Physical Methods

➢ Atomization
- Gas Atomization
- Water Atomization
- Cyrogenics Liquid Atomization
- Centrifugal Atomization

Atomization

<u>Atomization is the most important production method for metal powders</u>.
The process generally consists of three stages:

- melting
- atomization (dispersion of the melt into droplets)
- solidification and cooling.

additional processing becomes necessary before the powders attain their desired properties,(reduction of surface oxides, degassing, size classification, etc.)

Classification

For each of the process stages different methods can be used, resulting in a large number of variants.

Table 2.1 Variables in the processing steps of atomization

Melting		Melt disintegration		Solidification/Cooling
crucibles/liners	heating source	melt volume	energy input	heat transfer
● with	● induction	○ melt pool	● liquid/gas stream	● radiation
● without	● arc	● melt stream	● rotational energy	● convection
	● plasma	● melt film	● gas supersaturation	○ contact cooling
	● electron beam	○ melt droplet	○ ultrasonic vibrations	
			○ mechanical impact	
			○ hydrostatic pressure	
			○ electrostatic forces	

● commercially used; ○ experimental state

Melting

- In this stage **the most important criterion** is whether melting and melt distribution require a crucible system or not. Crucibles are one of the main sources for contamination of atomized powders.

- The **second criterion** is the heating source. Essentially all melting techniques known in metallurgy can be used, e.g., induction, arc, plasma, and electron-beam melting, but some of these may also contribute to contamination, as for example in arc melting.

Solidification

During the soldification and cooling stage, the **cooling rate** is the controlling parameter.

Cooling rate depends on:

- the dimensions of the liquid droplets or solid powder particles,
- the type of heat transfer from the particles to the surrounding medium.

The undercooling prior to nucleation and cooling rate are the controlling factors for determining the **microstructure of the powder particles**, as well as for the dimensions of the atomization unit.
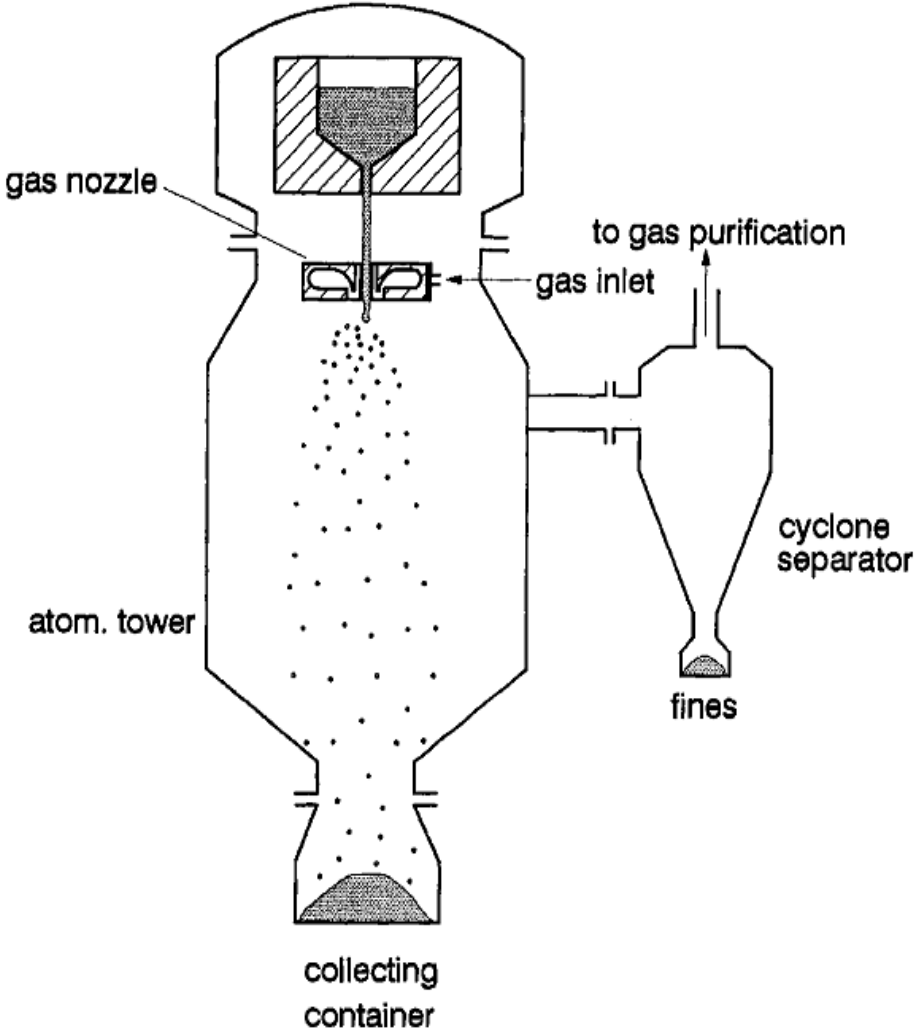
Depending on the parameters in each stage various disintegration methods are possible:

Disintegration/Dispersion

Disintegration step:
The energy for disintegration introduced into the melt;
by capillary forces *(melt drop process),*
mechanical impact *(impact disintegration),*
electrostatic forces *(electrodynamic atomization),*
liquid or gas streams or jets *(liquid or gas atomization) ,*
centrifugal forces (*centrifugal atomization),*
gas supersaturation of the melt *(vacuum atomization),*
or ultrasonics *(ultrasonic atomization) .*

Gas Atomization

gas nozzle

gas inlet

to gas purification

cyclone separator

atom. tower

fines

collecting container

Vertical atomisation unit

Air, nitrogen, argon or helium are used, depending on the requirements determined by the metal to be atomized.

Here, melted initial material is collapse with the gas within the chamber .

Heat is transfered from the liquid droplets to the surrounding gas. And liquid solidifies.

Atomization can be undertaken either in vertical or horizontal units.
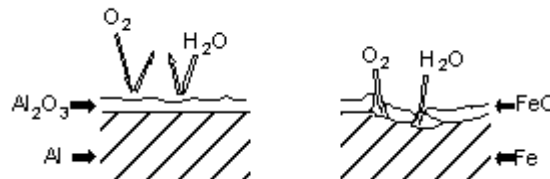
Gas Atomization

Production of Fine Particles;

- a high velocity of the atomizing fluid

- small melt stream (droplet) diameters

- high density, and low viscosity and surface tension of the melt

The nozzle design is an important key to success or failure of a gas atomization system.
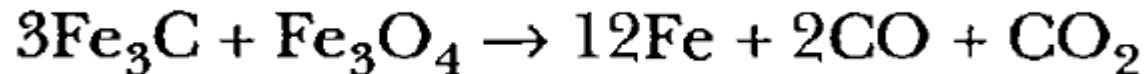
Gas Atomization

The mean particle size of gas atomized powders is in the range of 20-300 μm.

The particle shape is spherical or close to spherical.
Irregular particle shapes can only be produced in systems where reactions between the gas and the liquid metal cause the formation of solid surface layers. This is the case, for example, in the <u>air atomization of aluminium</u>.

Gas Atomization

- Melt atomization by **<u>air</u>** is used in the production of the so-called 'Roheisen Zunder' (RZ) iron powder. This process starts from a cast iron melt. The surface oxides formed during atomization are reduced by the inherent carbon of the cast iron particles during a simple subsequent annealing treatment

$$3Fe_3C + Fe_3O_4 \rightarrow 12Fe + 2CO + CO_2$$

Gas atomization

Inert gas atomisation is applicable for all metallic alloys which can be melted. The main application is for high alloy products such as stainless steel, tool steels, iron, nickel- or cobalt-base superalloy powders, as well as aluminium alloy powders.

Limiting factors are the availability of suitable crucible and auxiliary/helpful melting process materials. Powders from refractory metals with high melting temperature and highly reactive materials, such as titanium alloys, are usually produced by other methods.

Liquid atomization

• Water atomization   Cyrogenics Liquid atomization
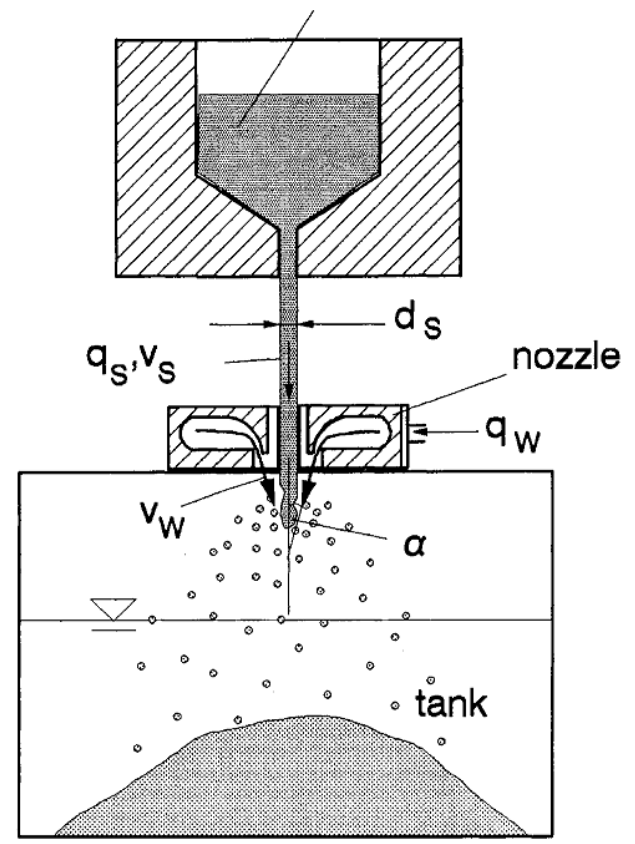
Water atomization,

Water atomisation is mainly used for
the production of iron base powders. Figure shows a
scheme for a water atomisation unit.

