

# Comparison of Four National Radium Standards

## Part 1. Experimental Procedures and Results

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## Part 2. Statistical Procedures and Survey

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### Part 1

The two United States primary radium standards have been compared with the British primary radium standard and the Canadian national radium standard (1) by an ionization method, using the NBS standard electroscop, (2) calorimetrically, using the Peltier-cooling radiation balance, (3) by means of a Geiger-Müller counter, and (4) using a scintillation counter. Where there is little or no difference in gamma-ray source self-absorption, the four methods should, and in fact do, give good agreement. In the case of the Canadian national radium standard the difference in the results obtained is an indication of a difference in source self-absorption.

#### 1. Introduction

During January and February 1954 the British primary radium standard and the Canadian national radium standard were at the National Bureau of Standards for the purpose of comparing these standards with the two United States primary radium standards at the Bureau. The intercomparisons were conducted over a period of 12 days and were made as exhaustive as possible, using the NBS electroscop, a Peltier radiation balance, and Geiger-Müller and scintillation counters.

#### 2. Historical Background

In August 1911 Mme. Pierre Curie prepared, in Paris, a primary radium standard consisting of 21.99 mg of the pure anhydrous radium chloride that had been used to determine the atomic weight of radium as 226.0. This 21.99 mg of radium chloride was sealed into a glass tube 32 mm long, having an internal diameter of 1.45 mm and a wall thickness of 0.27 mm.

At the same time Professor Otto Hönigschmid, in Vienna, made three radium-standard preparations from very pure radium chloride consisting of 10.11, 31.17, and 40.43 mg of radium chloride sealed in glass tubes about 32 mm long, having internal diameters of 3.0 mm and wall thicknesses of 0.27 mm, each tube having a platinum wire sealed in one end. This wire was presumably to prevent the accumulation of static charge within the tubes. The purity of the radium chloride was defined by a radium atomic-weight determination, resulting in a value of 225.97. Of these the 31.17-mg preparation was chosen as a secondary standard. Mme. Curie's 21.99-mg primary standard and Professor Hönigschmid's secondary standard are generally and respectively referred to as the 1911 Paris and Vienna radium standards.

In 1934, after 23 years had elapsed, some concern was felt lest the Paris primary standard, together with a number of secondary radium standards, might explode on account of the accumulation of helium and chlorine and possible devitrification of the containing tubes. Hönigschmid was at that time carrying out, in Munich, a further determination of the atomic weight of radium, and accordingly the International Radium Standards Commission asked him to prepare new standards, using the same salt as for the atomic-weight determination.

For his atomic-weight determination, which was carried out in the early part of 1934, Hönigschmid used approximately 4 g of radium chloride, containing 3 g of radium element, that had been placed at his disposal by the Union Minière du Haut Katanga. This salt was purified by Hönigschmid to a point where spectroscopic analysis by Gerlach showed a maximum of 0.002 to 0.003 percent of barium atoms. A value was obtained for the atomic weight of radium equal to 226.05, which is currently accepted.

Hönigschmid then used some 817 mg of this highly purified anhydrous radium chloride to prepare 20 new standards of radium. Exactly who asked him to do this is not now quite clear. According to Mlle. Chamie [1],<sup>1</sup> the International Radium Standards Commission, at the suggestion of Stefan Meyer, "entrusted Mr. O. Hönigschmid with the preparation of 20 standards, using the salt he had purified and used in measuring the atomic weight of radium." According to Hönigschmid himself, however, in a paper [2] presented after his death by Stefan Meyer, the 20 standards were prepared "at the wish of the Belgian radium company." These two versions are, however, not irreconcilable if one assumes that the suggestion of the Belgian company was made known to the International Radium Standards Commission, which then gave it its official sanction.

<sup>1</sup> Figures in brackets indicate the literature references on page 272.

The 20 new Hönigschmid standards were sealed into glass tubes on June 2, 1934, the glass tubing being similar to that used to seal the 1911 Vienna standard and having an internal diameter of 3.0 mm and a wall thickness of 0.27 mm. A platinum wire was sealed into the end of each standard.

One of the new Hönigschmid standards that was 42 mm long and contained 22.23 mg of radium chloride was selected as the new international standard, and its value was carefully compared with the 1911 Paris standard by gamma-ray measurements over a period of 4 years [1]. The Hönigschmid reference number for this standard is 5430. Hönigschmid states [2] that the error of a single weighing was not more than 0.02 mg. The gamma-ray comparison with the 1911 Paris standard showed a discrepancy, however, of 0.2 percent, corresponding to a weight of 22.27 mg as of June 2, 1934.

The first United States radium standard was brought to America in 1913 by Mme. Curie. This source contained 20.28 mg of radium chloride and was designated by the International Radium Standards Commission number IV (Vienna No. 6).

