



**IAEA**

International Atomic Energy Agency

# ***Roots, shoots and flowers of radioanalytical Chemistry - NAA and related fields***

Matthias Rossbach

Industrial Applications and Chemistry Section, NAPC

International Atomic Energy Agency – Vienna, Austria



# Contents

- **1) Historic developments**
- **2) Growth and diversification**
- **3) Success stories and examples**

## How it started

- **Wilhelm Conrad Röntgen (1845-1923) discovered in November 1885 a mysterious, penetrating radiation which he called x-rays.**
- **In March 1886 Henri Becquerel reported that uranium bearing compounds emit an invisible penetrating radiation which he called uranium radiation**



Henri Becquerel (1852-1908)

**Maria Sklodowska (1867-1934) studied physics and mathematics at the Sorbonne, Paris,**

**1895**

**She married Pierre Curie**

**1897**

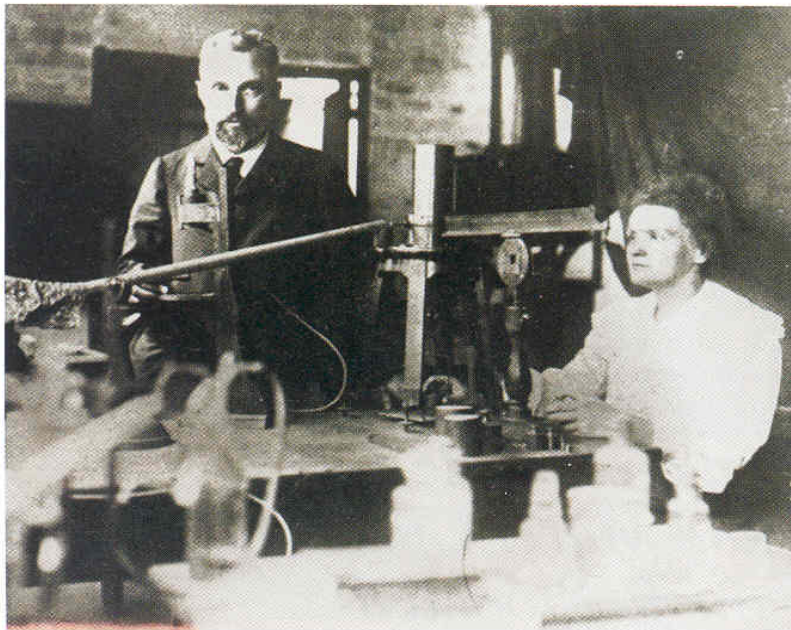
**Irène Curie was born**

**1898**

**Polonium and Radium was discovered**

**1903**

**Pierre and Marie Curie together with Henri Becquerel received the Nobel Price in physics**



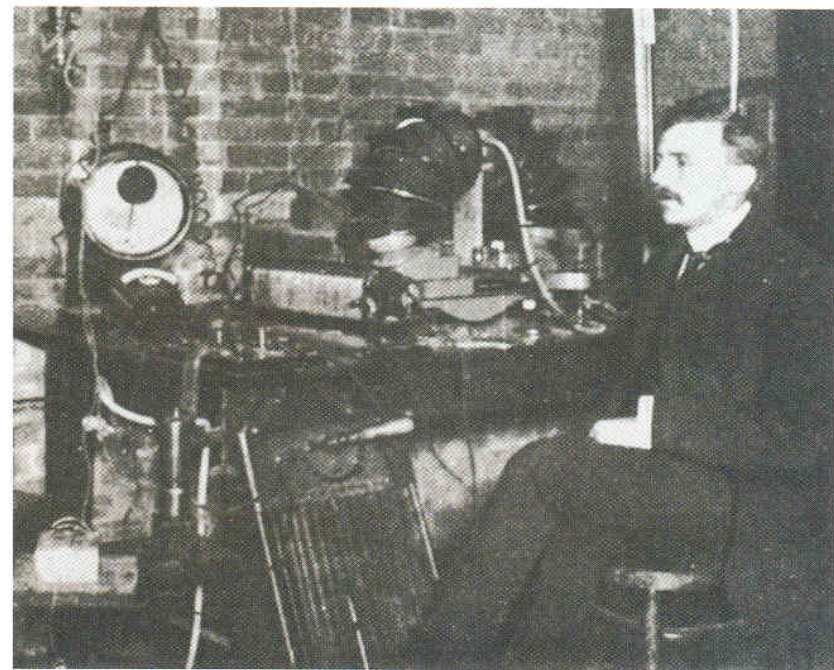
- **Marie started her PhD in 1897 to study Becquerel's radiation and its ionisation capacity in air.**
- **In July 1898 Marie called the 'nuclear property' of certain heavy elements to emit spontaneous radiation "radioactivity".**

## Discovery of new elements (1898)

- **Two natural minerals, Pitchblende ( $\text{UO}_3$ ) and Torbernit  $\text{Cu}(\text{UO}_2)_2 (\text{PO}_4)_2$  happened to be much more radioactive than pure U salts.**
- **by chemical separation they could isolate a substance being 400 times more radioactive than U. The new element behaved similar to Bi and was called Polonium.**
- **Later, tiny amounts of a second element, similar to Barium were obtained and called Radium.**

## Identification of different types of radiation, 1899-1900

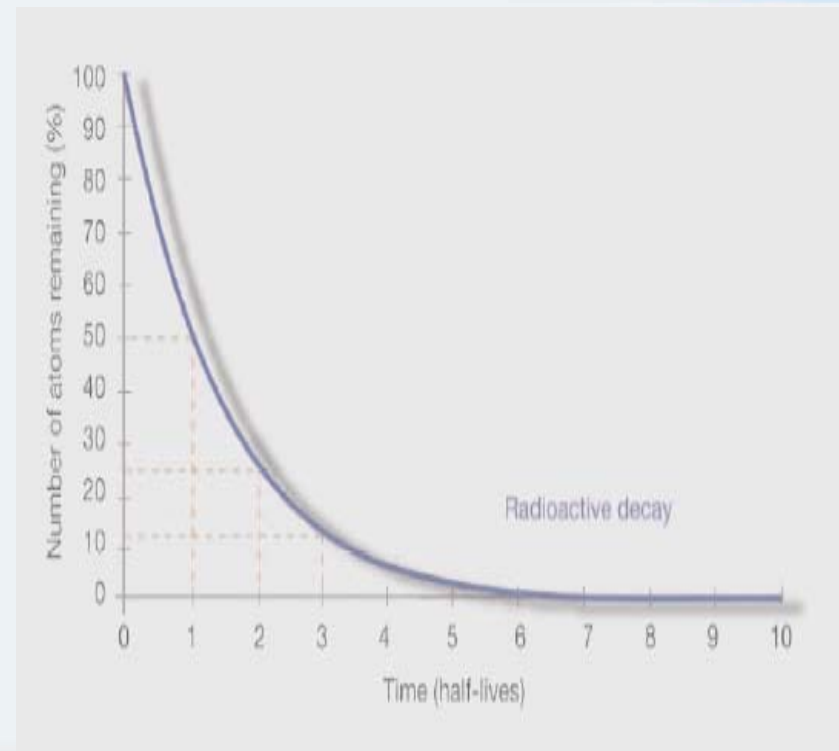
- **Ernest Rutherford (1871-1937) identified two types of radiation which he called alpha and beta radiation.**
- **Paul Villard (1860-1934) discovered a third type of radiation called gamma radiation.**
- **The nature and origin of this spontaneous radiation, however, was still mysterious.**



Ernest Rutherford (1871-1937)

## Ernest Rutherford and Frederick Soddy discovered the law of radioactive decay in 1903, $N = N_0 e^{-\lambda t}$

- “Emanation” of radioactivity is associated with the transformation of elements
- Radioactive decay is characterized by a specific half life,  $t_{1/2}$  or a decay constant,  $\lambda$
- Radioactive decay chains for U and Th were established
- Energy released in decay processes is million times higher than than chemical processes.



