

Experimental methods in physics

Surface analysis techniques

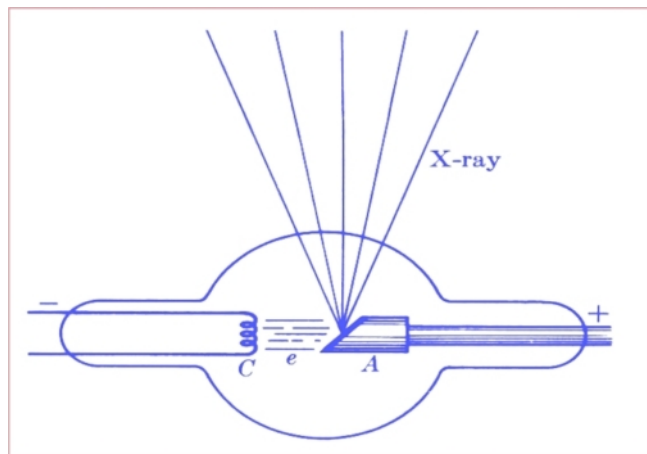
4. Sources and detectors

Jean-Marc Bonard

Academic year 09-10

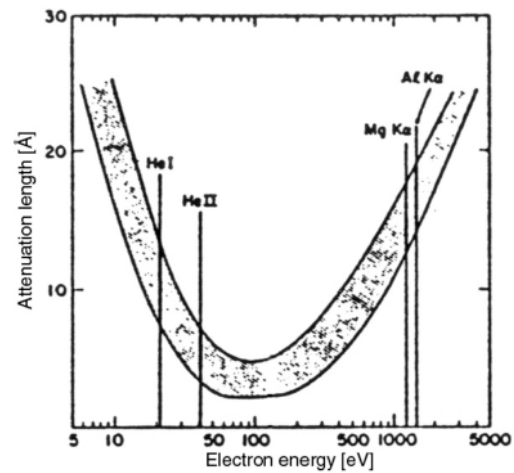
4. Sources and detectors

4.1. UV/X sources



Sources for photoelectron spectroscopy

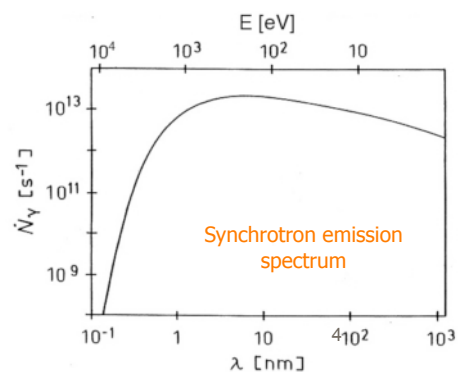
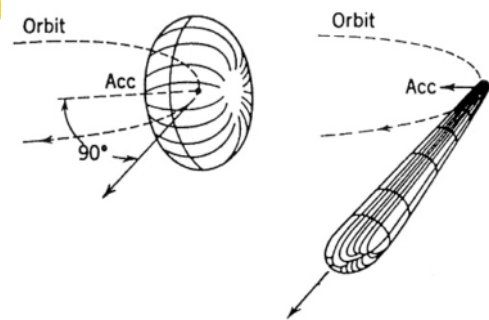
- Sources UV @ 21.2 eV (He)
 - Electric discharge in a He gas
 - High intensity
 - Nearly monochromatic
- X-ray sources
 - Bombardment of a metallic surface by high-energy electrons
 - Sources @ $\sim 1.5\text{keV}$: Al, Mg...
 - Monochromator often used to enhance energy resolution
- Synchrotron radiation
 - Higher brightness than conventional sources
 - Coherent and polarised light
 - Variable energy
 - Allows to cover energy range corresponding to minimal mean free path



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Synchrotron radiation

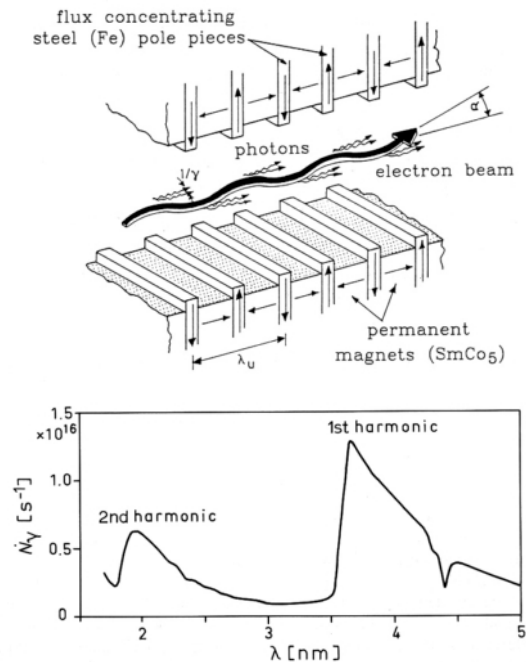
- Electron emit synchrotron light when deflected
 - Continuous spectrum
 - Low energy electrons: isotropic emission
 - Relativistic electrons: emission in a cone of low divergence angle tangent to the trajectory
- Synchrotron: Deflection of high energy electrons ($> 600\text{ MeV}$) by deflecting magnets



Synchrotron radiation II

Use of wigglers

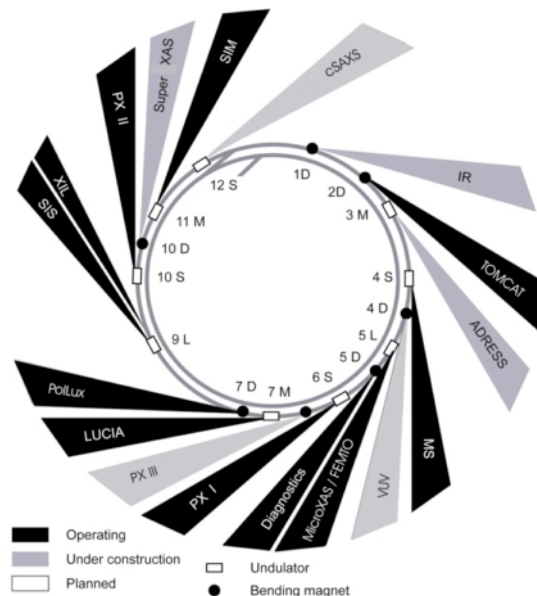
- | Periodic transverse magnetic field
- | Constructive/destructive interferences between beams emitted at each deflection
- | Coherent emission
- | ~1000x more intense emission than with a simple deflector
- | Smaller emission energy range



The "Swiss Light Source"

Synchrotron at PSI / Villigen (AG)

