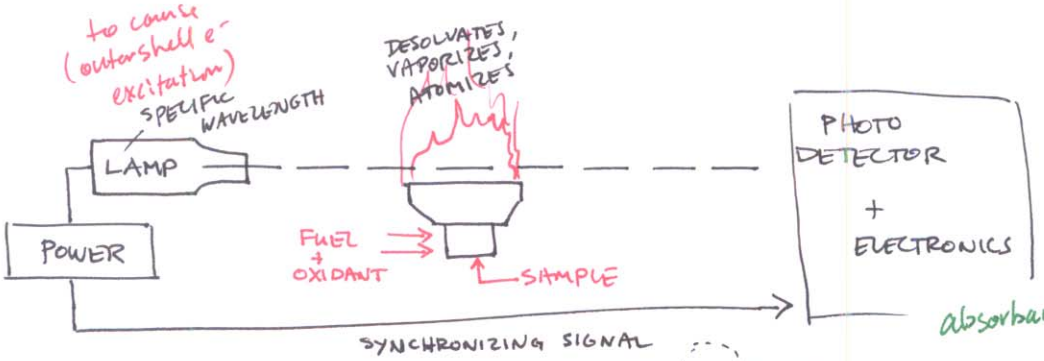
- QUANTITATIVE ANALYSIS OF APPX. 70 ELEMENTS

EXAMPLE APPLICATIONS (turn of century):
- TRACE IMPURITIES IN ALLOYS & PROCESS REAGENTS
- WATER ANALYSIS
- AIR SAMPLING
- DIRECT SOLIDS ANALYSIS

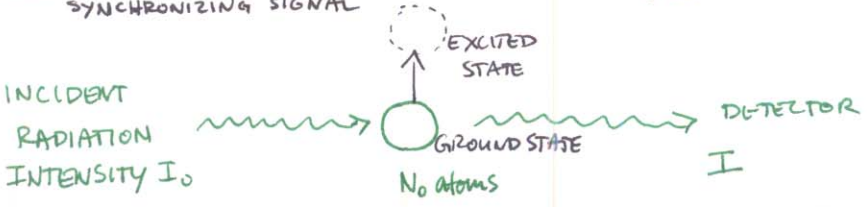
- SAMPLES: SOLIDS, LIQUIDS*, GASEOUS
  MOST OFTEN — DISSOLVE SOLID IN A LIQUID
  SMALL SIZE 1 mg AND UP

- LIMITATIONS: ppb to ppm DETECTION LIMITS
  CAN'T ANALYZE FOR NOBLE GASES, HALOGENS, S, C, N
  SINGLE-ELEMENT TECHNIQUE * Note newer machines offer multielement

- ANALYSIS TIME: FEW MINUTES + SAMPLE PREP + CALIBRATION



absorbance $\text{Signal} = \log \frac{I_0}{I} \propto N_0$

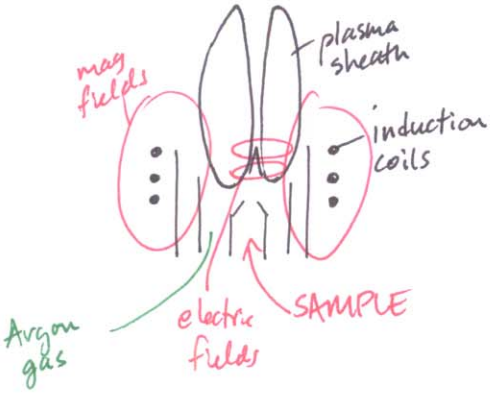


(ii) INDUCTIVELY COUPLED PLASMA (ICP) ATOMIC EMISSION SPECTROMETRY

- GENERAL USE
  - SIMULTANEOUS MULTIELEMENT ANALYSIS (OVER 70 ELEMENTS TOTAL)
- EX. APPLICATIONS
  - COMPOSITION OF METALS & ALLOYS
  - TRACE IMPURITIES IN METALS, ALLOYS, REAGENTS, SOLVENTS
  - ANALYSIS OF GEO., BIO., ENVIRON. MATERIALS
  - WATER
  - PROCESS CONTROL