The starting material is melted and metallurgically
treated in a separate furnace and then fed into a
tundish. The tundish provides a uniformly flowing
vertical melt stream, which is disintegrated into
droplets in the focal area of an arrangement of several
water jets.
The impact from the high pressure stream of water
leads to disintegration of the flowing metal

A high energy input to the water stream is needed.

Scheme for a water atomisation unit.

Liquid atomization

• Water atomization   Cyrogenics Liquid atomization

In water atomization, a high pressure water stream is forced through nozzles to form a disperse phase of droplets which then impact the metal stream. In this method, large quantities of energy are required to supply the water at high pressure.

This production method is significant for low and high alloy steels, including stainless steel.

Because of oxide formation, water atomization is ***not likely to be used in the atomization of highly reactive metals*** such as titanium and the super alloys. In general, water atomized powders **are irregular in shape**, with rough oxidized surfaces.

Liquid atomization

• Water atomization   Cyrogenics Liquid atomization

In cyrogenic liquid atomisation,.
The Krupp Company (Germany) introduced a novel version of atomization in which the melt is atomised with cryogenic liquid gas (argon or nitrogen) at −200℃. During the process, the pressure of the liquid gas is increased up to 300 bar, while a recooling unit prevents the temperature from rising in spite of compression and prevents the cryogenic liquid from vaporizing instantaneously at the jet opening.

Liquid atomization

- Water atomization: Cyrogenics Liquid atomization

In cyrogenic liquid atomisation,.

The resulting powder has the following properties:

– It is much purer than the powder atomized with water and can be compared to the quality of the gas atomized powder.

– The cooling rate is ten times higher than in gas atomization and almost reaches the quality of water atomization. Particles of 100 μm in diameter, for example, are quenched for approximately 106 K/s.

– The powders are, as in gas atomization, spherical and have an average size of 6–125 μm. show satisfactory results in cold forming, while having a good flowability. Gas atomized powders have poor green strength

Centrifugal atomization

The basis of centrifugal atomization is the ejection of molten metal from a rapidly spinning container, plate or disc.
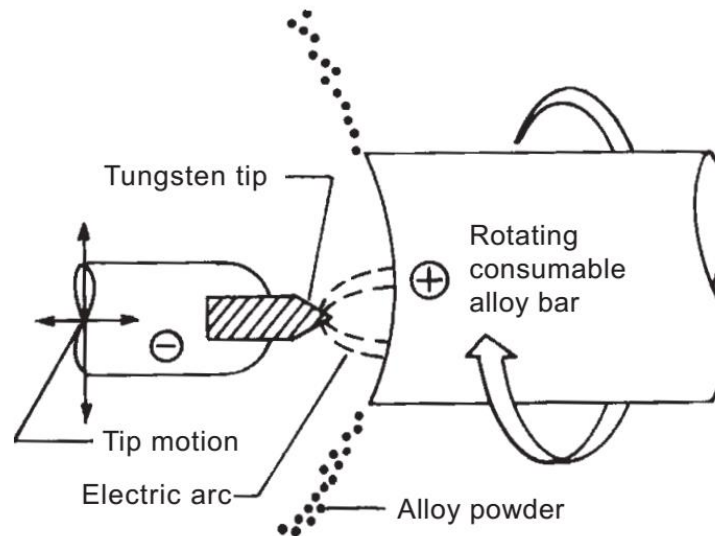
- The material in the form of a rod electrode is rotated rapidly while being melted at one end by an electric arc. Molten metal spins off the bar and solidifies before hitting the walls of the inert gas filled outer container.

Centrifugal atomization

The process was developed primarily for the atomization by high purity low oxygen content titanium alloys and superalloys.

Powder particles are smooth and spherical with an average diameter of ~200 μm; the size range is 50–400 μm. Typically, yields run to ~75% for –35 mesh powder.

Centrifugal atomization

Particle size distribution

- Accurately controlled rotation of the anode is important so as to obtain in a desired range.

- as the surface tension of the liquid metal, centrifugal forces (related to rotation speed) to some extent by the 'aerodynamics' of the droplets trajectory through the inert cover gas.

Centrifugal atomization

- Spherical metal powders made by either REP (rotating electrode process) or gas atomization are not well suited for cold pressing into green compacts to be followed by sintering. They are used in more specialized applications where consolidation is achieved by hot isostatic pressing (HIP) or some other high temperature method in which inter particle voids are more readily closed

ATOMIZATION

Solidification and Cooling

The cooling rate →the powder particle shape, and microstructure

Cooling occurs by

- heat transfer via radiation

- heat flow through the medium which is in contact with the melt.

The cooling rate during solidification depends on;

- The melt volume

- The heat flow

Small melt volumes favor rapid cooling.

Atomization under vacuum or reduced pressure conditions results in relatively low cooling rates
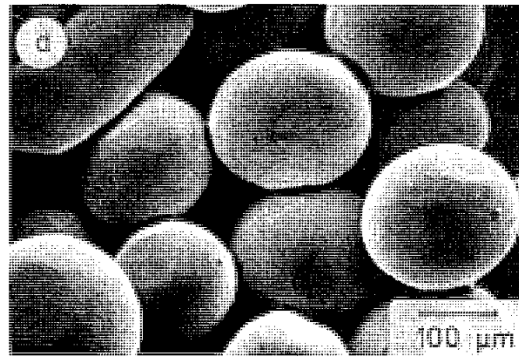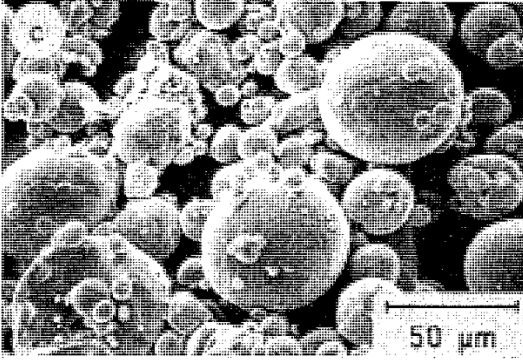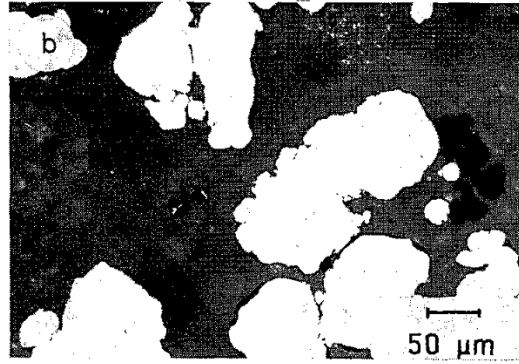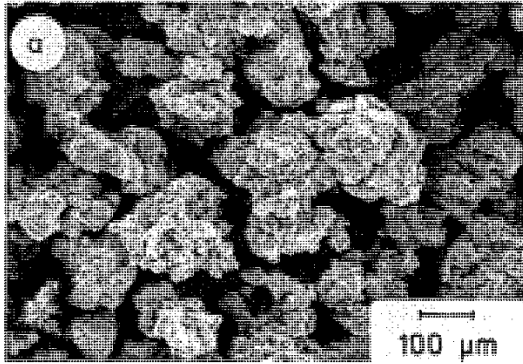
ATOMIZATION

The microstructure of the powder particles is determined by nucleation and growth factors.

• After nucleation has occurred, the relation of the growth rate of the solid from the liquid and the diffusion rate in the liquid determines the microstructure.

A large undercooling increases the growth/diffusion ratio

Low growth/ diffusion ratios result in dendritic microstructures as a consequence of segregation.

With increasing cooling rate, the particles tend to form microcrystalline structures, combined with other non-equilibrium states such as high defect concentrations or metastable phases, which promote sintering effectively. Even non-crystalline (amorphous) structures can be obtained.

water atomisation (a), b

gas atomisation (c)

rotational atomisation (d)

Spherical particles result from the solidifying droplets in gas and centrifugal atomization as a result of surface tension.
Water atomised powders can be produced with very irregular particle shapes for high green strength requirements, but particles close to spherical can also be produced if good flowability and tap density are required.

Advantages of atomization,
1. Freedom to alloy
2. All particles have the same uniform composition
3. Control of particle shape, size and structure
4. High purity
5. Lower capital cost

Fine particle sizes are favored by:
(a) Low metal viscosity
(b) Low metal surface tension
(c) Superheated metal
(d) Small nozzle diameter, i.e. low metal feed rate.
(e) High atomizing pressure

Atomization

Sphericity of a metal powder is favoured by:
(a) High metal surface tension
(b) Narrow melting range
(c) High pouring temperature
(d) Gas atomization, especially inert gas
(e) Long flight paths

Trends for Future Development

• ultra-high purity
  ultra-rapid cooling rate
  ultra-fine particle size

Powder characterization and microstructure control in powders

The success of any powder metallurgical process depends to a great extent on the complete characterization and control of the metal powders.

