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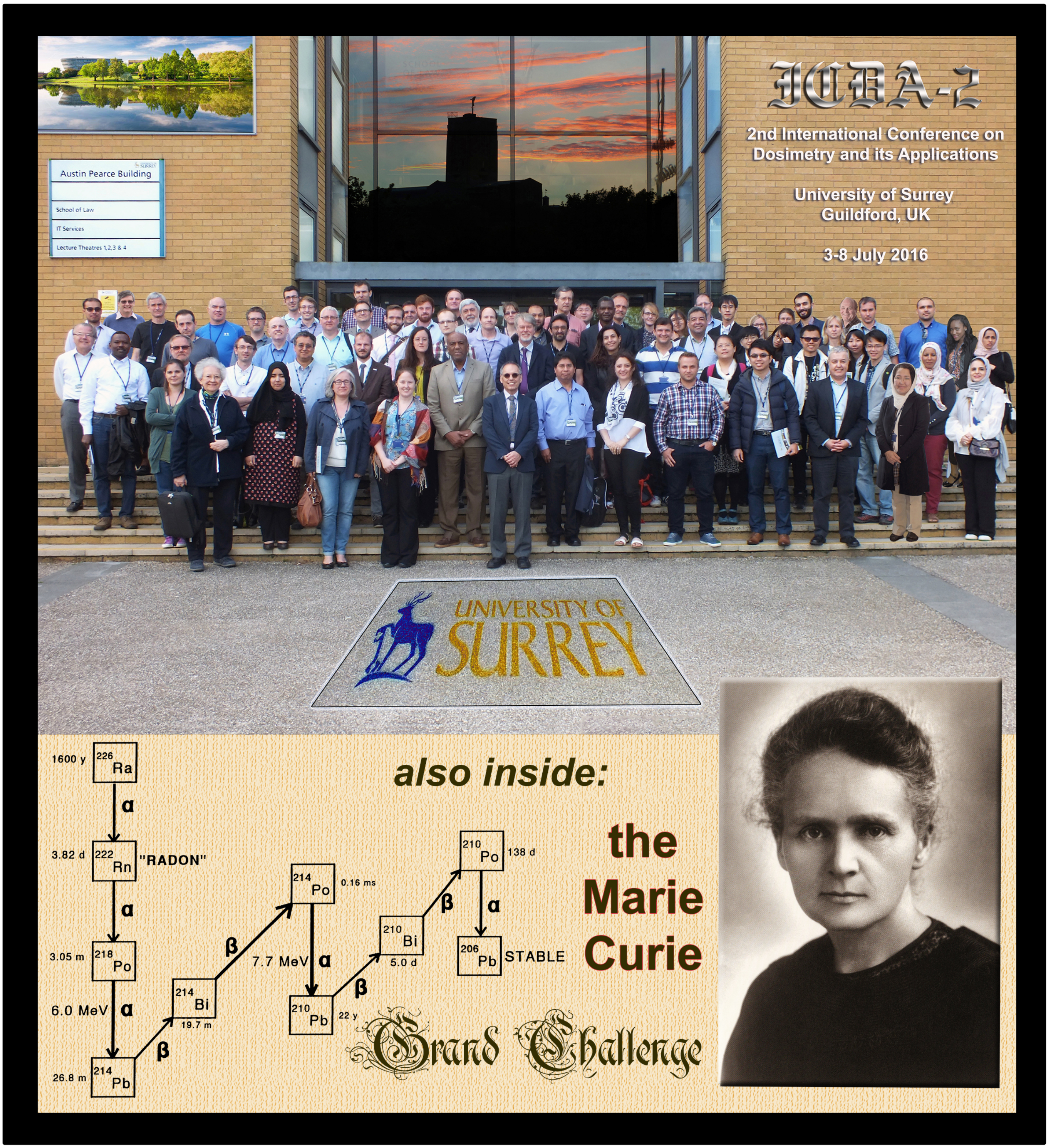

Marie Curie's Last Radium Standard – Grand Challenge

The last of the radium-226 standards that Marie Curie personally handled is destined for a radioactive materials waste dump. The challenge to the scientific community is to present a rationale for why this standard source, which 100 years ago was one of the most valuable standard artifacts in the world, should not face such an ignoble fate.