## Important consequences of these new findings:

- New model of the atom (Rutherford and N. Bohr, 1911-1913)
- Periodic system was reformed and complemented
- $\beta$  - rays are high energetic electrons
- Special Theory of Relativity was formulated (A. Einstein, 1905)
- $E = m c^2$
- Quantum theory was formulated (M. Planck, 1900)
- Applications of radioactivity in Chemistry, Biology, Geophysics, Astrophysics and Medicine
- New disciplines of research emerged, e.g. particle Physics or radiocarbon dating



**BUVARD**

**PLOMBIÈRES·les·BAINS (Vosges)**

EAUX HYPERTHERMALES (74°) TRÈS RADIO·ACTIVES  
**ESTOMAC · INTESTIN · RHUMATISME**  
**MALADIES DES FEMMES · MALADIES NERVEUSES**

Altitude: 456<sup>m</sup>

Cure d'Air

Séjour de repos



Environ pittoresques

Sapinières

Nombreuses excursions

*A 6 heures de Paris,  
Trains rapides, voitures directes.*

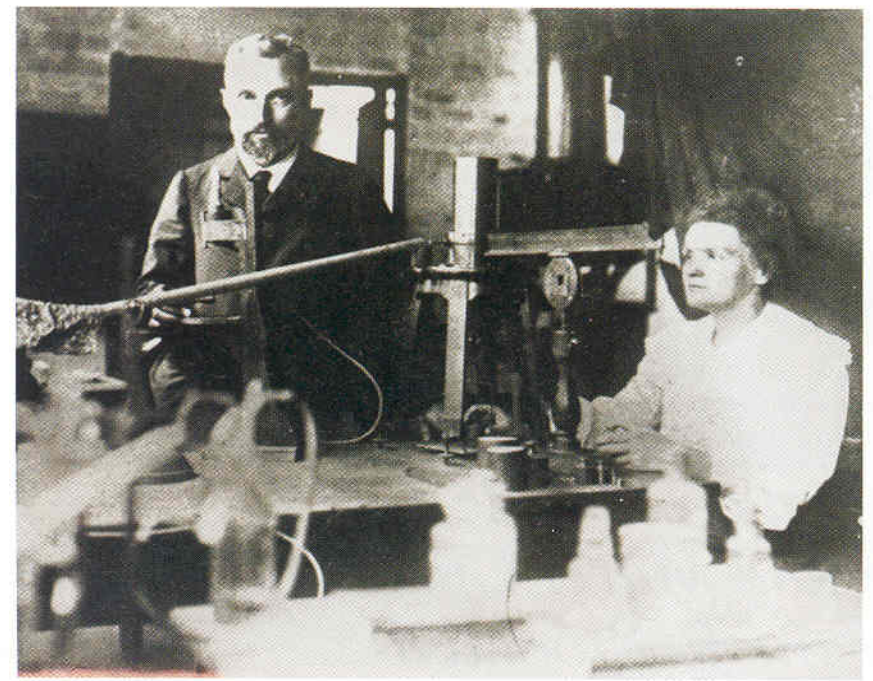
**SAISON DU 15 MAI  
AU 30 SEPTEMBRE**

Pour renseignements s'adresser au **SYNDICAT D'INITIATIVE**

COHENDET, FRÈRES - LYON  
SPÉCIALITÉ DE BUVARDS

## Marie Curie (1867-1934)

- 1898 discovery of Po and Rn
- 1903 PhD “Recherches sur les substances radioactives”
- 1903 Nobel Price in Physics
- 1907 atomic mass of Rn  $226.45 \pm 0.5$  (today’s value: 226.025)
- 1911 Nobel Price in Chemistry
- 1914 Radium Institute in Paris



## Irene Curie (1897-1956) and Frederic Joliot (1900-1958)

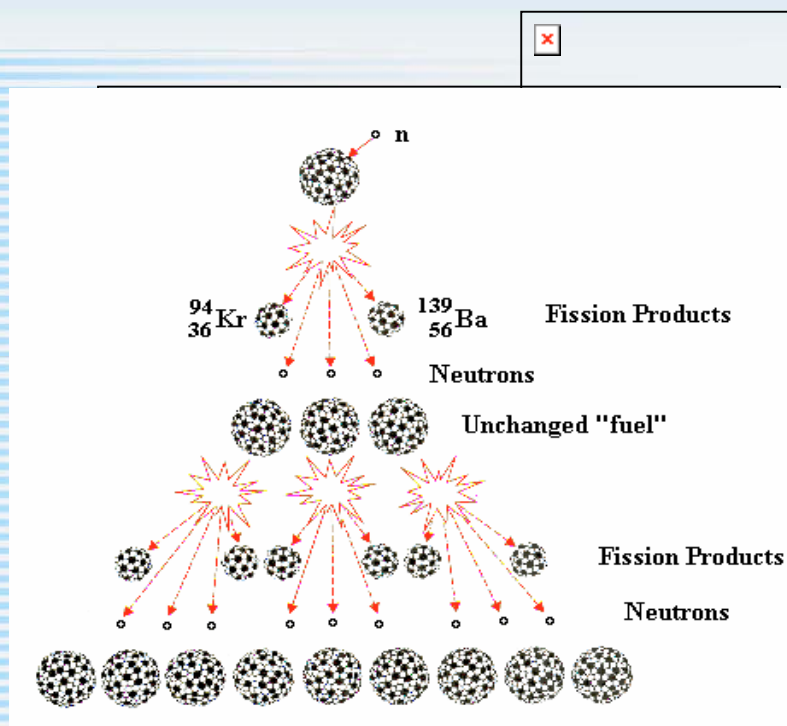
- 1919 Started working at the Radium Institute
- 1925 PhD in physics
- 1926 married Frederic Joliot
- 1933 discovered pair production ( $e^+ e^-$ )
- 1934 discovered artificial radionuclides  $^{27}\text{Al}(\alpha n)^{30}\text{P}$
- 1935 Irene and Frederic Joliot-Curie obtain the Nobel Price in Chemistry



## Other important discoveries and applications

- 1930 Wolfgang Pauli (1900-1958) postulated the beta decay to be associated with a new particle, the neutrino
- 1931 Paul Dirac predicted the positron  $e^+$
- 1932 James Chadwick discovered the neutron
- 1932 John Cockcroft and Ernest Walton produced with a particle accelerator  ${}^7\text{Li} + p \rightarrow \alpha + \alpha$
- 1932 Harold Urey discovered stable hydrogen isotope 'deuterium'
- 1934 Ernest Lawrence produced radionuclides at the cyclotron in Berkeley
- 1934 Enrico Fermi produced radionuclides by neutron irradiation
- 1935 first application of radionuclides in biology ( ${}^{32}\text{P}$  in rats, O. Chiewitz and G. de Hevesy)

## Towards uranium fission



- 1934 Enrico Fermi and co-workers bombarded all chemical elements with neutrons, including Uranium
- They discovered 5 radionuclides with different half lives but did not belong to element 91
- They concluded neutron capture and beta decay did produce trans-uranium elements
- The study of 'trans-uranium' elements was also taken up by Otto Hahn, Lise Meitner and Fritz Strassmann between 1935-1937

The search for trans uranium elements (blue) ended up in the discovery of fission into several lighter elements (green)

1																	18
H 1																	He 2
Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	Ne 10
Na 11	Mg 12											Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Md 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
Cs 55	Ba 56	La 57 71	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	/	Rn 86
/	Ra 88	Ac 89	Th 90	Pa 91	U 92	93	94	95	96								

## **Towards uranium fission**

- 1937** Irene Joliot-Curie published results of neutron irradiation of uranium with a radionuclide  $T_{1/2} \approx 3.5$ h similar to lanthanum, possibly a trans-uranium element
- October 1938** O. Hahn verified the results and suspected Radium isotopes
- December 1938** the activity behaved like Barium
- 6 January 1939** published the results as ‘Uranium decays into barium and lanthanum’. They had discovered the uranium fission.
- 11 February ‘39** L. Meitner and M. Frisch publish the theoretical explanation of uranium fission in “Nature”. 200 MeV per fission process released
- 2 December 1942** Enrico Fermi produced the first self sustained chain reaction below the Stadium of the Chicago University

# Nobel prize laureates in the field of radiochemistry and nuclear chemistry

## Prize in chemistry

1908	E.Rutherford	Modes of radioactive decay, Rn characterization
1911	M.Curie	Discovery of Po and Ra
1921	F.Soddy	Concepts of isotopes, change of Z in radioactive decay
1922	F.W.Aston	Separation of stable isotopes of Ne
1934	H.C.Urey	Discovery of deuterium, cosmic abundances
1935	F.Joliot/I Curie	Production of artificial radionuclides
1943	G.von Hevesy	Use of radioisotopes as tracers development of neutron activation analysis (with H.Levi)
1944	O.Hahn	Discovery of nuclear fission (with F.Strassman)
1951	E.M.McMillan G.T.Seaborg	Discovery of Np and Pu
1960	W.F.Libby	$^{14}\text{C}$ + $^3\text{H}$ dating methods



# Nobel prize laureates in the field of radiochemistry and nuclear chemistry

## Prize in physics

1901	W.C.Rontgen	Production and characterization of X-rays
1903	H.Becquerel M.Curie, P.Curie	Discovery of radioactivity
1935	J.Chadwick	Discovery of neutron
1938	E.Fermi	Search for transuranium elements
1939	E.O.Lawrence	Development of cyclotron
1951	J.D.Cockroft E.T.S.Walton	Development of accelerator
1961	R.L.Mossbauer	Isomer shifts in $\gamma$ -ray emission
1963	M.Goeppert-Mayer J.H.D.jensen, E.P.Wigner	Fundamental nuclear structure
1968	L.Alvarez	Electron capture decay
1983	W.F.Fowler	Nucleosynthesis of elements in stars

