

FINDING EKA-IODINE: DISCOVERY PRIORITY IN MODERN TIMES*

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Missing Members of the Periodic Table and the Discovery of the Heaviest Halogen

The International Union of Pure and Applied Chemistry (IUPAC) currently recognizes 111 elements for the modern periodic table (1). The discovery timeline for most of these elements can be traced clearly to a specific person or group; however, many elements discovered in modern times have a more nuanced history. Over fifty elements were discovered in the 19th century as advances in technology allowed many of Mendeleev's predictions to be proven, but the unexpected discovery of the noble gases and the difficulty placing the large numbers of rare earth elements on the periodic table cast doubt on periodic table dogma. This changed when H. G. J. Moseley's (1887-1915) measurements established that only seven elements—43, 61, 72, 75, 85, 87, 91—between hydrogen and uranium remained unknown at the start of the 20th century (2, 3). With few unknown elements remaining, the probability of discovering and naming a new member of the periodic table dropped drastically. Competing discoveries appeared for all of Moseley's "missing" elements, and the validity of some claims remained controversial for decades. The race to characterize element 85 provides perspective on how history often influences the course of and credit for scientific discovery.

Element 85, eka-iodine in Mendeleev's terminology, was chemically characterized in 1940 by postdoctoral researcher Dale R. Corson (b. 1914), graduate student

Kenneth R. MacKenzie (1912-2002), and Emilio Gino Segrè (1905-1989). The three Lawrence Berkeley Laboratory (LBL) workers reported the results of bombarding a sample of bismuth (^{209}Bi) with 32 MeV α particles in the newly completed 60-inch cyclotron in Berkeley (4-7). Under these conditions, a radioactive sample with a half-life of 7.5 hours was formed, a phenomenon they attributed to ^{211}Sb . Unlike many reports of element discovery in the early 20th century, the LBL researchers were able to perform chemical analyses on and to track the radioactivity of the samples during the treatments (6). While Corson, MacKenzie, and Segrè are widely recognized as the discoverers of element 85 (8), through the 1920s several discoveries of eka-iodine were claimed, disputed, and refuted—some proclaimed that eka-iodine could not even exist. (Table 1).

Searching in Sand: Alabamine and Dekhine

Because families of elements possess similar physical properties, early investigators assumed that eka-iodine would have a low melting point, be diatomic in its elemental state, and form salts with metals. Since elements at heavier periods often resemble their $n+1$ and $n-1$ neighbors more than their lighter congeners, eka-iodine also was expected to be radioactive and metallic like polonium. Searching for eka-iodine in substances that contained other halogens was deemed a reasonable strategy for finding the missing element by early researchers.

Table 1: Reports on the Existence of Element 85

Researchers	Country	Date	Isotope	Technology	Source	Proposed Name	Name Derivation
Loring (58, 59)	UK	1922	None ^{a, b}	Numeric analysis	NA	-	-
Loring (60, 61)	UK	1925	NIS ^b	Cathodic X-ray determination	Pyrolusite	-	-
Hahn (62)	Germany	1926	None ^b	Chemical separation	²²⁸ Ra	-	-
Friend (63)	UK	1926	NIS ^b	Chemical separation & cathodic X-rays	Dead Sea water Brazilian monazite and sea water	-	-
Allison (11)	USA British	1931	NIS	Magneto-optic ^c	Brazilian monazite and sea water	Alabamine	Alabama
Toshniwal (64)	India	1933	NIS ^b	UV spectra	Iodine	-	-
De (16)	British India	1937	NIS	Chemical separation ^d	Travancore monazite	Dakin	Dacca
Anderson (65)	Denmark	1938	NIS	Chemical separation ^e	Various	-	-
Hulubei & Cachois (22, 23)	France	1936					
Loring (66)	UK	1939	218	Decay X-rays	²²² Rn	Dor	world peace
Minder (34)	Switzerland	1940	218	α -particle detection ^f	²²² Rn	Helvetica	Switzerland
Corson, Mackenzie & Segrè (5)	USA	1940	211	Cyclotron & α -particle detection	²⁰⁹ Bi + a	Astatine	Unstable
Valadares (30)	Portugal	1941	218	Decay X-rays	²²² Rn	-	-
Minder & Leigh-Smith (35)	Switzerland & UK	1942	216	α -particle detection ^g	²²⁰ Rn	Anglo-helvetium	England & Switzerland
Karlik & Bernert (33)	Austria	1942	218	α -particle detection	²²² Rn	Viennium	Vienna
Karlik & Bernert (36)	Austria	1943	216	α -particle detection ^h	²²⁰ Rn	Viennium	Vienna
Karlik & Bernert (38)	Austria British	1943	215	α -particle detection	²¹⁹ Rn	Viennium	Vienna
De (17)	India	1947	NIS	Chemical separation ^d	Travancore monazite	Dakhine	Dakin & eka-iodine