In 1936 two of the twenty Hönigschmid preparations were acquired as the United States primary radium standards. They are each designated by two numbers, namely, 5437, XIV and 5440, XV. The arabic numerals are those given by Hönigschmid, and the roman numerals are those assigned by the International Radium Standards Commission and imply that the standards have undergone gamma-ray comparison with the 1911 Paris and Vienna standards. The lengths of these two United States standards are 36 and 37 mm, and they contained 50.22 and 26.86 mg, respectively, of radium chloride as weighed by Hönigschmid on June 2, 1934. These weights correspond to 38.23 and 20.45 mg of radium element. The weights derived from a comparison with the Paris and Vienna 1911 standards corresponded, however, to only 38.13 and 20.38 mg, respectively, of radium element, as of June 1934.

The British primary radium standard is designated by one number only, namely, 5432. It is solely a standard by weight and was not compared with the 1911 Paris and Vienna standards. It is, however, one of the original Hönigschmid preparations sealed on June 2, 1934. Its length is 38.8 mm, and its salt content corresponds to 15.60 mg of radium element, as of that date. This standard replaced the first British radium standard, which had been in the custody of the National Physical Laboratory since 1913. This earlier standard was designated by the International Radium Standards Commission number III (Vienna No. 3).

The United States and British primary radium standards, as can be seen from figure 1, have low ratios of volume of salt to volume of tube. It is therefore to be expected that with the standards in a horizontal position and the grains of radium chloride distributed evenly along the tube their gamma-ray source self-absorption would be very nearly the same.

The Canadian national radium standard is however shorter and of smaller diameter than the Hönig-

schmid preparations, and it is tightly packed (fig. 1). It was sealed in June 1930 by the Union Minière du Haut Katanga, its contents, and that of six other sources in the custody of the National Research Council, having been taken from two tubes of radium chloride that had been prepared by the Union Minière in June 1924. Its weight was derived by gamma-ray comparison in 1933, in Paris and Vienna, with the 1911 standards, and it is designated by the number XIII. It is understood that no corrections for possible differences in self-absorption were made in these gamma-ray comparisons. Its length is 10.5 mm, its internal diameter 1.5 mm, and its salt content corresponds, according to the gamma-ray comparison with the 1911 radium standards, to 24.23 mg of radium element, as of June 1934. Information on all four national standards is summarized in table 1.

TABLE 1. Description of four national radium standards

	A <sup>1</sup> U. S. primary radium standard	B British primary radium standard	C Canadian national radium standard	D U. S. primary radium standard
Reference numbers.....	5437, XIV	5432	XIII	5440, XV
Radium content as given by:				
1. Hönigschmid's weighings.....	38.23 mg	15.60 mg	-----	20.45 mg
2. Comparison with Paris and Vi- enna 1911 stand- ards, as of June 1934.....	38.13	-----	24.23 mg	20.38 mg
Length of glass tube....	36 mm	38.8 mm	10.5 mm	37 mm
Internal diameter of tube.....	3 mm	3 mm	1.5 mm	3 mm
Tube wall thickness....	0.27 mm	0.27 mm	0.25 mm	0.27 mm

<sup>1</sup> For convenience, A, B, C, and D are used here and elsewhere in this paper to identify these radium standards.

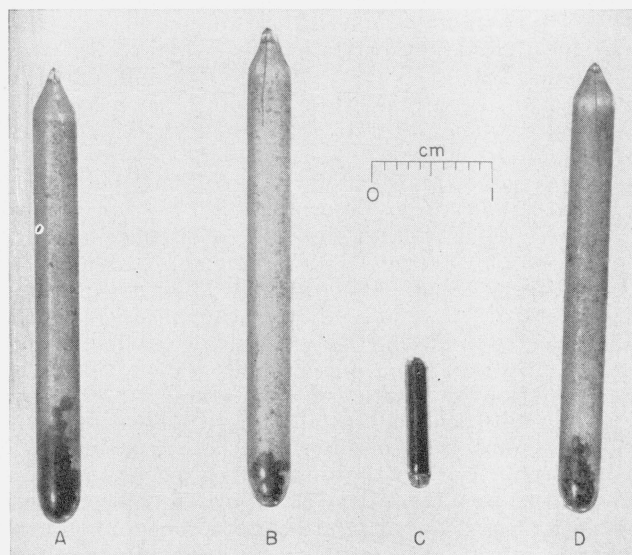


FIGURE 1. Four national radium standards.

A, American; B, British; C, Canadian; and D, American.

In view of the uncertainties that exist and the differences between the Hönigschmid weights and their weights as derived by comparison with the 1911 Paris and Vienna standards [3], it has recently been suggested that new radium standards be prepared from about 1 g remaining of Hönigschmid's original "atomic-weight" material. Another possibility lay in a recheck of the present standards. With this end in view, United States primary radium standard 5440, XV was taken to the United Kingdom in the summer of 1952 and to Canada in the autumn of the same year. At the National Physical Laboratory, in Teddington, and at the National Research Council Laboratories, in Ottawa, it was compared, by gamma radiation, with the British primary radium standard, 5432 [4] and the Canadian national radium standard, XIII [5]. The results obtained by these laboratories are discussed later in connection with the data given in table 3.