1960's

- SAMPLES
  - LIQ. MOST COMMON 5 - 50 mL OF SOL'N
    10 to 500 mg DISSOLVED SOLIDS
- LIMITS
  - ppm to ppb
  - NO NOBLE GASES
  - NOT GOOD FOR HALOGENS, SOME NONMETALS, ALKALI ELEMENTS, CAN'T DO CESIUM ?
- TIME
  - MIN. to HOURS + PREP TIME



- ICP IS AN EXCITATION SOURCE FOR ATOMIC EMISSION SPECTROMETRY
  ARGON - HIGHLY IONIZED BY ELEC & MAG FIELDS THAT CREATE COLLISIONS & RESISTIVE HEATING (10000 K)

ATOM → EXCITED STATE → GROUND STATE

EXCITED STATE ← ENERGY FROM PLASMA

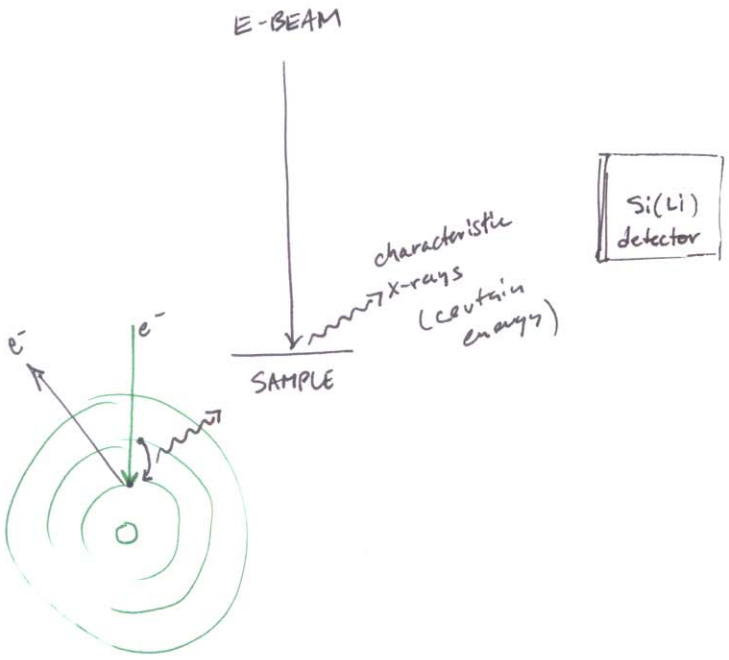
GROUND STATE ⇝ PHOTON (CHARACTERISTIC)

DETECT WITH SPECTROMETER

HIGHER CONC. → MORE EMISSION

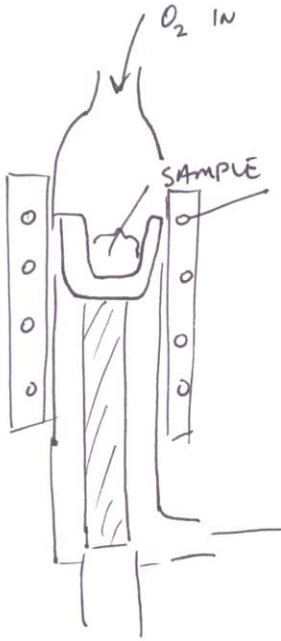
(iii) ENERGY DISPERSIVE X-RAY SPECTROSCOPY SPECTROMETRY (EDS) OR (EDX)

- GENERAL
  - QUALITATIVE & QUANTITATIVE ELEMENTAL ANALYSIS OF SOLIDS
  - USED WITH AN SEM!
- EX. APPLICATIONS
  - CHEMICAL ANALYSIS OF SMALL SOLID SAMPLES — NON DESTRUCTIVE!
  - METAL, ALLOY COMPOSITIONS
  - ELEMENTAL DOT MAPPING
- SAMPLES
  - ANY DRY SOLID, HOWEVER SMALL
- LIMITS
  - ABOUT 0.1 TO 1% FOR MOST ELEMENTS, BETTER WITH STANDARDS
  - USED WITH AN SEM.
- TIME
  - FAST! A COUPLE MINUTES FOR EVERYTHING.



