The Dawn of Radiochemistry

By J. P. Adloff and H. J. MacCordick

Centre de Recherches Nucléaires, Laboratoire de Chimie Nucléaire, B.P. 28,
67037 Strasbourg Cedex 2, France

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Abstract

Chemical research on radioactivity started in 1898. That year, three short key Notes by the Curies reawakened the topic of uranic rays discovered two years earlier by Becquerel. The discoveries of polonium and radium were milestones in the history of nuclear sciences. The exegesis of the Notes reveals the progress and processes which ineluctably led within a few months to the announcement of the existence of elements in amounts invisible at that time.

1. Introduction

The photographic plate by which radioactivity was discovered was the first known radiation detector. It was merely qualitative but nevertheless quite useful in seeking compounds other than those of uranium which could also produce an effect on photosensitive materials. During the years 1896 to 1898 Becquerel’s discovery stimulated a search for these strange rays and led to a short flare of false or at least doubtful observations. In an extensively documented review on this period, Lawrence Badash points out ‘how a proliferation of related phenomena can obscure the relevant facts, and how a sterile approach can effectively kill a newborn science" [1].

The interest of scientists consequently faded rather rapidly after the initial excitement aroused in 1896 by Becquerel’s Notes in the *Comptes Rendus.* The next important announcement, just 2 years later, was that thorium and its compounds were capable of blackening a photographic plate. This observation was made by another physicist, Gerhardt S. Schmidt (1865-1949), also a leader in the study of phosphorescence, at Erlangen in Germany [2-4]. The discovery of the radioactivity of thorium was published on February 4, 1898.

It might appear obvious today that the search for substances sharing the peculiar property of uranium and its compounds should have been a logical and systematic process following Becquerel’s observation. It is amazing how few *scientists* followed this approach. Apart from Schmidt, a young woman in Paris entered the scene: this was Marie Curie, who missed by two months the discovery of the radioactivity of thorium.

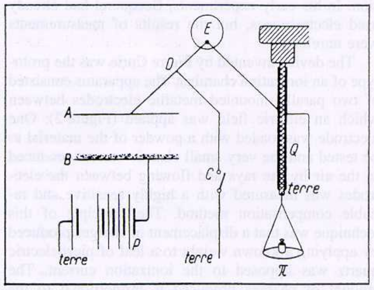
2. Marie Curie’s first Note: April 12, 1898 [5]

Marie Curie (née Marya Sklodowska, 1867-1934) came to Paris in 1891 and obtained a "licence" in mathematics and physics in 1894. The following year she married Pierre Curie (1859-1906), a physicist renowned for his work in magnetism and crystal symmetry (Figure 1). Together with his brother Jacques, he had discovered the piezoelectric effect in 1882.


Fig. 1. Pierre Curie and Marie Curie, about 1898

Becquerel’s discovery had raised a puzzling problem. The uranium salts appeared to maintain an undiminished ability to blacken a photographic plate in the course of time. What was the origin of this continuous emission of energy? Marie Curie, who was thinking of a subject for her thesis, decided to investigate the new phenomenon.

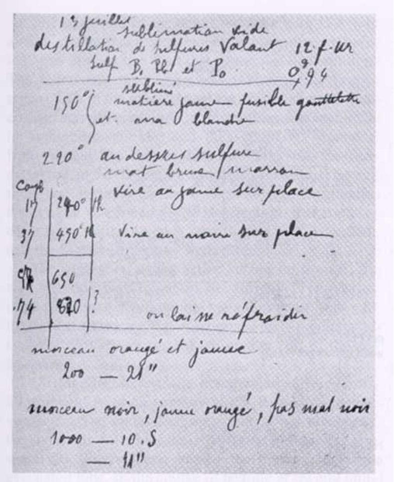
At this point, little progress would have been made without the genius of Pierre Curie. Besides blackening a photographic plate, the uranic rays also rendered air conducting for electricity. This property was much more amenable to quantitative measurement of the action of the rays, and thus of the intensity of their emission. In his early experiments, Becquerel had already used electroscopes, but the results of measurements were unreliable.



The device invented by Pierre Curie was the prototype of an ionization chamber. The apparatus consisted of two parallel-mounted metallic electrodes between which an electric field was applied (Figure 2). One electrode was loaded with a powder of the material to be tested and the very small electric current produced in the air by the rays and flowing between the electrodes was measured with a highly sensitive and reliable compensation method. The principle of this technique was that a displacement of charges produced by applying a known weight to a leaf of piezoelectric quartz was opposed to the ionization current. The amount of charges produced is proportional to the length and thickness of the foil of the leaf and to the stretching strength.