The question also arises as to what is desired in a radium standard. In order to derive the mass of any radium preparation in terms of the standard by gamma-ray measurements it is necessary to know both the absorption of the containers of the preparation and standard and also the self-absorption of the radium salts themselves. In NBS certificates the results are stated in terms of milligrams of radium when contained in a Thüringen glass tube having a wall thickness of 0.27 mm, together with an empirical absorption correction for the container in question. Only calorimetric measurements can give the ratios of the true radium contents, irrespective of absorption but in this case it is necessary to know the date of sealing of the preparation in order that correction may be made for the growth of polonium. A small fraction of the gamma-ray energy is absorbed and measured by the calorimeter, but any difference in absorption between two sources will represent only a small correction to the already small contribution of gamma-ray energy emission (about 7%) to the total energy emission.

### 3. Measurements With the NBS Standard Electroscop

The NBS standard electroscop [6] and measuring system were used, without modification, for this comparison of four national radium standards. The ionization chamber consists of a 10-cm cube free-air volume, with walls made of 1 cm of lead and a ½-cm aluminum inner lining. A gold leaf is suspended near the center of the chamber. A 10-μ quartz fiber at the free end of the leaf provides a fine line for projection. The fiber image is magnified approximately 100 times and projected onto a metric scale. The discharge of the electroscop is measured by timing the transit of the image between two fixed points on the scale 6 cm apart.

The source indexing system consists of a V-shaped trough of ½-in. Lucite on an aluminum stand. The stand can be moved along a line perpendicular to the face of the ionization chamber or rotated about its own vertical axis. Preparations are centered in the trough opposite the center of the

chamber, so that measurements are made perpendicular to the axes of symmetry of the preparations.

The four standards were measured relative to each other by comparison of each of the six possible combinations of pairs. Independent measurements were made on each pair by each of three different observers at source distances of 66.5 cm and 74.1 cm from the chamber. The entire series of measurements was repeated twice.

The following procedure was adopted for comparing each pair of standards:

1. The trough was placed at the distance selected and parallel to the chamber face.
2. A standard was held horizontally and tapped lightly until the salt was distributed uniformly along the length of the capsule, as in figure 2.
3. The standard was placed in the trough and centered.
4. Three observations of the discharge time were made and recorded.
5. The trough was rotated 180 degrees, and three more observations were made.
6. Procedures 1 to 5 were repeated with the second standard of the pair.
7. Procedures 1 to 6 were repeated for both members of the pair at the second distance from the electroscop.

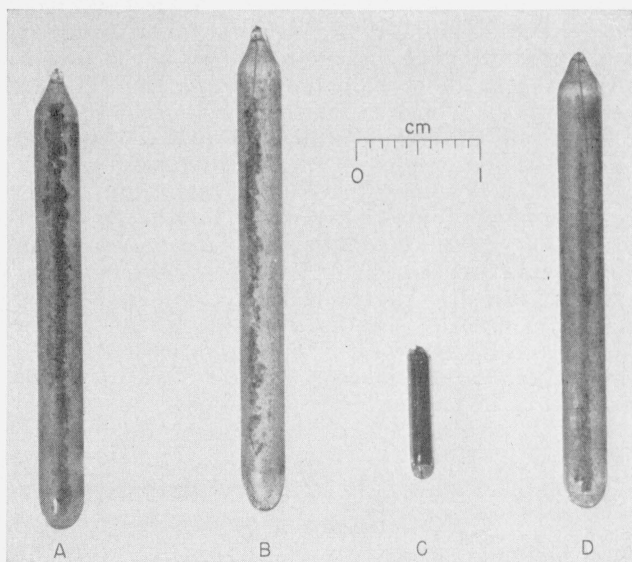


FIGURE 2. Four national radium standards, with the grains of salt in the three Hönigschmid standards distributed along the length of the tubes.

A, American; B, British; C, Canadian; and D, American.

### 4. Comparison by Geiger-Müller Counter

The Geiger-Müller counter used for this comparison was a neon-halogen-filled tube. The tube itself was surrounded by a sheath of lead ¼ inch thick so that the soft gamma rays, the spectrum of which might be varied by source absorption to a greater extent than that of the higher-energy gamma rays, would not be counted. The resolving time of the counter was determined by the two-source method to be 211 μsec ± 5 percent. The correction for re-

solving time applied to the data ranged from 1.1 to 2.7 percent.

The source holder of the NBS standard electro-scope was used to position each standard in turn in these measurements, and the standards were tapped so that, in the case of the more loosely packed Hönigschmid standards, the grains would be distributed uniformly along the tube.

In order to eliminate any possible effects due to drift a series of measurements was carried out on each pair of international standards. Thus, in the comparison of *A* and *B*, measurements were carried out with *A* and *B* arranged in "packages" in the following order: *A, B, B, A; B, A, A, B; A, B, B, A; and finally, B, A, A, B*. Similar package measurements were made on each of the other five pairings of the four international standards.

A total of about 80,000 counts was taken on each of the 16 members of the 4 packages comprising a pair comparison. Thus in the comparison of *A* and *B* a total of some 640,000 counts were made with *A* in position and 640,000 with *B*.

