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Standards of radium-226: from Marie Curie to the International Committee for Radionuclide Metrology

B.M. Coursey*, R. Collé, J.S. Coursey

Ionizing Radiation Division, Physics Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899-8460, USA

This article is dedicated to the memory of Wilfrid B. Mann (1908–2001), past president of the ICRM and past Editor-in-Chief of Applied Radiation and Isotopes. His early account of the origins of radionuclide metrology appeared as the first paper in this Journal, The preparation and maintenance of standards of radioactivity, 1956. Appl. Radiat. Isot. 1, 3–23.

Abstract

In the early part of the 20th century, the pioneers of radioactivity research, led by Marie Curie, Ernest Rutherford and Stefan Meyer, formed a *Commission internationale des étalons de radium*. The Commission made arrangements for the preparation and intercomparisons of the international standards of radium, which were identified as the Paris standard and the Vienna standard. Otto Hönigschmid from Vienna prepared a first set of international secondary standards in 1912 and a second set in 1934. In both instances, these secondary standards were compared by gamma-ray measurements with the Paris and Vienna standards. The usage of these international standards of radium in the 20th century is described. Published by Elsevier Science Ltd.

1. The first radium standards 1902–1912

Much has been written about Maria Sklodowska Curie and her extraordinary accomplishments in physics and chemistry. See, for example, the popular biography *Madame Curie* authored by her youngest daughter Eve (Curie, 1937). In this account, we will concentrate on the quantitative aspects of her work with radium, and how the early work with radium standards presaged the present system of international radionuclide metrology. Marie Curie's first experiments to establish the existence of radium as a separate element began with 100 g of pitchblende from St. Joachimstal in the present Czech Republic. (Excellent reviews of the early chemistry and the origins of the radium industry are given by Silverman (1950) and Landa (1982).) Marie Curie's next experiments were with 500 g of carnotite from the western US provided by the US Geological Survey. These early investigations suggested that she would need large quantities of raw materials to extract weighable amounts of the element. She then obtained 100 kg of pitchblende, courtesy of the Austrian Academy of Sciences. This was soon exhausted as well. Ultimately, Marie and Pierre Curie obtained 8 metric tons of pitchblende residues (for the cost of shipping) from St. Joachimstal, and by 1902 she had extracted one decigram of the element radium.

As soon as the remarkable properties of radioactivity were known, a large number of chemists initiated programs to separate radium and the longer-lived daughter products from the uranium, actinium and thorium series. Physical measurement standards were then needed to compare purity and yield of products from different laboratories. Clearly, standards of mass—amount of substance—would be useful. Arthur Eve, a collaborator of Rutherford's at McGill University, proposed as a standard 1 kg of thorium nitrate in a thin-walled, cylindrical glass vessel 16 cm in diameter with radiation filtered through 1 cm of lead (Eve, 1906). Note that the standard calls for a unit quantity of a purified compound, in a specified geometry, and with a specified filter to remove lower-energy radiations.

*Corresponding author. Tel.: +1-301-975-5584; fax: +1-301-869-7682.

E-mail address: bert.coursey@nist.gov (B.M. Coursey).

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A more obvious international standard would be based on the mass of the element radium. This ^{226}Ra standard would have to be free of "mesothorium" (^{228}Ra) and free of barium element contamination from the chemical purification. The chemists from the Curie Institute soon had competition from other "radioactivity laboratories" in Europe and North America (e.g., Soddy, 1911). In the decade following the discovery of radioactivity, Marie and Pierre Curie and Rutherford received Nobel Prizes—in large part for their elucidation of the nature of radioactivity as a result of their careful measurements of ^{226}Ra and its decay products. A consensus developed that an international radium standard was needed (Boudia, 1997).

The first formal action on establishing an international standard came 12–15 September 1910 at the International Congress of Radiology and Electricity in Brussels. A special international committee was appointed to report to the Congress on the best means to be adopted to fix an international radium standard. The members of the committee and their institutions at the time are given in Table 1. Although many on the committee had worked in Rutherford's laboratory at McGill University, Rutherford and the other committee members were keenly aware of Marie Curie's special place in the field.[1] It was agreed that the unit of activity would be named the "Curie",[2] and the quantity of a radioactive substance corresponding to 1 Ci would be that amount equivalent to radon emanations from one gram of ^{226}Ra. The more successful instruments of the day for comparing different radium sources were gold-leaf electroscopes in which the radium and daughter gamma rays were filtered through 1 cm of lead. The main contribution to air ionization came from the high-energy gamma rays of radium B (^{214}Pb) and radium C (^{214}Bi). Thus, sealed ^{222}Rn sources could be compared directly with sealed ^{226}Ra preparations with ^{222}Rn in equilibrium. The committee reported to the congress on the final day (September 15th) and their suggestions were adopted by the Congress (Rutherford, 1910). Marie Curie was asked to prepare a standard of approximately 20 mg mass radium.