The compensation of the opposite currents from the ionization chamber and from the quartz was controlled by the motion of the foil of a quadrant electrometer. The progressive accumulation of charges on the collecting electrode tends to deviate the foil from its rest position. This is counteracted by applying progressively a weight to the quartz leaf. Eventually the charges from the chamber are completely compensated and are equal to the amount of charges conveyed by the quartz, as calculated from the weight and from the time during which the weight is applied. For the first time, the emission of uranic rays could be quantified on the basis of the intensity of the current (in the picoampere range) or of the charge in e.s.u. units.

The handling of this device required considerable skill, but Marie Curie now had an invaluable tool for routine measurements. She did not always calculate values for the current but listed in her notebooks the strength of the sources in terms of the weight in grams and the application time in seconds (Figure 3). The device invented by Pierre Curie was rapidly adopted by most researchers in the field and remained in use at the authors’ Laboratory until the early 1950’s.



13 juillet
sublimation vide
distillation de sulfures Valant 12 f. ur
sulf B, Pb et Po 0g,94
sublimé
150° matière jaune fusible gouttelettes
et [illegible] blanche
290° au dessus sulfure
mat brun / marron
Coup
17 | 240° 1h vire au jaune sur place
37 | 450° 1h vire au noir sur place
47 | 650
74 | 870 | ? on laisse refroidir
morceau orangé et jaune
200 — 21"
morceau noir, jaune orangé, pas mal noir
1000 — 10.S
— 11"

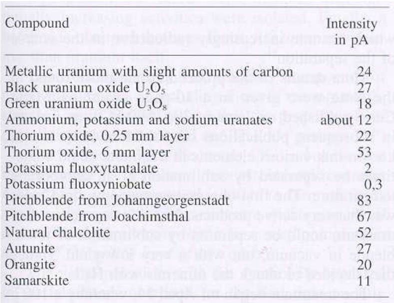
On February 11, 1898, Marie Curie started a systematic search for elements and compounds capable of imparting electrical conductivity to air. She tested all samples at hand or borrowed them from various collections; materials consisted of ‘a large number of metals, salts, oxides and minerals" [5]. The complete list was later recapitulated in her doctoral dissertation [6]:

"1. All metals and metalloids commonly available and a few rarer and pure compounds from Mr. Etard’s collection at the Ecole de Physique et de Chimie Industrielles de la Ville de Paris.

2. The following rare substances: gallium, germanium, neodymium, praseodymium, niobium, scandium, gadolinium, erbium, samarium and rubidium (samples lent by Mr. Demarcay); yttrium, ytterbium together with a new erbium (samples lent by M. Urbain).

3. A large number of rocks and minerals."

Marie Curie’s first Note was presented at the Academy by her former Professor Gabriel Lippman (1845-1921), who was also member of the examination board of her Thesis in 1903 and a Nobel Prize Laureate in 1908 for the invention of a method of colour photography. Curiously, the paper does not bear the name of Pierre Curie, without whom the experiments would not have been possible. Part of the data reported in [5] are shown in Table 1.



Compound	Intensity in pA
Metallic uranium with slight amounts of carbon	24
Black uranium oxide U_2O_5	27
Green uranium oxide U_3O_8	18
Ammonium, potassium and sodium uranates	about 12
Thorium oxide, 0,25 mm layer	22
Thorium oxide, 6 mm layer	53
Potassium fluoxytantalate	2
Potassium fluoxyniobate	0,3
Pitchblende from Johanngeorgenstadt	83
Pitchblende from Joachimsthal	67
Natural chalcolite	52
Autunite	27
Orangite	20
Samarskite	11

With two exceptions, all compounds contained U or Th, and the intensity was roughly proportional to the fraction of the element in the compound. This behaviour had already been observed by Becquerel, who concluded that the property of making air conducting was specific for the element uranium, independently of its state or chemical combination. An important step towards this conclusion was the measurement of uranium metal, which produced the same emission as uranium salts, but with greater intensity owing to the higher concentration of the element. The recognition of the proportionality between the uranium content and the intensity was the première of *radioanalytical chemistry.*

However, the result of the second sample in Table 1 was confusing. It was convenient to take the intensity of metallic uranium as a reference. Even if the metal prepared by Moissan by reduction of uranium oxide with carbon was not quite pure, as indicated, it was difficult to understand why the black U_20_5 exhibited a 10% higher intensity. This odd behaviour appears also, still unexplained, in Marie Curie’s thesis and has been properly clarified by R. L. Wolke *[7].*

Marie Curie emphasized that all minerals which were active contained the element uranium or, as she had found independently of Schmidt, the element thorium. The most important result was that pitchblende, a massive variety of uraninite ($U0_2$), is nearly 4 times more active than metallic uranium, and chalcolite (also known as metatonbernite), $Cu(UO_2)_2(PO_4)_2$, 6-8 H_20, is about twice as active as the metal. The Note’s key sentence actually states how Marie Curie will pursue her research: "*This fact is quite remarkable and suggests that these minerals may contain an element much more active than uranium (itself)*".