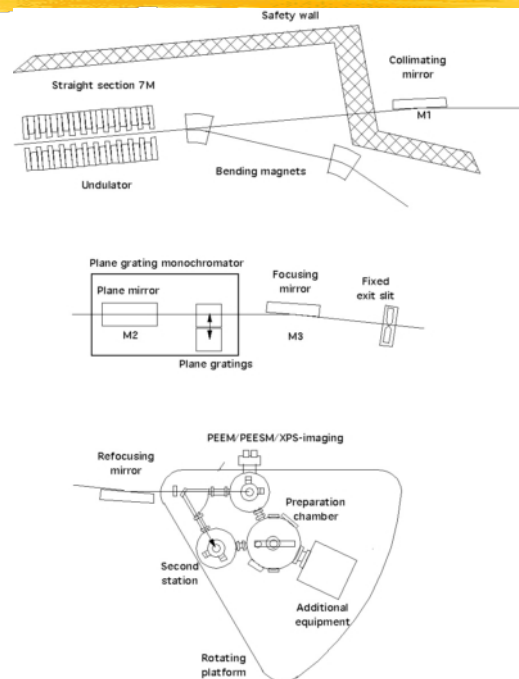
- | Storage ring
- | Six arcs
 - | Deflecting magnets
- | Six straight sections
 - | Wigglers
- | Nine "beamlines" currently in operation
 - | SIS: Spectroscopy of surfaces/interfaces
 - | IR/VUV: IR/UV spectroscopy
 - | SIM: Microscopy of surfaces/interfaces
 - | PX: Protein crystallography
 - | MS: Materials science (diffraction)
 - | ...



| <http://sls.web.psi.ch>

E.g., spectromicroscopy beamline

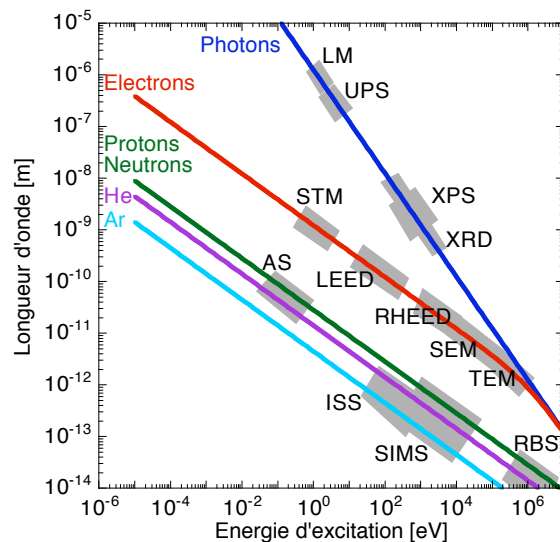
- | Source: wiggler
- | Aligning optics
- | Monochromator
- | Instruments mounted on a rotative platform



4. Sources and detectors

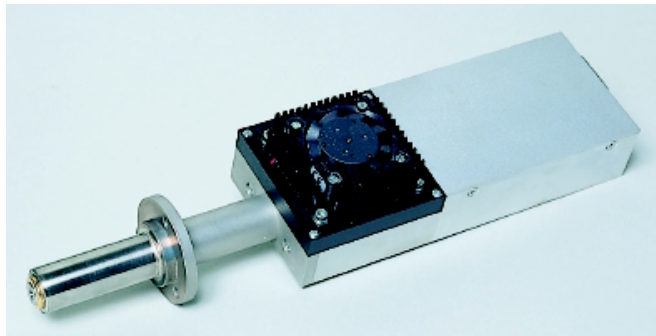
4.2. Spectrometry

- | Two stages
 - | Energy/mass selection
 - | Detection
- | Interaction products
 - | IR-VIS photons
 - | X-rays
 - | Electrons
 - | Ions
 - | Neutral particles



4. Sources and detectors

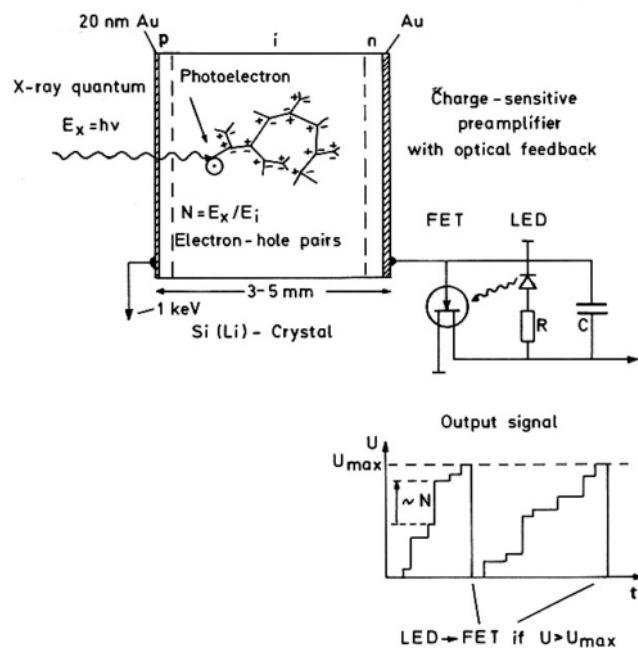
4.2.1. X-ray spectrometry



EDX Kratos μ EDX1400 detector

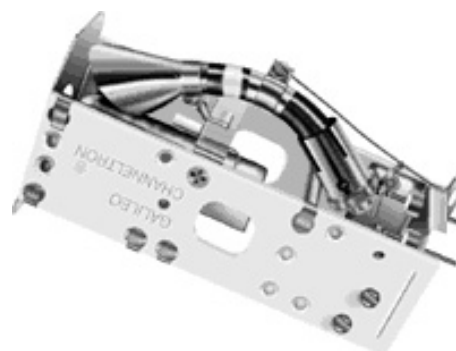
X-ray detection

- X-ray produces electron-hole pairs in a semiconductor
- Number of created charges proportional to photon energy (5 keV \approx 1300 pairs)
- Charge pulse converted to voltage difference by electronics
 - Amplification by a FET
 - Voltage at FET output constant until detection of next X-ray
 - Reset by a LED when maximal voltage reached
- Can also detect protons and α particles



4. Sources and detectors

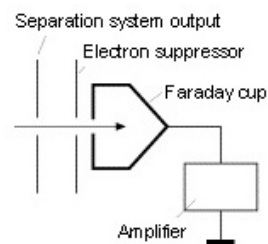
4.2.2. Electron spectrometry



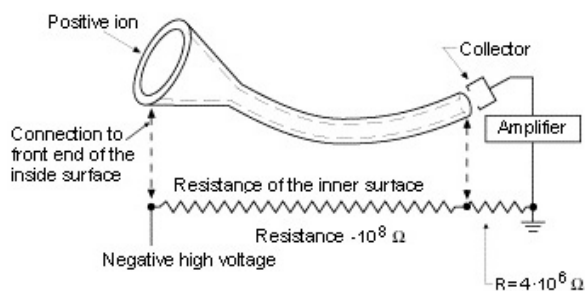
Electron detector "Channeltron"

Electron detection I

- Very low electron current
(XPS: 10^{-15} A $\approx 10^4$ e⁻/s)
- Faraday cage connected to an electrometer
 - ▮ Noise: $\leq 10^{-16}$ A
 - ▮ Absolute measurement
- Electron multiplier
 - ▮ Noise: $\leq 10^{-20}$ A
 - ▮ Fast
 - ▮ Relative measurement