(vi.) COMBUSTION ANALYSIS

- DETERMINATION OF C, S, N, H, & CONTENT IN SOLIDS
- SAMPLES : SOLIDS (BULK), POWDER
- TIME : A FEW MINUTES



C IN SAMPLE FORMS CO, CO_2

(vii) OTHER : OPTICAL EMISSION (OE) SPECTROMETRY

- FAST DETERMINATION OF COMPOSITION OF SOLIDS
- SIMILAR PRINCIPLE AS ICP, BUT USES A DC ARC OR SPARK OR FLAME → DISCHARGE TO ENERGIZE ATOMS & ANALYZES EMISSION SPECTRUM
- SAMPLE MUST CONDUCT (METALS, SOME GEO SAMPLES)

X-RAY FLUORESCENCE (XRF)

- SIMILAR TO EDS & WDS, BUT USES AN X-RAY SOURCE
- SOLIDS USUALLY
- FAST!
- DOWN TO ATOMIC # 11 (Na)
- SOME PHASE INFORMATION

(V.) MASS SPECTROMETRY (SPARK SOURCE)

- QUALITATIVE & QUANTITATIVE ANALYSIS OF INORGANICS, TRACE IMPURITIES IN MATERIALS

EX. APPLICATIONS:

- IMPURITIES IN SILICON FOR SEMICONDUCTORS
- METALS IN ORES (Au, Ag, Pt)
- TOXIC ELEMENTS IN WATER SAMPLES
- ALLOY COMPOSITIONS

SAMPLES:

- SOLIDS, SOLID RESIDUES
- Mg TO μg SIZE
- PREP: CONDUCTIVE - MAKE INTO ELECTRODE
  NON CONDUCTIVE - MIX WITH GRAPHITE OR Ag POWDER

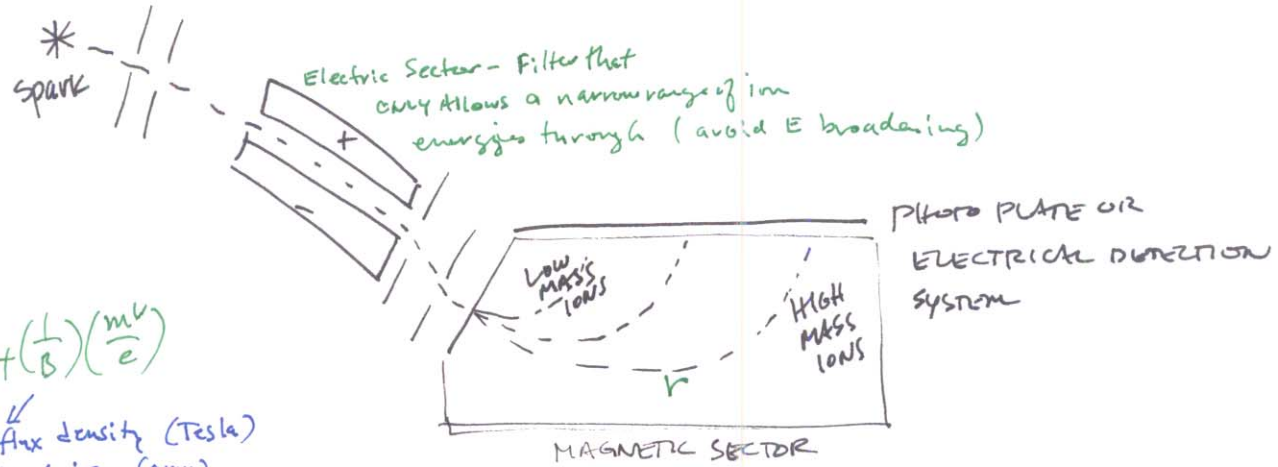
LIMITS:

- ppb LEVELS
- CONTAMINATION FROM PREP.