In the autumn of 1911, Rutherford and Marie Curie met at the Solvay Conference in Brussels and agreed to ask Stefan Meyer of the Institut für Radiumforschung in Vienna to prepare a second standard. Rutherford assigned his young graduate student, James Chadwick, the task of devising an instrument to compare two different radium preparations (Rutherford and Chadwick, 1912). On 25–28 March 1912, the International Committee met in Paris to compare the two standards. Rutherford's apprehensions about the meeting were expressed in a personal letter to Boltwood on 18 March (Badash, 1969; Brown, 1997)

> I have not much doubt but that the two standards will be found in very good agreement, but it will be a devil of a mess if they are not. That is one of the reasons that I must be there to act as arbitrator between the two parties. I have developed a balance method of a gamma ray comparison, with which I think I can compare two nearly equal standards [to] an accuracy of 1 in 1000. I suppose, however, we shall not worry if the agreement of the two standards is within 1 in 300 or 400.

Chadwick's method was used as well as another ionization method designed by Pierre Curie using his piezoelectric quartz crystal (Chavaudra, 1995). The agreement between the Paris and Vienna standards was 2 parts in 1000 (Geiger, 1984). Of course there was general relief that this close agreement was good enough, but Hönigschmid was careful to point out later that he used calibrated weights in his mass measurements while Marie Curie did not! Rutherford's account of the Paris meeting was published in *Nature* in April, 1912 (Rutherford, 1912). Meyer and von Schweidler's account of the meeting in German is given in Meyer and von Schweidler (1916). Geitel, Eve and Boltwood did not attend the meeting. Interesting descriptions of Rutherford's and Curie's preparations for the meeting have been given by Brown (1997) and Boudia (1997), respectively.

Table 1
Commission internationale des étalons de radium (1912)[a]

Marie Curie	Sorbonne University, Paris
André Debierne	Sorbonne University, Paris
Ernest Rutherford	Manchester University, Manchester
Frederick Soddy	Glasgow University, Glasgow
Otto Hahn	Berlin University, Berlin
Hans Geitela	Gymnasium Wolfenbüttel, Braunschweig
Stefan Meyer	Academy of Sciences, Vienna
Egon R. von Schweidler	University of Innsbruck, Innsbruck
Arthur S. Eve	McGill University, Montreal
Bertram Boltwooda	Yale University, New Haven

[a] For further information on these members of the commission see: Fricke (1992) and Badash (1969).

[1] In later years many of those who worked for Rutherford and others who greatly admired his work would propose the unit the Rutherford (rd) for radioactivity (Dorsey, 1921; Curtiss, 1948) but these proposals were never adopted. Under Curtiss' proposal 1 rd would equal 1 MBq.

[2] Frame (1996) has commented on the deliberations in choosing the name for the unit and the ambiguity in who was being honored.