Principle of the Faraday cup

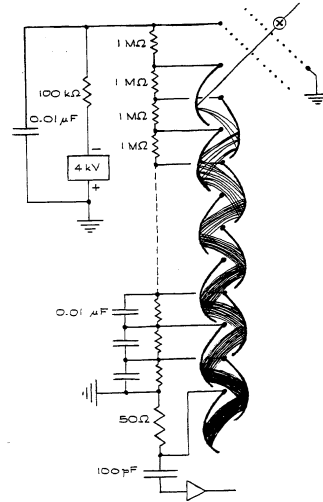


Configuration of the Channeltron

Electron detection II

Dynode

- 10-20 sheets interconnected by a resistance cascade
- Sheets covered by material having a high secondary electron emission rate
- Electron impacting on first dynode provokes emission of several secondary electrons
- Secondary electrons accelerated towards next dynode
- Amplification from dynode to dynode

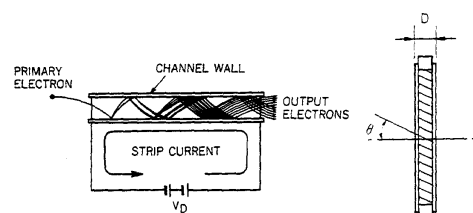
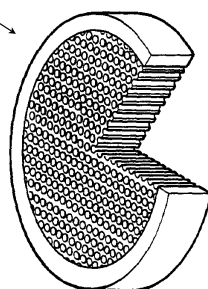


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Electron detection III

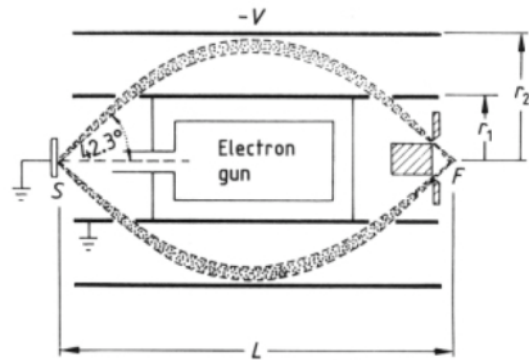
Channeltron / Channelplate

- Continuous dynode
- Semiconducting tube with high resistivity ($10^9 \Omega$) and high secondary electron emission rate
- Limited to $\sim 10^7$ detections/s
- Spatially resolved detection: channelplate
- Can also detect
 - Ions
 - X-rays



Cylindrical analyser

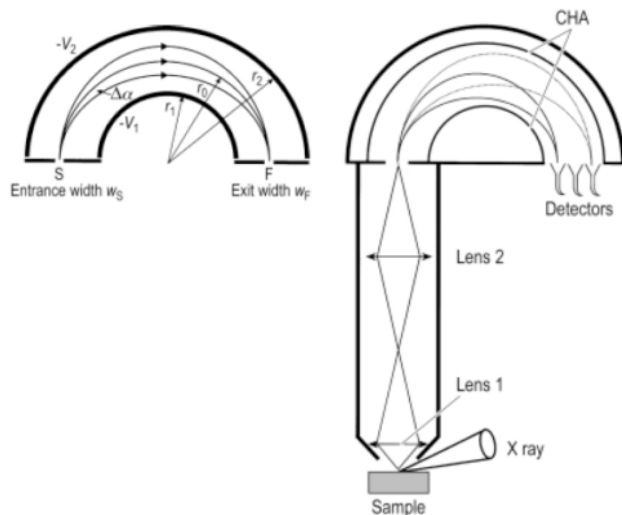
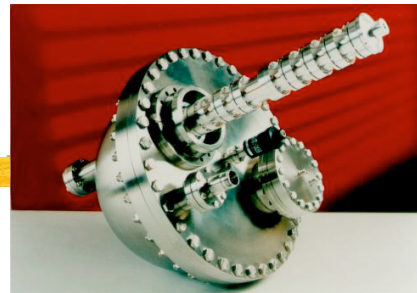
- Electron trajectory perpendicular to equipotentials
- $E = 1.31 \text{ eV} / \ln(r_2/r_1)$
- Precise angle of acceptance (42.3°): imposed geometry
- Inner cylinder earthed
- Outer cylinder at $-V$
- Medium resolution ($E/\Delta E \approx 100$)
 - Auger spectroscopy: one analyser
 - Photoelectron spectroscopy: two analysers in series



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Hemispherical analyser

- Electron trajectory parallel to equipotentials
- $E = e \cdot (V_2 - V_1) / (r_2/r_1 - r_1/r_2)$
- Lens assembly before analyser
 - Enhances electron collection
 - Decelerates electrons before analysis: enhances resolution
- Advantages
 - Better resolution than cylindrical analyser ($E/\Delta E \approx 1000$)
 - Measurement as a function of electron take-off angle possible

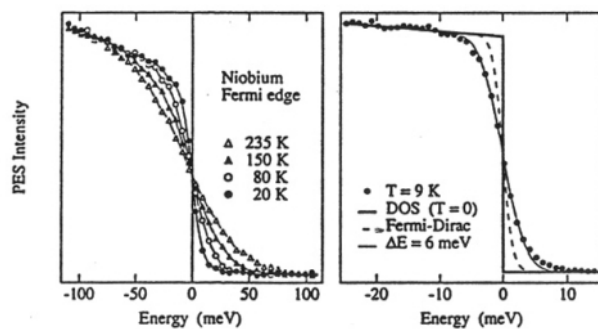
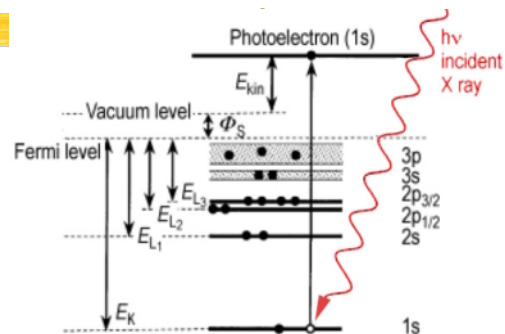


Energy resolution

Analysis in energy

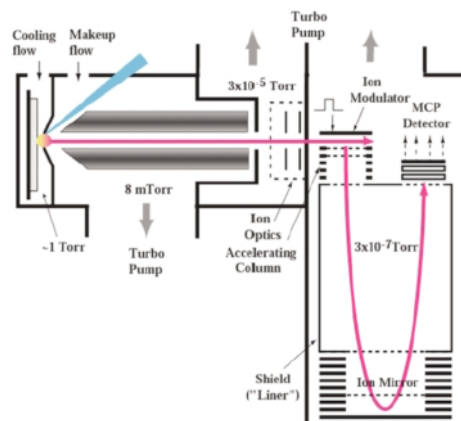
- Kinetic energy allows to determine the binding energy E_B
- $E_{kin} = h\nu - E_B - \phi_s$
- ϕ_s : work function of the sample
- Best attainable resolution: a few meV

- Example: Distribution of electrons around the Fermi level in Nb



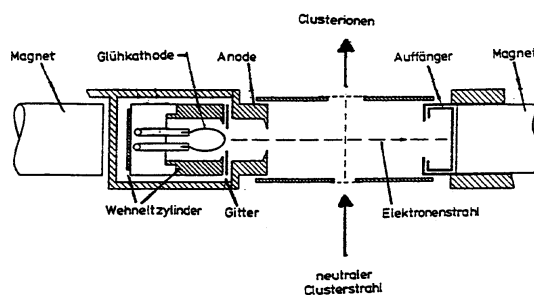
4. Sources and detectors

4.3. Detection of atoms and molecules



4. Sources and detectors

4.3.1. Ionisation



Detection of neutral particles

- Energetic particles
 - Production of secondary electrons on a target
 - Detection with a channeltron

■ Low energy particles: Production of ions

- Ionisation by electrons
 - Electron beam of ~ 100 eV
- Photoionisation
- ...

