THE TROUBLED STORY OF POLONIUM: AN EARLY CONTROVERSY IN RADIOCHEMISTRY

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Last November the worldwide media reported what may have been the first murder by radioactive poisoning in "a case that has all the mystery and menace of a political thriller" [1, 2]. The victim, 43-year-old Alexander V.Litvinenko, a former Russian KGB officer and outspoken critic of the Kremlin, died on November 23, 2006 in London from the ingestion of polonium, spreading alarm across the capital as police discovered traces of radiation in three places that the former spy had visited. On his deathbed Litvinenko accused Russian President V.V.Putin of a "barbaric and ruthless" [1] murder.

Polonium 210, an isotope of one of the rarest elements in the earth's crust, is a difficult-to-produce substance about 250 million times as toxic as cyanide that emits 5,000 times more α-particles than the same amount of radium. It is dangerous when breathed, ingested, or injected. A by-product of the nuclear industry, it cannot be detected by normal radiation-detection devices so it should be relatively easy to smuggle across borders.

This mysterious poisoning incident raises still debated questions on the availability of polonium [3], its lethal amount [4], its transfer to the victim [5], and the contamination of people and surroundings [6]. It also prompts us to examine a first conflict in the young science of radiochemistry that arose more than a century ago when the discovery of polonium by Pierre and Marie Curie was questioned.

In 1898, two years after (Antoine) Henri Becquerel (1852-1908) discovered "uranic rays," research on radioactivity shifted from physics to chemistry. In that year Pierre (1859-1906) and Marie Curie (1867-1934) discovered two elements, in invisible quantities, that they identified solely by the emission of the new radiations (Fig.1-3). In a first publication (April 12, 1898), Marie Curie recorded that certain uranium-bearing minerals, in particular, pitchblende (Fig.4), emitted more rays (*i.e.,* were more *active*) than metallic uranium and concluded, "this fact is quite remarkable and suggests that these minerals may contain an element much more active than uranium itself…" [7]. Three months later, on July 18, 1898, this hypothesis was confirmed in a second publication, "On a new substance, radio-active, contained in pitchblende" [8]. From a hundred-gram batch of the mineral, the team separated by fractional hydrolysis and vacuum sublimation of sulfides (Fig.5) a compound that accompanied bismuth during the procedure and carried an activity 400 times more intense than that of uranium: "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" [8] (Fig.6).

Figure 1. The 1903 Nobel Prize in Physics was awarded one half to Antoine Henri Becquerel (left) "for his discovery of spontaneous radioactivity" and the other half to Pierre Curie (middle) and Marie Curie, née Sklodowska (right) "for their joint researches on the radiation phenomena discovered by Professor Henri Becquerel" (Courtesy, the Nobel Foundation)

Figure 2. Postage stamps honoring Becquerel and the Curies are numerous. Here are a few. From left to right. 1. France. Henri Becquerel. Issued February 4, 1946. Scott Catalogue No. B202 (2 + 3 fr.). 2. Monaco. Pierre and Marie Curie. 90th Anniversary of the Discovery of Radium. Issued July 14, 1988. Scott Catalogue No. 852 (150 fr.). 3. France. Marie Curie with Evaporating Dish with Radium Glow. Issued October 23, 1967. Scott Catalogue No. 1195 (60 c.). 4. Cameroon. Pierre Curie with Symbols for Radium and Polonium. Issued October 10, 1986. Scott Catalogue No. C336 (500 fr.). 5. Afars and Issas. Marie Curie and Radium. Issued August 23, 1974. Scott Catalogue No. C86 (10 fr.). 6. Poland. Marie Curie and Radium. Issued March 5, 1992. Scott Catalogue No. 3081 (3500 zl.). 7. San Marino. Marie Curie and RaA (Polonium). Issued April 21, 1982. Scott Catalogue No.1025 (60 l).
(All Stamps, Courtesy, Foil A.Miller)

Figure 3. Pierre and Marie Curie in their laboratory located in the basement of the Parisian École de Physique et Chimie Industrielles, rue Lhomond (1898).
(Courtesy, Archives Curie et Joliot-Curie)

Figure 4. Czechoslovakia postage stamp publicizing Joachimstahl (Jachymov), the area in Bohemia where pitchblende was first discovered and which was the source of the ore used by the Curies. It features a radioactive burst, the sun, and atom symbol. Issued August 29, 1966. Scott Catalogue No. 1413 (60 h.). (Courtesy, Foil A.Miller)