1.1. 1912 series of Hönigschmid standards

Some of the most careful gravimetric measurements at that time were carried out by Otto Hönigschmid in Meyer's laboratory in Vienna as part of his efforts to measure the atomic weight of radium (Hönigschmid, 1911). The International Committee asked Hönigschmid to prepare a set of radium ampoules suitable for use as standards by metrology institutes in different countries. The "primary standards" were a special designation for the Paris standard of Marie Curie and the Vienna standard maintained by Stefan Meyer. The "secondary standards" were prepared as weighed samples of radium chloride from material extracted from St. Joachimstal pitchblende, which was said to be practically free of mesothorium (^{228}Ra). These were compared by gamma-ray measurements with the Paris and Vienna standards and certificates for each standard were signed by Stefan Meyer, Marie Curie and, as president of the commission, Ernest Rutherford (Meyer, 1945a, b, c). In Rutherford's letters in *Nature*, he refers to an international "committee", but the certificates are titled in French *Commission internationale des étalons de radium*. Perhaps they made the transition from "committee" to "commission" at the March 1912 meeting. The 1912 standards were of the order of 10–20 mg of $RaCl_2$, such that their emission rate would be comparable to the Paris standard of 21.99 mg $RaCl_2$ and the three standards maintained in Vienna with masses of 10.11, 31.17 and 40.43 mg $RaCl_2$. The standard of 31.17 mg was designated "the Vienna standard". The disposition of the original seven secondary standards is given in Table 2 (Meyer and von Schweidler, 1916). Recipient national metrology institutes included the Physikalisch-Technische Reichsanstalt (PTR, Berlin), the National Physical Laboratory (NPL, Teddington), and the National Bureau of Standards (NBS, Washington). The certificate for the NBS Standard No. 6 is shown in Fig. 1. The certificate for the NPL Standard No. 3 is shown in Smith (1975). These standards were put to immediate practical use in support of the new world-wide radium industry. The radium work at the NBS was undertaken by Noah Dorsey who was the first chief of the Radium Section and later published important work on protection measures for radium workers (Dorsey, 1921).

2. Commercial pressures for internationally compatible radium measurements

In the two decades following its discovery radium became the most valuable material on earth, its price eventually peaking near $125,000 (US) per gram of element. Carnotite from Colorado and Utah in the USA was competitive as a raw material with the pitchblende deposits from St. Joachimstal. The US industry led by the Radium Chemical Company became one of the most important suppliers to the growing international market. Some of the richest deposits in the world were found in January 1913 in the Belgian province of Congo in Africa and, after the war, these were developed by the Union Minière du Haut Katanga of Brussels. However, World War I interrupted production, commerce and research. (James Chadwick was in Berlin working with Hans Geiger at the Physikalisch-Technische Reichsanstalt (PTR), and was held prisoner as a foreign national for the duration of the hostilities!).

The high value of radium during this period put great pressures on accurate measurements to assure equity in trade. We give three amusing examples here. WWI began 28 July 1914 and on 1 August, Glenn Donald Kammer from the Pittsburgh radium works of the Radium Chemical Company, set sail for England with a case containing 4 g of radium valued at $500,000 (Silverman, 1950). The trip was widely covered by

Table 2
Reproduction of a table taken from Meyer and von Schweidler (1916) giving the disposition of the initial seven secondary standards. As indicated, these standards were sent to France, Germany, England, the United States, Sweden, Japan and Portugal; and each was directly compared against the Paris and Vienna primary standards[a]

Land	ein-geschmolzen am	Wiener Messung $RaCl_2$ (mg)	Pariser Messung	Gewähltes Mittel
Frankreich	4. Okt. 1912	22.47	22.42	22.45
Deutsches Reich	4. Okt. 1912	19.73	19.74	19.73
England	4. Okt. 1912	21.10	21.16	21.13
Ver. Staaten Amerika	1. Juli 1913	20.29	20.28	20.28
Schweden	1. Juli 1913	9.74	9.71	9.73
Japan	1. Juli 1913	9.80	9.80	9.80
Portugal	1. Juli 1913	9.07	9.11	9.09

[a] As indicated in the table, the agreement in the comparisons against the two primary standards was well within a few tenths of a percent, which is a precision that still rivals contemporary radionuclidic metrology.

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.

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. $RaCl_2$. (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 %.

Pour les mêmes 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. $RaCl_2$. (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 %.

President of the Commission

E Rutherford

Fig. 1.

newspapers in Europe and North America. The material was intended for Manchester, Greenwich, Sheffield, Northampton and Hull—all medical centers that would use the radium in therapy. Kammer was dismayed to find that all the purchasers were afraid that that the US radium was contaminated with ^{228}Ra, and they insisted on a separate analysis by the NPL in Teddington. After months of arguing, Northhampton paid for the mesothorium analysis at NPL who found negligible contamination of the US radium with ^{228}Ra. NPL then convinced the other centers that the mesothorium tests were unnecessary.

Another dispute arose in 1919 when Marie Curie wrote to the NBS that her institute questioned the accuracy of standard samples prepared by the Radium Chemical Company that had supposedly been certified at NBS. These samples had been shipped to the Banque du Radium in Paris who had then requested analyses at the Curie Institute. The guarded response to Mme Curie from the NBS Director was that the samples for the New York company had been carefully compared in Washington against Standard No. 6, which she herself had certified in 1912. The matter was resolved when one of the NBS scientists visited Paris and contacted the Banque du Radium. He found that this institution was a commercial broker and that the radium samples had been re-packaged by clerks before they were sent to Marie Curie's laboratory. But, the clerks were sure they had done a careful job of transferring the radium!