Initial evidence in favour of this hypothesis appears in the next sentence, since Marie Curie knew how to prepare chalcolite. "*I have prepared chalcolite by the Debray method with pure products; this artificial chalcolite is not more active than other uranium salts*". Marie Curie then concluded that the unknown element exists only in the uraniferous minerals which are more active than metallic uranium. A third mineral, autunite, a phosphate of Ca and $U0_2$, also exhibited an anomalous, although less spectacular, activity that was higher than in uranium.

Interestingly enough, the samples investigated included two potassium compounds with feeble activities. Marie Curie assigned the activity of potassium fluoxytantalate and niobate to the elements Ta and Nb. Neither of these elements has long-lived natural radio-isotopes. It may therefore be assumed that Marie Curie unknowingly discovered the radioactivity of ^{40}K. The potassium oxyfluotantalate in question was probably Marignac’s salt, $K_4Ta_4O_5F_4$, with a specific ^{40}K activity of 4 Bq g On the other hand, Marie Curie did not report a signal from rubidium (^{87}Rb) or from samarium (^{147}Sm), which have much higher specific activities (88 Bq g^{-1} for RbCl and 122 Bq g^{-1} for Sm_2O_4. This may be due to the lower energies of the emitted radiations but, in any case, the activities would be close to the limit of detection.

At this stage, further search for the identity of the supposed element became a matter of paramount importance and urgency. Pierre Curie himself was fascinated by Marie's findings; on March 18 he abandoned his own research projects and joined his wife in the adventure.

When Marie Curie's Note reporting the radioactivity of thorium appeared, Schmidt hastened to announce to the French scientists that *he* was the discoverer of the phenomenon and published the following month in the *Comptes Rendus* a one-page summary of his original paper [3].

3. The second Note: July 18, 1898 [8]

The title of Marie Curie's second publication was signed with Pierre Curie (as first author) and announced that the search for "the element much more active than uranium" was successful: "On a new substance, radio-active, contained in pitchblende". This was also the first appearance of the word *radio-active.* The Curies omitted the hyphen the following year. The Note was presented at the Academy by Henri Becquerel who, surprisingly, was not associated with the two most important publications of the Curies.

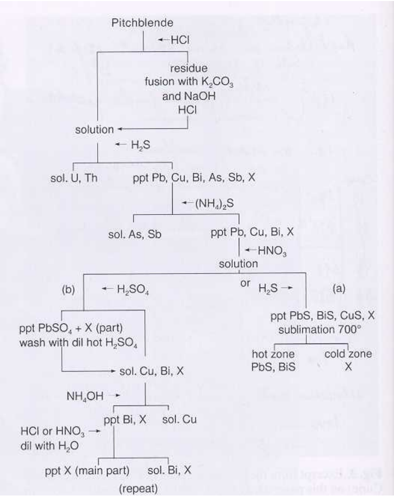
It is noteworthy that research on radioactivity now turned from physics to chemistry. Neither Pierre nor Marie Curie were chemists and they had to ask for assistance. The collaboration of Gustave Bémont (1867-1932) is acknowledged in a footnote. Bémont was "Chef de Travaux", i.e. in charge of practical training for the students at the Ecole Municipale de Physique et Chimie Industrielles in Paris. The handwriting of Bémont appeared in the Curies' notebooks on May 5, 1898 [9]. Bdmont was associated with the discovery of radium, as co-author of the third Note of the Curies [10]. This paper suggests that he was a close collaborator during the period May to December 1898. Apart from that, however, he remained the "forgotten man of radioactivity".

The chemical analysis of pitchblende was neither particularly difficult nor innovative. The method followed the classical scheme of analysis given by Fresenius and could be carried out in cookbook fashion. Besides, pitchblende had already been analysed long before and the material was known to contain several metals such as Cu, As, Sb, Bi and Pb.

However, the Curies were now able to follow the procedure by a new and highly sensitive method, involving the measurement of radioactivity of the element searched. In a biography of Pierre Curie published in 1924 [11], Marie Curie explained: "The method we have used is a new one for *chemical research based on radioactivity.* It consists in separations performed with the ordinary procedures of analytical chemistry, and in the measurement of the radioactivity of all compounds separated. In this way, one can recognize the chemical character of the radioactive element sought; the latter is concentrated in fractions which become increasingly radioactive in the course of the separation".

More details of the procedure than those found in the Note were given in a 10-page report by Marie Curie published on January 30, 1899 [12], as well as in subsequent publications on polonium [13]. It was known that various elements in a mineral could sometimes be separated by sublimation at an appropriate temperature. The first observation made by the Curies was that very active products, 20-fold more active than uranium, could be separated by sublimation of pitchblende in vacuum, but with a very low yield. Hence they decided to attack the minerals with HCl.