Figure 5. Sublimation experiment of a mixture of bismuth, lead, and polonium sulfides, handwritten by Pierre Curie. The symbol "Po" appears for the first time in the Curies' laboratory notebook on July 13, 1898, five days before the publication of the discovery.
(Courtesy, Hélène Langevin)

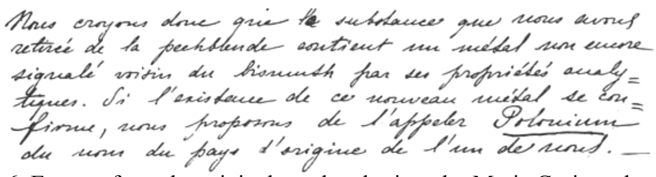
Nous croyons donc que la substance que nous avons retirée de la pechblende contient un métal non encore signalé voisin du bismuth par ses propriétés analytiques. Si l'existence de ce nouveau métal se confirme, nous proposons de l'appeler Polonium du nom du pays d'origine de l'un de nous. —

Figure 6. Excerpt from the original text handwritten by Marie Curie and presented to the Académie des Sciences by Gabriel Lippmann (1845-1921; 1908 Nobel physics laureate). (Courtesy, Archives Académie des Sciences)

Figure 7. French postage stamp issued in 1998 to commemorate the 100th anniversary of the discovery of radium with a reproduction of Marie Curie's handwritten inscription, "Le Radium."
(Courtesy, Jean-Pierre Adloff)

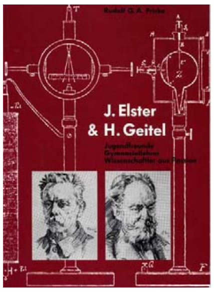

Figure 8. Cover page of Rudolf Fricke's monograph on Julius Elster and Hans Geitel, "youthful friends, high school teachers, scientists by passion"

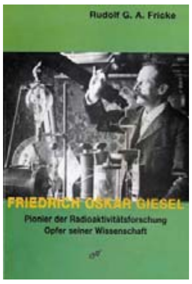

Figure 9. Cover page of Rudolf Fricke's monograph on Friedrich Oskar Giesel, "Pioneer in research in radioactivity, victim of his dedication to science"

This assertion about the element was unique in the history of chemistry. None of the criteria required at the time were available: isolation of a pure compound, determination of the atomic weight, and spectral analysis of the supposed element. Eugène Demarçay (1852-1904), the discoverer of europium and an eminent authority on spectroscopy, could not distinguish any new characteristic lines apart from those of the impurities. The Curies admitted, "this fact does not favor the idea of the existence of a new metal" [8]. The amount of polonium in the sample was a few nanograms (10^{-9} g.), obviously in at the time.

On December 26, 1898 the Curies announced the discovery of a second "strongly" radioactive substance similar to barium [9]. Its activity in a final batch was 900 times that of uranium. This time spectroscopic analysis [10] revealed lines that could not be assigned to any known element: "We think this is a very serious reason to attribute it [the most intense line] to the radioactive part of our substance. The various reasons that 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" [9] (Fig.7).The spectroscopic proof for the existence of radium eclipsed the discovery of polonium. From 1899 on, P.Curie pursued investigations on Becquerel rays, and M.Curie worked on the chemical treatment of uranium ores. Her obsession was the determination of the atomic weight of the new element. On March 28, 1902 she obtained the value of 225.9 (A recent figure is 226.0254) from 120 mg. of pure radium chloride, one million times more active than uranium [11].

The Curies' discoveries provoked an immediate interest in Germany. Julius Elster (1854-1920) and Hans Geitel (1855-1923), science teachers at the *Gymnasium* (high school) in Wolfenbüttel near Braunschweig (Brunswick), learned of the discovery of polonium a few days after it was reported in Paris. They immediately began to treat a sample of uranium ore taken from their collection of minerals, and two months later they announced: "We were able to confirm the very interesting discovery of Mr. and Mrs. Curie, namely that substances, which to a high degree have the property of conferring electrical conductivity to air, can be separated chemically from Joachimsthal pitchblende" [12].

Elster and Geitel maintained an avid interest in physics and over a period of 40 years published about two hundred papers on electric conductivity of gases, atmospheric electricity, the photoelectric effect, and radioactivity [13] (Fig.8). In radioactivity (about 40 publications) their work dealt for the most part with properties of Becquerel rays and atmospheric radioactivity. They were the first to suggest that radioactivity could not result from a chemical reaction, but rather from a transformation on the atomic scale, while the Curies favored the absorption of cosmic radiations by heavy atoms such as uranium and thorium. Experiments performed by the German team showed that the Curies' hypothesis was "highly improbable." In a letter of December 30, 1898 to his friend, Charles-Edouard Guillaume (1861-1938; 1920 Nobel physics laureate), Pierre Curie acknowledged: "Elster and Geitel are certainly persons who most thoroughly investigated the question of uranic rays (and that in a foreign country!), and I would not be surprised if they soon produced excellent results" [14].