By 1921, the cost of radium and the demands from medical centers were so high that Marie Curie was dismayed that she could not afford radium for her own research. This came to the attention of some prominent women in the US and Mrs. William Brown Meloney organized the women of America to collect $100,000 (US) to buy Marie Curie a gram of radium. The money was collected and the Pittsburgh company prepared the materials from carnotite from the US. The radium would normally have been valued at $120,000, but the company provided it for the $100,000 that had been subscribed. Ten sealed tubes of 100 mg Ra each were prepared and sent to NBS where they were compared by gold-leaf electroscope with Standard No. 6 from the International Radium Standards Commission. The certificate for the one gram of radium (shown in Fig. 2) was presented to Marie Curie by President Harding in a ceremony at the White House in May 1921. During this visit to America, Marie Curie also visited the Pittsburgh radium factory and the NBS (Curie, 1923) where she doubtless held discussions with Noah Dorsey and others on the techniques in use for measurements of these 10 samples and the one she had questioned two years earlier. A fascinating look at the NBS laboratories she visited in Washington is given in a "public health study of a typical radium laboratory" (Williams, 1924).

At the end of the decade, Marie Curie asked her benefactors to help her once again to obtain one gram of Ra, this time for a Radium Institute in her native Poland (Towpik and Mould, 1998). This time the American women collected $50,000 (the price had dropped!) and a check was presented to Marie Curie by President Hoover at the White House. She used the money to buy the radium from the Belgian factory who used raw materials from the Congo. More efficient separations chemistry and discoveries of more high-grade ores (in Canada and South America as well as Africa) had combined to reduce the unit price of radium. But the number of applications and the associated metrological needs continued to increase. Gram quantities were needed for radium helmets used in external beam therapy, while milligram quantities were needed for interstitial therapy with both radium needles and radon in sealed glass tubes. The interstitial therapy was initially referred to as "endocurie therapy", while today it is universally known as "brachytherapy". Measurements were also needed to prevent fraudulent sales of materials that contained little or no radioactivity (Frame, 1992). Finally, measurements were increasingly needed for small amounts—that is, microgram quantities of Ra—particularly in solution form. These were used to standardize methods for measuring Ra in water for use in comparing therapeutic spas throughout the world.

2.1. 1934 series of Hönigschmid standards

By the early 1930s there were increasing concerns about the long-term integrity of the 1912 Hönigschmid standards. The two points most often discussed were the possible build-up of ^{4}He gas in the sealed vessels, and the unknown effect of long-term alpha-particle irradiation on the Thuringian glass itself. After almost 90 years there is no evidence that either of these effects has resulted in loss of one of the original standards but, nevertheless, the concerns were real. The International Commission asked Hönigschmid to undertake preparation of a new set of standards, and this time he used material from the Union Minière du Haut Katanga that was also essentially free of mesothorium contamination. Meyer, in an obituary for Professor Hönigschmid in 1945, gave an account of the preparation of the 1934 standards (Meyer, 1945a, b, c). The new standards were compared with the Paris and Vienna standards identified earlier.

From recent correspondence located at NIST, one can see that obtaining the new standards was not an easy, straightforward task. In order to buy the 1934 standard, NBS had to first negotiate a price and delivery schedule with the Radium Chemical Company in New York. They in turn placed an order with the Union Minière in Brussels. The certificates state that the sample was weighed by Hönigschmid on 2 June 1934. However,

UNITED STATES OF AMERICA
Department of Commerce
Bureau of Standards - S. W. Stratton, Director

CERTIFICATE FOR RADIOACTIVE MATERIAL

Submitted for measurement and certification

By the Radium Chemical Company, Pittsburgh, Pa. Distributers

For the Standard Chemical Company, Pittsburgh, Pa. Makers

And presented by

THE PRESIDENT OF THE UNITED STATES OF AMERICA
ON BEHALF OF THE WOMEN OF AMERICA
to

Madame Marie Sklodowska Curie,
Paris, France.
May 20, 1921.