These properties also influence the behavior of the powder during compaction and sintering, and the composition, structure and properties of the sintered material.
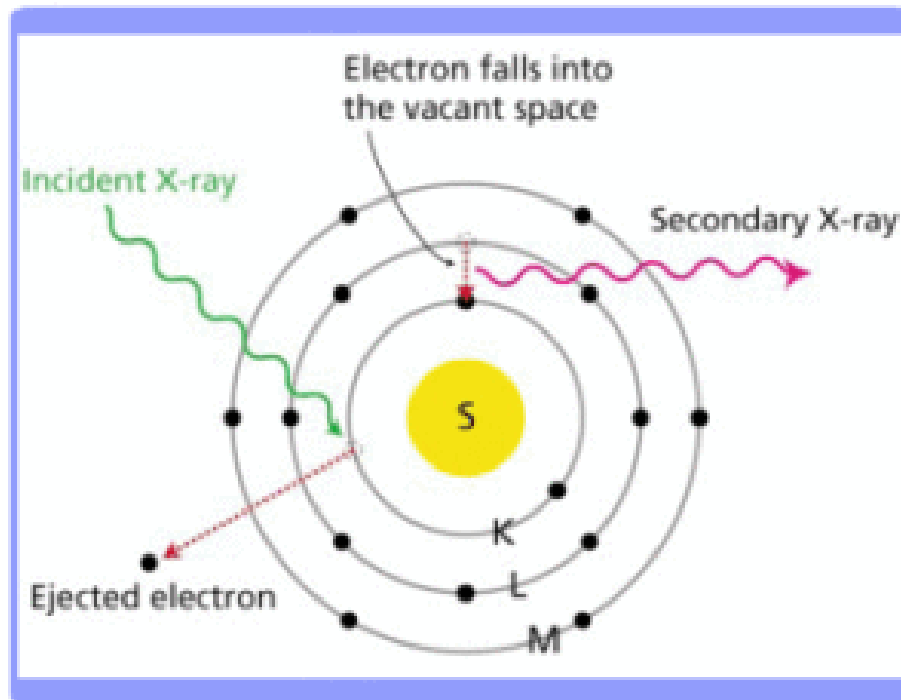
Chemical Composition and Structure

The levels of impurity elements in metal powders can be very significant to both the processing and properties of the final product. It is necessary to know whether such elements are present in their elemental form or whether they are present in the form of a chemical compound
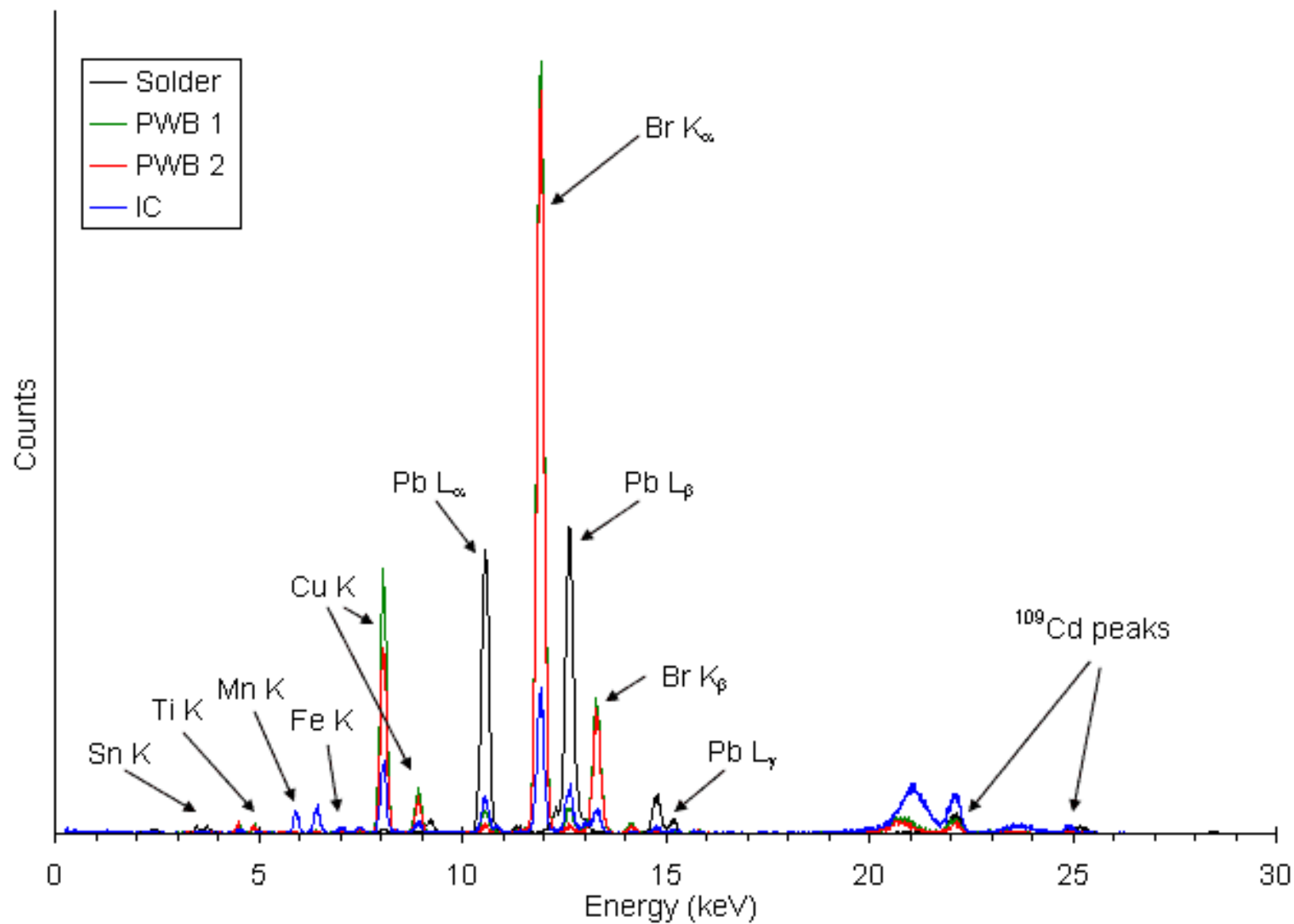
- Practically any metal powder adsorbs significant quantities of gases and water vapour from the atmosphere during storage.

  - The amount of such contamination increases with decreasing particle size and with increasing chemical activity of the surface.

Some of Chemical Characterization Techniques ;