The two German friends reported the discovery of polonium to Friedrich Oskar Giesel (1852-1927), Chief Chemist at the quinine factory Büchler in Braunschweig [15] (Fig.9). Fascinated by the finding, Giesel decided to search for the new element, a prospect that became even more challenging after the discovery of radium. Thus began the career of the prolific, leading German figure in the new field of radioactivity – a competitor and controversialist of the French team. Giesel realized immediately, like Pierre Curie and at about the same time, that residues left after the processing of uranium ores for the glass industry were a cheap and abundant waste that ought to contain the new elements. In this respect Giesel was very fortunate. He acquired 10 kg. of uranium-free residues from the chemical Company E. de Haën, located in List near Hanover. In his spare time he followed the procedure described by the Curies and separated a strongly radioactive substance that, however, did not behave like polonium and bismuth but instead accompanied barium. Using a further supply of 200 kg. of residues, Giesel confirmed the result and nearly anticipated the discovery of radium, but in the meantime the Curies' report was published.

On their side, in September, 1898 the Curies, who were close to running out of pitchblende, turned to the Austrian Government for the purchase of residues from the uranium mines in Joachimsthal. They received free of charge a first batch of 100 kg. of residues, followed by 1000 kg. one year later. The Curies regularly purchased the material, and by the time of Pierre Curie's death (1906) they had processed about 23 tons of residues with an estimated content of 12 g. of radium. This figure may appear important. However, the Curies' activities were largely surpassed by the German production of radium. By mid-1899 Giesel had acquired 1000 kg. of residues from List and was offering radium at a nominal price to anyone who wanted it. His products were much more active than those of the Paris team. Thus he was the first to observe, among other phenomena, the self-luminosity and color change of radium salts, the luminescence of Sidot blende excited by α-rays, and the physiological effects of the radiations.

Giesel began an epistolary collaboration with the French couple. Thirteen letters addressed to the Curies from December, 1899 to November, 1902 are known; unfortunately the replies were lost in the destruction of the Büchler plant during World War II [14]. Meanwhile, Willy Marckwald (1864-1942), *Privatdozent* at the Universität Berlin, a newcomer to the field, announced the discovery of radiotellurium, supplanting polonium. One of the harshest controversies in the early history of radiochemistry, which lasted four years, ensued.

Further work on polonium did not appear for several years. The Curies still had doubts about the element whose existence they had announced hesitantly. Apart from the activity of the "pseudo-bismuth" considered as polonium, they could advance no other argument for its existence. In January, 1902, nearly four years after the discovery of the element, they stated: "Experiments over several years show that the activity of uranium, thorium, and radium does not change with time, - and they complemented this assertion in a footnote, - on the contrary, polonium makes an exception; its activity decreases slowly with time. This substance is a kind of bismuth; it has not yet been proven that it contains a new element" [16].

The Curies could not foresee how detrimental this last sentence would be with respect to their discovery of polonium. They continued: "It differs in several aspects from the other radioactive substances: it does not emit radiations that are deflected in a magnetic field [which was wrong] and does not produce induced activity [which is correct]" [16]. Giesel was quickly convinced of the authenticity of radium, but like the Curies, he doubted the existence of polonium. Alluding to non-materialist theories of the origin of radioactivity [17], he asked the Curies: "Are you also inclined to believe that the concept "polonium" does not correspond to a material reality, but results merely from a displacement of ether?" [18]. At the 1900 International Congress of Physics in Paris, the Curies also wondered: "Which is the source of energy of the Becquerel rays? Should it be sought inside the radioactive bodies themselves or outside?" [19]. Giesel also observed the unexpected decrease in the radioactivity of polonium. Furthermore, spectral analysis performed in Germany did not reveal any line of the supposed element.

The element polonium became even more suspicious after the discovery of *induced radioactivity,* that is, the process by which any substance in the close vicinity of radium became radioactive itself [20]. Giesel then supposed that polonium was nothing other than "inducedly activated bismuth." He had dipped a freshly split fragment of bismuth into a solution of radium bromide. After a few days it was intensively radioactive, giving off α-radiation, as expected for polonium [21]. He was joined by the Curies: "One may wonder if radioactivity which is apparently a spontaneous phenomenon is not merely an induced effect in certain substances" [22].