This certifies that each specimen of the above mentioned radioactive material, as described below, has been compared with the Radium Standard of the National Bureau of Standards, and that from the data so obtained the equilibrium intensity of the measurable gamma radiation has been computed to be equivalent to that from a quantity of radium whose mass is specified in the right hand column of the following table of values.

Designating numbers of tube*			External dimensions of tube (millimeters)		Combined weight of tube and contents (milligrams)	Computed radium element equivalent° (milligrams)
Assigned by makers	Assigned by the Bureau of Standards					
	Serial	Test	Length	Diameter		
1	4082	Tex.31302-40	41.9	3.77	554.7	100.7
2	4083	" " 41	35.0	3.66	465.3	101.3
3	4084	" " 42	38.5	3.91	541.9	100.9
4	4085	" " 43	40.5	3.82	552.6	101.0
5	4086	" " 44	38.5	3.76	517.7	100.9
6	4087	" " 45	37.7	3.92	537.5	100.5
7	4088	" " 46	36.0	3.62	479.3	101.2
8	4089	" " 47	36.8	3.81	505.6	100.9
9	4090	" " 48	39.4	3.84	546.9	101.1
10	4091	" " 49	33.6	3.72	462.8	101.6

° The computed radium element equivalent specified in the right-hand column represents a quantity of radium in radioactive equilibrium with its first four derivatives, being hermetically sealed in a tube of Thuringian glass having walls 0.27 millimeters thick.

The residual uncertainty in the numerical value of the radium element equivalent of these several specimens does not exceed 0.7 of one percent.

Observations extending over 25 days indicate that the radium contained in these specimens is now in radioactive equilibrium.

* [illegible] material herein certified is divided into ten lots each sealed in a separate [illegible] and designated by the respective numbers shown in the first three columns of the above table. [illegible]

S. W. Stratton

Fig. 2.

when NBS ordered the sample in 1936 there were no assurances that it had been measured against the Paris and Vienna standards. Leon Curtiss at NBS wrote to Lord Rutherford, president of the International Commission, asking his assistance in having the sample measured in Paris and Vienna. Curtiss had done a postdoctoral fellowship with Rutherford in the Cavendish Laboratory in 1924–1926. With Rutherford's assistance—and cash payments from NBS to Paris and Vienna—measurements were made, and certificates for the two standards of the US (Nos. 5437 and 5440) were finally received. Marie Curie was involved in the decisions to prepare the second set of standards, but she died on 4 July 1934, just one month after the standards were prepared. Her daughter, Irène Joliot Curie, took her place on the International Commission and the 1934 Hönigschmid standard certificates bear her name.

Table 3
The 20 Hönigschmid Standards of 2 June 1934[a]

Sample	Mass RaCl2 (mg)	Location
5433	12.53	—
5435	13.05	—
5421	17.75	was at AB, but not there now
5426	19.19	PTB, Braunschweig
5432	20.50	NPL, Teddington
5430	22.23	France
5440	26.86	NBS, Gaithersburg
5431	27.15	was at Union Minière, now at AB
5427	27.96	VNIIM, St. Petersburg
5428	30.75	IRK, Vienna
5425	31.73	NRC, Ottawa
5422	32.56	Possibly at one time at Lab. Curie, Paris
5429	33.34	—
5424	37.64	PTB, Braunschweig
5434	38.88	AB, Germany
5438	50.00	Possibly at one time at Lab. Curie, Paris
5437	50.22	NBS, Gaithersburg
5436	52.72	—
5442	134.93	at AB, May have been dissolved
5441	137.34	—

[a] Summary prepared by David Smith, NPL from a questionnaire distributed by D. Smith, NPL, Teddington and Nikolai Karmalitsyn, VNIIM, St. Petersburg in 1989.

AB denotes a commercial firm in Braunschweig, Germany. (The company is presently organized as AEA Technology.)

The primary standards from 1911 denoted Nos. I, III and IV are maintained at the Institut für Radiumforschung und Kernphysik der Universität Wien (IRK). (The present name of the institute is Institut für Isotopenforschung und Kernphysik (IIK) der Universität Wien and the remaining samples are stored in Seibersdorf, Austria.)

In 1989, David Smith of the NPL distributed a questionnaire on radium standards as an action of Section 2 of the Comité Consultatif pour les Étalons de Mesure des Rayonnements Ionisants (CCEMRI) (Smith, 1989). His table, reproduced here as Table 3, gives notes on the location at that time of the 20 standards prepared in 1934.