The treatment began on April 14, whereby a 100 g sample of pitchblende was first ground and then subjected to the action of HCl. The mineral was "two and a half times more active than uranium", and thus probably from Joachimsthal (Table 1) [14]. Insoluble residues remained which were generally very active, and these were solubilized in acids after fusion with a mixture of potassium carbonate and sodium hydroxide.



The Curies and Bémont used several procedures in parallel runs, although only one is described in the Note. The flow chart shown in Figure 4 has been drawn up in accordance with the procedures described in references [8] and [12].

The treatment of the acidic solution with H_2S was already a significant step, since the precipitate of sulfides was more active than that of the residual solution. The latter contained U and Th, although the occurrence of Th in the mineral was not previously mentioned. The activity contained in the sulfides was insoluble in ammonium sulfide, and thus could be separated from As and Sb. The residual insoluble sulfides were dissolved in HNO_3 after addition of H_2S0_4, the activity was partially carried by lead sulfate. Eventually, the activity was found in the last fraction, that contained only bismuth. At each step the activity increased, and the inactive fractions were discarded.

The separation of the active substance from Bi by wet methods was found to be difficult. The Curies used fractional precipitation by addition of water to the acidic solution. The fractions which precipitated first were those that carried the greater part of the activity.

On June 6, Marie Curie precipitated sulfides from a nitric acid solution containing Pb, Bi and the active substance. She underlined the result in her notebook: the solid was *150 times more active* than uranium. The same day, Pierre Curie heated the precipitate in an evacuated tube. In the course of heating at several hundred degrees, the bismuth and lead sulfides remained in the hottest part of the tube, while a thin black layer of powder carrying the activity condensed in the cooler part at 250-300 C. That day, the Curies succeeded in preparing a sample 330 times more active than uranium.

By repeating the various steps, fractions with continually increasing activities were isolated. Finally, a batch was obtained that was about *400 times more active* than uranium itself.

The Curies carefully verified that "compounds of nearly all elements... including those of the rarest substances" were not active and that the property of radioactivity was limited to U and Th and "perhaps Ta".

The Note ends with the words "*We...believe that the substance we recovered from pitchblende contains a heretofore unknown metal, similar to bismuth in its analytical properties. If the existence of this new metal is confirmed, we propose that it be named polonium in honor of the native land of one of us*".

The name polonium with the symbol Po appeared in the laboratory notebook for the first time on July 13, in the handwriting of Pierre Curie (Figure 3). Prior to polonium, four elements were given names referring to countries: germanium, ruthenium, gallium and scandium. But the designation "polonium" had a provocative significance, since as a state Poland had virtually disappeared in 1795, being parcelled out between Prussia, the Austrian Empire and Russia. At the time when Marie Curie had left her homeland, a Grand Dukedom of Warszaw had been constituted, but politically it was a mere dependence of Russia.

The announcement of the existence of a new element that remained invisible and could be identified solely on the basis of its emission of "uranic rays" was unique in the history of chemistry. It had become customary that no such claim was considered valid until a pure substance had been isolated, the atomic weight of the element determined and its spectral lines measured. Eugene Demarcay (1852-1904), who was a recognized expert in spectroscopy, examined the spectrum of the new element but, to the disappointment of the Curies, could not distinguish any new characteristic line apart from those of impurities. The authors admitted that "...this fact does not favour the idea of the existence of a new metal".

The mass equilibrium ratio ^{238}U to ^{210}Po is 1.34 X 10^{10}. Pitchblende may contain as much as 80% of uranium [14]. Accordingly, the 100 g sample used by the Curies may have contained of the order of 6 ng of Po. Even with a 100% separation yield, such amounts were naturally invisible and far below the sensitivity limits of spectroscopical detection attainable at that time. One of the largest preparations of polonium in the early history of radioactivity was carried out by Marie Curie and Andre Debierne (1874-1949), who started with several tons of the residue from the sulfuric acid extraction of uranium ore. Their final product weighed about 2 mg and probably contained about 0.1 mg (0.45 Ci) of polonium. The spark spectrum of this material revealed for the first time a few lines characteristic of the element, 12 years after its discovery [13]. The largest reported amount of natural ^{210}Po is about 40 Ci. It was extracted from a residue of 37 tons of lead oxide from the Port Hope radium refinery [15].

The isolation of polonium from uranium had thus been accomplished, although the Curies were unaware of the genetic relationship between the two elements. They considered the whole material as a mixture. They also knew nothing at the time of the phenomenon of radioactive decay. In this sense, it was a matter of chance since the separations were performed within 3 months, which was a short time with respect to the 138-day half-life of polonium. It was only a few years later that the Curies noticed with astonishment and great perplexity that polonium was progressively disappearing. Moreover, the Curies could not imagine that they were dealing with *tracer* amounts of the new element. By simple reasoning, the substance in the ore that was more active than uranium itself must obviously be present in very small amount, since it had not yet been found. However, it was not evident at first that this amount was below the limit of any chemical means of detection.