Pierre Curie himself, five years after the announcement of the discovery, admitted: "Of all strongly radioactive substances, radium is the only one for which it could be proven unequivocally that it contains a new element" [23]. The assignment of the position of the new element in the periodic table does not seem to have preoccupied the discoverers. In 1898 the terminal part of the table was unoccupied beyond ${}_{83}Bi$ with the exceptions of ${}_{90}Th$ and ${}_{92}U$. The new radioactive element followed bismuth along the chemical treatment; thus it could be assumed that the two elements bore similar chemical properties and should be close neighbors in the table. The only plausible position was that of $_{86}$Eka-Te, overlooked by the Curies, who had no reason to suppose that it was the missing analogue of tellurium; as far as they knew, it had the properties of bismuth. In a Faraday Lecture before the Chemical Society of London Dmitrii Ivanovich Mendeleev (1834-1907) expounded on still undiscovered elements and predicted "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" [24]. In this reasoning Mendeleev anticipated the properties of element 84 but mistook *dvi-tellurium* for *eka-tellurium*.

At the end of 1901 Marckwald obtained from the chemical firm Richard Sthamer in Hamburg several kilograms of residues from the treatment of Joachimsthal uranium ore with the goal of separating radioactive products. He extracted about one percent by weight of very active bismuth oxychloride (BiOCl) from the material. After several abortive attempts to separate the radioactive component from bismuth by precipitation as attempted by the French team, he succeeded by using electrolysis: The first metal that plated out was quite active, leaving most of the bismuth in solution. In a still simpler experiment Marckwald dipped a polished bismuth rod into a hydrochloric acid solution of the mixture; a thin film deposited spontaneously, and after a few days, the entire radioactive component was separated, leaving the bismuth solution almost inactive [25]. This was the goal vainly pursued by the Curies.

In a further investigation Marckwald showed that the radioactive substance was more electronegative than antimony, suggesting that it belonged to the Se-Te group rather than to the Sb-Bi group [26]. He succeeded in separating the activity from tellurium: "By processing 6 kilos of bismuth oxychloride derived from about 2000 kg of pitchblende, I have recovered 1.5 g. of radiotellurium. The metal was converted to the chloride, and the tellurium was precipitated with hydrazine hydrochloride. The tellurium is still quite active at this point, but a single additional precipitation suffices to yield almost inactive tellurium. The filtrate contains the active substance, still contaminated by bismuth, tin, and some tellurium" [26].

After these experiments Marckwald's reasoning seemed sound: chemically, the element could not be the Curies' polonium; physically, the activity of his element remained constant, therefore it could not be polonium. Encouraged by these observations, Marckwald "provisionally" named the new substance "radiotellurium" [26].

Marckwald's "radiotellurium" was too much to accept for Marie Curie, who possessed a visceral sense of ownership for polonium and felt outraged by the new name given to her element. "Frau" Curie reacted vigorously in German to Marckwald's assertions [27]. Obviously, she regretted the misfortunate (She wrote *misinterpreted*) words of the unlucky footnote [16], to which "Marckwald gave a significance that they did not bear." She said that the Curies 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 radiotellurium that was carried by bismuth and that emitted easily absorbed rays was identical with polonium. The only difference would be that "Mr. Marckwald's polonium did not suffer a decrease in activity" [27]. She warned that only long-term measurements over months had shown the decay of the activity of polonium; one of her polonium sources had taken 11 months to lose half of its activity, and she defied Marckwald to prove the constancy of the activity.

Neither of the two authors was completely correct. The chemical properties of polonium were undoubtedly those of Eka-Te. In early 1904 Frederick Soddy (1877-1956; 1921 Nobel chemistry laureate) commented: "Prof. Marckwald states that the activity of his body [radiotellurium] is permanent… this seems to be physically irreconcilable according to our present knowledge of the nature of α-rays… It is to be hoped that Prof. Marckwald will give some account of the measurements by which he has concluded that the activity of radiotellurium is constant… Most men of science will agree with Mme. Curie in protesting against a new name given to polonium… The practice of rechristening well-known bodies and sending them back to the country of their origin with new names and as new discoveries, which seems to be prevalent among some German organic chemists, would, If adopted in the case of radioactive bodies lead to the recognized number being exactly doubled" [28].

The situation was already confused enough with the increasing number of new radioactive species found in uranium and thorium ore residues. Marckwald reacted immediately, protesting against the insinuation and saying that he had already begun measurements before Soddy's suggestion [29]. The controversy subsided in January, 1905 when Marckwald reported that radiotellurium decayed with a half-life of 139.8 days [30]. One year later Marie Curie announced with great satisfaction that she had found a half-life of 140 days with five specially prepared polonium sources, one prepared by her usual method of fractional precipitation and the other four by the "very convenient" method used by

Mr.Marckwald: “This provides definitive proof that the body studied by Mr.Marckwald under the name *radiotellurium* is identical with polonium” [31].