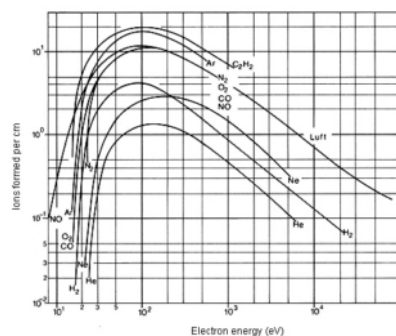
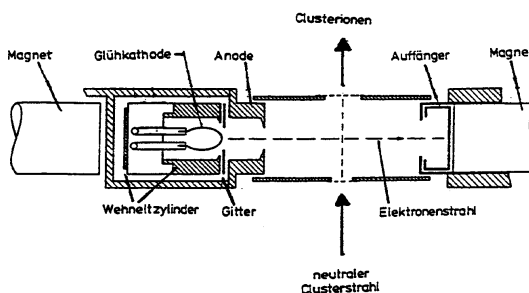


Fig. 4.14
Specific ionization S for various gases by electrons exhibiting energy level E



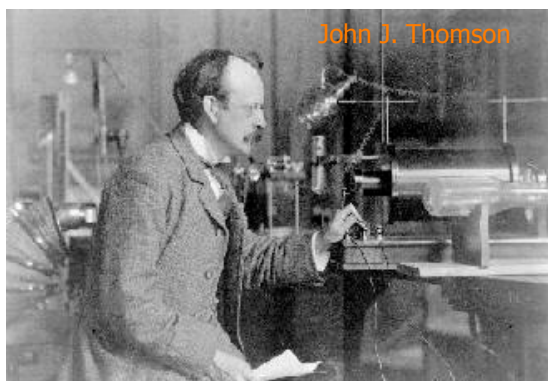
Ionisation methods

Ionisation methods	Sample	Form of sample	Mass	Advantages
Electron Impact (EI)	low mass, volatile	gas, liquid or solid	<1,000 amu	Hard method, widely used
Photoionization	low mass, volatile	gas	<1,000 amu	Hard method
Chemical Ionization (CI)	low mass, volatile	gas, liquid or solid	<1,000 amu	Soft method
Electrospray (ESI)	peptides, proteins, non-volatile	liquid chromatographic	<200,000 amu	Soft method, multiple ionisation
Fast Atom Bombardment (FAB)	carbone hydrates, organometallics, peptides	dispersed in a viscous matrix	<6,000 amu	Soft method
Matrix Assisted Laser Desorption (MALDI)	peptides, proteins, nucleotides	dispersed in a solid matrix	<500,000 amu	Soft method, very high masses

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4. Sources and detectors

4.3.2. Mass spectrometry - history



Mass spectrometry

Goal

Detection of particles as a function of their mass/charge ratio: m/q

Lorentz force $\vec{F} = q(\vec{E} + \vec{v} \times \vec{B})$

Radial acceleration

Radius of curvature r , velocity v

$$m/q = Er_1/v^2 \quad m/q = Br_2/v$$

Thomson (1897): electron

Dempster (1918): magnetic sector

Aston and Thomson (1920): discovery of isotopes

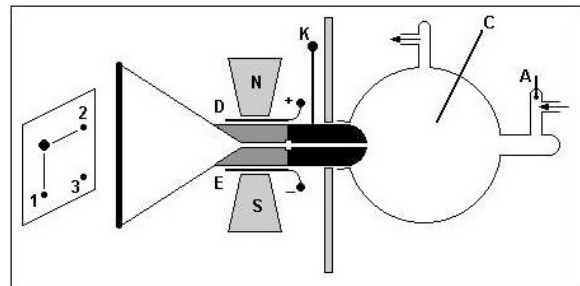
Experiment of Thomson and Aston parabola spectrometer

Gas in chamber C

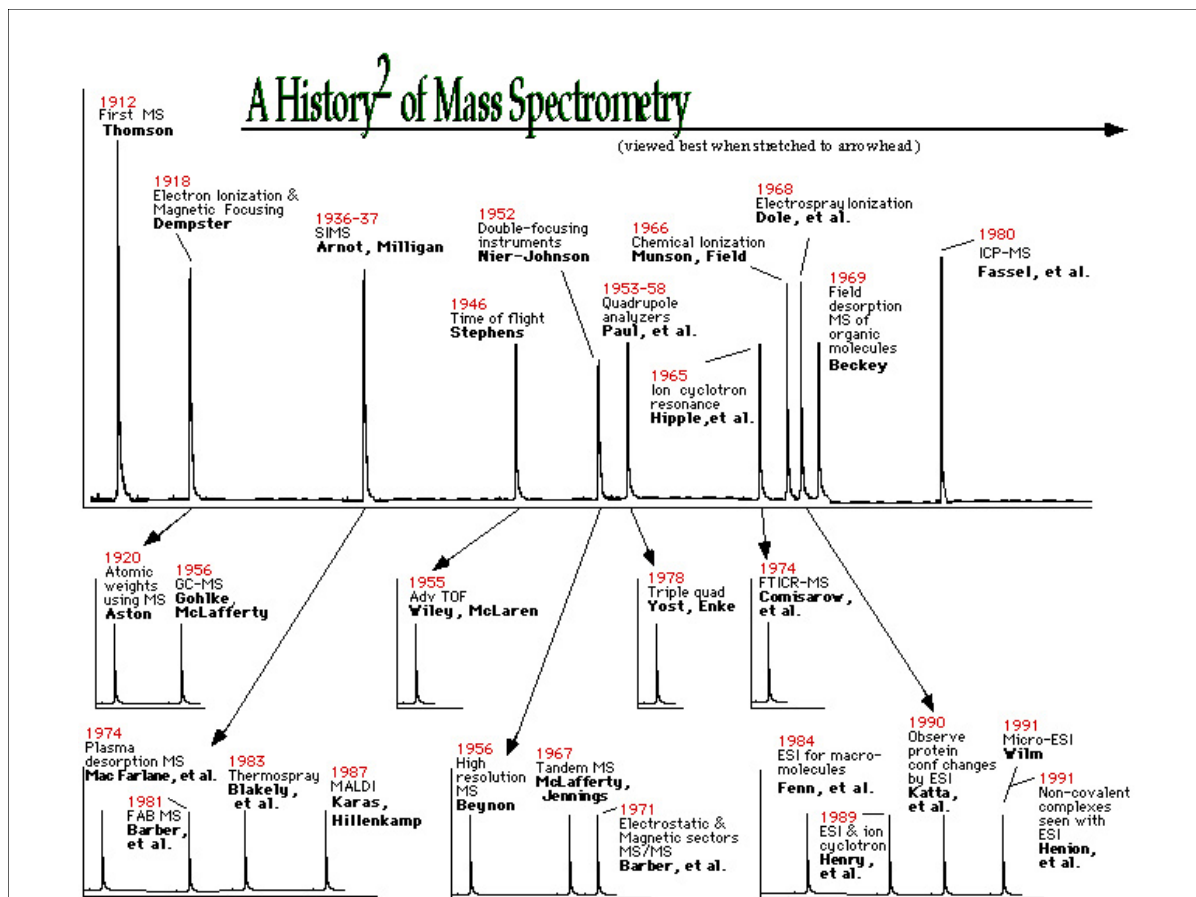
"Cathodic rays" (electrons) produce "Kanalstrahlen" (ions)