### 5. Comparison by Scintillation Counter

The scintillation counter consisted of a thallium-activated sodium-iodide crystal mounted on the face of a photomultiplier tube. The resolving time of the counter and amplifier was  $5 \mu\text{sec} \pm 10$  percent, and the corrections applied to the data varied from 0.3 to 0.8 percent. The discriminator was set to accept pulses corresponding to gamma-ray energies greater than 1 Mev. Thus, as for the NBS standard electro-scope and the Geiger-Müller counter, the effect of source self-absorption of the lower-energy gamma rays should not be apparent. The sodium-iodide crystal and photomultiplier were mounted adjacent to the Geiger-Müller counter so that counts on each source could proceed concurrently with both counting systems. Exactly the same pairing and packaging order of sources as was used for the Geiger-Müller counter comparison was, ipso facto, also used in the scintillation-counter measurements. The counts for each source in position were of the order of 400,000 compared with 80,000 in the case of the Geiger-Müller counter.

### 6. Measurements With the Radiation Balance

A modification of the radio-balance originally designed by Callendar [7] for the measurement primarily of radiant energy has recently been described [8], which is suitable for the measurement of the energy emission from radioactive materials. This modification of the radio-balance has been renamed the radiation balance, its most important feature being the ability to balance the energy emission from a radioactive source either against Peltier cooling or the energy emission from another radioactive source, or both.

None of the radiation balances constructed previously was large enough to accommodate the large Hönigschmid standards, and, accordingly, a new one was constructed for this purpose. This balance is described in detail separately in this issue [9]. It

differed essentially from the first one, however, in that its larger cups were made from gold instead of copper.

### 7. Radiations Measured

The radiation from radium in equilibrium with all its products consists of five energetic alpha-particle groups, including that of polonium; three main groups of beta particles, the most energetic being that from the transition of radium E to radium F with a maximum energy of 1.17 Mev; and a complexity of gamma rays, the most energetic being from the excited levels of radium C'.

Three of the methods described here and used to compare the radium contents of the four national radium standards were essentially gamma-ray comparisons. With the thicknesses of lead used, or the discriminator setting, the chief contribution to the gamma-ray effect would be from the energetic radium C' gamma rays (above 0.6 Mev in the case of the electro-scope and Geiger-Müller counter and above 1 Mev in the case of the scintillation counter).

In contrast, the radiation balance measures primarily the energy emitted in corpuscular form. Some 93 percent of the energy produced by radium and its daughters down to radium D is associated with particulate emission, the remaining 7 percent of the energy produced being associated with the gamma radiation. The wall thickness of the gold cups was such as to absorb completely the most energetic beta particles from radium E. Some 12 percent of the energy associated with the gamma rays is also absorbed. Of the 7 percent of the total energy produced that is associated with the gamma-ray emission, another 1 percent (for the Canadian standard) or 1.5 percent (for the Hönigschmid standards), corresponding, respectively, to 0.07 and 0.1 percent of the total energy produced, will be absorbed in the sources themselves. The difference of 0.5 percent between the source self-absorption of the Canadian and Hönigschmid standards corresponds therefore to a difference of only 0.035 percent of the total energy produced, which is negligible. Any smaller differences in gamma-ray source self-absorption of the three Hönigschmid standards are also therefore negligible so far as the measurements in the radiation balance are concerned. The alpha-particle and beta-particle absorption is complete; a correction must be made, however, for the growth of radium E and polonium, which will not be in equilibrium with the radium.

### 8. Results

The results obtained with the radiation balance, measuring the sources singly and in every combination of pairs, are summarized in table 2. In this table the order of measurement is represented by reading from left to right and down the table.

From the results in table 2 the following best estimates for the energy absorbed (in microwatts) from sources *A, B, C, and D* have been deduced:

<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>
6293.4	2569.8	4131.0	3360.7

TABLE 2. Energy absorption, in microwatts

Source	Energy absorbed	Source	Energy absorbed	Source	Energy absorbed	Source	Energy absorbed
B.....	2571.0	A-B..	3727.1	D-B..	788.6	C-B..	1561.2
C.....	4127.1	C-D..	776.0				
D.....	3371.6	A-D..	2935.6				
A.....	6285.2	A-C..	2164.2				

In table 3 are shown the complete results for the six pairs of standards, using the NBS standard electroscop, Geiger-Müller counter, scintillation counter, and radiation balance. In the last line of the table are shown the weight ratios for the same six pairs. The weight of the Canadian standard (C) is, however, only a derived weight, and for this reason, any ratio involving this derived weight is shown in quotation marks. The ratios A/B, A/D, and B/D are, however, the ratios of Hönigschmid's own weighings.