# A Nuclear Chronology



- **Hiroshima & Nagasaki 1945**
- **“Atoms for Peace” 1953, Eisenhower**
- **Creation of the IAEA 1957**
- **Non-Proliferation Treaty 1968**
- **Three Mile Island 1979**
- **Chernobyl Accident 1986**
- **In 2003 there were 441 NPRs in 30 countries producing 359 GW**



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***Growth and diversification***  
**of analytical radiochemistry**

M. Rossbach

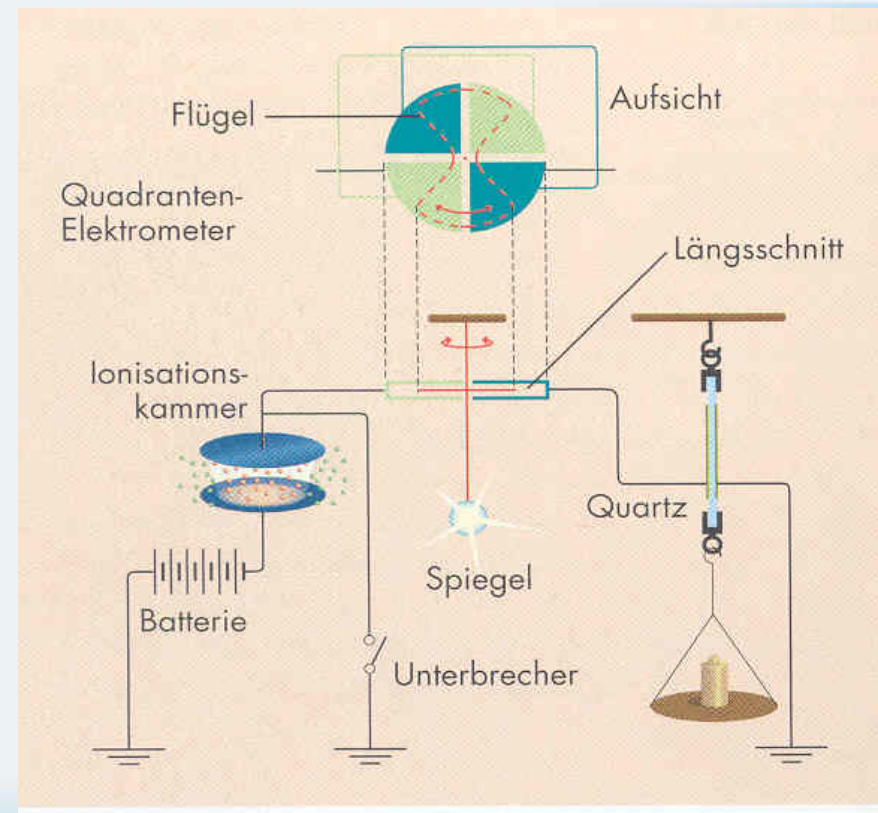
Industrial Applications and Chemistry Section

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## The physical principle

- detection of radioactivity was used to guide the chemical separation of radioactive elements
- First detectors were based on piezo-electric effect and used the observation of  $\alpha$ -particles ionising air



## Other early instruments

- **W. Crookes, 1903, invented the ‘Spintharoscope’, a ZnS coated foil that emits sparks when a particles impinge. Through a small magnifying glass these sparks can be seen.**



<http://www.unitednuclear.com/spintharoscope.htm>

Our Standard Spintharoscope looks & operates the same, but is powered by a minute amount of Uranium ore, instead of Americium <sup>241</sup>. The brightness & frequency of scintillations are considerably less.



Special quantity pricing is available to schools, museum shops, and other learning institutions. Please email or call us for details.



**New!** SUPER Spintharoscope: \$30.00 **New!**  
also still available:  
Standard Spintharoscope: \$20.00

## Standards and units

- **1 Curie (Ci) was defined as the radon emanation from 1 g of radium ( $^{222}\text{Rn}$ , 3.8 d,  $^{226}\text{Ra}$ , 1600 y)**
- **BIPM, 1950: 1 Ci =  $3.7 \times 10^{10}$  disintegrations per s**
- **1 Becquerel (Bq) = 1 disintegration per s ( $\alpha$ ,  $\beta$ , and  $\gamma$  rays have to be considered together)**
- **1 Sievert (Sv) = dose equivalent index,  $\text{Jkg}^{-1}$**

## Standards and units

- In 1911 Marie Curie prepared a standard from pure radiumchloride. The preparation was repeated in Vienna and the results differed only by 0.2 %.





COMMISSION INTERNATIONALE DES ÉTALONS DE RADIUM.

CERTIFICAT.

Das als Chlorid dargestellte Radiumpräparat Nr. 6 entstammt St. Joachimstaler Uranpechblende und ist demnach praktisch frei von Mesothorium.

Es enthält 21.50 Milligramm Salz.

Es wurde am 1. Juli 1913 eingeschlossen in ein Glasröhrchen (Thüringer Glas) von 0.27 mm Wandstärke, äußerem Durchmesser 3.2 mm, Länge 42 mm, an dessen Ende ein feiner Platindraht eingeschmolzen ist.

Dasselbe wurde als **Secundärer Standard** an den Wiener Etalons und an dem internationalen Standard in Paris nach mehreren  $\gamma$ -Strahlungsmethoden unabhängig voneinander geeicht.

Der  $\gamma$ -Strahlung nach ist es im Jahre 1913 äquivalent 20.28 mg RaCl<sub>2</sub>. (Die jährliche Abnahme beträgt etwa 0.4 Promille.)

Unter Zugrundelegung der Atomgewichte von

226 für Radium  
35.457 für Chlor  
79.916 für Brom

entspricht dies

15.44 mg Ra-Element,  
20.28 mg RaCl<sub>2</sub>,  
26.36 mg RaBr<sub>2</sub>.

Die Genauigkeit dieser Angabe wird auf 0.2% für gesichert gehalten.

La Préparation de Chlorure de Radium contenue dans l'ampoule Nr. 6 provient de la pechblende de St. Joachimsthal. Elle est donc pratiquement exempte de Mesothorium.

Elle contient 21.50 Milligrammes de sel.

Le sel a été enfermé le 1/7/13 dans un tube de verre (Verre de Thuringe.) Epaisseur du verre 0.27 mm; Diamètre extérieur 3.2 mm; Longueur 42 mm. Un fil de platine fin a été soudé à l'extrémité du tube.

En qualité d'**Étalon secondaire** l'ampoule a été comparée à l'Étalon de Vienne et à l'Étalon International de Paris, au moyen de méthodes de mesures basées sur le rayonnement  $\gamma$ . La comparaison a été faite indépendamment à Vienne et à Paris.

D'après son rayonnement  $\gamma$ , la Préparation équivaut en l'année 1913 à 20.28 mg. RaCl<sub>2</sub>. (La diminution par année est de 0.4 pour mille.)

En adoptant les poids atomiques suivants:

Radium . . . 226  
Chlore . . . 35.457  
Brome . . . 79.916

on déduit la teneur correspondante en Radium élément et en Bromure de Radium:

Ra 15.44 mg.  
RaCl<sub>2</sub> 20.28 mg.  
RaBr<sub>2</sub> 26.36 mg.

La précision de ces résultats est considérée comme assurée à une approximation de 0.2%.

Specimen No. 6 of Radium is prepared as chloride from pitchblende of St. Joachimsthal and is consequently practically free from Mesothorium.

It contains 21.50 Milligrammes of salt.

It was enclosed the 1/7/13 in a glass tube (Thuringian glass) of 0.27 mm thickness, exterior diameter 3.2 mm, length 42 mm, a thin platinum wire being fused into the end of the tube.

It is calibrated as **Secondary Standard** by comparison with the Vienna-Standard and with the International Standard at Paris, several independent  $\gamma$ -ray methods being used.

Measured by the  $\gamma$ -radiation, it is in the year 1913 equivalent to 20.28 mg. RaCl<sub>2</sub>. (The yearly decay is about 0.4 per mille.)

Taking the atomic weights

226 for Radium  
35.457 for Chlorine  
79.916 for Bromine

this corresponds to

15.44 mg Ra-element,  
20.28 mg RaCl<sub>2</sub>,  
26.36 mg RaBr<sub>2</sub>.

These statements are considered correct to 0.2%.