TIME:

PREP: 1-6 hr, ANALYSIS 1hr - 2hrs

- HIGH VOLTAGE SPARK CREATES IONS OF THE MATERIAL (30 kV)

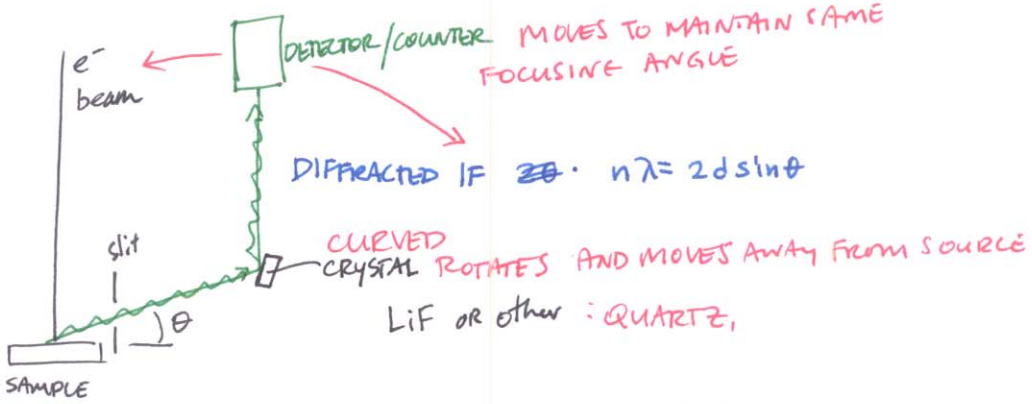


$$r = 144\left(\frac{1}{B}\right)\left(\frac{mV}{e}\right)$$

B = mag flux density (Tesla)
m = mass of ion (amu)
V = accel voltage (V)
e = charge state of ion

(iv) WAVELENGTH DISPERSIVE X-RAY SPECTROMETRY (WDS)

- GENERAL
  - SIMILAR TO EDS, BUT MUCH MORE ACCURATE & PRECISE
  - USED WITH AN SEM-TYPE SETUP
- EX. APPLICATIONS
  - TRACE ELEMENT ANALYSIS IN SOLIDS
  - IDENT. OF COMPOUNDS
  - DOT MAPPING (2-D OR 3-D W/ ION MILL)
  -
- SAMPLES
  - SAME AS EDS
- LIMITS
  - ABOUT 0.1% OR BETTER FOR MOST STUFF
- TIME
  - 10 to 30 MINUTES



DIFFERENT X-RAY ENERGIES →

DIFFERENT WAVELENGTHS →

DIFFERENT DIFFRACTION ANGLES

- RECORD X-RAY INTENSITY AS A function OF CRYSTAL ANGLE.
- CONVERT ANGLES OF PEAK POSITIONS TO λ USING BRAGG'S LAW. $n\lambda = 2d\sin\theta$
- RELATE λ TO SPECIFIC ELEMENTS.

λ to ENERGY RELATION:

(b.) PHASE IDENTIFICATION

(i.) X-RAY DIFFRACTION (POWDER) XRD

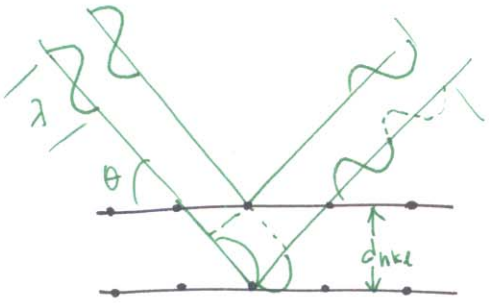
GENERAL: CRYSTAL STRUCTURE INFORMATION

APPLICATIONS:
- I.D. OF PHASES IN UNKNOWNS
- CHARACTERIZATION of SOLID STATE PHASE TRANS. (T, P)
- LATTICE PARAMETER/TYPE DETERMINATION
- CRYSTALLOGRAPHIC ORIENTATION OF SINGLE CRYSTALS
- ANISOTROPIC THERMAL EXPANSION ANALYSIS
- ANALYSIS OF SOLID SOLUTIONS
- PHASE DIAGRAM DETERMINATION

SAMPLES: CRYSTALLINE SOLIDS - POWDER OR BULK
1 mg OR MORE
VERY LITTLE PREPARATION

LIMITS: MUST BE CRYSTALLINE
MUST BE A KNOWN PHASE FOR ID (JCPDS OR NBS PDF)
NO NANOCRYSTALLINE

TIME: <1 hr to 16 hr



DIFFRACTION - BRAGG'S LAW $n\lambda = 2d\sin\theta$

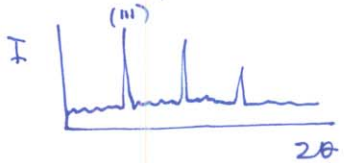
$$d = \left(\left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2\right)^{-1/2}$$ ORTHO TETRAG. CUBIC

cubic: $d = \dfrac{a}{(h^2+k^2+l^2)^{1/2}}$ → fcc: hkl all odd or all even

bcc: h+k+l = even!