Eventually, in a final publication (June 1, 1906), Marckwald surrendered, proposing to replace the name radiotellurium by polonium in the future [32]. However, before the sentence announcing the decision, he insisted once again that the chemical properties of the radioelement were identical with those of eka-tellurium. He 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” [33]. Nevertheless, Marckwald was vexed and was unconvinced that the original polonium of the Curies was not a mixture of radioactive species. For her part Marie Curie was still reluctant to acknowledge 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 polonium should be available in weighable amounts” [31].

The polonium quarrel paralleled a second French-German dispute, this time between André Debierne (1874-1949) and Giesel [34]. Both parties claimed the discovery of a third radioactive element in uranium ores, actinium for Debierne and emanium for Giesel. The argument that lasted several years hampered the otherwise deferent attitude of Giesel towards the Curies. The only way to settle the controversy was to compare the properties of the two supposed elements. After Giesel had repeatedly and vainly invited Debierne to provide a sample of actinium and sent to Marie Curie part of his own product, he decided to take the initiative and bring his emanium to Paris. This was the first and last encounter between the French and German protagonists. The confrontation did not resolve the dilemma, and Giesel deplored the stingy, condescending Parisian reception. Further experiments confirmed the identity of the two radioactive products, and the story ended in 1907. Giesel stated, “I shall not permit a disparagement of the discoveries that I made entirely of my own” [35], but most historians now recognize Debierne as the discoverer of actinium. At least Giesel has his own *post mortem* recognition with the engraving “Entdecker des Aktiniums” on his tombstone in Braunschweig.

Of course, the Curies were not happy with the suspicions. In a letter of September, 6, 1905 to Waldemar Voigt (1850-1919) [36] Pierre Curie complained: “Madame Curie and I, as well as Mr. Debierne, were very offended by the latest publications of Mr. Giesel and Prof. Marckwald. There is only one radioactive element in the series of the Rare Earths, and this was discovered by Debierne, who named it actinium. Mr.Giesel isolated the same element several years later than Debierne; he called it emanium and asserted that Debierne's “actinium” did not exist. Nonetheless, we had informed Mr. Giesel right from the beginning that his material was the same as that obtained by Debierne. Such behavior coming from a man of such standing as that of Mr. Giesel is most unfortunate…. Moreover, there is at present only one strongly radioactive element that can be precipitated by hydrogen sulphide. Mr. Marckwald named his material “radiotellurium;” this product has exactly the same properties as those of polonium, and we see no reason for striking out the name of the first strongly radioactive element that we discovered. Arguments on questions of priority involve discussions that are unworthy of men of science and we greatly regret that Messrs. Giesel and Marckwald oblige us to partake in such matters” [14].

After the quarrel with Marckwald, Marie Curie was still not content. The isolation and identification of polonium as an element remained to be accomplished. This was expected to be much more difficult than for radium. The concentration of polonium in uranium ore is 4,000 times less than radium, *i.e.,* about 0.04 mg. per ton. The treatment of vast amounts of residues of uranium ores could not be pursued in the miserable shed where the Curies alone separated enough radium for the determination of the atomic weight of the radioelement.

In 1904 the French industrialist Émile Armet de Lisle, whose factory in Nogent, near Paris, would soon provide radium for medical use, began to collaborate with Marie Curie. De Lisle benefited from Marie Curie's technical suggestions, and in return she profited from his large technical facilities. Paul Razet, a chemist from Pierre Curie's *École*, investigated various methods for the concentration of polonium. The selected procedure required several workmen at the Nogent plant; after nearly one year Razet obtained about 200 g. of a poloniferous material 3,500 times more active than uranium [37]. Marie Curie and André Debierne pursued the concentration and eventually separated a few milligrams of a very active substance containing 1 to 2 percent polonium, *i.e.,* about 0.1 mg. of the element. The spectral analysis revealed seven new rays, of which four could be attributed with certainty to polonium. This was the definitive proof of the element, 12 years after its discovery. The authors concluded: “We intend to measure the spectra again after the decay of polonium to ascertain the identification of the rays. It is also hoped to see the spectrum of the element formed in polonium. According to theory it could be lead” [38].