- XRF
- XRD
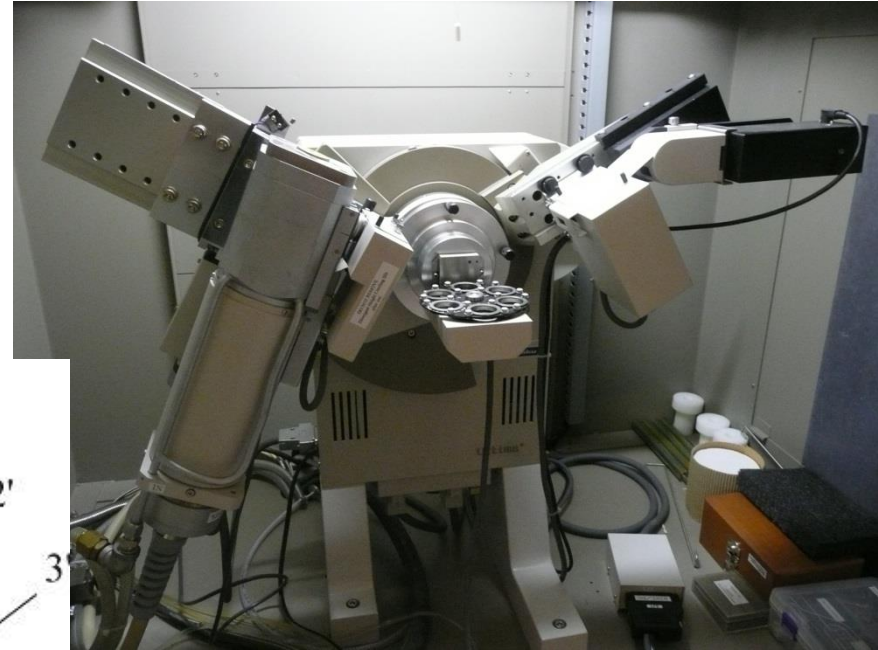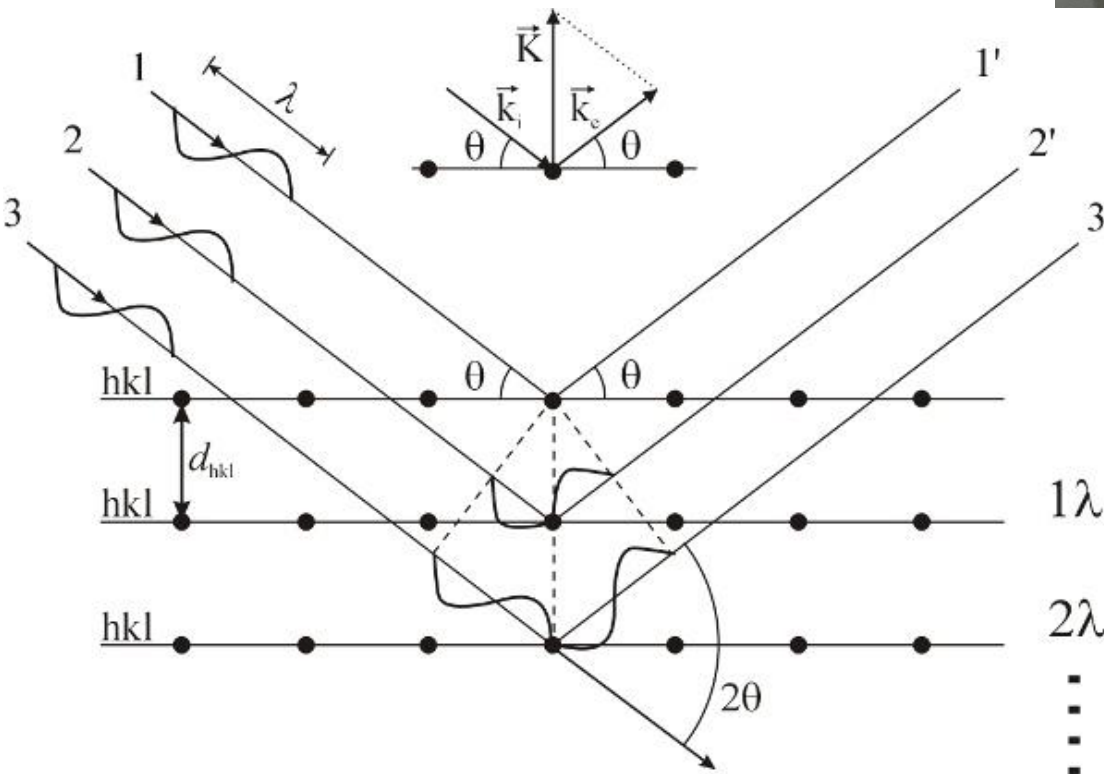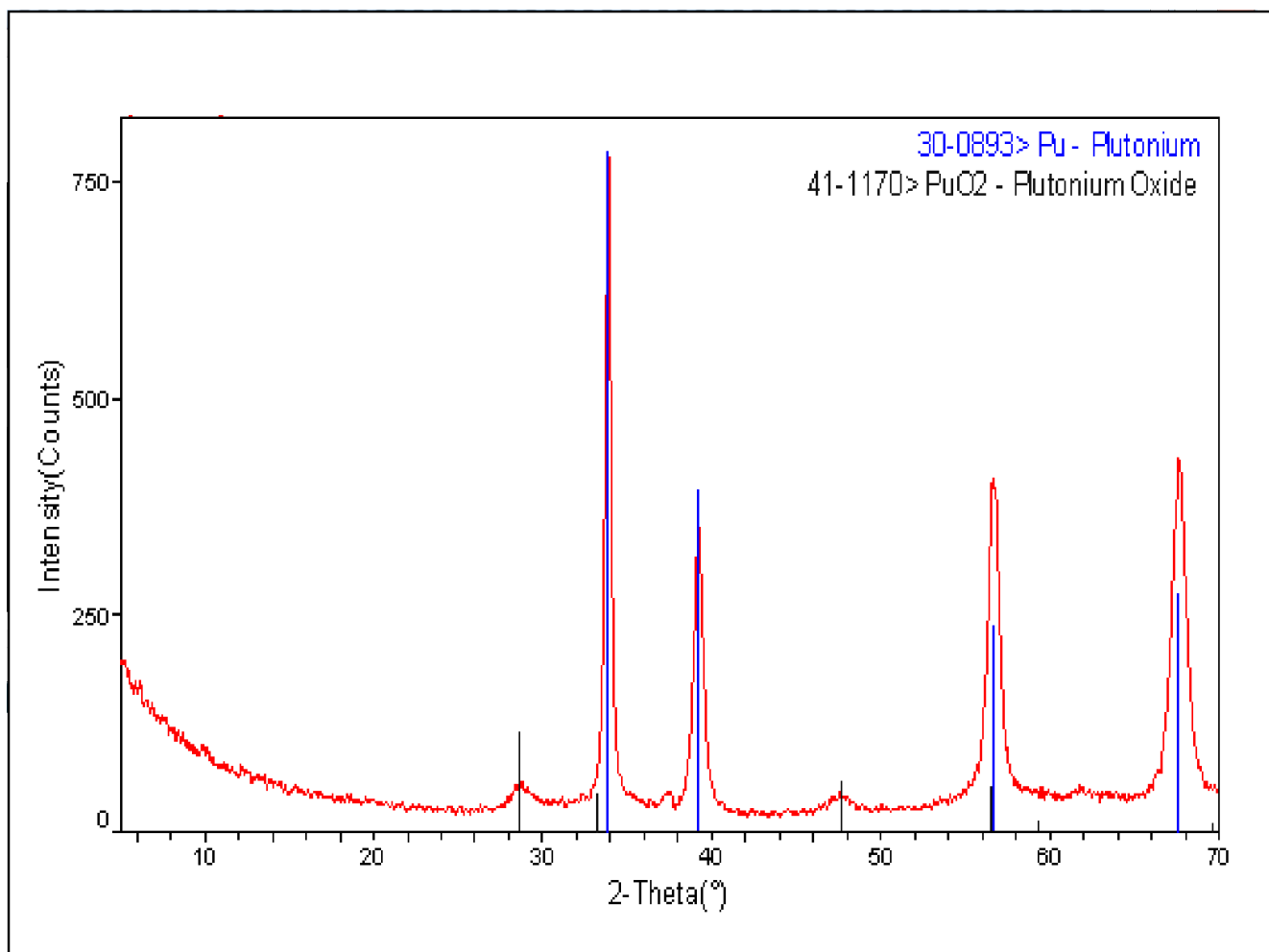- EDX or EDXS

XRF; X-Ray Fluorescence

Periodic Table — Key to Energy Values in keV

Key: (top) $K_{\alpha 1}$ $K_{\beta 1}$ — (symbol) Au — (Z) 79 — (bottom) $L_{\alpha 1}$ $L_{\beta 1}$

Element	Z	$K_{\alpha 1}$	$K_{\beta 1}$	$L_{\alpha 1}$	$L_{\beta 1}$
H	1				
He	2	0.851			
Li	3	0.052			
Be	4	0.110			
B	5	0.185			
C	6	0.282			
N	7	0.392			
O	8	0.526			
F	9	0.677			
Ne	10	0.851			
Na	11	1.04	1.07		
Mg	12	1.25	1.30		
Al	13	1.49	1.55		
Si	14	1.74	1.83		
P	15	2.02	2.14		
S	16	2.31	2.46		
Cl	17	2.62	2.82		
Ar	18	2.96	3.19		
K	19	3.31	3.59		
Ca	20	3.69	4.01	0.34	
Sc	21	4.09	4.46	0.40	
Ti	22	4.51	4.93	0.45	0.46
V	23	4.95	5.43	0.51	0.52
Cr	24	5.41	5.95	0.57	0.58
Mn	25	5.90	6.49	0.64	0.65
Fe	26	6.40	7.06	0.70	0.72
Co	27	6.93	7.65	0.78	0.79
Ni	28	7.48	8.26	0.85	0.87
Cu	29	8.05	8.90	0.93	0.95
Zn	30	8.64	9.57	1.01	1.03
Ga	31	9.25	10.26	1.10	1.12
Ge	32	9.89	10.98	1.19	1.21
As	33	10.54	11.73	1.28	1.32
Se	34	11.22	12.50	1.38	1.42
Br	35	11.92	13.29	1.48	1.53
Kr	36	12.65	14.11	1.59	1.64
Rb	37	13.39	14.96	1.69	1.75
Sr	38	14.16	15.83	1.81	1.87
Y	39	14.96	16.74	1.92	2.00
Zr	40	15.77	17.67	2.04	2.12
Nb	41	16.61	18.62	2.17	2.26
Mo	42	17.48	19.61	2.29	2.40
Tc	43	18.41	19.61	2.42	2.54
Ru	44	19.28	21.66	2.56	2.68
Rh	45	20.21	22.72	2.70	2.83
Pd	46	21.18	23.82	2.84	2.99
Ag	47	22.16	24.94	2.98	3.15
Cd	48	23.17	26.09	3.13	3.32
In	49	24.21	27.27	3.29	3.49
Sn	50	25.27	28.48	3.44	3.66
Sb	51	26.36	29.72	3.61	3.84
Te	52	27.47	30.99	3.77	4.03
I	53	28.61	32.29	3.94	4.22
Xe	54	29.80	33.64	4.11	4.42
Cs	55	30.97	34.98	4.29	4.62
Ba	56	32.19	36.38	4.47	4.83
La	57	33.44	37.80	4.65	5.04
Ce	58	34.72	39.26	4.84	5.26
Pr	59	36.02	40.75	5.03	5.49
Nd	60	37.36	42.27	5.23	5.72
Pm	61	38.65	43.96	5.43	5.96
Sm	62	40.12	45.40	5.64	6.21
Eu	63	41.53	47.03	5.85	6.46
Gd	64	42.98	48.72	6.06	6.71
Tb	65	44.47	50.39	6.28	6.98
Dy	66	45.99	52.18	6.50	7.25
Ho	67	47.53	53.93	6.72	7.53
Er	68	49.10	55.69	6.95	7.81
Tm	69	50.73	57.58	7.18	8.10
Yb	70	52.36	59.35	7.41	8.40
Lu	71	54.06	61.28	7.65	8.71
Hf	72	55.76	63.21	7.90	9.02
Ta	73	57.52	65.21	8.15	9.34
W	74	59.31	67.23	8.40	9.67
Re	75	61.13	69.30	8.65	10.01
Os	76	62.99	71.40	8.91	10.35
Ir	77	64.89	73.55	9.19	10.71
Pt	78	66.82	75.74	9.44	11.07
Au	79	68.79	77.97	9.71	11.44
Hg	80	70.82	80.26	9.99	11.82
Tl	81	72.86	82.56	10.27	12.21
Pb	82	74.96	84.92	10.55	12.61
Bi	83	77.10	87.34	10.84	13.02
Po	84	79.30	89.81	11.13	13.44
At	85	81.53	92.32	11.42	13.87
Rn	86	83.80	94.88	11.72	14.32
Fr	87	86.12	97.48	12.03	14.77
Ra	88	88.46	100.14	12.34	15.23
Ac	89	90.89	102.85	12.65	15.71
Th	90	93.33	105.59	12.97	16.20
Pa	91	95.85	108.41	13.29	19.70
U	92	98.43	111.29	13.61	17.22
Np	93	101.00	114.18	13.95	17.74
Pu	94	103.65	117.15	14.28	18.28
Am	95	106.35	120.16	14.62	18.83
Cm	96	109.10	123.24	14.96	19.39
Bk	97	111.90	126.36	15.31	19.97
Cf	98	114.75	129.54	15.66	20.56
Es	99	117.65	132.78	16.02	21.17
Fm	100	120.60	136.08	16.38	21.79
Md	101				
No	102				
Lr	103				

Groups: IA, IIA, IIIB, IVB, VB, VIB, VIIB, VIII, IB, IIB, IIIA, IVA, VA, VIA, VIIA, VIIIA. Lanthanides 57–71; Actinides 90–103.