Accelerated by cathode K

Crossed electric and magnetic fields



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Mass spectrometers

Analyser	Avantages
Quadrupole	Fast scanning, resolution ($M/\Delta M$) of $\sim 10^4$
Sector (magnetic and/or electrostatic)	High resolution (10^5)
Time-of-Flight (TOF)	No mass limit (in theory), high current, resolution of 10^3 (10^4 with a reflectron)
Ion Cyclotron Resonance (ICR)	Very high resolution (10^6), exact mass



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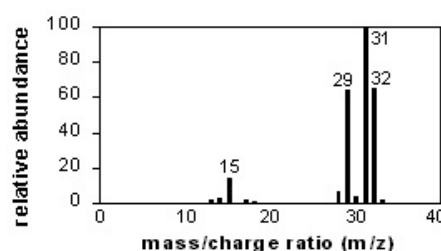
Mass spectrometry

Identification of molecules

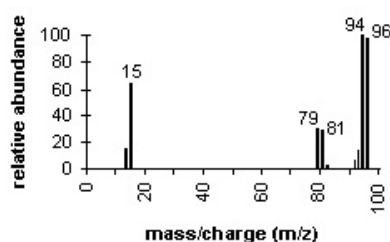
- Fragments
- Isotopes
- Multiple ionisation...

Wide use

- Gas-phase chromatography
- Secondary ion mass spectrometry (SIMS)
- Residual gas analysis
- ...from the atom to high molecular weight proteins...



ions	m/z
CH_3OH^+	32
$\text{H}_2\text{C}=\text{OH}^+$	31
$\text{HC}\equiv\text{O}^+$	29
H_3C^+	15



$\text{Br}-\text{CH}_3$	m/z = 15
(79)BrCH ₃	m/z = 94
(81)BrCH ₃	m/z = 96

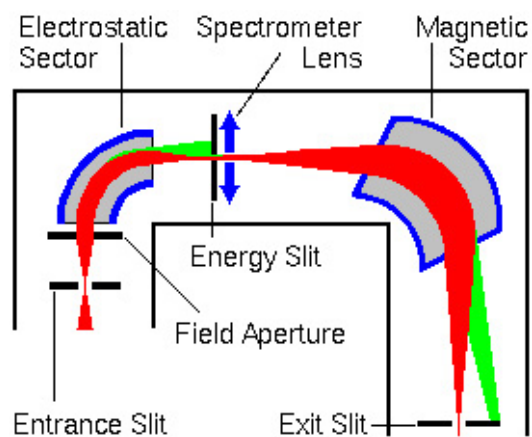
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4. Sources and detectors

4.3.3. Mass spectrometry: sector spectrometer

Sector spectrometer

- Development of Aston and Dempster's spectrometers
- Sector analyser
 - | Constant radius of curvature
 - | Constant acceleration energy
 - | Mass selection by varying E or B
- Magnetic sector introduced chromatic aberrations
 - | Ions with same mass do not necessarily have the same energy
 - | Mass and energy focussing: double sector



Sector spectrometer II

- Used mostly for dynamic SIMS
- Typical resolution of $M/\Delta M = 20000$
- Limited mass transmission (≤ 500 amu)
- Ion optics behaves like a lens system: direct imagery
- Resolution: ~ 50 nm
- Detection of only one mass at one time
- Mattauch-Herzog geometry: simultaneous detection of several masses →

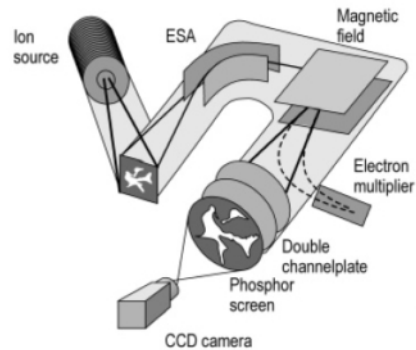


Fig. 3.19. Basic set-up of a direct imaging magnetic sector instrument. The stigmatic secondary ion optics consists of an electrostatic analyzer (ESA) and a magnet sector field.

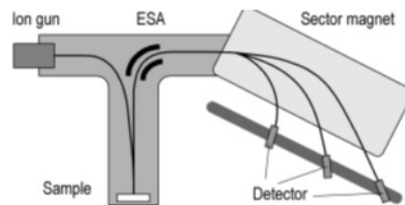


Fig. 3.20. Schematic drawing of a Mattauch-Herzog magnetic-sector instrument with simultaneous mass detection.

4. Sources and detectors

4.3.4. Mass spectrometry: quadrupole spectrometer

Quadrupole spectrometer

Principle

- Gas ionised by electrons (emitted by a hot filament cathode)
- Ions directed to spectrometer entrance
- Charge/mass selection by a quadrupole
- Detection by a Faraday cage, channelplate...

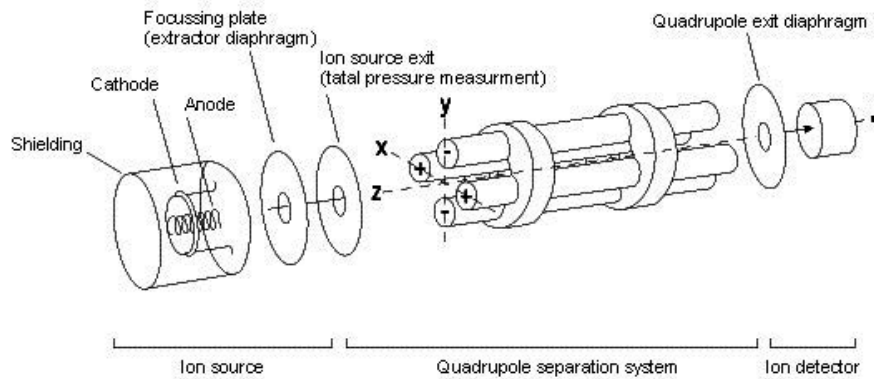


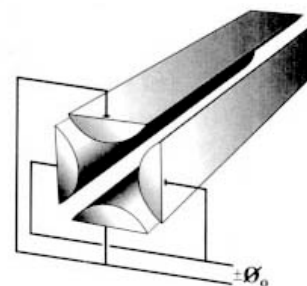
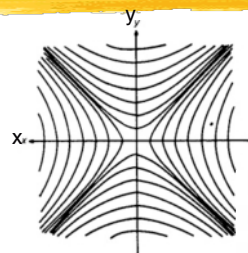
Fig. 4.2
Schematic for quadrupole mass spectrometer

