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Growth and diversification
of analytical radiochemistry

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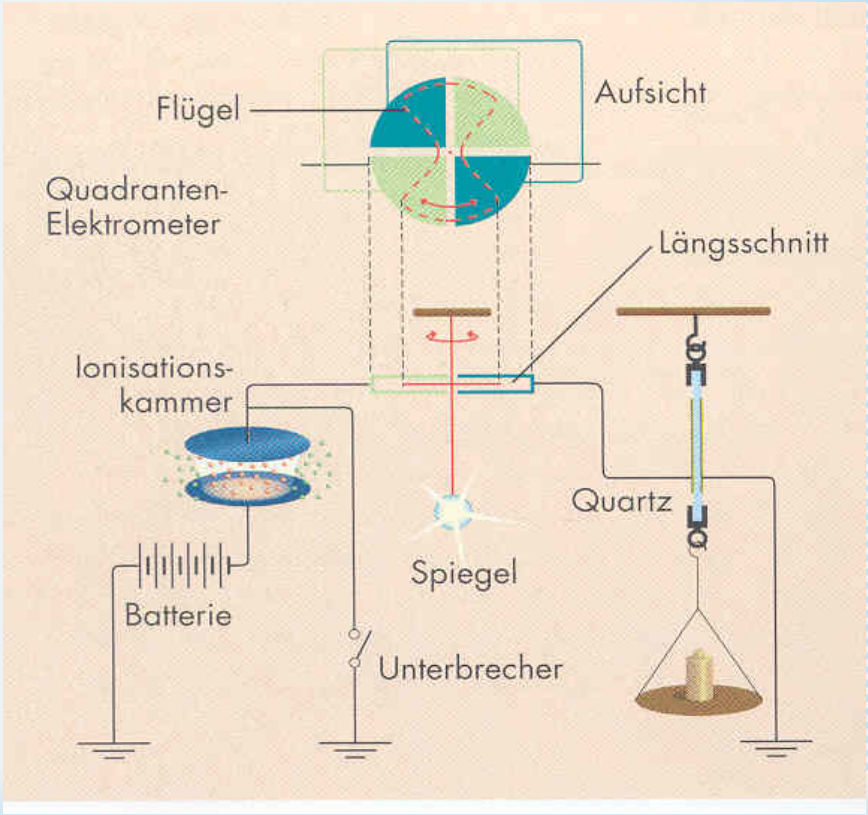
The physical principle

- 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 α–particles ionising air



Other early instruments

- **W. Crookes, 1903, invented the 'Spinthariscope', 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/spinthariscope.htm

Standards and units

- 1 Curie (Ci) was defined as the radon emanation from 1 g of radium (^{222}Rn, 3.8 d, ^{226}Ra, 1600 y)
- BIPM, 1950: 1 Ci = 3.7×10^{10} disintegrations per s
- 1 Bequerel (Bq) = 1 disintegration per s (α, β, and γ rays have to be considered together)
- 1 Sievert (Sv) = dose equivalent index, 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 Mesothor.

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 22 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 γ-Strahlungsmethoden unabhängig voneinander geeicht.

Der γ-Strahlung nach ist es im Jahre 1913 äquivalent 20·28 mg $RaCl_4$. (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 $RaCl_4$,
26·36 mg $RaBr_2$.

Die Genauigkeit dieser Angabe wird auf 0·2 % für gesichert gehalten.

Für die Wiener Messung
Stefan Meyer

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 Mésothorium.

Elle contient 21·50 Milligrammes de sel.

Le sel a été enfermé le 1/VII 1913 dans un tube de verre (Verre de Thuringe.) Epaisseur du verre 0·27 mm; Diamètre extérieur 3·2 mm; Longueur 22 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 γ. La comparaison a été faite indépendamment à Vienne et à Paris.

D'après son rayonnement γ, la Préparation équivaut en l'année 1913 à 20·28 mg. $RaCl_4$. (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.
$RaCl_4$ 20·28 mg.
$RaBr_2$ 26·36 mg.

La précision de ces résultats est considérée comme assurée à une approximation de 0·2 %.

Pour les mesures faites à Paris
M. Curie

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

It contains 21·50 Milligrammes of salt.