Element Index

Actinium - Ac 89
Aluminum - Al 13
Americium - Am 95
Antimony - Sb 51
Argon - Ar 18
Arsenic - As 33
Astatine - At 85
Barium - Ba 56
Berkelium - Bk 97
Beryllium - Be 4
Bismuth - Bi 83
Boron - B 5
Bromine - Br 35
Cadmium - Cd 48
Calcium - Ca 20
Californium - Cf 98
Carbon - C 6
Cerium - Ce 58
Cesium - Cs 55
Chlorine - Cl 17
Chromium - Cr 24
Cobalt - Co 27
Copper - Cu 29
Curium - Cm 96
Dysprosium - Dy 66
Einsteinium - Es 99
Erbium - Er 68
Europium - Eu 63
Fermium - Fm 100
Fluorine - F 9
Francium - Fr 87
Gadolinium - Gd 64
Gallium - Ga 31
Germanium - Ge 32
Gold - Au 79
Hafnium - Hf - 72
Helium - He 2
Holmium - Ho 67
Hydrogen - H 1
Indium - In 49
Iodine - I 53
Iridium - Ir 77
Iron - Fe 26
Krypton - Kr 36
Lanthanum - La 57
Lawrencium - Lr 103
Lead - Pb 82
Lithium - Li 3
Lutetium - Lu 71
Magnesium - Mg 12
Manganese - Mn 25
Mendelevium - Md 101
Mercury - Hg 80
Molybdenum - Mo 42
Neodymium - Nd 60
Neon - Ne 10
Neptunium - Np 93
Nickel - Ni 28
Niobium - Nb 41
Nitrogen - N 7
Nobelium - No 102
Osmium - Os 76
Oxygen - O 8
Palladium - Pd 46
Phosphorus - P 15
Platinum - Pt 78
Plutonium - Pu 94
Polonium - Po 84
Potassium - K 19
Praseodymium - Pr 59
Promethium - Pm 61
Protactinium - Pa 91
Radium - Ra 88
Radon - Rn 86
Rhenium - Re 75
Rhodium - Rh 45
Rubidium - Rb 37
Ruthenium - Ru 44
Samarium - Sm 62
Scandium - Sc 21
Selenium - Se 34
Silicon - Si 14
Silver - Ag 47
Sodium - Na 11
Strontium - Sr 38
Sulphur - S 16
Tantalum - Ta 73
Technetium - Tc 43
Tellurium - Te 52
Terbium - Tb 65
Thallium - Tl 81
Thorium - Th 90
Thulium - Tm 69
Tin - Sn 50
Titanium - Ti 22
Tungsten - W 74
Uranium - U 92
Vanadium - V 23
Xenon - Xe 54
Ytterbium - Yb 70
Yttrium - Y 39
Zinc - Zn 30
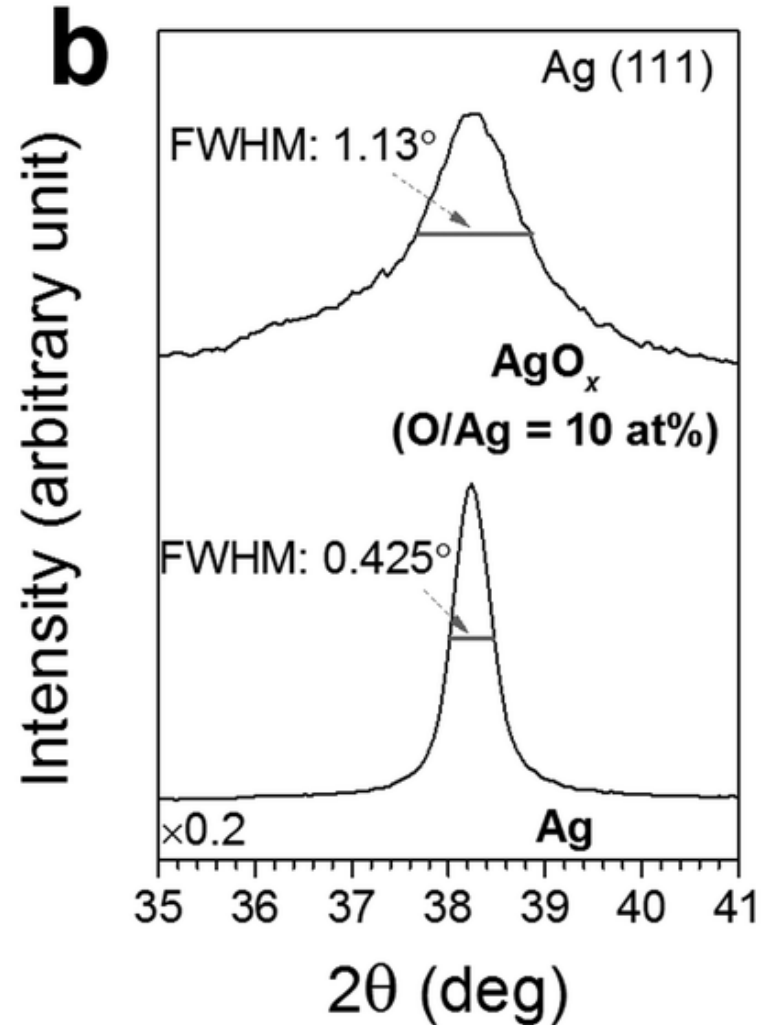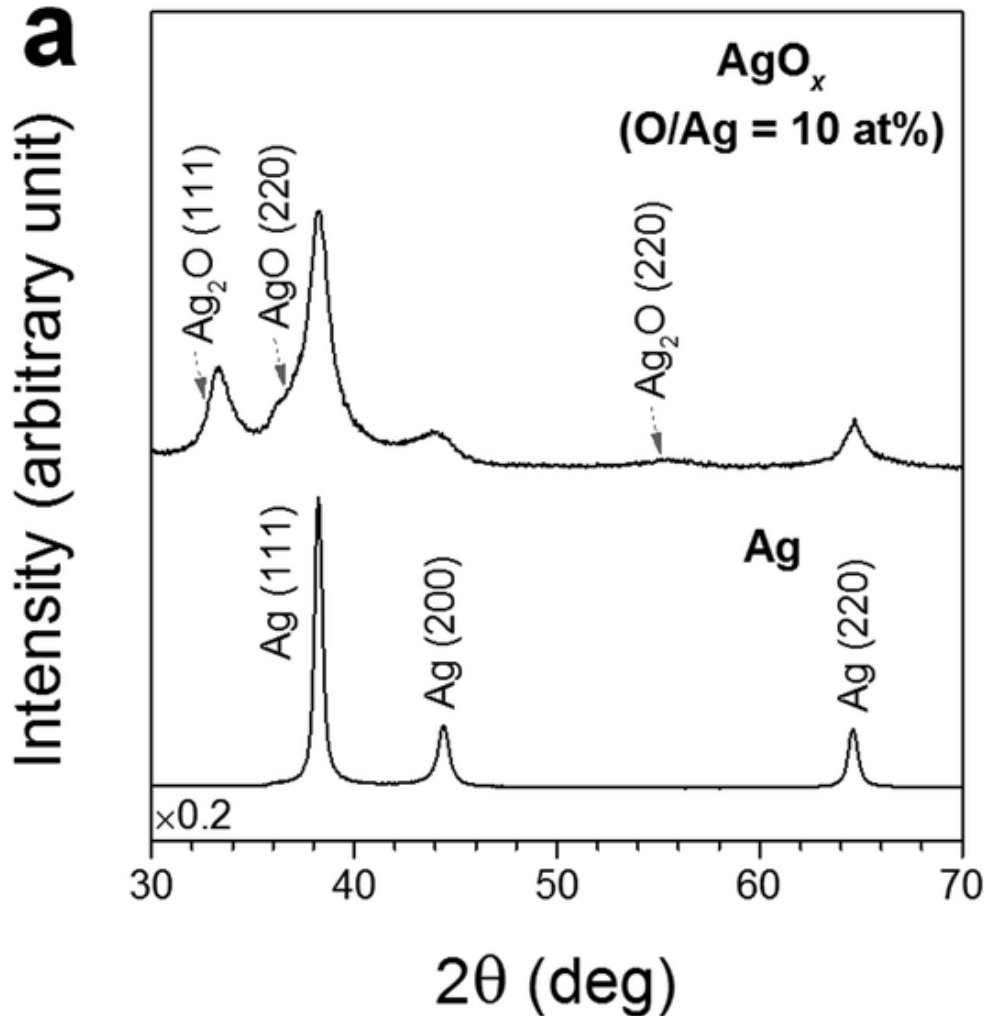Zirconium - Zr 40