Für die Wiener Messung

Stefan Meyer

Pour les mêmes faits à Paris

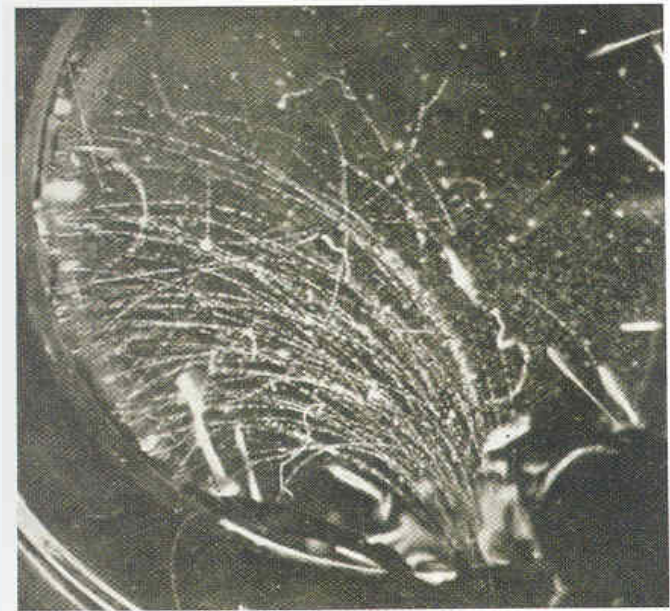
M. Curie

President of the Commission

E. Rutherford

## More instruments to detect ionising radiation

- **1908-1912: Rutherford and Geiger developed the Geiger-Mueller Zaehlrohr**
- **1912: Charles T.R. Wilson developed the ionisation chamber**
- **1932: J. Chadwick used a Wilson chamber connected to an oszilloscope and discovered NEUTRONS**



## Discovery of induced radioactivity

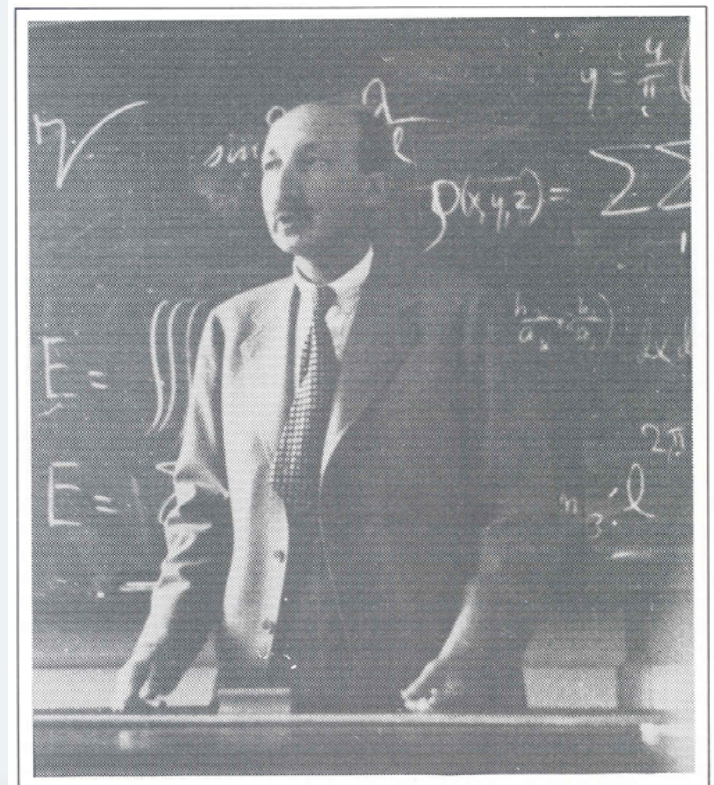
1934, Frederic Joliot-Curie irradiated an Al foil with  $\alpha$ -particles from a Po source. He detected  $e^+$  and neutrons. When he removed the source, neutron emission stopped but  $e^+$  continued to be detected with a  $t_{1/2}$  of 3 min 15 s. The reaction



was the first detection of induced radioactivity.

Proof of the new element was made by chemical separation!

## George de Hevesy and Hilde Levi invented Neutron Activation Analysis in 1936



## The early days

- **O.R. Frisch, Hevesy and Levi prepared Geiger counters at the Institute of Theoretical Physics in Copenhagen.**
- **They prepared a neutron source by mixing pulverized metallic beryllium with radon in a glass ampoule**

**The neutron source:  ${}^9\text{Be} + {}^4\text{He} \rightarrow {}^{12}\text{C} + \text{n}$**

**Using  $\alpha$  particles from radon ( $t_{1/2} = 3.8 \text{ d!}$ )**

## The first NAA experiment

- **“Hevesy took out of a cupboard a number of REE samples and handed it over to me saying: ‘Well, take this one and try it’”.**
- **H. Levi took Dysprosium and irradiated it with the neutron source.**
- **After irradiation she could not detect anything**
- **Some time later she checked the empty holder and the counter rattled away!!**

## The advent of NAA

- **The high cross section of REE was used to detect these in other materials.**
- **Not the energy of the gamma rays but the half live was used for identification.**
- **The advent of intense neutron sources from graphite moderated, air cooled natural uranium research reactors (e.g. Oak Ridge X-10,  $10^{12}$  n/cm sec) in 1945 boosted the use of NAA**

## The advent of NAA

- **Shortly afterwards (1950) Na(Tl) detectors and single channel analysers became available.**
- **Most work was still relying on radiochemical separation prior to measurement.**
- **Computers allowed to use automatic peak area determination only from 1960 onward.**
- **Only by 1965 high resolution Ge(Li) detectors and the first multi channel analysers became available.**



## Diversification of NAA techniques

- The search for trans uranium elements stimulated the development of “*Rapid Radiochemical Procedures*” published in 1961 by Kusaka and Meinke
- Fast ADCs and amplifiers were introduced into high count rate systems → short lived radionuclides (e.g. G. Westphal and F. Grass, Vienna, Austria)
- Use of guided neutron beams extracted from RRs (in conjunction with cold sources) opened opportunities for ‘prompt gamma NAA’ (e.g. Henkelmann and Born, 1973, Grenoble, France)

## Diversification of NAA techniques

- **The use of radiotracers generated a vast development in investigating element distributions in living organisms and the environment → isotope dilution analysis**
- **Mössbauer discovered the resonance absorption of  $\gamma$  quanta and this effect developed a new analytical tool.**
- **The radioactive equilibrium opened a whole suit of age determinations, e.g. U/Pb, U/He, K/Ar, Rb/Sr, as well as  $^{14}\text{C}$  and tritium methods.**

## Diversification of NAA techniques

- **Syre and Dodson (1957) published first work on “NAA of Mediterranean potsherds”**
- **V. P. Guinn (1961) published first forensic applications bullet lead and gun shot residue analysis**
- **P. Savel (1963) reported radiochemical determination of As in a few mm of a single human hair**
- **R.E. Jervis (1970) determined low levels of Hg in samples of environmental and nutritional interest**
- **J. Versieck et al (1981) provided reliable results in body fluids by RCNAA in the 10 µg/ml – 0.01 ng/ml range**

## Development of $k_0$ standardisation

- **F. Girardi et al. (1965) introduced the single comparator method using  $k$  factors for NAA**
- **A Simonits, F. De Corte, J. Hoste (1975) published the Au based  $k_0$  standardisation method**
- **F. De Corte (1987) published the comprehensive  $k_0$  data catalogue**
- **1992 KAYZERO/SOLCOI software was released**
- **2003 new  $k_0$  data catalogue for PGNAA was issued by the IAEA**
- **2005 “ $k_0$ -IAEA software” was introduced and distributed**



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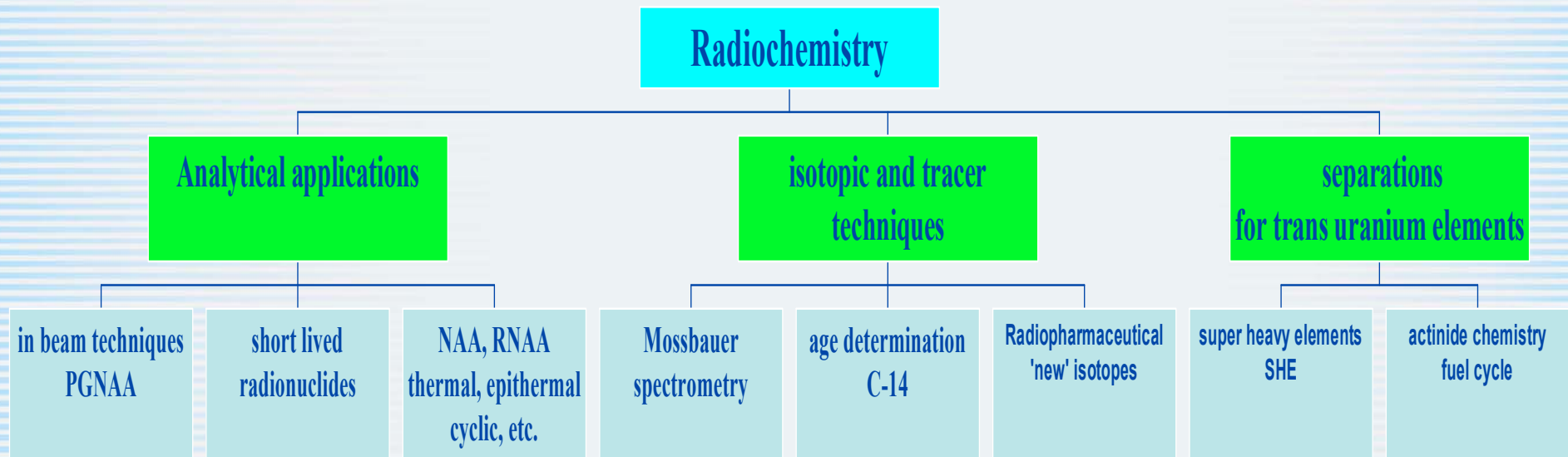
*Flowers of NAA*  
Success stories and examples