By 1910 three radioactive families of radium, uranium, and thorium were partially unravelled, but the final (stable) product of the radium series was still in question. Sir Ernest Rutherford (1871-1937; 1908 Nobel chemistry laureate), one of the leading figures in radioactivity, wondered if the formation of lead in the decay of polonium could be proven. He immediately acknowledged: "Apart from the interest of obtaining a weighable quantity of polonium in pure state, the real importance of the present investigations of Mme. Curie lies in the probable solution of the question of the nature of the substance in which the polonium is transformed… It is a matter of very great interest and importance to settle definitively if polonium changes into lead… The outlook is very promising that the experiment of Mme. Curie and Debierne will settle this question conclusively" [39].

The Curies' polonium was ^{210}Po, the main natural isotope of the element, decaying with a half-life of 138.376 days to ^{206}Pb, the stable end product of the radium family [40]. A number of other isotopes appear in the natural decay series with short half-lives, precluding chemical studies. The tiny amount of polonium recovered from uranium ores or from aged radium salts (0.2 mg. of polonium per gram of radium at equilibrium) is still insufficient for the usual chemical research. Until 1944 all the work on the element was conducted at the trace level. With the advent of nuclear reactors with intense neutron fluxes the transmutation of bismuth to polonium became economically feasible [41]. The reaction is currently used for the production of milligram quantities of polonium, and the radioelement is no longer extracted from uranium ores. The chemical behavior of polonium and its compounds is that expected for an eka-tellurium element, as Marckwald anticipated with his "radiotellurium".

One of the difficulties of working with ^{210}Po is its high specific activity of 1.66×10^{11} Becquerel per mg. The intense radiation of milligram samples quickly decomposes most organic complexing agents and even the solvents. Crystal structures of solids are quickly destroyed or altered. For this reason it would be desirable to work with an isotope of lower specific activity. Bismuth bombarded with protons in a cyclotron produces a mixture of ^{208}Po (half-life, 2.898 years) and ^{209}Po (half-life, 102 years). The latter would reduce radiation effects about 600-fold, but the yield in terms of weight would be far below the μg (10^{-6} g.) scale.

^{210}Po decays by emission of 5.3 MeV α-particles that are readily absorbed in thin walls. Sealed sources are harmless and because of that are not detected with the usual control systems. The handling of polonium requires special precautions. In terms of radiotoxicity it is one of the most noxious radioelements in cases of internal contamination, *i.e.,* when polonium is ingested or inhaled in the organism. Acute or deadly accidents were reported when intense polonium sources became available in research laboratories [42]. A related case occurred at the Curies' laboratory in 1941. Sonia Cotelle, a former technician of Marie Curie's, inhaled a lethal amount of polonium dispersed after the explosion of a distillation vessel. She died two weeks later. Irène Curie, who was standing behind Sonia, was shielded by the body of her collaborator and felt no immediate harm.

Marie Curie could not foresee that polonium would lead to the discoveries of the neutron (by James Chadwick in 1932), artificial radioactivity (by Frédéric Joliot and Irène Curie in 1934), and nuclear fission (Otto Hahn and Fritz Strassmann in 1939), and thus to the emergence of the nuclear era of mankind. Mixtures of polonium and beryllium were commonly used neutron sources, especially to initiate a fission chain reaction in nuclear reactors and nuclear weapons.

In concluding his 1903 Nobel physics lecture, delivered belatedly on June 6, 1905, Pierre Curie wondered: "Whether mankind benefits from knowing the secrets of Nature, whether it is ready to profit from it or whether this knowledge will not be harmful for it" [43]. He had experienced wittingly on himself the biological effects of radium [44], and he foresaw that its prolonged action could lead to death: "It can even be thought that radium could become very dangerous in criminal hands" [43].

As we have seen at the beginning of our article, Pierre Curie's fear was recently confirmed in the poisoning of Alexander V. Litvinenko, with polonium in place of radium. Marie Curie could never have imagined this dreadful application of *her* polonium.

References and Notes[1]

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3. Various commercial devices containing polonium are available for suppression of static electric charges and dust and in smoke detectors. They contain a few thousand Becquerels, an amount permitted in the United States by the U.S. Nuclear Regulatory Commission (The Becquerel, a unit of radioactivity, is defined as one disintegration per second). According to "United Nuclear," a firm that sells radioactive materials, "You would need 15000 of our polonium-210 needle sources at a total cost of about $1 million to have a toxic amount".

[1] Сохранён авторский вариант библиографического описания. – *Прим.ред.*

4. The lethal dose is estimated to be about 1 microgram (10^{-6} g). Larger amounts of polonium may be kept in nuclear research laboratories and nuclear power plants. Substitution and handling is extremely risky. Also, see Amato, I. How Polonium Poisons // *Chem. Eng. News,* December 4, 2006, *84* (49), 15; Fine, N. Polonium Poisoning // *Chem. Eng. News,* January 29, 2007, *85* (5), 4.