X-ray Diffraction

nλ=2dsinθ - Bragg's Law

X-Ray Diffraction

$$t = \frac{0.9\lambda}{B_{size}\cos\theta_B}$$
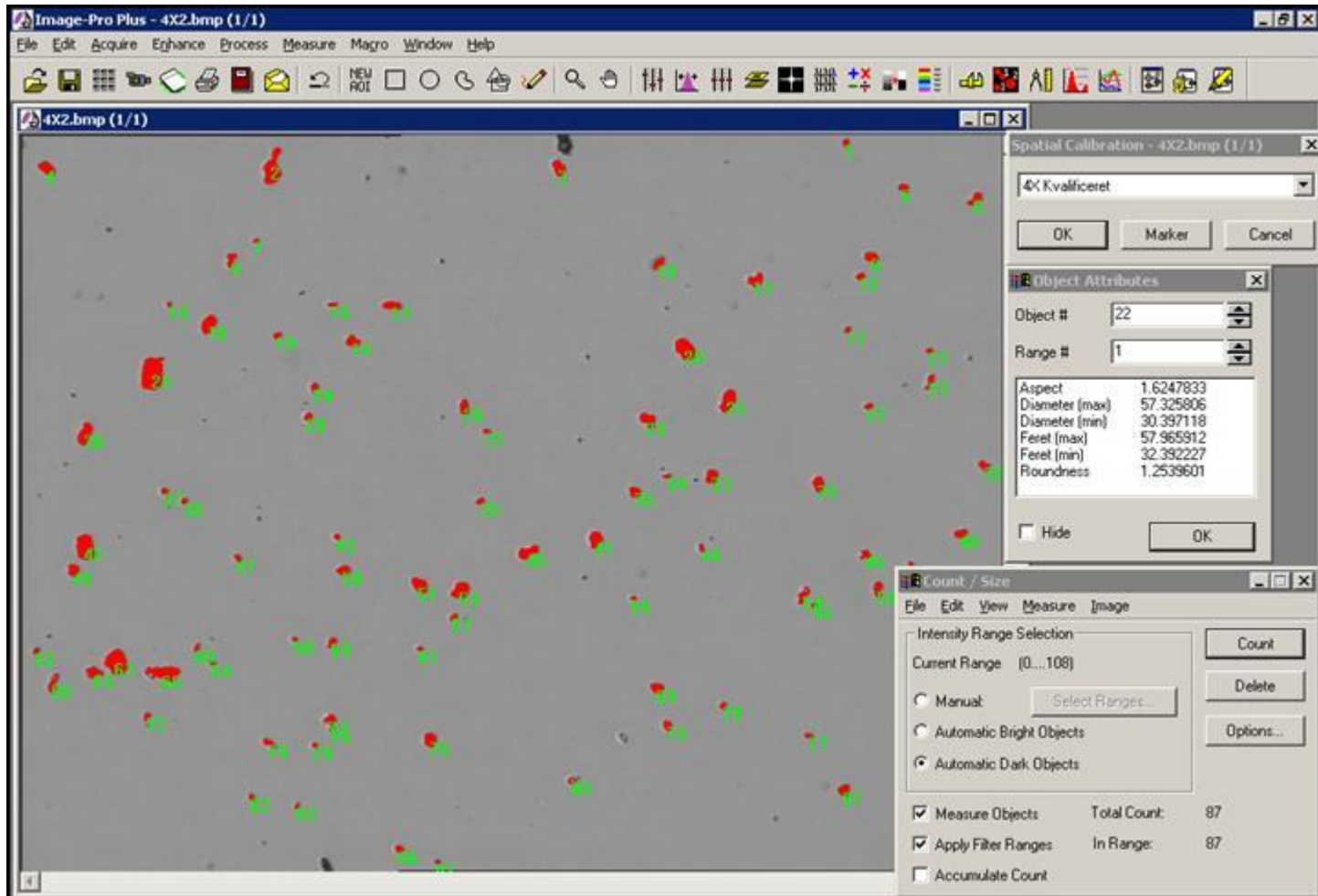
Scherrer Equation

Useful for particles less than 100nm

Optical Microscope

The optical microscope method is applicable to particles in the size range 0.8-150 μm. Below that, Electron Microscopy is needed.
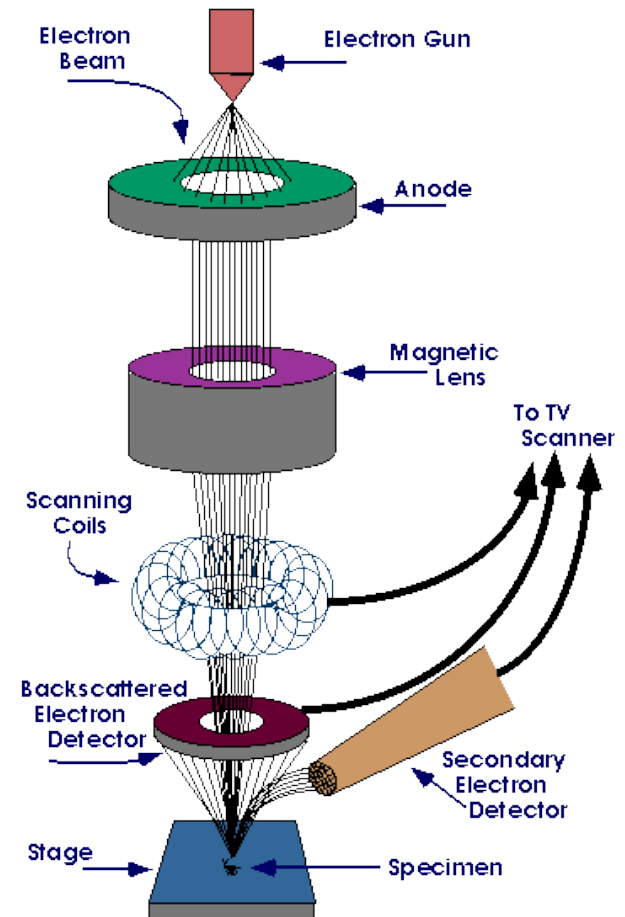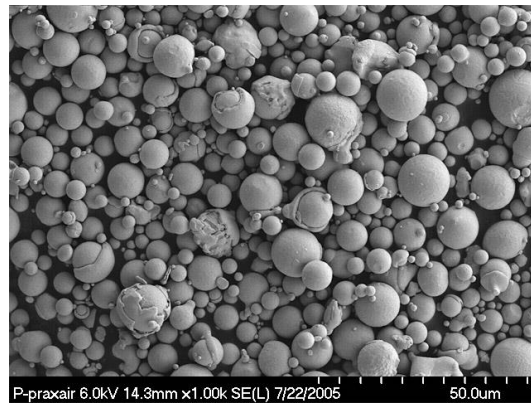
Optical Microscope

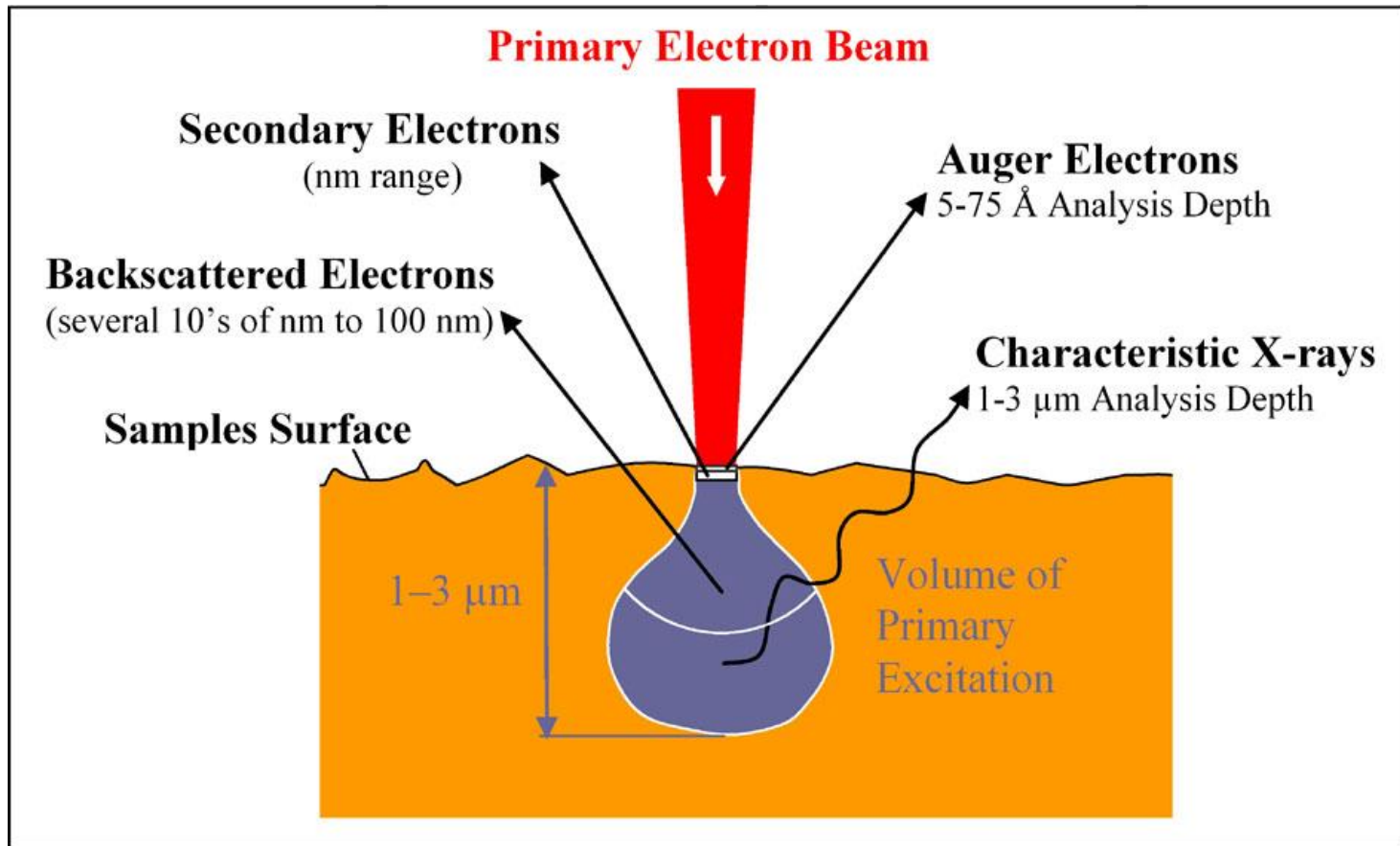There are image analyser programs to determine particle sizes and distribution from the optical (and/or electron) microscopy images