Quadrupole spectrometer II

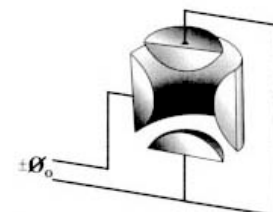
Hyperbolic field

- Instable for charged particles
- Potential U on opposing electrodes (distance of $2 \cdot r_0$)
- Potential $-U$ on two other electrodes
- Superposition of constant potential U with alternative potential V

$$\Phi = [U + V \cos(\omega t)] \cdot (x^2 - y^2) / r_0^2$$
- Ideally: electrodes with hyperbolic section
- In practice: cylindrical electrodes



- Based on same principle: ion trap



Quadrupole spectrometer III

Principle

- Electrodes +: transmit ions with $m/q > M_1$
- Electrodes -: transmit ions with $m/q < M_1$
- $M_1 = V / (14.4 \omega^2 r_0^2)$
- Resolution: determined by
 - U/V ratio
 - Length and radius of quadrupole
- Generally
 - ω remains constant
 - Ion selection by varying U, V with U/V constant

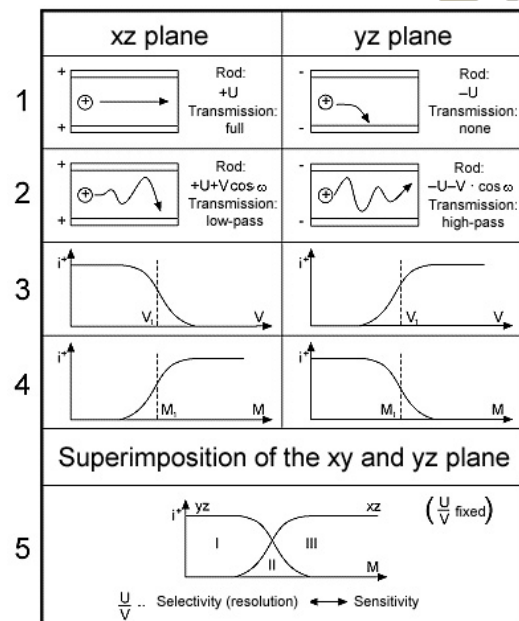


Fig. 4.5
Phenomenological explanation of the separation system

Quadrupole spectrometer IV

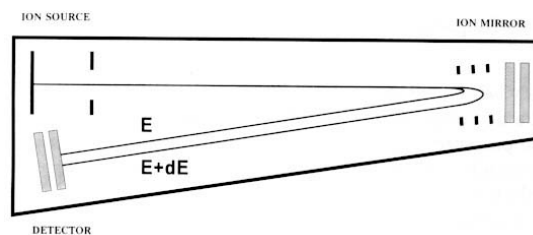
- Simple principle, moderate cost
- Limits
 - Middle resolution ($M/\Delta M \approx 500$)
 - Masse limited to ~ 500 amu
 - Low transmissivity (<1% of selected ions reach detector)
 - Spectrum acquisition by scanning U and V: huge loss of information

4. Sources and detectors

4.3.5. Mass spectrometry: time-of-flight spectrometer (ToF)

Time-of-flight spectrometer

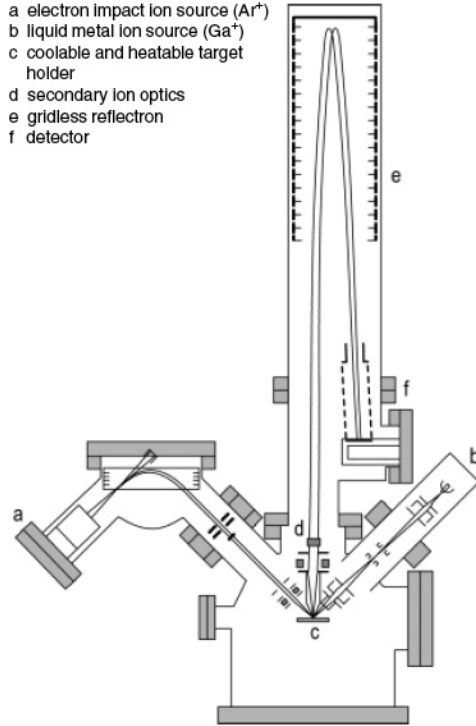
- Does not have a quadrupole's drawbacks
 - High masses
 - Efficient selection and detection
- Acceleration of ions with $U_0 = 2-8 \text{ keV}$
 - Ions with same energy
 - Velocity varies with $(m/q)^{0.5}$
 - Measurement of time of flight for a given distance L :
$$t^2 = (m \cdot L^2)/(2q \cdot U_0) \propto m/q$$
- Dispersion of initial ion velocity
 - Compensation by using an ion mirror (reflectron)



Time-of-flight spectrometer II

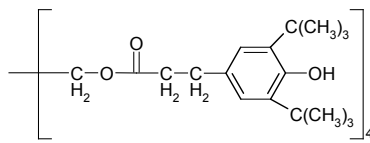
- Measurement of time of flight
 - Possible only with ion pulses
 - Pulsed ion beam: primary or secondary
- Mass resolution $m/\Delta m \approx 10000$
 - Long flight distance (1 - 1.5 m)
 - Measurement of time-of-flight with 0.1 ns precision
- Advantages
 - No mass limit
 - Detection of all masses with same polarity in the secondary ion pulse
 - Possibility of detecting ions as a function of position on sample surface

- a electron impact ion source (Ar^+)
- b liquid metal ion source (Ga^+)
- c coolable and heatable target holder
- d secondary ion optics
- e gridless reflectron
- f detector

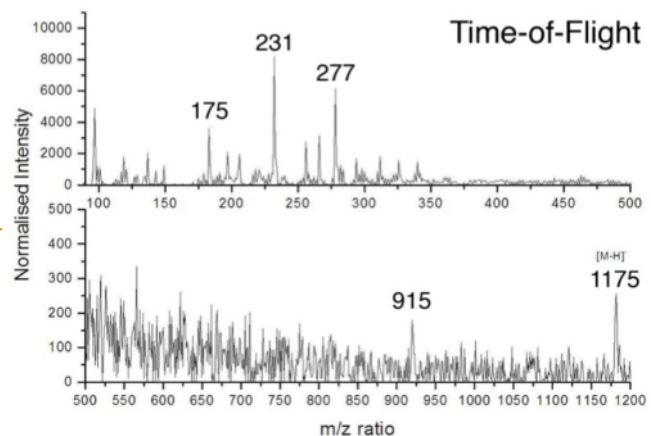
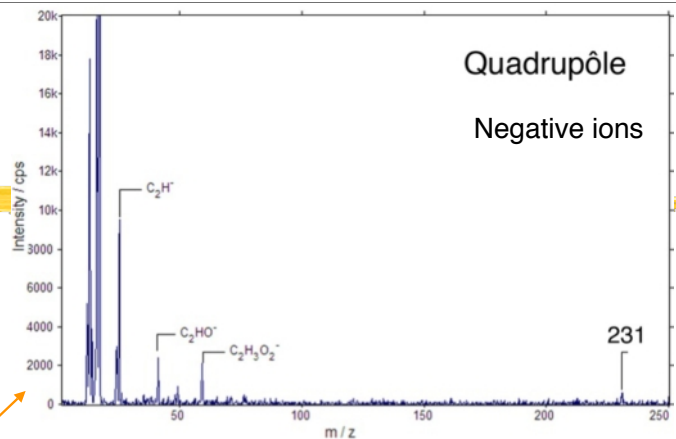