M. Rossbach

IACS, IAEA Vienna



# Development of different disciplines

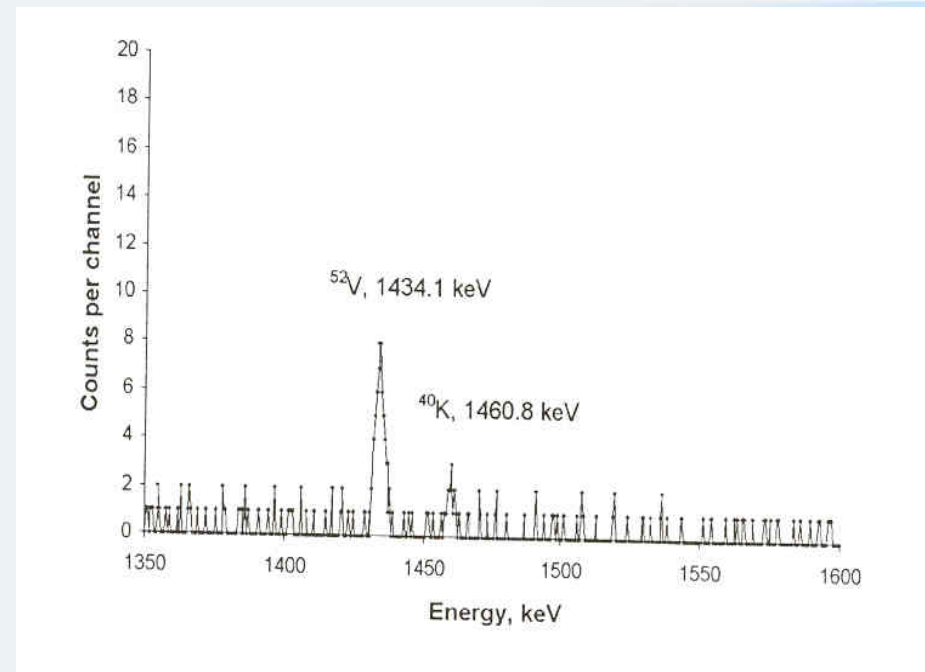


# Radiochemical separations

- **removal of interfering components up to  $5 \times 10^7$ , hence**
- **great improvement of the signal/background ratio**
- **essentially blank free nature of analysis**
- **optimisation of resulting radioactive product by choosing best irradiation conditions (thermal/epithermal neutrons, (n,g), (n,p), (n,2n) reactions... and**
- **optimisation of counting conditions (Compton suppression, coincidence counting, well type detectors etc.)**

## Examples of RNAA

- **Determination of V in blood**
- **$^{52}\text{V}$  was separated from 250 mg of freeze dried blood, irradiated for 12 min. in  $5 \times 10^{12}$  n/cm<sup>2</sup> s and counted for 7 min. on a well type detector**
- **Mean:  $23 \pm 14$  pg/ml**





## Examples of RNAA

- Cosmo-chemical investigations of long lived radionuclides, e.g.  $^{53}\text{Mn}$ ,  $^{129}\text{I}$ , or  $^{26}\text{Al}$
- determination of Si in high purity materials by distillation of  $\text{SiF}_4$  and counting  $^{31}\text{Si}$  with LSC. Detection limit: 3 ng/g

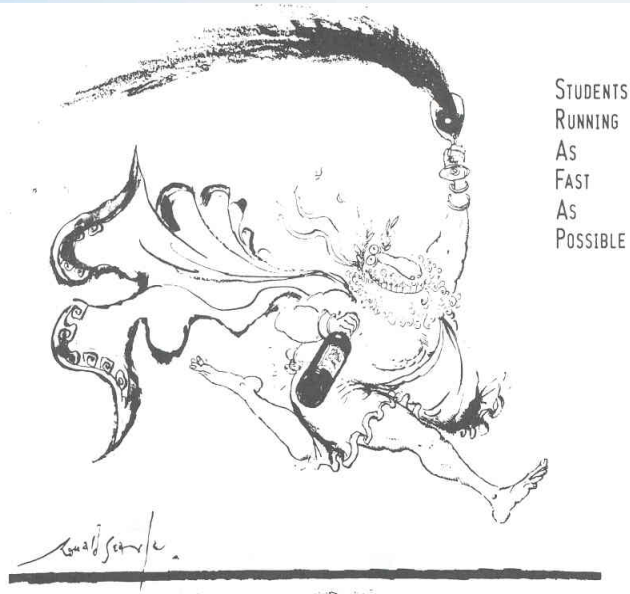


FIG. 1. A meteorite's history.

## Fast chemical separations for trans-uranium elements

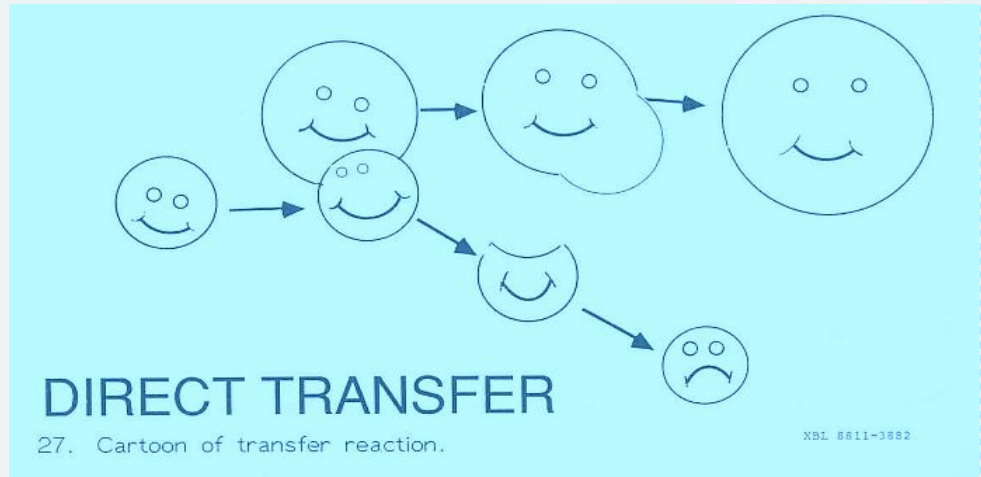
- Following the discovery of neutron capture/ $\beta$  decay of uranium the search for trans uranium elements began
- Research on fission products lead to the development of fast chemical separation techniques (SRAFAFAP).
- The LBL 88-inch Cyclotron in Berkeley, USA made possible the fusion of TUE with heavy ions, e.g  $^{16}\text{O}$ ,  $^{22}\text{Ne}$  or  $^{48}\text{Ca}$
- Half life of the product nuclides decrease with increasing mass

# Search for super heavy elements (SHE)



STUDENTS  
RUNNING  
AS  
FAST  
AS  
POSSIBLE

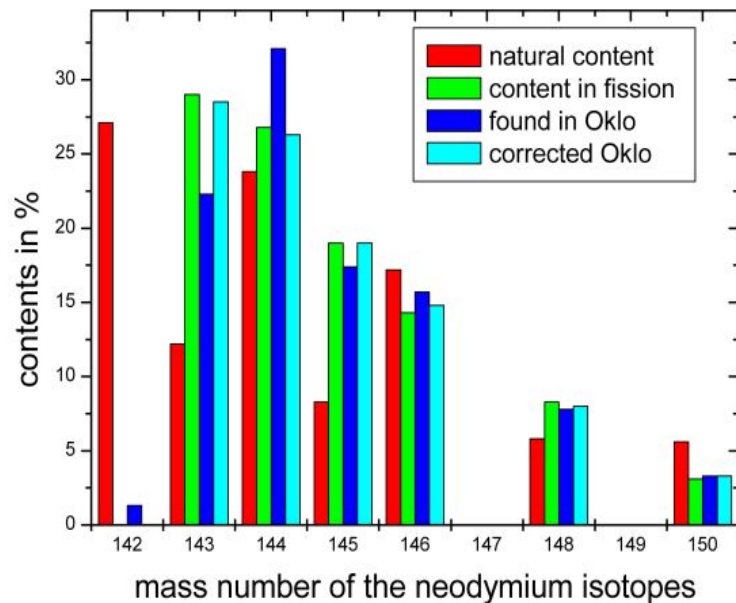
14. SRAFAP (Students Running As Fast As Possible). (TT, see Fig. 9).