In 1910 the International Conference on Radiology and Electricity met in Brussels and a special committee including Marie Curie (Sorbonne University, Paris), Ernest Rutherford (Manchester University, Manchester) and Stefan Meyer (Academy of Sciences, Vienna) were asked to report on a means for establishing a standard for radium. Marie Curie prepared a standard source of 21.99 mg of radium chloride (the Paris Standard) and Stefan Meyer's institute prepared a set of three primary standards (the Vienna standards). The Vienna standards of 10.11 mg, 31.17 mg and 40.43 mg $RaCl_2$ were prepared by Otto Hönigschmid. In 1912 Rutherford and others arranged a comparison of the Paris and Vienna standard (the 31 mg source) with a gamma-ray comparison instrument built by his student James Chadwick. Following the successful intercomparison, Hönigschmid was asked to provide a set of seven secondary standards for use by national measurement laboratories around the world. Secondary Standard Number 6 was sent to the National Bureau of Standards (NBS) in Washington, DC. The mass of $RaCl_2$ on July 1, 1913 as measured by Curie was 20.28 mg and by Meyer 20.29 mg. The certificate, in French, English and German, was signed by Curie, Rutherford and Meyer.

The standard was received in the US in December 1913 and immediately placed in use for calibration of radium preparations for US medical and research applications and for export. During WWI and the immediate aftermath, the US industry had the global market for radium. Essentially all of the source material for export came through NBS as purified, sealed sources for gamma-ray comparison with the NBS standard. Standard No. 6 was the US primary standard and was used to calibrate other working standards of higher and lower mass.

The original 1913 standards were replaced in 1934 by a second set of standards prepared by Hönigschmid; Marie Curie died one month after their preparation. Her daughter, Irene Joliot-Curie, took her place on the International Radium Commission and supervised the intercomparisons of the 1934 standards with the Paris standard, which was then maintained at the Bureau International des Poids et Mesures (BIPM) in Sèvres, France. Irene Joliot-Curie retained two of the 1934 standards in her laboratory and took Standard No. 5430 to the BIPM in exchange for the original Paris standard. The US received standards No. 5440 (26.74 mg of $RaCl_2$) and No. 5437 (50.05 mg $RaCl_2$) in 1937. The NBS scientist, Leon Curtiss, who received these two sources had spent two years as a postdoctoral student with Rutherford at the Cavendish Laboratory in Cambridge. He spent much of 1935-1936 corresponding with Lord Rutherford to ensure that the sources were properly calibrated in Paris and Vienna prior to shipment to the US.

The three standard sources that came to the US were used to calibrate tens of thousands of sources for medical applications – principally for cancer therapy – and industry.

From 1914 to 1942, the NBS performed about 38,000 certification measurements on radium sources that totaled about 390 g, and an estimated commodity value of $21 M (1928 US dollars), which corresponds to over $300 M in 2015 dollars. The last recorded usage of the 1934 Hönigschmid standards was

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in 1956 when Wilfrid Mann used a microcalorimeter to compare the US standards with those of Germany and Canada.

Following these measurements, Mann designed brass containers with screw cap lids – equipped with glass tops to allow visualization of the glass ampoules. The glass tops were soon blackened by the radiation from the sources.

The containers were last closely inspected in 1995, although the lead storage cave where they are stored is checked periodically for any sign of radon leakage from the sources.

The fate of the Curie radium sources. Radium-226 was quickly replaced after the discovery of artificially-produced radiation sources. Sealed sources of radium for interstitial and intracavitary treatments gave way to radionuclides such as iridium-192. The higher-energy gamma-ray teletherapy sources (cesium-137 and cobalt-60) that replaced radium were replaced in turn by electron and proton accelerators. The NBS, now named the National Institute of Standards and Technology (NIST), discontinued calibrations of radium sources for medical applications in 1989, and the medical calibration laboratories in the US continued to offer calibrations for only a few years after that. One by one, the research centers that had retained the original 1913 and 1934 standards moved on to other pursuits and disposed of the sources as radioactive waste. At present, it is believed that the three sources retained at NIST are the last of those certified by Marie Curie and Irene Joliot-Curie.

Beyond their value as historical artifacts, what can be said of these sources that is of scientific interest? At the time of their preparation, elemental radium was separated from pitchblende from St. Joachimstal in the present Czech Republic (1913 standards) and from pitchblende from the Belgian Congo (1934 standards). They were certified to be low in barium, from the chemical separation, and low in mesothorium (although the radium-228 would have long ago decayed). Radium-226 has a half-life of 1600 years, and the 1913 standard has essentially achieved secular equilibrium with all the daughter products including the lead-210 and daughters. Lead-210 has a half-life of 22.3 years, and 5 half lives is usually considered sufficient for equilibrium. Using a value of about 160 $\mu W\ mg^{-1}$ for the power of radium-226 in equilibrium with its daughters, Source No. 6 has a power of about 3.2 mW. The five alpha particles emitted in the decay chain become helium-4 atoms. One can calculate from the 102 year decay of source No. 6 this would amount to 78 μg of helium-4, but the permeation rate of He through glass is sufficient to prevent a significant internal pressure. The alpha-particle radiation damage to the glass ampoules, however, must be significant, and this alone has led to the trepidation in handling the sources over the past half century.