Comparison

- Irganox1010 molecule



- Mass: 1176.78 amu
- Quadrupole
 - Some characteristic ions at low masses only
 - Signal intensity decreases rapidly with increasing mass
- Time-of-flight
 - Detection of characteristic fragments and molecular ion

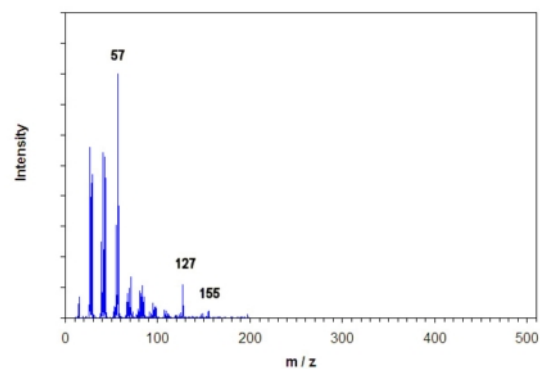


Comparison Quadrupole - ToF

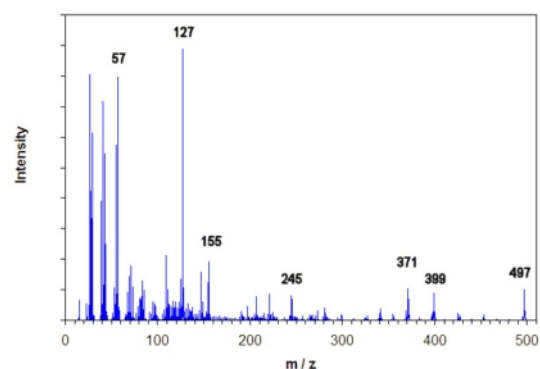
- Surface with unknown contaminant
- Quadrupole
 - Limited in mass to $m/q \sim 160$ in that case
 - Decrease in intensity of factor 10 between peaks at 57 and 127 amu
- Time-of-flight
 - Characteristic fragments with high mass
- Identification
 - Database
 - High mass fragments determine often the identification

www.minisims.com

Contaminated Area - Quad Positive Spectrum

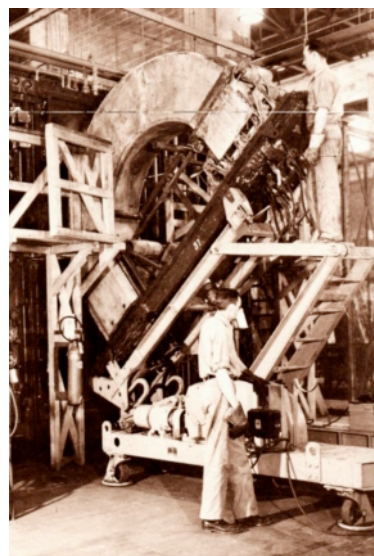


Contaminated Area - ToF Positive Spectrum



4. Sources and detectors

4.4. The "Calutrons"

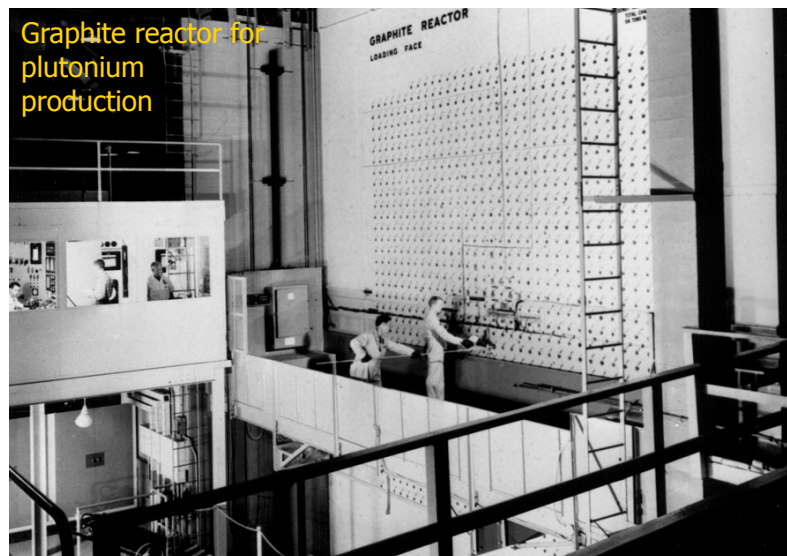


Going back...

- 1920
 - Studies of Thomson and Aston
 - Existence of isotopes
- 1938
 - O. Hahn and F. Strassmann discover nuclear fission of uranium
 - Less than one week later, the possibility of an atomic bomb is mentioned
- 1939
 - E. Fermi and J. Dunning task A. Nier with the separation of uranium isotopes
- 1941
 - The feasibility of an atomic bomb is accepted (1/11/1941)
 - Critical mass: between 2 and 100 kg of ^{235}U (0.7% in natural uranium)
 - No separation technique, no moderator
- 1942
 - The site of Oak Ridge is chosen for uranium enrichment

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Uranium enrichment I



- Fission of ^{235}U produce neutrons
- $^{238}\text{U} + n^0 \rightarrow ^{239}\text{Pu}$

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Uranium enrichment II

Gas diffusion

- | Diffusion rate varies with molecular weight
- | UF_6 diffuses through fine and porous filters (10 – 100 nm)
- | Weight difference between $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$: < 1%
- | Enrichment factor of $\sim 0.14\%$ per cycle
 - | Natural uranium: 0.7% ^{235}U
 - | Military grade: 88% ^{235}U
 - | 4000 diffusion stages
- | 12'000 workers

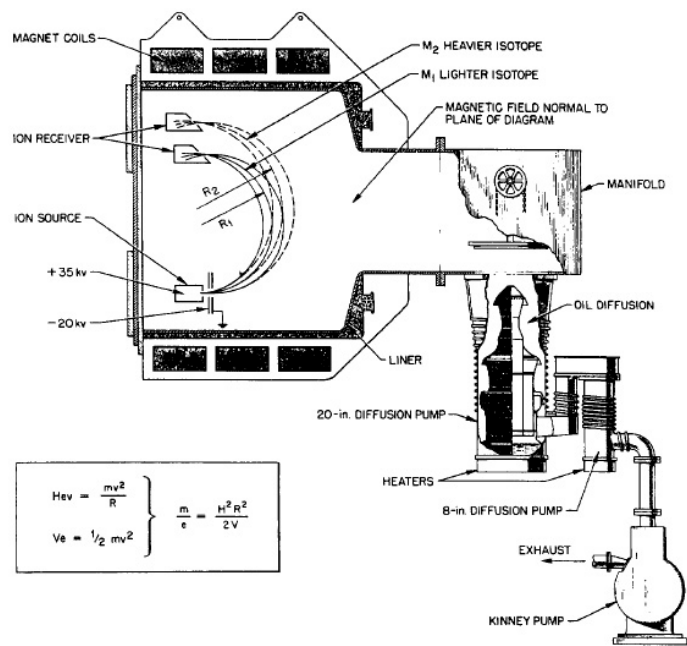


Gaseous diffusion plant in Oak Ridge

Uranium enrichment III

Electromagnetic separation

- | Proposed by E.O. Lawrence in 1942
- | 180° magnetic sector
- | Separation of $\sim 2.5\text{mm}$ after an arc of 45cm radius
- | "Calutron"
CALifornia University cycloTRON