## Isotopic and tracer techniques

- **Isotopes, being produced in RRs and from cyclotrons are sensitive probes behaving exactly as their parent elements in environment and in biological systems**
- **Some isotopes are being produced naturally by cosmic radiation and can be used for age determination**
- **Isotope dilution analysis is an elegant alternative for analysing large collectives, e.g. amount of blood in the human body**

## Example



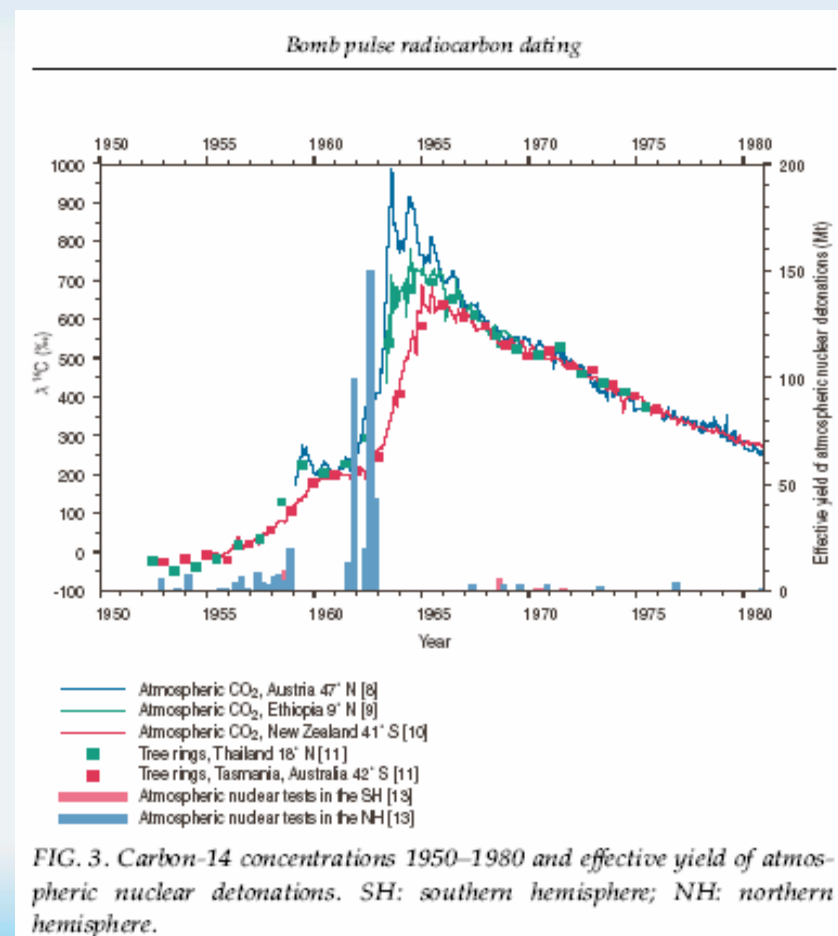
- The natural reactor of Oklo, Gabun was discovered by careful isotopic analysis of the isotope ratio of several elements (U, Nd, Dy)
- burnup was calculated to be  $4 \cdot 10^5$  MW·h. 10 t of uranium have fissioned and 4 t of Pu have formed 2 billion years ago

## Examples

- **Radiolabelled compounds are used for speciation analysis, e.g.  $^{75}\text{Se}$  for metabolic studies (seleno-proteins)**
- **Analysis of Cr in plasma of dialysis patients revealed the active contamination of fresh dialysate by the instruments and resulted in elevated Cr in liver tissue**
- **Method validation and optimisation using radiotracers have resulted in improved performance of e.g. Hy-AAS, ICP-OES and ICP-MS.**

## Examples

➤  $^{14}\text{C}$  bomb pulse dating is a versatile method for determination of age, provenance, fraud, and other forensic applications using AMS



## Analytical applications

- **Epithermal NAA**
- **Photon activation analysis**
- **Charged particle AA**
- **Prompt gamma NAA**
- **NAA with 14 MeV neutrons**
- **Cyclic NAA**
- **Pulsed reactor NAA**
- **INAA by delayed neutrons (U, Th)**
- **Derivative NAA**
- **Monostandard and  $k_0$  NAA**
- **Large sample NAA**



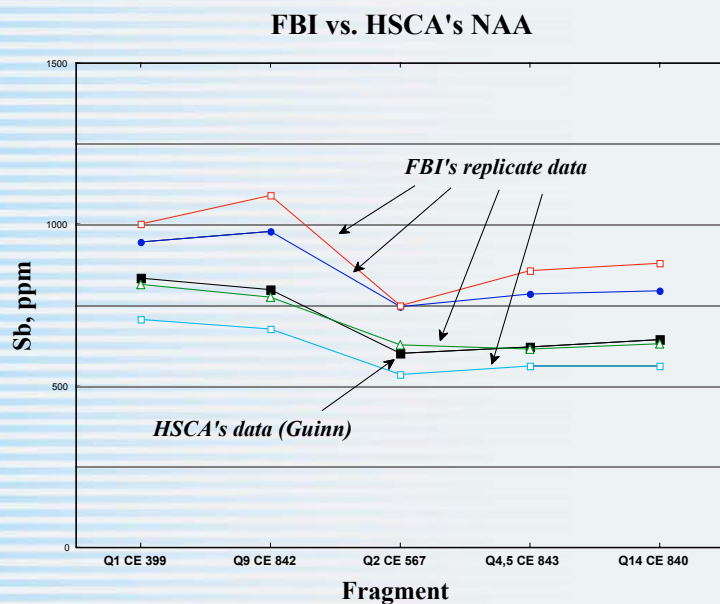
# Thermal neutron activation analysis

- **based on nuclear properties → matrix independent**
- **multielement capabilities**
- **no sample dissolution required → basically blank free**
- **high sensitivity for many elements**
- **physical principle well understood → high accuracy**
- **Uncertainties can be controlled → low uncertainty**
- **dynamic range for many orders of magnitude**
- **intrinsic quality control by multi nuclide analysis**

## Major fields of applications

- **Geological mapping**
- **Environmental monitoring**
- **Health related studies**
- **Trace contaminants in high purity materials**
- **Industrial quality control**
- **Occupational health studies**
- **Paleo-climatic studies in ice cores**
- **forensic applications**
- **certification of reference materials**
- **halogen analysis in hydrocarbons**
- **Metabolic studies in animal and humans**
- **Trace elements in agriculture and food industry**

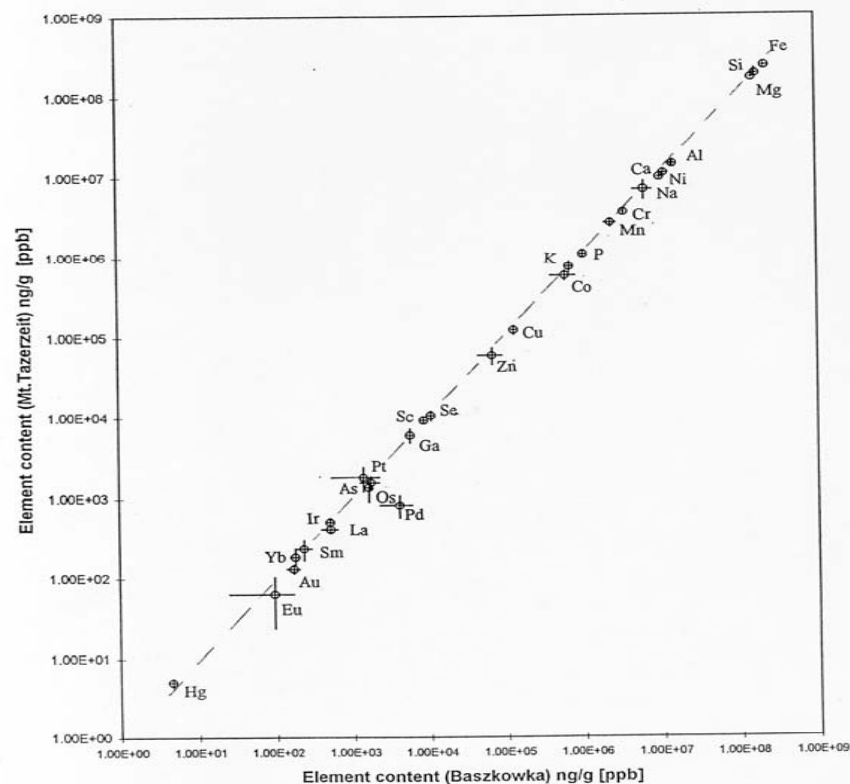
## Examples



- **Neutron Activation and the JFK Assassination (K.A. Rahn, L.M. Sturdivan, 2004)**
- **JFK assassination in 1963, FBI investigation in 1964 and V. Guinn did NAA in 1977**
- **Results confirmed that only two bullets struck the victims**