Scanning Electron Microscopy

It is also a direct method to measure particle size of the particles. Optical microscopy or electron microscopy can be used to determine particle size
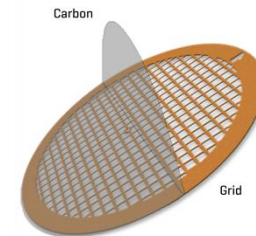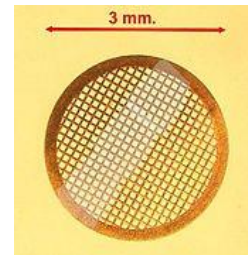

P-praxair 6.0kV 14.3mm x1.00k SE(L) 7/22/2005   50.0um

LEO 1550 VP

Electron Beam
Electron Gun
Anode
Magnetic Lens
To TV Scanner
Scanning Coils
Backscattered Electron Detector
Secondary Electron Detector
Stage
Specimen

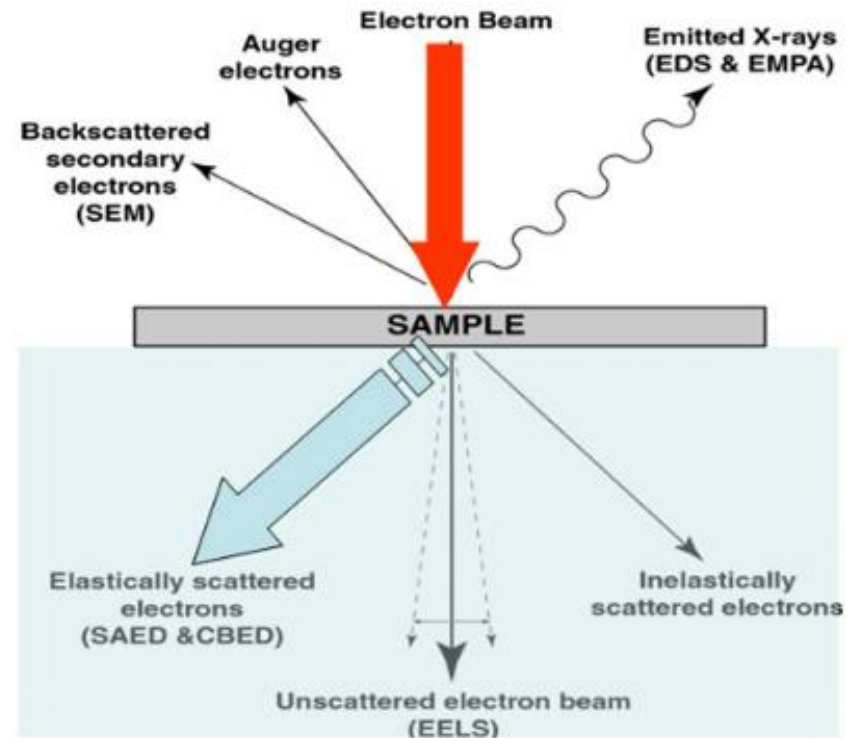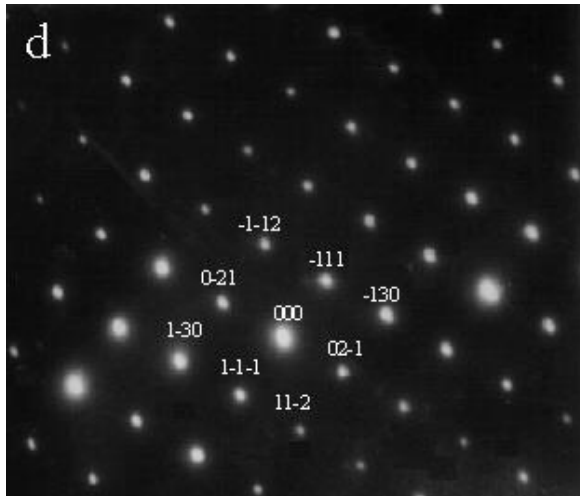# Scanning Electron Microscopy

Energy Dispersive X-ray Spectroscopy

Transmission Electron Microscopy

electron gun

anode

condenser lens

specimen

objective aperture lens

intermediate lens

projector lens

fluorescent screen
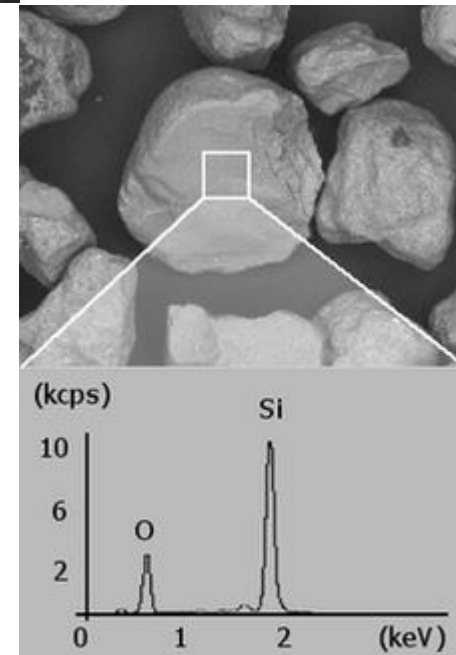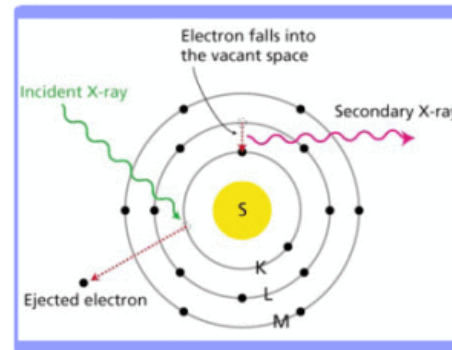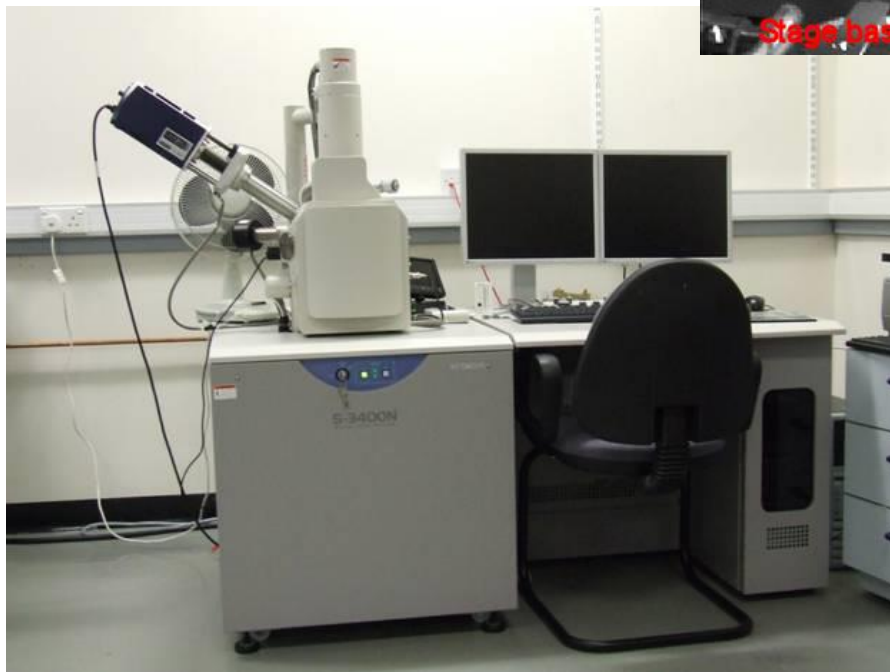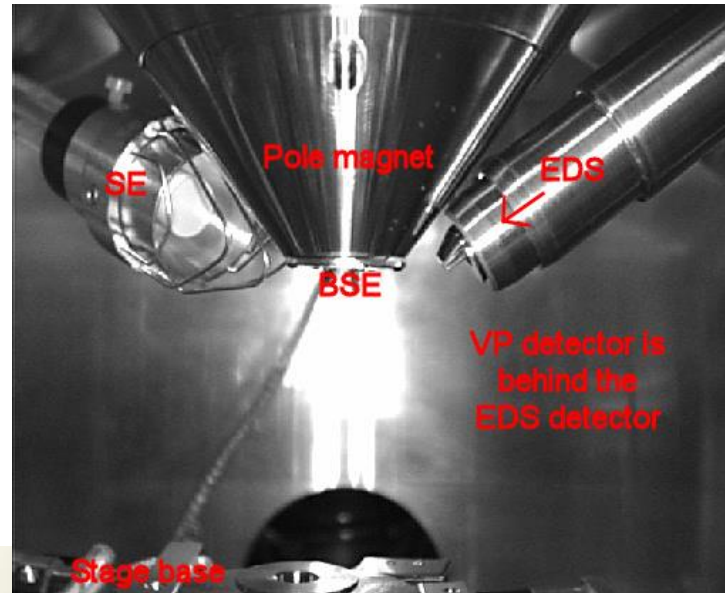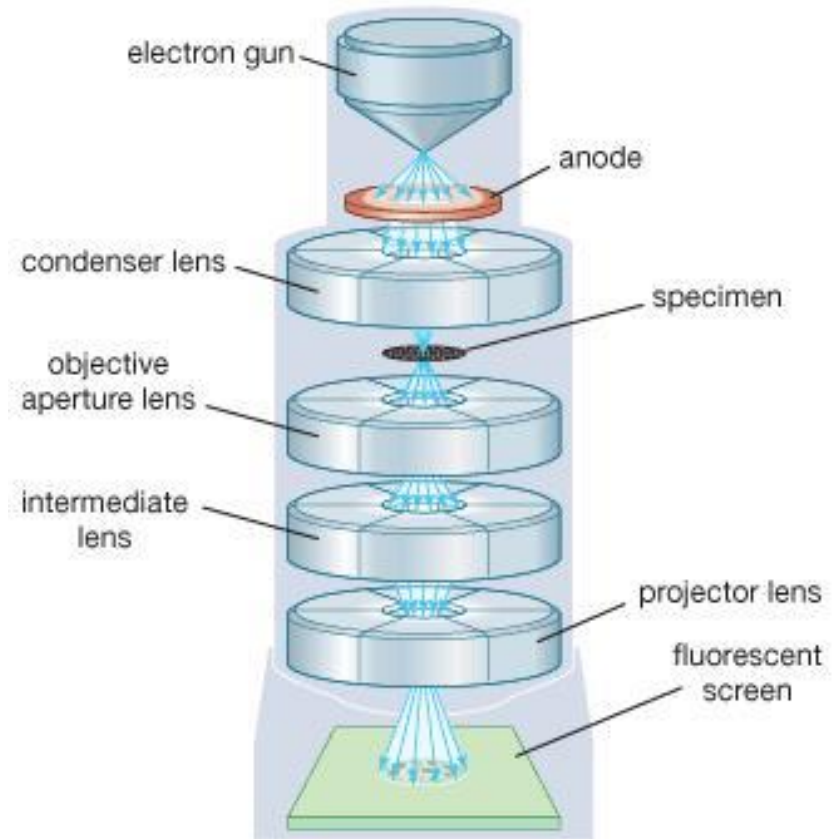
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3 mm.