Without knowing it, the Curies had invented the use of carriers; in the final step the polonium was effectively *carried* by bismuth. The words "tracers", "chemistry at the tracer level", "carriers", are terms that arose from the pioneer work of the Curies and that introduced the classical vocabulary of radiochemistry.

The assignment of polonium in the Periodic Table of the elements does not seem to have preoccupied the discoverers. At the time, the terminal part of the Table was unoccupied beyond $_{83}$Bi, with the exceptions of $_{90}$Th and $_{92}$U. In principle, the new element could have fitted into any of the vacant positions.

It appeared remarkable that the polonium was concentrated in the bismuth fraction. This affinity led Marie Curie to consider that the two elements had similar chemical properties. Radionuclides are, however, often carried physically by any kind of solid. As pointed out by Wolke [7], polonium hydroxide, $PoO(OH)_2$, and polonium sulfide, PoS, are co-precipitated at trace concentrations with $Bi(OH)_3$ and insoluble sulfides, but this behaviour does not necessarily imply a strong chemical resemblance.

Nevertheless, it seemed reasonable to assume that polonium should be situated not too far from Bi in the Periodic Table. The insolubility of the sulfide as well as other properties of the elements in groups 1, 2, 17 and 18 [in the IUPAC version of the Periodic Table] preclude for polonium the positions 87 Eka-Cs, 88 Eka-Ba, 85 Eka-I and 86 Eka-Xe. Rare earths are not carried by sulfides, and this further excludes the 89 Eka-La position.

In a Faraday Lecture given before the Chemical Society of London in 1889, Mendeleev expounded on still undiscovered elements, and predicted that "in the series which contains Hg = 204, Pb = 206 and Bi = 208 ...there exists an element analogous to tellurium which ... can be described as *dvi-tellurium*" [16]. He anticipated the properties of the element Z = 84 that were later confirmed when larger amounts of polonium became available. Nevertheless, Mendeleev had made a mistake: the element which he anticipated was *dvi-selenium* or *eka-tellurium.*

As will be pointed out in the Epilogue, the persistence of Marie Curie in considering that the chemistry of Po should be closely similar to that of Bi turned out to be detrimental to the discoverers of the element.

The second Note of the Curies also ended the short story of polonium for several years. Now the Curies were on the verge of another, much more important, discovery. All the same, Marie Curie conserved a sentiment of ownership for polonium, which she defended with emotion, vehemence, and even with aggressiveness. In one sense, she was right, owing to the role of her polonium in the discoveries of the atomic nucleus, the neutron, artificial radioactivity and fission.

4. The third Note: December 26, 1898 [10]

The title of the third Note, like the second one, announced the discovery of a radioactive element and bore one additional word: "On a new *strongly* radioactive substance contained in pitchblende".

The notebook entries of the Curies were interrupted from July to November 11th 1898. Polonium had been found in the sulfide fraction precipitated from the soluble part of the pitchblende. Even before their announcement of the discovery of polonium, the Curies probably pursued the analysis of the residual solution, suspecting that the latter might contain still another radioactive substance. They focused their attention on the sulfides because it was easier to search for the activity concentrated in this material. Bismuth and other metals whose sulfides were insoluble were the carriers of Po. This role was now ensured by barium, which fortunately was present in sufficient amount in the mineral.

Few details on the procedure appear in the Note. The Curies began with a recapitulation of the properties of Po in order to emphasize the strikingly different nature of the "new radio-active substance". It behaved like "nearly pure barium": it was not precipitated by hydrogen sulfide or ammonium sulfide, nor by ammonia. On the other hand, the sulfate and the carbonate were insoluble in water. The high solubility of barium chloride in water, and its insolubility in concentrated HCI and in alcohol proved to be of particular importance in the concentration of the radioactive sub stance. Finally, the spectra showed the characteristic pattern of pure barium.

The authors concluded that the new radioactive substance must be contained in the barium. They advanced three reasons in favour of this hypothesis First, Marie Curie verified that "normal" barium was inactive. For this purpose, she undertook fractional crystallizations on 50 kg of commercial barium chloride until a final amount of 10 g was obtained an which showed no activity. Accordingly, the radioactive substance was *not* barium.

The second proof was the progressive concentration of the radioactive substance in the course fractional crystallization of barium chloride. The first hydrated chloride was 60 times more active than uranium. Upon dissolution in water, followed by partial precipitation with alcohol, the solid was much more a active than the solution. The Curies pursued the progressive concentration until the activity of the chlorides was *900 times* higher than that of uranium. At this point they had to cease the experiment because lack of material. They concluded that the solubility the chloride of the radioactive element must be low than that of barium chloride. Later, the precipitation of chlorides from water-alcohol mixtures was replaced by the more efficient procedure of crystallization of chlorides or bromides from water alone.