## Examples

- Analysis of extra terrestrial material such as moon rock or meteorite
- Two different meteorites fallen in 1935 and 1991 showed identical NAA composition,  $R = 0.998$
- It could be proven that both rocks belong to a common parent body



## Examples

- **Two strands of Napoleon's hair (0.1722 mg and 0.2151 mg) were analysed using INAA.**
- **Being a multi element technique, As, Cr, Hg, Sb and Zn could be determined simultaneously**
- **Results suggest that As poisoning was not the major reason for Napoleon's death**

TABLE 1. ELEMENT CONCENTRATIONS (ppm) OF ARSENIC, CHROMIUM, MERCURY, ANTIMONY AND ZINC IN SAMPLES OF NAPOLEON'S HAIR

	Hair 1	Hair 2
Arsenic	1.85 ± 0.11	3.05 ± 0.18
Chromium	7.65 <sup>a</sup>	10.5 ± 1.9
Mercury	1.84 <sup>a</sup>	3.98 ± 0.29
Antimony	4.47 ± 0.27	4.32 ± 0.38
Zinc	35 <sup>a</sup>	58 ± 13

<sup>a</sup> Information value.

## Examples



- **Heterogeneous material such as waste or metal scraps difficult to homo-genize can be analysed by large sample NAA**
- **1 kg of waste was analysed using the  $k_0$  approach and compared with results after homogenisation**
- **Similarly Cd in plastics and shredded computer waste was determined in 1.5 kg samples**

# Determination of EOX in fatty tissue

- Organic compounds that contain chlorine, bromine or iodine substituents
- Lunde (1972) determined Br in marine oils by NAA
- Lunde and Steinnes (1975), Gether *et al.* (1979) determined EOX in fish oils by INAA
- Newsome *et al.* (1993) determined EOC1 in fish lipid by INAA at Dalhousie SLOWPOKE

Comparison of total EOC1 (NAA) and total PCB and Chlorinated Pesticides (GC-MS) in Fish Samples from the Great Lakes

Fish Species	PCB + OC, ppm lipid	NAA, ppm	Unaccounted, %
Bass	28.4	138	79.5
Bullhead	4.1	87.1	95.3
Carp	1.1	73.4	98.5
Eel	6.2	44.3	86.0
Herring	6.7	93.4	92.8
Perch	3.6	130	97.2
Smelt	1.5	108	98.6
Trout	6.4	98.1	93.2

# Prompt gamma neutron activation analysis



- Investigation of fission products in nuclear waste
- Archaeological investigations
- Hydrogen in fullerenes
- Non-destructive boron analysis
- BNC therapy



# Standard Reference Materials analyzed for certification by PGAA

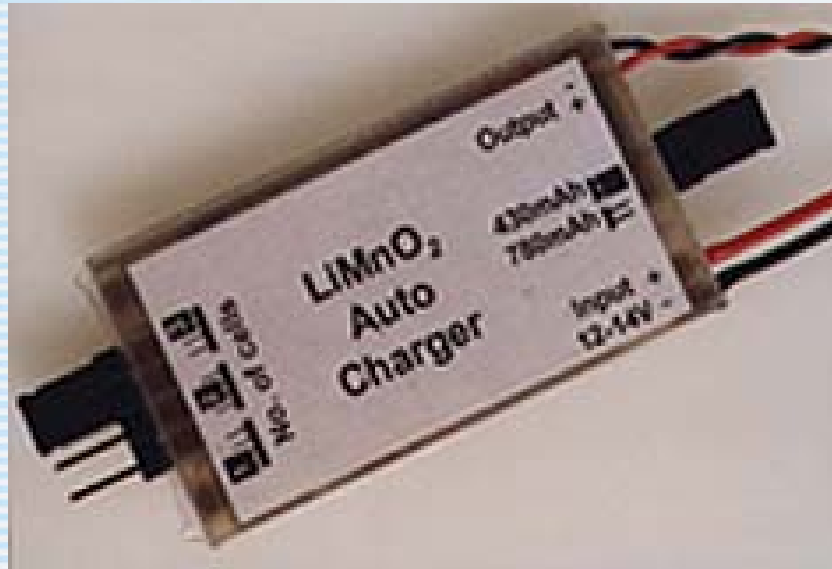
SRM Identification	H	B	C	N	Na	Al	Si	S	Cl	K	Ca	Ti	Zn	Cd	Sm	Gd
1216 Modified silica	•		•													
1244-1247 Inconels		•														
1261a-1265a Steels		•														
1515 Apple Leaves		•		•					•							
1547 Peach Leaves		•		•					•							
1548 Total diet		•						•	•							
1548a Mixed Diet		•		•	•				•	•						
1566b Oyster Tissue	•	•	•	•				•	•	•						
1570a Spinach	•	•		•	•			•	•	•	•			•		
1573a Tomato Leaves	•	•	•	•				•	•	•	•			•	•	•
1575a Pine Needles		•							•	•						
1632c Coal	•	•	•					•	•	•						
1643b Water		•														
1761-1767 Steels		•														
1848 Lube oil additive	•	•						•	•				•			
1941 Marine Sediment		•					•	•		•		•		•	•	•
2682-2685a Coals	•	•	•	•		•		•								
2702 Marine Sediment														•		
2781 Domestic Sludge		•		•					•	•				•		

## Example

- **Gold coins are being analyzed by PGAA for major and trace metals.**
- **Major metals: Ag and Au**
- **Trace metals: Al, Ti, Fe, Cl, V, Mn, Co, Cd, Nd, Sm, and Gd.**
- **The ratios of the trace metal concentrations provides a signature that represents the location of the ore deposit.**



## Example



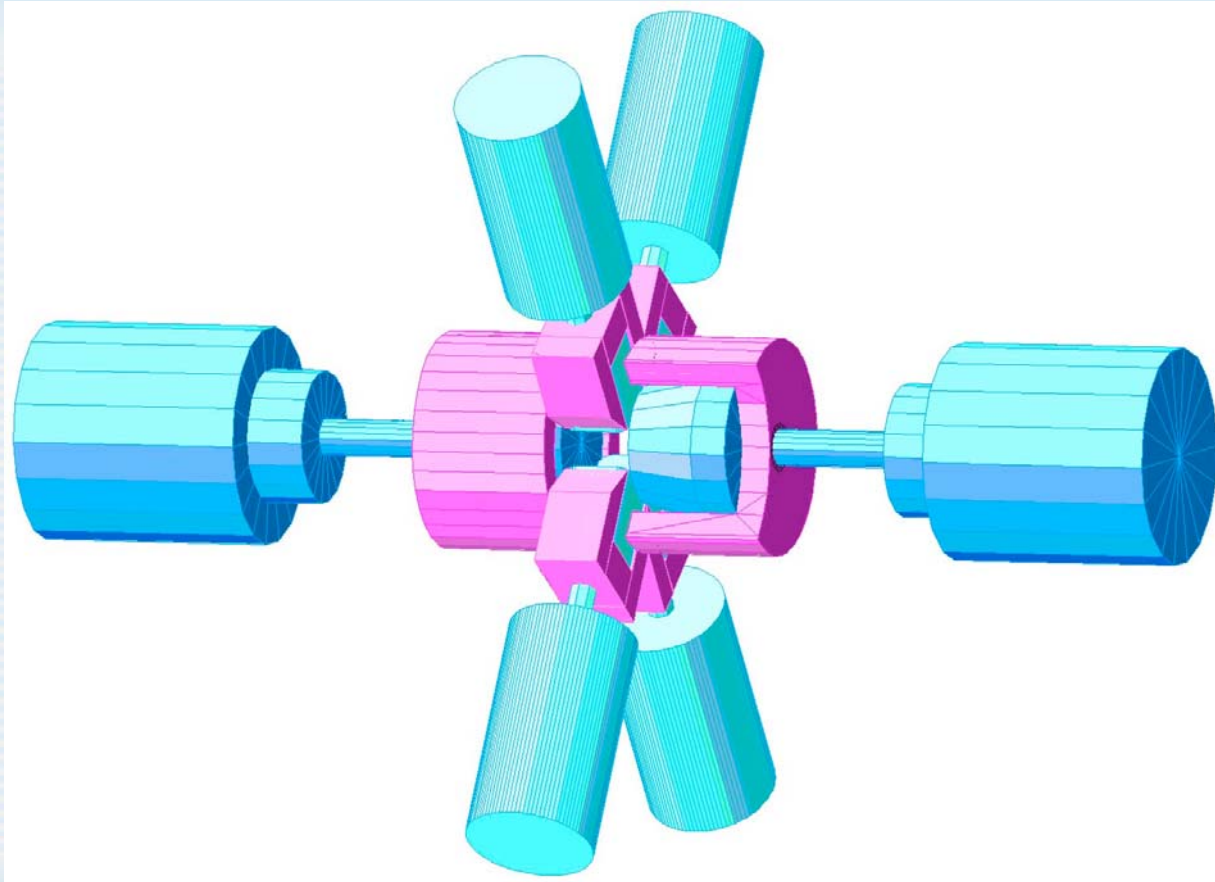
- **New battery materials are being analyzed for hydrogen.**
- **Hydrogen is not desired in the battery material and different processes are being examined to determine the hydrogen content.**
- **PGAA appears to be one of the only methods available that can measure hydrogen at this trace concentration level.**

## Future trends

- Installation of a new analytical system of PGA (called MPGA) at JAERI, Japan (an assembly of multiple Ge detectors with sophisticated coincidence system is now being set up for PGA at the cold neutron beam line).
- Construction of a proton accelerator research complex (called J-PARC). Spallogenic neutrons are generated by a large accelerator and are used for nuclidic analysis.