3. International intercomparisons of radium standards

Bilateral intercomparisons of radium standards must have taken place during the period 1920–1940. We have, for example, correspondence from the Director of the NPL to the Director of NBS 13 June 1921, which begins "In reply to your letter of March 29th, we have conducted an extensive search through our records, in the hope of finding instances where specimens of radium have been measured at both the Bureau of Standards and the NPL.... Unfortunately, although we have handled a good deal of American radium, almost wholly from the Radium Chemical Company, we can find no evidence that the figure...". So, it would appear that metrology institutes did comparisons mainly to resolve disputes on commercial transactions. Other comparisons with university laboratories in Germany, France, the UK and elsewhere were probably more common. In 1928, Curtiss made a comparison of the NBS standard with standards from the Cavendish laboratory. By this time he had built a radium calibration range much better suited for protection of the operator when measuring milligram radium sources (Curtiss, 1928). The main tool for gamma-ray intercomparisons was still the gold-leaf electroscope.

After World War II, many nations recognized the need for radioactivity standards of fission-product nuclides which could be used in industrial applications. Cyclotrons also became more widely available for production of nuclides, many of which had commercial applications. The expanding metrology groups around the world moved quickly to perfect the traditional methods and to develop new coincidence methods that could take advantage of scintillation detectors with improved resolution and faster electronics. But it was perhaps natural for those conducting international comparisons to look first to radium standards as the 1600 year half-life would obviate the problems associated with shipments by sea of shorter-lived nuclides.

Wilfrid Basil Mann, a young Englishman, was one of the first of this generation after WWII to take on the challenge of comparing the Hönigschmid standards from several countries. Mann developed a radiation balance after the design of Callendar (1910). It was described as a twin-cup Peltier-effect microcalorimeter. It was used in comparison of the Hönigschmid

standards of the US (5437 and 5440), United Kingdom (No. 5432), Canada (No. 5425) and Germany (No. 5426). Gamma-ray measurements were also made with an electroscope (Loftus et al., 1957; Geiger, 1984). It is interesting to comment on the calorimetric approach. Rutherford and his colleagues had recognized the utility of using calorimeters to measure the power from radioactive substances (Rutherford et al., 1930). In their 1930 book, Rutherford summarizes available data on power measurements and lists the calculated power corresponding to radium plus daughters as "140.1 g calories per hour". This corresponds to 162.8 $\mu W\,mg^{-1}$of Ra plus daughters. Mann reported a value of 164.58 $\mu W\,mg^{-1}$ "uncorrected for growth of polonium or of radium E" (Davenport et al., 1954). Using currently available nuclear-decay data, Collé (Collé and Zimmerman, 2002) calculated a value of 158.7 $\mu W\,mg^{-1}$. The main value of Mann's calorimeter was not as an absolute detector, but that it could be used to compare two standards without the source-geometry uncertainty introduced in gamma-ray comparisons at a distance from the electroscope. The most careful calorimetric measurements of radium standards were those of Yudin and coworkers in St. Petersburg (Christmas et al., 1988) who paid special attention to the energy loss from gamma rays that escaped the calorimeter and energy gains from build-up of ^{210}Pb plus daughters. The measured power per unit mass for any given radium sample will depend on the dimensions of the heat sink and on the time elapsed since encapsulation of the radium, but should be of the order of 160 $\mu W\,mg^{-1}$ with no contribution from the ^{210}Pb sub-series. In radioactive equilibrium, the ^{210}Pb sub-series will add an additional 34.2 $\mu W\,mg^{-1}$.

Comparative measurements with the calorimeter and various electroscopes were made in a number of laboratories including NBS, NPL, PTB, NRC, IRK and the Union Minière, Brussels. In every instance, the measurements served to confirm the ratio between any two standards as equal to the mass ratio from Hönigschmid. As a result, in 1959 an ad hoc study group of the CCEMRI of the Comité International des Poids et Mesures recommended that the whole system of international Hönigschmid standards be considered as the international standard.

At the International Summer School on Radionuclide Metrology held at Hercig Novi in 1972, Wilfrid Mann gave a summary of the many international measurements of the 1934 Hönigschmid standards (Cavallo et al., 1973). In the absence of an International Radium Standards Commission, the responsibilities for international radium and radon metrology have been assumed by Section 2 of the CCRI and by members of the International Committee for Radionuclide Metrology (ICRM) and their several working groups.

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