- MEASURE INTENSITY AS $f(\theta)$ (INTENSITY & POSITION)
  - ATOM TYPE & POSITION
  - AMT. OF SAMPLE
- ID PEAKS - (hkl)
- ID unknowns

→ λ OF X-RAYS UNIT CELL ($Cu\ K_{\alpha 1}$ $\lambda = 0.1542$ nm)



(ii) WDS

- MAY BE USED FOR PHASE IDENTIFICATION

(iii) OPTICAL MICROSCOPY + IMAGE ANALYSIS

- LOOK AT PHASES, ID BY COLOR, SHAPE

(iv) SEM/EDS

- LOOK AT SHAPE, CHECK COMPOSITION

(v.) NMR

(VII) NUCLEAR MAGNETIC RESONANCE (NMR)

GENERAL & APPS.:
- PHASE ANALYSIS
- ELECTRONIC STRUCTURE IN METALS
- MAGNETIC STRUCTURE
- ENVIRONMENT OF ATOMS IN SOLIDS
- DEFECT STUDIES
- STRUCTURE OF ORGANIC COMPOUNDS / ISOMER IDENTIFICATION
- COPOLYMER RATIO STUDIES (ORGANICS)

SAMPLES: INORGANIC POWDER, WIRE, FILMS
ORGANICS DISSOLVED IN SOLVENT

TIME: 30 MIN - 48 hrs.

ATOMS OR ISOTOPES HAVE DIFFERENT RESPONSE TO MAGNETIC FIELD

- RADIO FREQUENCY (RF) SPECTROSCOPY INVOLVING THE INTERACTION OF NUCLEAR MAGNETIC DIPOLE OR ELECTRIC QUADRUPOLE MOMENTS WITH EXTERNAL OR INTERNAL MAGNETIC FIELDS OR ELECTRIC FIELD GRADIENTS

* RF FIELD APPLIED → NUCLEAR SPIN SYSTEM RESPONDS & CHANGES → DETECTOR SENSES CHANGE
APPLIED w/ MAGNETIC FIELD

"CHEMICAL SHIFT" — values tabulated & used to determine structure

FOR FREE NUCLEI, RESONANCE FREQUENCY ν_0 IN APPLIED MAGNETIC FIELD H_0 IS:

$$\nu_0 = \left(\frac{\gamma}{2\pi}\right) H_0$$

DIFFERENT FOR EVERY ELEMENT / ISOTOPE

γ = GYROMAGNETIC RATIO

(c.) MICROSTRUCTURE

- MORPHOLOGY OF PHASES, GRAIN SIZE, MICROCONSTITUENTS, VOLUME DEFECTS (POROSITY, INCLUSIONS)

(i) OPTICAL METALLOGRAPHY / IMAGE ANALYSIS

- PHASES BY APPEARANCE, RESPONSE TO ETCHANT, COLOR, ↓ MICROCONSTITUENTS

— CROSS SECTION PREPARATION —

SECTIONING
GRINDING
POLISHING

- VOLUME DEFECTS (INCLUSIONS) BY MORPHOLOGY
- POROSITY / PHASE AMOUNTS BY IMAGE ANALYSIS
- PARTICLE SIZE

(ii) SCANNING ELECTRON MICROSCOPY (SEM)

- WILL SEE IN LAB
- 10 - 100,000X, EVEN 500,000 X WITH FIELD EMISSION GUN
- LOTS OF ACCESSORIES — EDS
  - MAGNETIC CONTRAST
  - VOLTAGE / CURRENT CONTRAST (screen w/ bias)
  - CRYSTAL ORIENTATION DATA
  - MECH. TEST; HOT/COLD
- LOTS OF SIGNALS TO ANALYZE — X-RAY
  - BEI
  - SEI
  - Augen
  - Current, voltage
- GOOD FOR X-SECT. OR FRACTURE SURFACES, ETC.