The third and last argument was the decisive one. This time, the spectroscopic test was successful. Demarcay observed in the spectrum of the radioactive barium chloride several lines which could not be assigned to any known element [17]. The wavelength the most intense line was 3814.8 A (a recent value 3814.42 A). The intensity of the line increased with the radioactivity of the sample from "very weak" the first sample up to "notable" for the sample with 900-fold activity of that of uranium. The authors conclude "We think this is a very serious reason to attribute it [the line] to the radio-active part of our substance. The various reasons which we have enumerated lead us to think that the new radioactive substance contains a new element, to which we propose to give the name *radium*".

This name, followed by a question mark, appeared in the notebook for the first time on December 18. The chemical behaviour of the new substance was much easier to determine than that of polonium. Clearly, it belonged to the family of the alkaline earths, for which the best fingerprint is the insolubility of the sulfates. Indeed, the statement "radium sulfate more soluble in concentrated H_2S0_4 than barium sulfate" also with a question mark, was written by Pierre Curie.

Besides the spectroscopic analysis, a second "official" proof for the existence of radium would have been the determination of the atomic mass. Marie Curie was aware of this exigence. She determined the amount of chlorine present in the radiferous anhydrous barium chloride and compared it to that of a batch of ordinary barium chloride. The calculated atomic masses of the radioactive material were *always slightly higher,* but still within limits of errors. Obviously, the amount of radium was too low to change the apparent atomic mass of Ba, 137.4 (now 137.327).

From the equilibrium mass ratio of ^{238}U to ^{226}Ra, and assuming a quantitative separation yield, it is calculated that the amount of radium present was, at the most, of the order of 30 µg.

The determination of the atomic mass of radium became an obsession for Marie Curie that lasted for years. In successive trials, as the radiferous barium became more and more enriched in radium, the measured atomic mass increased. Eventually, on July 21, 1902 she published the value of 225± 1 (now 226.0254). This astonishingly close value was obtained with a self-luminous sample of 0.120 g of $RaCl_2$ with a Ra:Ba ratio of 10^6, which was *one million times* more active than uranium [18]. Now radium could be definitely placed in the 88 Eka-Ba position in the Periodic Table.

The first preparation of radium, as noted by the Curies, "contains very likely a high proportion of barium; nevertheless, the radio-activity is considerable. Hence the radio-activity of radium must be *enormous*". The authors now compared the radioactivity of the four known radio-elements: U, Th, Po and Ra. The last two left an image on a photographic plate within half a minute, U and Th only after exposure times of several hours.

When the Curies ran out of material, they were aware that the concentration procedure of radium in radiferous barium should be pursued. They were also aware that vast amounts of raw material would be necessary in order to prepare "visible" or at least much larger quantities of Po and Ra. In a footnote of the publication reporting the discovery of radium, the authors thanked Professor M. Suess of the University of Vienna, also Corresponding Member of the French Academy, for his intervention with the Austrian Government. The latter offered to the Curies free of charge 100 kg of a uranium-free residue from the treatment of the Joachimsthal pitchblende [14]. The residue still contained Po and Ra. "This shipment will greatly facilitate our research" concluded the authors.

With the foregoing discovery of polonium, the Curies had oddly enough begun with the most difficult part of the work. In its own right, radium had outstanding advantages; its concentration in the ore was about 5000 times greater than that of polonium; it is a true chemical analogue of barium, from which it can be separated and it could be readily assigned to its correct place in the Periodic Table.

The Nobel Prize for Physics was attributed in 1903 to "H. A. Becquerel for his discovery of spontaneous radioactivity and to P. and M. Curie for their joint researches on the radiation phenomena". At this time, no mention was made of the discoveries of polonium and radium. Thus it is perhaps significant that Becquerel travelled alone to Stockholm; in the meantime, the Curies were allegedly occupied with their teaching duties.

In 1911, Marie Curie received the Nobel Prize in chemistry "for her services to the advancement of chemistry by the discovery of the elements radium and polonium, by the isolation of radium, and for the study of the nature and compounds of this remarkable element".

5. Epilogue

L. Badash stated that the "great discoveries of 1898 [of Po and Ra]... served to renew interest in radioactivity. The moribund subject was resurrected and interest now never flagged until radioactivity merged into atomic physics and evolved into nuclear physics" [19].

During the year 1898, the discovery of uranic rays also stimulated research outside of France. Julius Elster and Hans Geitel in Wolfenbuttel (Germany) published a first paper on November 11, 1898 [20]. Their work was mainly directed toward verifying the first (and erroneous) interpretations of the phenomenon of radioactivity, but they also confirmed the "very interesting discovery" of the Curies, since they succeeded in the chemical isolation of a strongly active substance from Joachimsthal minerals. Stefan Meyer (1872-1949) in Vienna began a study of the rays of radium a few months after the discovery of the element. Like Suess, he aided the Curies in obtaining the shipment of residues of uranium ore.