# Detector assembly to be installed

Each detector (clover-type) consists of four individual Ge detectors.



## Field portable instruments



## ...and neutron sources/generators

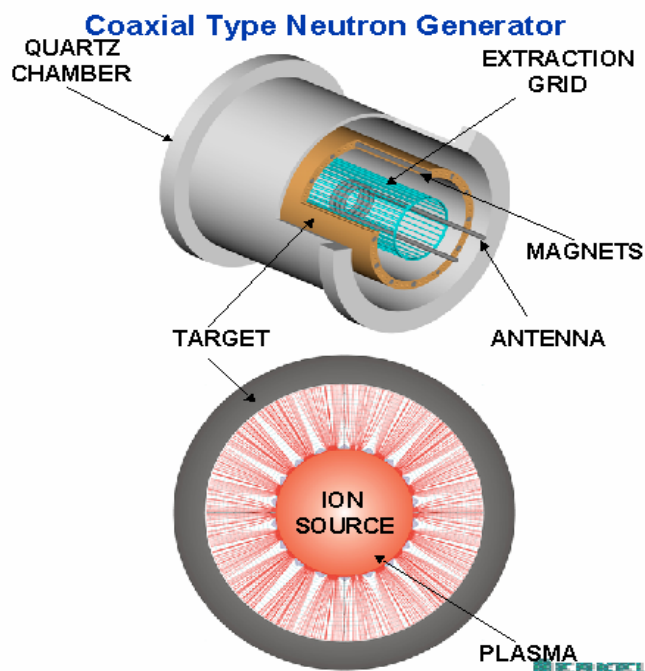


Neutron generator used for coal online analysis, working time : 8000 h

# DD-neutron generators

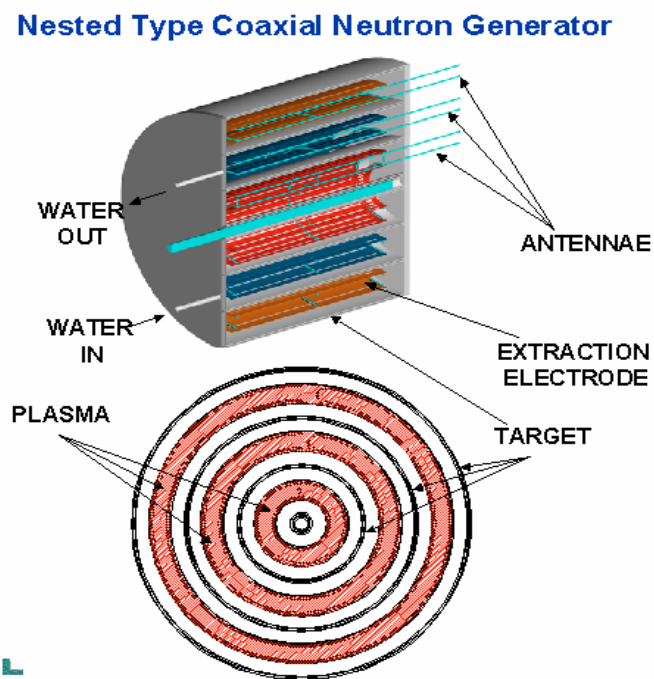


## Nested-Type Neutron Generator Increases Target Area



For D-D neutron output  $\sim 1.2 \times 10^{12}$  n/s  
 For D-T neutron output  $\sim 3.5 \times 10^{14}$  n/s

Accelerator and Fusion Research Division

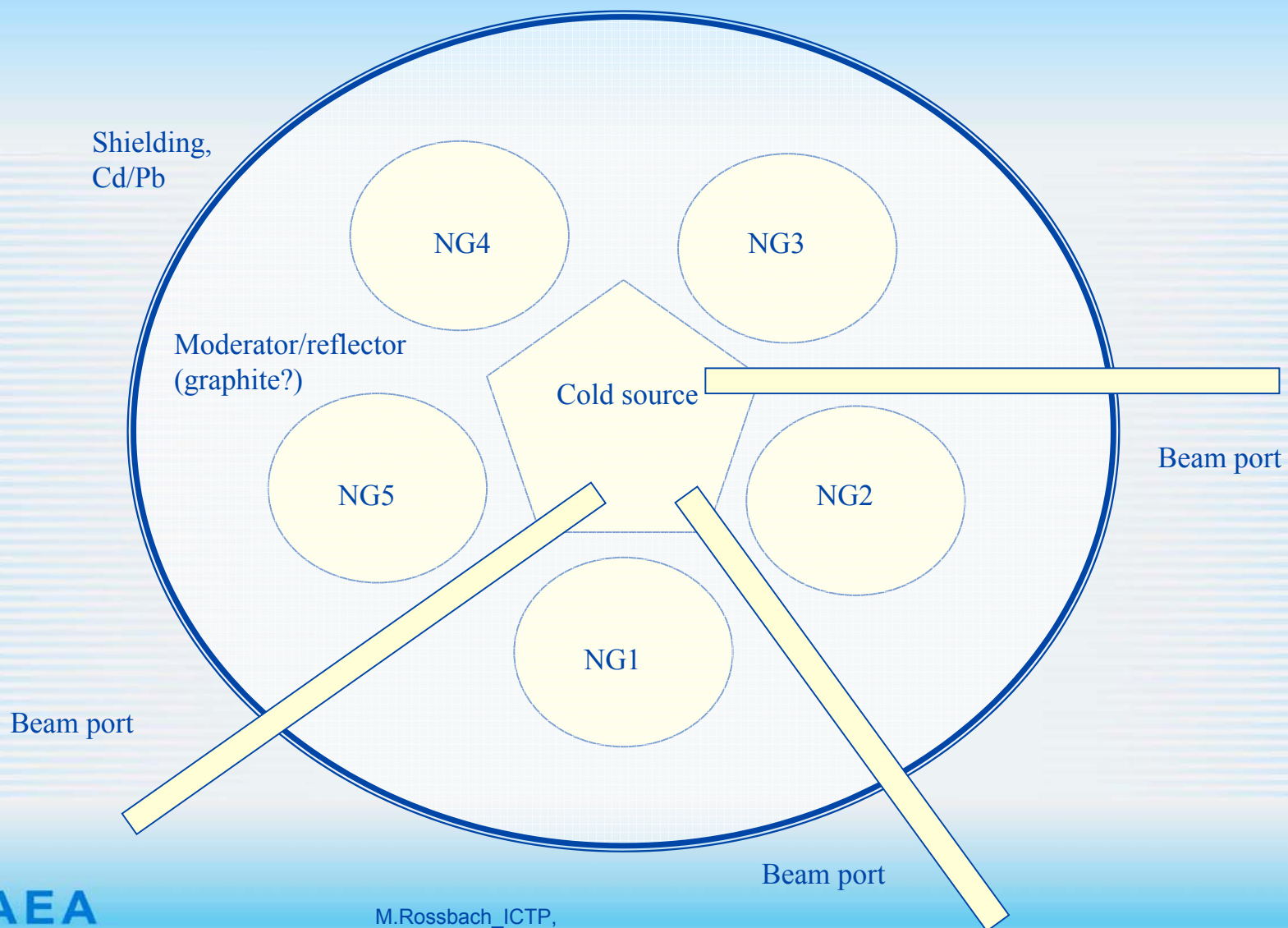


For D-D neutron output  $\sim 1.6 \times 10^{13}$  n/s  
 For D-T neutron output  $\sim 4.5 \times 10^{15}$  n/s

Ion Beam Technology Program



## Possible configuration of a neutron irradiation facility based on a neutron generator assembly



## Hyphenated techniques and combinations

Low energy X-ray detector  
for major elements e.g. Al, Si...

High energy X-ray detector for  
trace elements e.g. Cr, Ti, V, Fe,  
Ga...

HPGe  
 $\gamma$ -ray  
detector



**Thank you**