TABLE 3. Adjusted results for the ratios of the four international standards

Method	A/B	A/C	A/D	B/C	B/D	C/D
NBS standard electroscop.....	2.441	1.570	1.870	0.6429	0.7661	1.192
Geiger-Müller counter.....	2.461	1.582	1.885	.6430	.7659	1.191
Scintillation counter.....	2.478	1.579	1.889	.6370	.7624	1.197
Radiation Balance.....	2.449	1.523	1.873	.6220	.7647	1.229
Weighing.....	2.451	"1.578"	1.869	"0.6438"	.7628	"1.185"

For comparison with these values the ratios obtained by Perry [4], using the NPL standard ionization chamber with gold-leaf electroscop, an ionization chamber with a Lindemann electrometer, and a Geiger-Müller counter for B/D were, respectively, 0.7669, 0.7657, and 0.7669. The result obtained for the gamma-ray ratio C/D by Michel [5], using the NRC precision ion chamber and Lindemann electrometer was 1.192. Michel, from geometrical considerations, then calculated the source absorption of each standard and corrected the gamma-ray ratio to give a weight, or content, ratio of C/D equal to 1.185. The direct gamma-ray ratios obtained both by Perry and Michel are in excellent agreement with the results shown in table 3.

A check on the internal consistency of the results shown in table 3 can be provided by assuming that A, B, and D are so much alike that there are negligible differences in source absorption for high-energy gamma rays, and none at all in the case of the calorimeter, where 93 percent of the energy absorbed is particulate, so that any change due to absorption of the 7 percent of gamma rays and secondary electrons would be even more negligible. A check can then be run on the results for A, B, and D by dividing the quantity characteristic of each in each determination by the Hönigschmid weight of each standard. This characteristic quantity is scale divisions per second for the NBS standard electroscop, counts per second for the counters, and microwatts

for the radiation balance. In each case the characteristic quantity is as of February 1954, and the mass of radium element is as of June 1934. It is not necessary for this check to correct for the 20-year decay of radium as this is the same constant for each standard.

The results of this internal precision check are shown in table 4, in which the figures quoted are the characteristic quantity, divisions, or counts per second or microwatts, divided by the mass of radium element present and normalized to make the "best average" equal to 100.00 in each case.

TABLE 4. Radioactive effect per milligram of radium element (Normalized to make the best average equal to 100.00)

Method	A	B	D	Best average	Standard deviation of the individual results
NBS standard electroscop.....	99.93	100.31	99.88	100.00	0.23
Geiger-Müller counter.....	100.31	99.90	99.51	100.00	.40
Scintillation counter.....	100.52	99.42	99.47	100.00	.62
Radiation balance.....	100.03	100.10	99.86	100.00	.13

The values of the best average should, in turn, enable one to form an estimate of the precision of Hönigschmid's weight determinations, in which, according to Hönigschmid himself [2], the error of a single weighing was not more than 0.02 mg. A statistical survey of the results was carried out with the cooperation of W. S. Connor and W. J. Youden, and resulted in the best estimates of the mass of radium element in A, B, and D given in table 5. The methods adopted to arrive at these best estimates, and also the best estimates given in table 3 for the ratios of pairs of standards, are described by Connor and Youden in part 2 of this paper.

TABLE 5. Best estimates, in milligrams, of the masses of the Hönigschmid radium standards, as of June 2, 1934

Standard	A	B	D
Hönigschmid's mass.....	38.23	15.60	20.45
Mass derived from NBS standard electroscop.....	38.227	15.611	20.446
Mass derived from Geiger-Müller counter.....	38.235	15.598	20.443
Mass derived from scintillation counter.....	38.235	15.595	20.444
Mass derived from the radiation balance.....	38.235	15.608	20.435

## 9. Mass of Radium Element in the Canadian National Standard

By comparing the calorimetric ratios given in table 3 with the "weight" ratios, it is clear that the derived weight of the Canadian national radium standard (C) is low by about 3 percent. However, this does not allow for the difference in sealing date,

which involves a compensating polonium-growth correction of about 1.8 percent. By comparison of the "weight" ratios with the NBS standard electro-scope ratios, it is also confirmed that no source self-absorption correction could have been made in deriving the certified weight of radium in the Canadian standard. However, from the data available it is possible to derive a value for this mass of radium.

The experimentally determined ratios of the energy absorbed in the radiation-balance cups per unit mass of radium element for *A*, *B*, and *D* are 164.62, 164.73, and 164.34  $\mu\text{w}/\text{mg}$ , respectively. Taking the best average value of 164.58  $\mu\text{w}/\text{mg}$  of radium element, the mass of the radium in the Canadian national radium standard is found to be equal to 25.10 mg, as of June 1934, uncorrected for the growth of polonium or of radium E.

Using the Curie-Yovanovitch equation, as corrected for new values of the decay constants by Jordan [8, 10], the energy increments due to growth of polonium-210 in *A*, *B*, and *D*, on the one hand, and in *C*, on the other, are found to be equal, respectively, to 12.2 and 16.2  $\text{cal g}^{-1} \text{hr}^{-1}$  inclusive, of nuclear recoil energy, the separation and sealing dates being, respectively, May 25, 1934, and June 2, 1934, for the Hönigschmid standards, and June 1924 and June 1930 for the Canadian national standard. The growth of radium E will contribute, in proportion, another 0.8 and 1.0  $\text{cal g}^{-1} \text{hr}^{-1}$ . Subtracting the contributions of polonium-210 and nuclear recoils and of radium E from the energy absorbed from *A*, *B*, and *D* in the radiation-balance cups gives a total energy absorption for all three sources equal to 11103.0 instead of 12223.9  $\mu\text{w}$  (as of February 1954).