5. Andrei Lugovoy and Dmitrii Kovtun, both former agents of the FSB (the successor organization of the KGB) sat with Litvinenko in the Millennium Hotels's Pine Bar as he drank a cup of tea containing polonium, traces of which were found in the cup (Murphy, K.; Rotella, S. A tall, elusive Russian and a cup of poison tea // *Los Angeles Times*, February 10, 2007.

6. Traces of polonium were identified at the localities of the poisoners and the victim.

7. Sklodowska Curie, M. Rayons émis par les composés de l'uranium et du thorium. *Compt. rend.* 1898, *126,* 1101–1103.

8. Curie, P.; Curie, M. Sur une substance nouvelle radio-active, contenue dans la pechblende. *Compt. rend.* 1898, *127,* 175–178. The word "radio-active," coined by Marie Curie, appears here for the first time. The Curies dropped the hyphen the following year. Before polonium, the first natural element to be discovered by its radioactivity, four elements were given names referring to countries: germanium, ruthenium, scandium, and gallium. However, "polonium" had a provocative significance because Poland had disappeared as a state in 1795, being parceled out between Prussia, the Austrian Empire, and Russia. At the time that Marie Curie had left her homeland (1891), a Grand Duchy of Warsaw had been constituted, but politically it was a mere dependency of Russia. The last radioactive element (and also the last element) discovered in nature is francium, found in 1939 by Marguerite Perey (1909–1975), Marie Curie's laboratory assistant (Adloff, J.-P.; Kauffman, G.B. Francium (Atomic Number 87), The Last Discovered Natural Element // *Chem. Educator* 2005, *10*, 387–394; DOI 10.1333/s00897050956a).

9. Curie, P.; Curie, M.; Bémont, G. Sur une nouvelle substance fortement radio-active, contenue dans la pechblende // *Compt. rend.* 1898, *127,* 1215–1217. Chemist Gustave Bémont was a collaborator of the Curies from May to December, 1898. He was *Chef de travaux*, *i.e.,* in charge of the practical training of students at the Parisian *École de Physique et de Chimie Industrielle* while Pierre Curie was a Professor there. His actual role in the discovery has not been elucidated, and he remains the "forgotten man of radioactivity."

10. Demarçay, J. Sur le spectre d'une substance radioactive // *Compt. rend.* 1898, *127,* 1218.

11. Curie, M. Sur le poids atomique du radium // *Compt. rend.* 1902, *135,* 161–163.

12. Elster, J.; Geitel, H. Versuche an Becquerelstrahlen // *Ann. Phys. Chem*. 1898, *66*, 735–740. The pitchblende mines near Joachimstahl (now Jachymov in the Czech Republic) belonged to the Austro-Hungarian Empire until 1919. They were the primary source of uranium ores for the production of radium (Zeman, A.; Benes, P. St. Joachimsthal Mines and Their Importance in the Early History of Radioactivity // *Radiochim. Acta* 1995, *70/71*, 23–29).

13. Fricke, R.G.A. *J.Elster & H.Geitel;* Döring Druck 3300: Braunschweig, 1992). An excellent, exhaustive account of the life and achievements of the two scientists.

14. Blanc, K. *Pierre Curie: Correspondances réunies et annotées;* EDP Sciences: Paris (in press). A collection of about 500 annotated letters sent and received by Pierre (and sometimes Marie) Curie as well as related letters and documents during the period 1879–1906.

15. Fricke, R.G.A. *Friedrich Oskar Giesel*; A.B. Verlag: 30302 D-Wolfenbüttel, 2001.

16. Curie, P.; Curie, M. Sur les corps radioactifs // *Compt. rend.* 1902, *134,* 85-87.

17. Crookes, W. Sur la source de l'énergie dans les corps radioactifs // *Compt. rend.* 1899, *128,* 176-178.

18. Giesel, F., letter to P. and M. Curie, January 12, 1900 // Blanc, K. *Pierre Curie: Correspondances réunies et annotées;* EDP Sciences: Paris (in press).

19. Curie P.; Curie, M. Les nouvelles substances radioactives et les rayons qu'elles émettent // *Reports of the International Congress of Physics*; Gauthier–Villars: Paris, 1900; Vol. III, p.79-106.

20. Curie, P.; Debierne, A. Sur la radioactivité induite provoquée par les sels de radium // *Compt. rend.* 1901, *132,* 548–551. Rutherford discovered that the transfer of radioactivity was due to a radioactive gas (radon) released by radium (Rutherford, E. Transmission of Excited Radioactivity // *Bull. Am. Phys. Soc.* 1901, *2*, 37-43).