Carbon

Grid

Transmission Electron Microscopy

10 1/nm

d

-1-12
-111
0-21
-130
1-30
000
02-1
1-1-1
11-2

Electron Beam

Auger electrons

Emitted X-rays (EDS & EMPA)

Backscattered secondary electrons (SEM)

SAMPLE

Elastically scattered electrons (SAED &CBED)

Inelastically scattered electrons

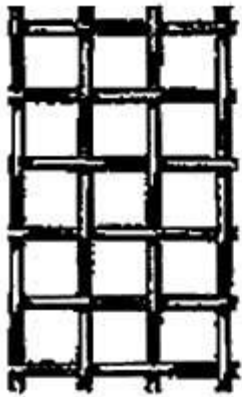Unscattered electron beam (EELS)
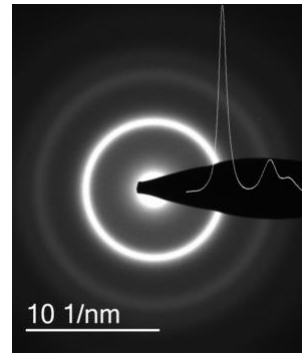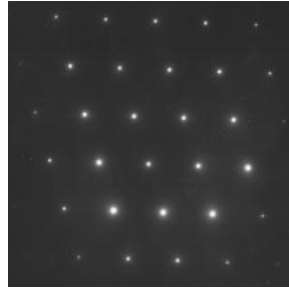
Sieving

Sieving is used to separate particles according to their particle sizes.

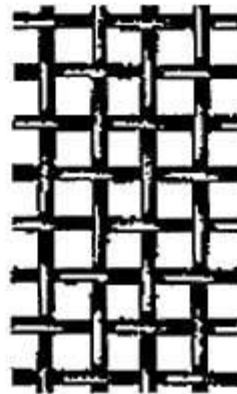# Sieving

Table shows sieve numbers and their corresponding openings in mm and inches.
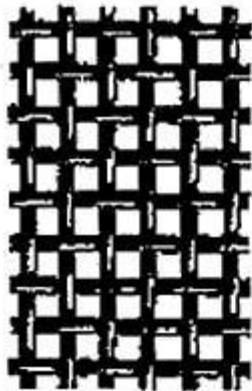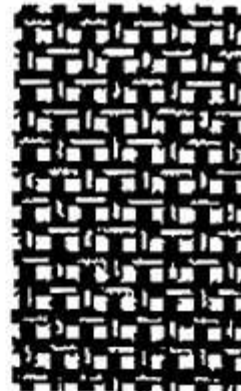
©Scrap Tire News

3 mesh

4 mesh

Mesh Screen Sizes

5 mesh

7 mesh

| (ASTM) U.S. Sieve Number	Particle Size	Tyler Screen Scale Equivalent	Sieve Opening Millimeters	Sieve Opening Inches	International Standard Organization Millimeters
3 ½		3 ½	5.660	0.223	5.6
4		4	4.760	0.187	
5		5	4.000	0.157	4
6		6	3.360	0.132	
7		7	2.830	0.111	2.8
8		8	2.380	**0.0937**	
10		9	2.000	0.0787	2
12		10	1.680	0.0661	
14		12	1.410	0.0555	1.4
16		14	1.190	0.0469	
18		16	1.000	0.0394	1
20		20	0.840	0.0331	
25		24	0.710	0.0280	0.71
30		28	0.590	0.0232	
35		32	0.500	0.0197	0.5
40		35	0.420	0.0165	
45		42	0.350	0.0138	0.355
50		48	0.297	0.0117	
60		60	0.250	0.0098	0.250
70		65	0.210	0.0083	
80		80	0.177	0.0070	
100		100	0.149	0.0059	
120		115	0.125	0.0049	
140		150	0.105	0.0041	
170		170	0.088	0.0035	
200		200	0.074	0.0029	
230		250	0.062	0.0024	
270		270	0.053	0.0021	
325		325	0.044	0.0017	
400		400	0.037	0.0015	

Sedimentation

If a particle with diameter d is dropped into a liquid, two forces act on it. Gravitational force and and the upward thrust of the liquid. (check the units)

Stokes Law

- Drag force $F_d = 6\pi\eta\, ru$

    η = viscosity

- Force of gravity

    $$F_g = \frac{4}{3}\pi r^3 \left(\rho_s - \rho_f\right)g$$

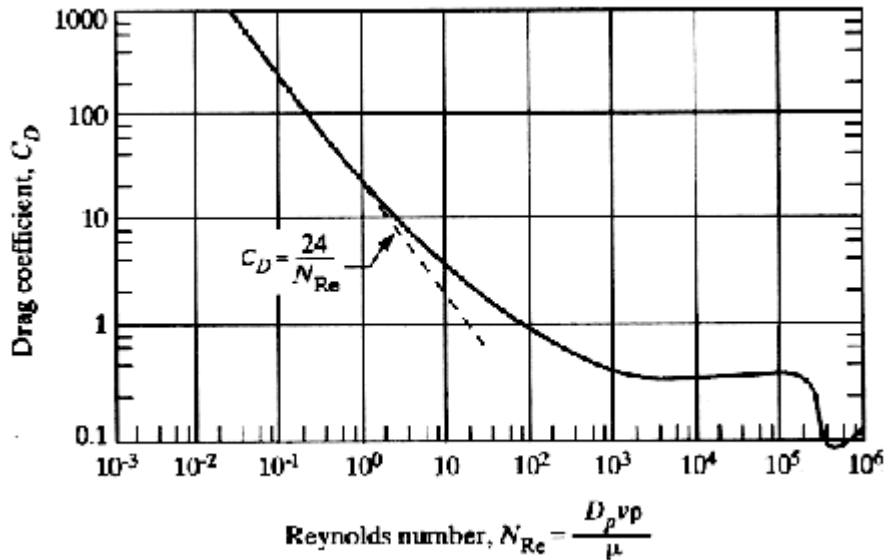- At terminal velocity $F_g = F_d$

- Solve for velocity

    $$u = \frac{d^2 g\left(\rho_s - \rho_f\right)}{18\,\eta}$$
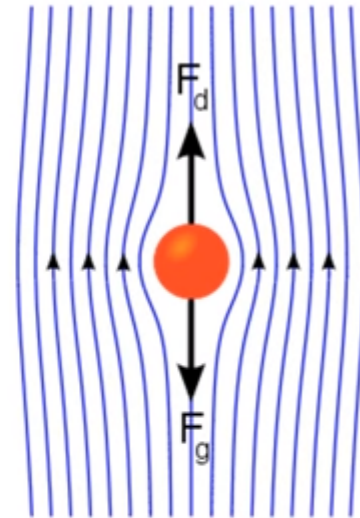
Gravity sedimentation is useful for particle size range 0.2 – 100 μm.

Sedimentation

After calculations, Reynold's number must be checked. If R<2, the result is real. If R>2, result is not real.

$$R = \frac{\rho \upsilon d}{\eta}$$

$$C_d = \frac{24}{R} + \frac{3}{\sqrt{R}} + 0.34$$

$$\upsilon^2 = \frac{4g(\rho_p - \rho)d}{3\,C_d\,\rho}$$

where; C_d is drag coefficient, ρ is density of fluid, υ is settling velocity, η is the viscosity, d is diameter of particle