In the case of the Canadian national standard, an energy production of 17.2  $\text{cal g}^{-1} \text{hr}^{-1}$  by polonium-210 and radium E corresponds to 20.0  $\mu\text{w}/\text{mg}$  of radium element, which, by a second approximation, is found to be equivalent to 489.7  $\mu\text{w}/24.48_5$  mg of radium element (the mass of radium as of June 1924). The corrected energy absorption from the Canadian national radium standard is therefore 3641.3 instead of 4131.0  $\mu\text{w}$ , as of February 1954. The radium content of the Canadian national radium standard, as of June 1934, is then obtained by multiplying the total weight of the Hönigschmid standards (76.28 mg as of June 1934) by the ratio of the corrected energy absorptions of February 1954. This gives the result that there were 24.36 mg of radium element in the Canadian national standard, as of June 1934. This value will, if anything, be on the low side, however, as some radium D on the walls of the original two tubes may have been lost on transfer when the Canadian standard was resealed in June 1930. In this event, the polonium-210 correction will have been too great.

## 10. Summary of Results

As a result of this intercomparison of national radium standards, the ratios of the weights ascribed to three of them by Hönigschmid have been confirmed. It would appear that the weights derived

from the comparison of the two United States standards with the 1911 Paris and Vienna standards are, therefore, too low; unless it were assumed that all of Hönigschmid's mass determinations were low in the same ratio. However, this is to be discounted because the Berlin standard was, by comparison with the 1911 standards, found to have a greater weight than that determined by Hönigschmid [1].

Relative to the Hönigschmid weights, the Canadian national radium standard is found to have a mass of radium element equal to 24.36 mg, which indicates that no correction for difference in source self-absorption was made in its comparison with the 1911 Paris and Vienna standards. The difference between this value and that obtained by comparison with the 1911 Paris and Vienna standards (24.23 mg as of June 1934) would indicate a self-absorption correction of 0.53 percent. The absorption correction determined by Michel [4] was 0.94 percent; the difference between these two values could be a measure of the loss of radium D and polonium-210 in the transfer of June 1930.

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## Part 2. Statistical Procedures and Survey

W. S. Connor and W. J. Youden

The statistical analysis of the observations on the four national radium standards is discussed. The readings made with the electroscopes, Geiger-Müller counter, and scintillation counter were adjusted by one formula, and the readings made with the radiation balance by a different formula. In each case the adjusted values of the standards satisfy a consistency criterion. Finally, the adjusted values were improved by making use of the proportional relationship between the masses and the radioactive effects of the standards.

### 1. Introduction

Four national radium standards were recently compared at the National Bureau of Standards, as described in part 1 of this paper. The unusual opportunity associated with the presence of four standards in one laboratory directed attention to certain statistical aspects of the intercomparison. The experimental procedures and results are described in part 1. Part 2 discusses the statistical analysis.

When two standards are compared, careful measurements provide an estimate for the value of one standard in terms of the other. A standard error may be calculated for this estimate. A third standard makes possible the additional experimental evaluation of each of the first two standards in terms of the third.

Suppose that three standards  $A$ ,  $B$ , and  $C$  are available. The experimental ratios  $a/b$ ,  $b/c$ ,  $c/a$  may each be determined by using exactly the procedure that would have been employed if just two standards had been available. None of the measurements made on  $A$  in estimating  $a/b$  are used in the estimation of  $c/a$ . Additional data for  $A$  are taken to determine  $c/a$ . There is a considerable advantage in this method because the precision of the comparison is improved by alternating the readings on the two standards under comparison. This alternation reduces the effects of drift in the instruments and changes in the environment. As soon as the ratios  $a/b$ ,  $b/c$ ,  $c/a$  have been determined there is a simple test for the consistency of the three ratios. The product of the three ratios should be unity. The discrepancy between this product and unity provides a measure of the errors in these ratios.

A similar consistency criterion was applied to the six ratios determined by the electroscopes, Geiger-Müller counter, and scintillation counter. Because a different statistical treatment was required for the measurements made with the radiation balance, those measurements are discussed separately.

The last section describes how the masses of the standards were used further to improve the estimates of the standards.

### 2. Comparison of the Standards by Means of Electroscopes, Geiger-Müller Counter, and Scintillation Counter

Using these methods, environmental conditions common to paired measurements introduce a common multiplicative error in the measurements. It is ad-

vantageous to express the results of paired measurements as ratios to eliminate this error.