It was enclosed the 1/VII 1913 in a glass tube (Thuringian glass) of 0·27 mm thickness, exterior diameter 3·2 mm, length 22 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 γ-raymethods being used.

Measured by the γ-radiation, it is in the year 1913 equivalent to 20·28 mg. $RaCl_4$. (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

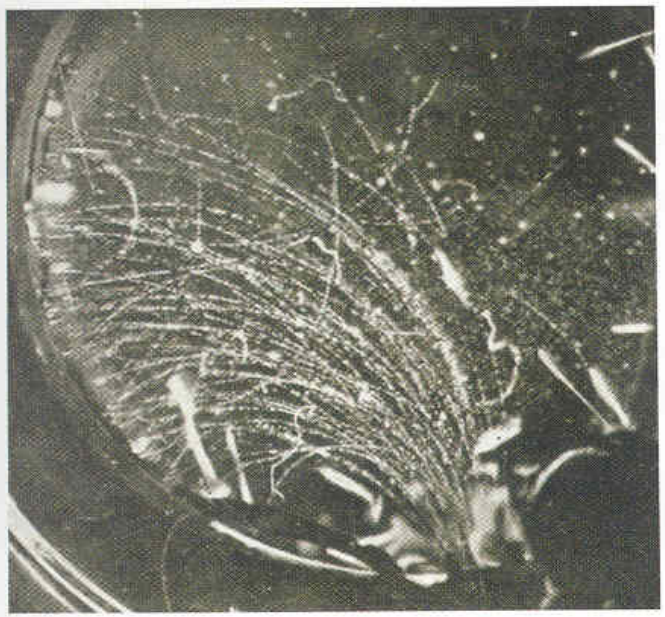
15·44 mg Ra-element,
20·28 mg $RaCl_4$,
26·36 mg $RaBr_2$.

These statements are considered correct to 0·2 %.

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

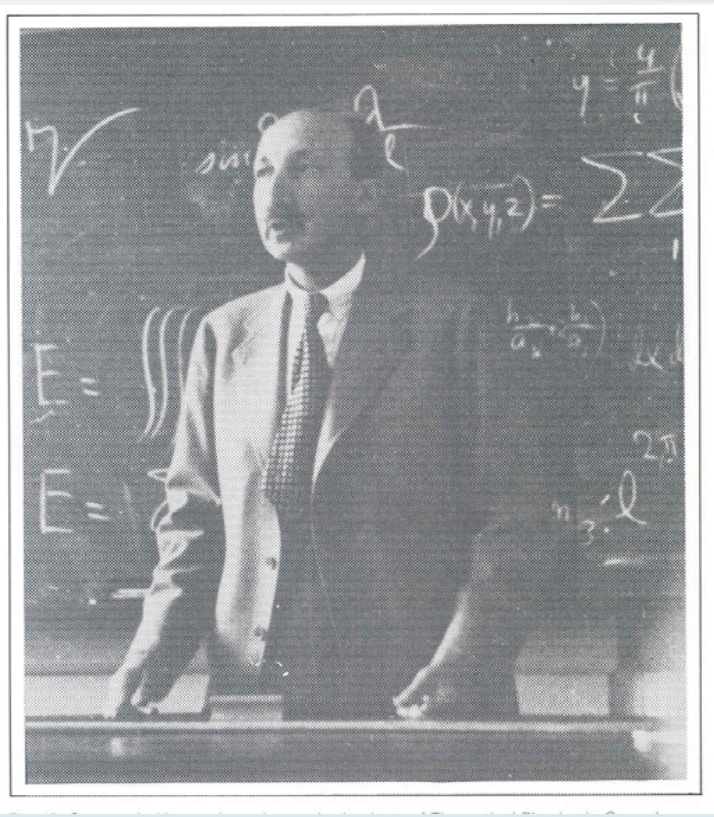
$$^{27}Al + \alpha \rightarrow {}^{30}P + n$$

$$^{30}P \rightarrow {}^{30}Si + e^+ + \nu$$

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: $^{9}Be + {}^{4}He \rightarrow {}^{12}C + n$

Using α particles from radon ($t_{1/2}$ = 3.8 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 γ 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}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