(iii) TRANSMISSION ELECTRON MICROSCOPY (TEM)

- 1000 X – 1 MILLION X
- < 1 nm RESOLUTION – RESOLVE ATOM LOCATIONS IN HRTEM!!
- CRYSTAL STRUCTURE INFO BY ELECTRON DIFFRACTION
- LATTICE IMAGING w/ INTERPLANAR SPACINGS < 0.1 nm
- METAL, CERAMIC, POLYMER, BIO MICROSTRUCTURES
- ID (STRUCTURE & COMPO.) OF PHASES, PRECIPITATES, CONTAMINANTS

SAMPLE PREP: PAIN IN THE BUTT!

5 mm THICK 3 - 5 mm ϕ. →

SECTION & ELECTROTHINNED OR ION MILLED.

DOWN TO 100 nm OR LESS

POWDERS - DISPERSED IN ALCOHOL & PLACED ON C FILM.

- ELECTRON DIFFRACTION DOWN TO 30 nm SIZE FEATURES
- ELEMENTAL MICROANALYSIS DOWN TO 30 nm

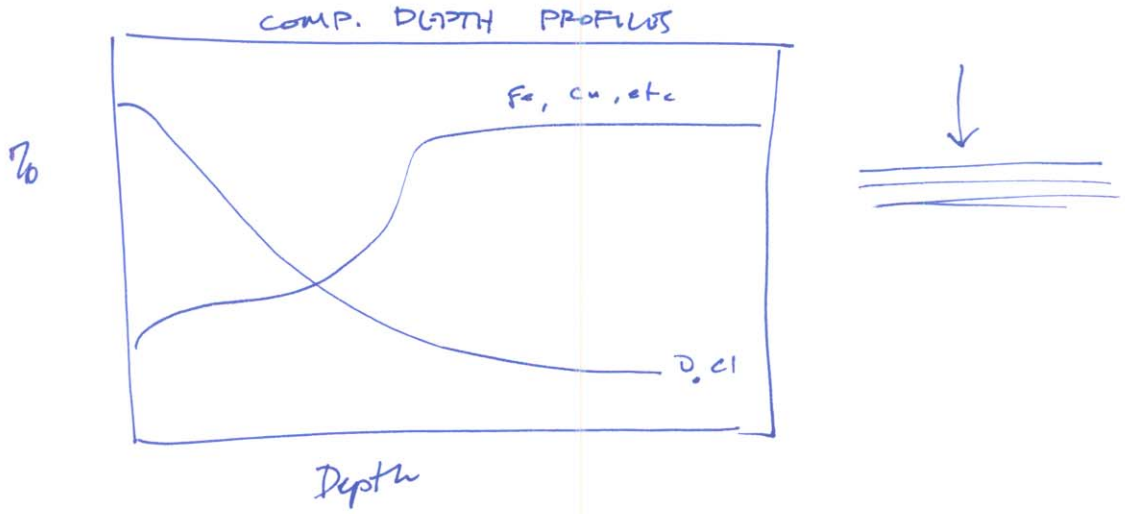
  0.5 TO 1.0 wt% AT BEST

  5% TYPICAL

- TIME 3 HR – 30 HR PLUS PREP (WEEKS)

(iv) AUGER ELECTRON SPECTROSCOPY

- 0-3 nm REGION NEAR SURFACE
- COMPOSITION OF SURFACE CONTAMINATION; CORROSION PRODUCTS
- PHASE ID



(v.) OTHER –

ATOMIC FORCE MICROSCOPY (AFM)

SCANNING TUNNELING MICROSCOPY (STM)

2. PHYSICAL PROPERTIES

a. THERMAL PROPERTIES & BEHAVIOR

— SEE HANDOUT —

b. ELECTRICAL PROPERTIES

— HANDOUT —

c. GRAVIMETRIC

d MAGNETIC

3. MECHANICAL PROPERTIES