There were four standards,  $A$ ,  $B$ ,  $C$ , and  $D$ . Therefore, the following six ratios could be determined experimentally:

$$a/b \quad a/c \quad a/d \quad b/c \quad b/d \quad c/d.$$

These provide opportunities to test the consistency of the data. For example, the products

$$a/b \times b/c \times c/a$$

$$a/b \times b/d \times d/a$$

$$a/c \times c/d \times d/a$$

$$b/c \times c/d \times d/b$$

should all be equal to unity. The discrepancies between these products and 1.0000 reveal the errors of the measurements. It is proper to make use of the information that the products should be exactly equal to one. The measured ratios may be adjusted by a least-squares technique to obtain new ratios  $\hat{A}/\hat{B}$ ,  $\hat{A}/\hat{C}$ , etc., which do in fact multiply out to unity for all combinations that should give unity. This includes not only three factor combinations such as

$$\hat{A}/\hat{B} \times \hat{B}/\hat{C} \times \hat{C}/\hat{A}$$

but also four factor products

$$\hat{A}/\hat{B} \times \hat{B}/\hat{C} \times \hat{C}/\hat{D} \times \hat{D}/\hat{A}.$$

The adjustment formula used on the data shown in table I is of the form

$$\frac{\hat{A}}{\hat{B}} = \sqrt[4]{\left(\frac{a}{b}\right)^2 \left(\frac{a}{c} \times \frac{c}{b}\right) \left(\frac{a}{b} \times \frac{d}{b}\right)},$$

where the lower case letters indicate the measured ratios.<sup>1</sup> The adjusted values (see table 3 in part 1)

<sup>1</sup> This adjustment formula is related to the adjustment formula for the difference between the estimates of two treatment effects in a balanced incomplete block (BIB) design, see R. L. Anderson and T. A. Bancroft, *Statistical theory in research*, p. 252 (McGraw-Hill Book Co., Inc., New York, N. Y., 1952). Since the two measurements in a pair, as  $a$  and  $b$  or  $c$  and  $d$ , are subject to a common multiplicative error, the logarithms of the two measurements in the pair are subject to a common additive error. Hence, the BIB design formula applies for the difference between the logarithms of the adjusted values, as  $\log \hat{A} - \log \hat{B}$ , and by taking antilogarithms, the above formula is obtained.

have the property that

$$\frac{\hat{A}}{\hat{B}} = \frac{\hat{A}}{\hat{C}} \times \frac{\hat{C}}{\hat{B}} = \frac{\hat{A}}{\hat{D}} \times \frac{\hat{D}}{\hat{B}}$$

The observed values do not meet this consistency requirement. The reconciliation among the results effected by the above least-squares technique introduces each standard symmetrically in the computation pattern and does not single out any one standard as a superstandard. After the relative values have been established, one standard may be given an agreed value, whereupon all other standards are determined without changing the relative values.

TABLE 1. Experimental results for the ratios of four standards

Method	a/b	a/c	a/d	b/c	b/d	c/d
Electroscope.....	2.4438	1.5675	1.8703	0.64246	0.76650	1.1918
Geiger-Müller counter.....	2.4746	1.5785	1.8784	.64489	.76789	1.1920
Scintillation.....	2.4847	1.5710	1.8930	.63921	.76186	1.1953

The above least-squares adjustment has long been used for other comparisons. Recently, it has been found that certain subsets of pairs selected from all possible pairs lead to convenient least-squares estimates.<sup>2</sup> Given that a reasonably small number of pairs will suffice to interrelate all the standards, there would appear to be some chance of success for an international program of comparison. Once a properly selected subset of pairings was obtained, the various national standards could be tied together with values that would give consistent comparisons among the standards.

### 3. Radiation-Balance Measurements

The radiation balance used in this work was suitable for measuring either a proportion of the energy emitted by one standard or the same proportion of the difference in energies emitted from two standards. This difference is determined by one measurement. The schedule of measurements included separate measurement on the four standards as well as the six possible differences between them. The precision of measurement of a difference was the same as the precision of measurement of a single standard.

Typical formulas for the least-squares estimates<sup>3</sup> for the 10 quantities follow:

$$\hat{A} = \frac{2}{5}a + \frac{1}{5}[(a-b) + b] + \frac{1}{5}[(a-c) + c] + \frac{1}{5}[(a-d) + d]$$

$$(\hat{A} - \hat{B}) = \frac{2}{5}(a-b) + \frac{1}{5}[(a-c) + (c-b)]$$

$$+ \frac{1}{5}[(a-d) + (d-b)] + \frac{1}{5}a - \frac{1}{5}b.$$

<sup>2</sup> W. J. Youden and W. S. Connor, Making one measurement do the work of two, *Chem. Eng. Progr.* **49**, 549 (1953); and W. J. Youden and W. S. Connor, New experimental designs for paired observations, *J. Research NBS* **53**, (1954) RP2532.

<sup>3</sup> For a discussion of the method of least squares, see R. L. Anderson and T. A. Bancroft, *Statistical theory in research*, p. 155 (McGraw-Hill Book Co., Inc., New York, N. Y., 1952).