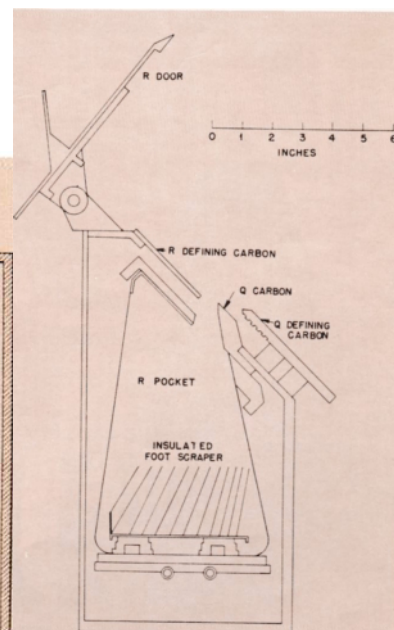
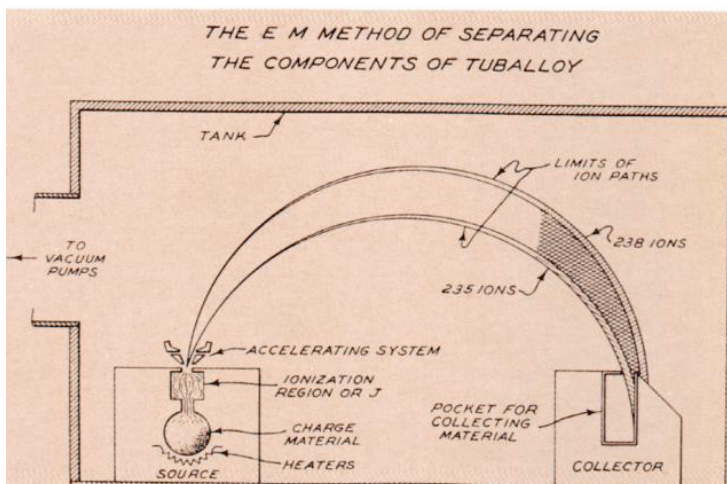
“Calutrons”

- Magnet of 4.6 m diameter
- Realised for a 100 MeV cyclotron
- Used for first separation trials



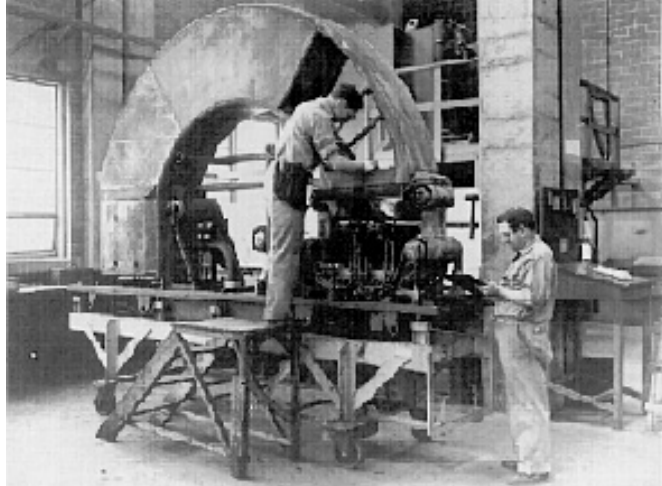
“Calutrons” II

- 864 α units: enrichment to 12%
- 216 β units: enrichment to 88%



“Calutrons” III

- | Base material: UCl_4
- | Separation of typ. 1-4 g/h
- | Collectors exchanged every ~100h
- | Graphite burned
- | Metallic uranium extracted from ashes
- | ~90% of evaporated material “lost” on the instrument walls
- | Periodic cleaning

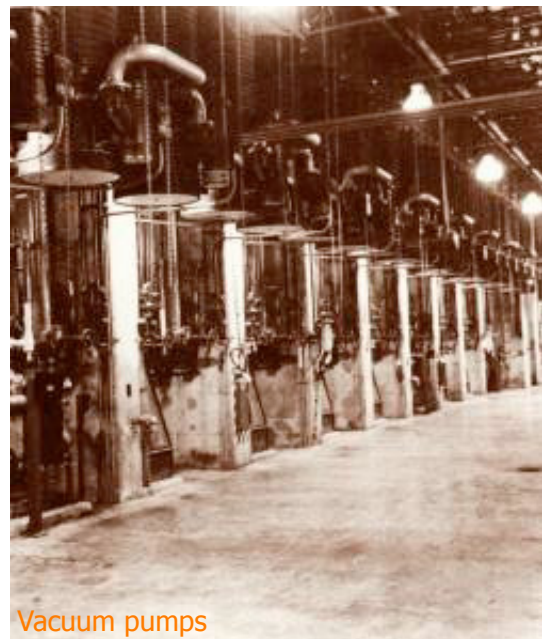


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“Calutrons” IV



Instrument control



Vacuum pumps

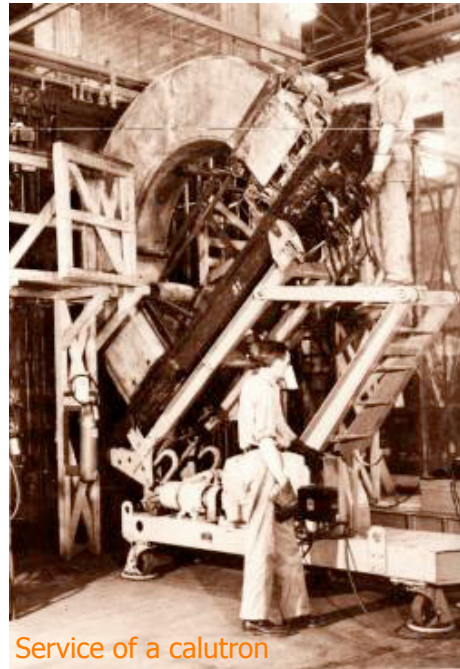
“Calutrons” V

■ Performances

- | August 1945: 42 kg of ^{235}U enriched to 88%
- | 5100 kg of natural uranium
- | 22'000 workers

■ After WWII

- | Used for separation of stable isotopes
- | Five original calutrons in used until March 1999
- | Research, medicine, industry...
- | E.g. 700 g/year of thallium 203 for medical imagery
- | Technique used in Iraq in 1992...



Service of a calutron