The Marie Curie Grand Challenge to the scientific community is to present reasons why these sources should be retained for perhaps another 100 years. Institutes interested in receiving these standard sources for historical or investigative research purposes must have regulatory approval to receive such sources, as well as a source transportation plan and project plan approved by the institution director and an authorized Radiation Safety Officer.

Suggestions should be sent to

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Gaithersburg, MD
September 2016

../Sources and photos

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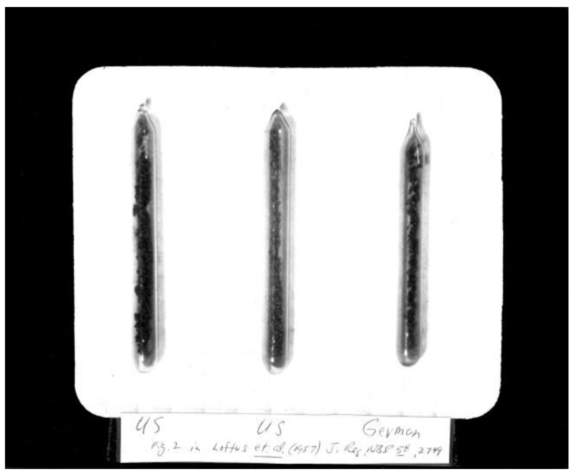

1934
Hönigschmid
Standards,
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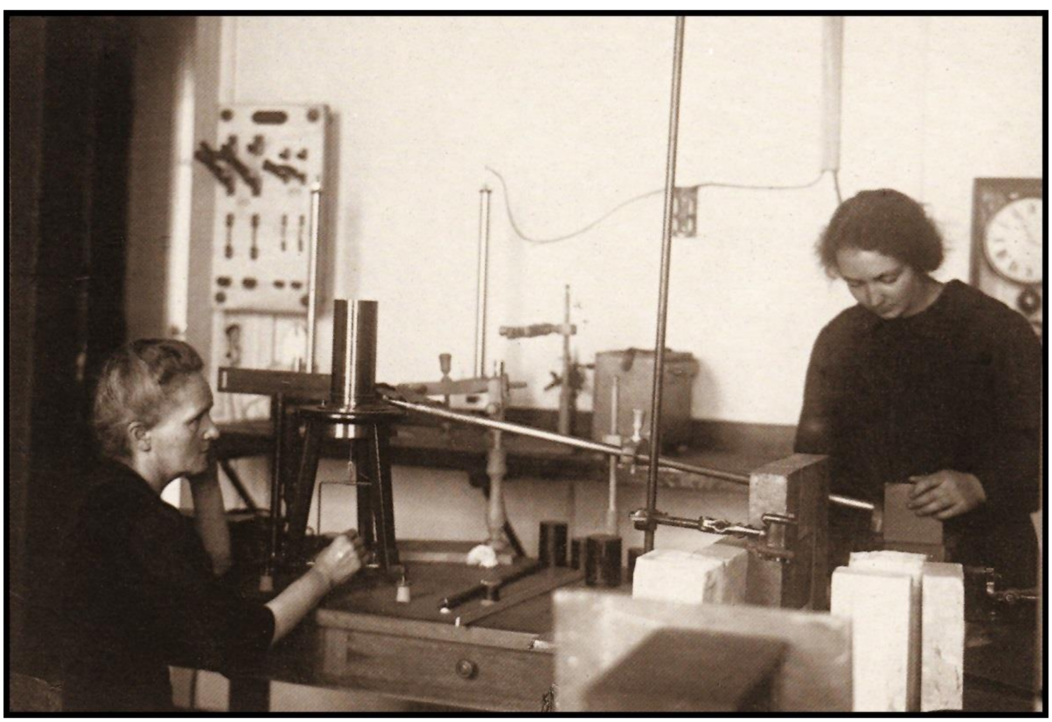

Marie Curie and her daughter Irene Joliot-Curie in their Paris Laboratory

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Secondarv Standard No 6 v2

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 $RaCl_2$. (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 $RaCl_2$,
26·36 mg $RaBr_2$.

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 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. $RaCl_2$. (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,
$RaCl_2$ 20·28 mg,
$RaBr_2$ 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. 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. $RaCl_2$. (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 $RaCl_2$,
26·36 mg $RaBr_2$.

These statements are considered correct to 0·2 %.

Für die Wiener Messung:
Stefan Meyer

Pour les mésures faites à Paris:
M. Curie

President of the Commission
E. Rutherford