When Ernest Rutherford (1871-1937) left the Cavendish Laboratory in Cambridge for McGill University in Montreal in August 1898, he had already shown that the uranic rays had two components, which he named for " convenience" the *a* and *ß* rays. This discovery was published in January 1899 [21].

In America, the Becquerel experiments were reviewed in April 1898 [22]. Interestingly enough, the discovery of radium was announced in the January 28, 1899 issue of *Scientific American,* scarcely one month after the publication had appeared in the *Comptes Rendus* [23]. The translation came to the attention of Bertram Borden Boitwood (1870-1927), one of the first Americans interested in radioactivity, as early as 1898 [19].

It was, however, in Germany that the discovery of the radioelements had the strongest impact. In List, near Hannover, the chemical Company E. de Haen produced uranium for the glass industry, using extracts from the Joachimsthal ore. On July 14, 1899, the proprietor of the plant, E. de Haen himself, stated in a short note that he had succeeded in separating radium; indeed, a batch produced by him was active enough to exhibit self-luminosity, a property observed for the first time [24]. The interest of de Haen was obviously commercial, since the radium preparations were offered for sale. Owing to the facilities of his factory, he was able to prepare strongly active sources more rapidly than the Curies, who treated 20 kg batches with their own hands.

Friedrich Oskar Giesel (1852—1927), chief chemist at a quinine factory in Braunschweig, was the "scientist" occupied with the treatment of the residues of the de Haen factory. Shortly after the publication of the discovery of Po by the Curies, he found that the residues of the treatment of the uranium minerals, rather than the ore itself, were also a convenient source for the extraction of radioactive substances. He followed the Curies' procedure and separated a substance that did not behave like Po but had properties *closer to those of barium.* Hence, Giesel had nearly anticipated the discovery of radium by Pierre and Marie Curie.

The material available to Giesel was much more active than that of the Paris team. Within a few years, he was producing radium and offering it at a nominal price to anyone who wanted it. He confirmed de Haen's observation of the self-luminosity of radiferous Ba, in particular of the non-hydrated salts, which was so intense that one could read by the bluish light emitted by radiferous barium bromide. In his first publications on August 9 and 24, 1899, Giesel described original observations, such as the colour change of active barium salts due to self-irradiation, the increase in the activity of radium during the first weeks following recristallization (i.e., the in-growth of active deposit), and noted the differences in the absorption of the rays emitted by Ra, "which traverse considerably a silver Thaler" and of those of Po that were completely absorbed by thin metallic foils [25-26]. He also observed the disappearance of the activity of the precipitated lead sulfides within the course of a few months.

Meanwhile, the Curies had begun the extraction of radium from several tons of residues from the Joachimsthal ores. The Vienna Academy of Sciences had intervened with the Austrian Government (the proprietor of the mine) to sell the material to the Curies at a low price, which Pierre and Marie paid from their own money. The tedious processing of the residues under primitive conditions has been popularized in various biographies, novels and movies. The problems encountered, the reasonings and the procedure are described in Marie Curie's thesis. This document has been analysed didactically by Wolke [7]. The sentence which summarized the success of the endeavour stated "we succeeded ... in extracting from ...thousands of kilograms of starting material a few decigrams of products".

André Debierne, a former student of Pierre Curie, had agreed to take over the large scale processing of the pitchblende residues. Advised by the Curies, he began looking for other active substances in the tailings. Logically, he selected the substances which did not precipitate with H_2S, but were precipitated completely with ammonia. This choice ought to exclude Po and Ra. In October 1899, he announced that he had discovered a new fraction which had properties of titanium but with an activity 100000 times higher than that of uranium [27].

Later he found that the new substance more closely resembled thorium, but it was also much more active than this element. Since it behaved in a manner different from that of the known radioelements, Debierne claimed the discovery of *actinium* [28].

In fact, Debierne's assertion was false. To our knowledge, it appears that his substance was a mixture of two thorium isotopes, ionium (^{230}Th) and radio-actinium (^{227}Th) with little, if any, of the element now known as actinium [29]. The error was quite understandable, however, owing to the extreme complexity of the mixture of natural radionuclides. The real discoverer of actinium was probably Giesel.

Marie Curie was aware of the importance of proving that Ra and Po were *elements.* She recognized that the demonstration would be much easier for Ra. For that reason, she worked untiringly to obtain radium in ever higher purity and in visible amounts in order to determine the atomic mass. It is understandable that, initially, the scientific community included sceptics, among whom were leading authorities. Even in 1906, Lord Kelvin argued that radium was a molecular combination of lead and helium, because both elements appeared spontaneously in radium.