21. Giesel, F. Über Polonium und die inducirende Eigenschaft des Radiums // *Ber.* 1903, *36*, 2368–2370.

22. Curie, P.; Curie, M. Sur la radioactivité provoquée par les rayons de Becquerel // *Compt. rend.* 1899, *129,* 714–716.

23. Curie, P. Recherches récentes sur la radioactivité // *J. Chim. Phys.* 1903, *1*, 409-443.

24. Mendeleev, D. The Periodic Law of the Chemical Elements // *J. Chem. Soc*. 1889, *55*, 634; Goldwhite, H. Mendeleev's Other Prediction // *J. Chem. Educ*. 1979, *56*, 35.

25. Marckwald, W. Über das radioactive Wismuth (Polonium) // *Ber.* 1902, *35*, 895-896.

26. Marckwald, W. Das radioactive Wismuth (Polonium) // *Phys. Z.* 1902/3, *4,* 51-54.

27. Curie, "Frau" M. Über den radioaktiven Stoff "Polonium" // *Phys. Z.* 1902/3, *4,* 234-235.

28. Soddy, F. Radio-tellurium // *Nature* 1904, *69*, 347.

29. Marckwald, W. Radio-tellurium // *Nature* 1904, *69*, 461.

30. Marckwald, W. Über das Radiotellur IV // *Ber.* 1905, *38*, 591–594.

31. Curie, M. Sur la diminution de la radioactivité du polonium avec le temps // *Compt. rend.* 1906, *142,* 273–276. Pierre Curie presented this note to the Académie des Sciences on January 29, 1906. He died in an accident on April 19, 1906.

32. Marckwald, W. Über Polonium und Radiotellur // *Phys. Z*. 1906, *7,* 369–370.

33. Shakespeare, W. *Romeo and Juliet*; Act II, Scene 2, lines 43-44.

34. Adloff, J.-P. The Centenary of a Controversial Discovery: Actinium // *Radiochim. Acta* 2000, *88*, 123-127.

35. "Eine Schmälerung meiner vollständig unabhängig gemachten Entdeckungen werde Ich nicht zulassen" (Giesel, F. Über Aktinium-Emanium // *Phys. Z.* 1904, *5*, 822-823).

36. Pierre Curie was befriended by Voigt, Professor of Physics at the Universität Göttingen, author of the theory of tensors. Both scientists had a common interest in symmetry in physical phenomena. Voigt had interpreted piezoelectricity discovered by Pierre Curie (Seymour, R.B.; Kauffman, G.B. Products of Chemistry: Piezoelectric Polymers: Direct Converters of Work to Electricity // *J. Chem. Educ.* 1990, *67*, 763–765).

37. Razet, P. Sur la concentration du polonium // *Le Radium* 1907, *4*, 135-139.

38. Curie, M.; Debierne, A. Sur le polonium. *Compt. rend.* 1910, *150,* 386-389. One of the largest reported amounts of natural polonium is about 9 mg., extracted from 37 tons of residues (Moyer, H.V. 1956 *Polonium* USAEC, TID-5221, Oak Ridge).

39. Rutherford, E. Properties of polonium // *Nature* 1910, *84*, 491-492.

40. By the end of 1911 more than 30 radioactive species had been identified. In the nomenclature introduced by E. Rutherford and H. Geiger "Radium F" referred to the present ^{210}Po (Rutherford, E.; Geiger, H. Transformation and nomenclature of the radioactive emanations // *Phil. Mag.* 1911, *22*, 621-629). The nomenclature was in use at the Curie laboratory until the 1950s (Joliot-Curie, Madame. *Les radioéléments naturels*; Hermann: Paris, 1946).

41. In a neutron flux bismuth is converted to radioactive ^{210}Bi, which decays with a 5-day half-life to ^{210}Po.

42. Rona, E. Laboratory Contamination in the Early Period of Radiation Research // *Health Phys*. 1979, *37*, 723-727.

43. Curie, P. Radioactive substances, especially radium. Nobel Lecture, June 6, 1905 // Nobel Foundation. *Nobel Lectures: Including Presentation Speeches and Laureates' Biographies: Physics 1901–1921;* Elsevier: Amsterdam-London-New York, 1967; pp 73–78; http://nobelprize.org/nobel_prizes/physics/laureates/1903/pierre-curie-lecture.pdf (accessed March 2007).
44. Becquerel, H.; Curie, P. Action physiologique des sels de radium // *Compt. rend.* 1901, *132,* 1289–1291.