The quantities  $a$ ,  $b$ ,  $(a-b)$ , etc., are measured quantities. The value for  $(\hat{A} - \hat{B})$  given by the above formula will agree exactly with the result obtained by subtracting the adjusted estimate  $\hat{B}$  from the adjusted estimate  $\hat{A}$ . This was not true for the recorded values. The total amount of energy measured for the standards is left unaltered by the adjustment. Slight shifts take place in  $a$ ,  $b$ ,  $c$ ,  $d$ ,  $(a-b)$ , etc., to achieve consistency among the results. The discrepancies between the measured quantities and the corresponding adjusted values afford a measure of the precision of the measurements. The calculation is shown in table 2. It should be noted that no quantity was measured twice. The replication is concealed. There are, of course, only four standards; that is, four quantities to be determined from the ten observations. This leaves six contrasts, i. e., six degrees of freedom, available for estimating the standard deviation.

TABLE 2. Calculation of standard deviation, in microwatts, for radiation balance

Standard	Observed	Adjusted	Difference	(Difference) <sup>2</sup>
	$\mu w$	$\mu w$	$\mu w$	$\mu w$
A.....	6285.2	6293.4	8.2	67.24
B.....	2571.0	2569.8	1.2	1.44
C.....	4127.1	4131.0	3.9	15.21
D.....	3371.6	3360.7	10.9	118.81
A-B....	3727.1	3723.6	3.5	12.25
A-C....	2164.2	2162.4	1.8	3.24
A-D....	2935.6	2932.7	2.9	8.41
C-B....	1561.2	1561.2	0.0	0.00
C-D....	776.0	770.3	5.7	32.49
D-B....	788.6	790.9	2.3	5.29

$$\text{Standard deviation} = \sqrt{\frac{264.38}{6}} = 6.6 \mu w.$$

### 4. Masses of the Radium Standards

Standards  $A$ ,  $B$ , and  $D$  were made from the same supply of radium salt. The weighings were made in the same day by Hönigschmid and are considered to have a maximum error of 0.02 mg. The various properties of the three Hönigschmid standards measured by the several methods used in this intercomparison are believed to be directly proportional to the masses of the standards. All the methods give relative values for the standards. In addition, the radiation balance measures the difference between any two standards directly. Standard  $D$  was arbitrarily given the value of unity and the values for  $A$  and  $B$  expressed relative to it. Table 3 contains some of the adjusted ratios from table 3 of part 1, including the ratios derived from Hönigschmid's weighings.



TABLE 3. Value of standard, when  $D$  equals 1.000

Method	A	B	D
Scintillation counter	1. 889	0. 7624	1. 000
Geiger-Müller counter	1. 885	. 7659	1. 000
NBS standard electro- scope	1. 870	. 7661	1. 000
Radiation balance	1. 873	. 7647	1. 000
Weighing	1. 869	. 7628	1. 000

For each method of measurement a plot may be made of the values of the standards against the corresponding masses. The resulting points should lie along a straight line that passes through the origin. Let  $m$  denote the mass and  $r$  the radioactive effect given by any one method of measurement in the relative units of table 3. If the error in  $r$  is  $k$  times as large as the error in  $m$  (as measured by the standard deviations), the slope  $b$  may be computed from the quadratic

$$b^2 + \frac{k^2 \sum m_i^2 - \sum r_i^2}{\sum m_i r_i} b - k^2 = 0,$$

where  $m_i$  and  $r_i$  ( $i=A, B, D$ ) are the masses and the corresponding radioactive effects for standards  $A, B$ , and  $D$  from table 3.<sup>4</sup> This method of determining  $b$  has the property that the sum of the squares of the perpendicular distances of the points ( $km_i, r_i$ ) from the line  $r=b(km)$  is minimized.

<sup>4</sup> For a discussion of this method, see W. Edwards Deming, Statistical adjustment of data, Exercise 6, 184 (John Wiley & Sons, Inc., New York, N. Y., Nov. 1944).

In general, any particular plotted point will not be located exactly on the fitted line. The plotted points are subject to errors of observation. The "best" estimates of the coordinates for the point are taken to be the coordinates of the point on the line nearest to the plotted point. These coordinates,  $m'_i$  and  $r'_i$ , are

$$m'_i = \frac{m_i + br_i}{1 + b^2} \quad \text{and} \quad r'_i = b \frac{m_i + br_i}{1 + b^2}.$$

This procedure for fitting lines was followed for each of the lines relating the measured radioactive property to the mass. For the electro-  
scope, Geiger-Müller counter, scintillation counter, and radiation balance,  $k$  was taken as 2, 4, 5, and 1, respectively. These values correspond to the errors given by table 4 of part 1, except for the scintillation counter, for which 5 was used instead of 6.

To obtain estimates for the masses, each value of  $m'_i$  was multiplied by Hönigschmid's value for  $D$ , i. e., 20.45 mg. These estimates are recorded in table 5 of part 1. In every case the result agreed with the assigned mass within the claimed weighing error. It is particularly interesting to observe that the estimates obtained from the line, using the radiation balance results, confirm the assigned masses. For this line the errors in  $m$  and  $r$  were taken to be the same, and therefore any displacement of the point to bring it on the line required equal changes in the experimental values for mass and energy.

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