As for Po, doubts and controversy followed the euphoria of the discovery. Apart from the activity of the "pseudo-bismuth" considered by the Curies as polonium, no other argument could be advanced in favour of its existence. Nearly four years after the discovery, the Curies stated that "experiments over several years show that the activity of U, Th, Ra and probably Ac ... does not change with time". On the other hand, they recognized that polonium progressively lost its activity. Hence they complemented the previous assertion by a footnote [30] indicating that "this substance [Po] is a kind of active bismuth; *it has not yet been proven that it contains a new element, ...* it does not emit radiations deviated by a magnetic field [which was wrong] and does not produce induced radioactivity [which was correct]". The doubts of the Curies could not have been expressed at a worse moment: Willy Marckwald in Berlin had claimed the discovery of a new radioelement in the bismuth fraction from a pitchblende residue, which *he was able to separate from bismuth.* One of the harshest controversies in the early history of radiochemistry followed.

Marckwald had received from the chemical firm Richard Stahmer in Hamburg several kilograms of residues from the treatment of uranium ores. Upon being asked to search for radioactive substances, he extracted about one per cent by weight of a very active bismuth oxide chloride, BiOCl. After several abortive trials to precipitate the active constituent, he succeeded with the help of electrolysis [31]. The first metal which plated out was quite active, leaving most of the Bi in solution. In a still simpler experiment, he dipped a Bi foil into the solution of the active BiOCl; a thin film deposited spontaneously and after a few days the entire activity was separated from Bi. This represented the goal which had been unsuccessfully pursued by the Curies.

In a following publication, on October 10, 1899, Marckwald showed that the radioactive substance was more electronegative than antimony, and suggested that it might belong to the S-Te group, rather than to the Sb-Bi group [32]. This proposal was upheld by the vacant Eka-Te position in the Periodic Table. The resemblance of the radioactive substance with Te was further confirmed by the reaction of SnCL with the active BiOCI, which produced brownish flakes that carried most of the activity. Furthermore, the latter did not appear to decrease with time. Therefore *it could not be polonium.* Encouraged by these observations, Marckwald named "provisionally" the new substance *radiotellurium* [33].

That was too much for Marie Curie, who felt outraged by the new name given to *her* polonium. On December 12, "Frau" Curie reacted vigorously to Marckwald’s assertions [34]. Obviously, she regretted the misfortunate (she wrote *misinterpreted)* words of the footnote to which "Mr. Marckwald gave a significance that they did not bear". She said that the Curies had never intended to suggest that polonium was anything more than activated bismuth, but only that they had not yet been able to prove that it was a new element. She was convinced that Marckwald’s radio-tellurium, which was carried by bismuth and emitted easily absorbed rays, was identical with polonium. The only difference would be that "Mr. Marckwald’s polonium did not suffer a decrease of activity". She warned that only long-term measurement over months had shown the decay of the activity of polonium, and she defied Marckwald to prove the constancy of the activity.

Neither of the two authors was completely right. The chemical properties of polonium were undoubtedly those of Eka-Te. On the other hand, Frederick Soddy (1877-1956) showed that Marckwald’s statement on the constancy of the activity of his radio-tellurium "seems to be physically irreconcilable with our present knowledge of the nature of *a* rays..." [35]. He concluded that "most men of science will agree with Mine Curie in protesting against a new name given to it [to polonium]". Soddy added that "the practice of rechristening well-known bodies and sending them back to the country of their origin with new names and as new discoveries, ... seems to be prevalent among German organic chemists. If adopted in the case of the radioactive bodies, [it] would lead to the recognized number being exactly doubled". At the time, the situation was already sufficiently confused as a result of the ever-increasing number of new radioactive entities found in uranium and thorium ores.

The controversy subsided when Marckwald reported in January 1905 that radiotellurium decayed with a half-life of 139.8 days [36]. One year later, Marie Curie announced with great satisfaction that she had found a half-live value of 140 days with sources of polonium prepared by her usual method of fractional hydrolysis of a solution of bismuth sub-nitrate, as well as with samples obtained by the "very convenient" method used by Mr. Marckwald [37]. "This provides definitive proof that the body studied by Mr. Marckwald under the name *radiotellurium* is identical with polonium."

Eventually, in a final publication dated June 1st 1906, Marckwald surrendered, proposing to replace in the future the name of radiotellurium by polonium [38]. However, before the sentence announcing the decision, he insisted once again that the chemical properties of the radioelement were identical with those of Eka-Te. Marckwald concluded by quoting from Shakespeare’s "Romeo and Juliet":

What’s in a name? that which we call a rose
By any other name would smell as sweet.

Nonetheless, Marckwald was vexed and remained unconvinced that the original polonium of the Curies was not a mixture of several radioelements. For her part, Marie Curie was still reluctant to acknowledge the conclusions of Marckwald that polonium was a homologue of tellurium: "By no means can one pretend that polonium exhibits the reactions of tellurium rather than those of bismuth ... To know its properties, pollonium should be available in weighable amounts ... " [37]. Five more years of work were necessary to reach this goal [13].

The discoveries of 1898 were the premises of a long story which ended by the mid-1930’s, when the first generation of radiochemists eventually unravelled the natural radioactive families.

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