NIS – no isotope specified

- a. Authors claimed element 85 could not exist
- b. Authors report not being able to isolate element 85
- c. Magneto optical method was later discredited (12, 13).
- d. Element 85 instability inconsistent with reported properties.
- e. Assumption that element 85 would separate chemically like iodine was disproven by chemical tests on synthetic samples from Berkeley (5).
- f. Disproved by Karlik and Bernert (32, 33).
- g. Disproved by Karlik and Bernert (40, 67).
- h. Disproved by Seaborg (68).

The first widely popularized claim of the existence of eka-iodine was reported by Fred Allison (1882-1974) at the Alabama Polytechnic Institute. Allison had developed a new method of analyzing materials, which he called the magneto-optic method (9). The technique relied on a time delay in the Faraday Effect, the rotation of plane-polarized light or other electromagnetic radiation passing through certain substances by an applied magnetic field. By rapidly switching the field on and off, he suggested that systematic patterns were observed because the time delay changed the position of the light passing through the analyte. Such a phenomenon would result in related substances giving a series of patterns that could be delineated even when contained in a single matrix. Allison examined typical halogen-containing compounds including sea water, hydrohalic acids, apatite, and Brazilian monazite sand, a source of rare earth minerals. In 1931, Allison's first paper describing eka-iodine was followed by a second article in 1932, where he suggested the name alabamine (Ab), derived from Alabama, for the new halogen (10, 11). He also described chemical tests on the alabamine, but its presence was determined exclusively by the magneto-optic effect. There is no time delay in the Faraday effect however (12), and in 1935, MacPherson demonstrated that Allison's observations were due to imperfections in the machine (13). So alabamine ceased to exist except on periodic tables and textbooks, where it remained well into the 1940s.

Rajendralal De, a little known Indian chemist working in Dacca (now Bangladesh, then British India), read about Allison's results prior to the revelation about the flawed methodology. De studied at the Kaiser Wilhelm Institute in Germany with Otto Hahn and Lise Meitner in the 1920s, when they had unsuccessfully looked for missing elements. Monazite sand such as Allison used in his research can be found in numerous locations around the world. The sand is occasionally found on beaches, such as in the Brazilian monazite which was used by Allison, or as Travancore monazite from the Travancore state in southwestern British India, which was studied by De. Like Allison, De believed monazite sand would contain substantial quantities of eka-iodine. He subjected the sand to a battery of chemical treatments and found a black, sublimable substance (14), which he identified as eka-iodine and named dakin (15, 16). Without access to an original copy of the 1937 pamphlet, De's reasoning for the name dakin cannot be deduced; however, it is probably named for Dacca, which sometimes is spelled Dhaka.

De published an update on his work in 1947 (17) and a review of his studies in 1962 (18). In his 1947 pamphlet, De proposed a revision to his original name. He recommended the name dekhine instead of his original suggestion of dakin. He argued that dekhine is evocative in sound to both dakin and eka-iodine. In his article, De describes in detail his method of purifying element 85 from Travancore monazite sand. De's description of eka-iodine is inconsistent with its chemical properties reported by the LBL group in 1940. Although he reports isolating milligram quantities, the intense radioactivity of even the longest-lived, 8-hours isotope of eka-iodine would have precluded De from safely handling the material. No other papers appear to cite De's 1947 pamphlet, and the only reference connecting De's 1947 pamphlet to any source is to Allison's discredited work.

Measuring X-rays Disrupted by Worldwide Conflict

World War I had ended before the search for element 85 commenced in earnest, but both World Wars had a significant influence on research efforts and the people intertwined in its discovery. When Romania entered World War I on the side of the Allies in 1916, a young Romanian, Horia Hulubei (1896-1972, Fig. 1) was selected to go to France and join the Aéronautique Militaire. Hulubei had studied physics and chemistry at the University of Jassy (Romania) until his country entered the war. Moving to France would have a profound impact on Hulubei's life and career. After the war Hulubei returned to Romania but was unable to continue his education until 1922 (19). After graduating from the University of Jassy in

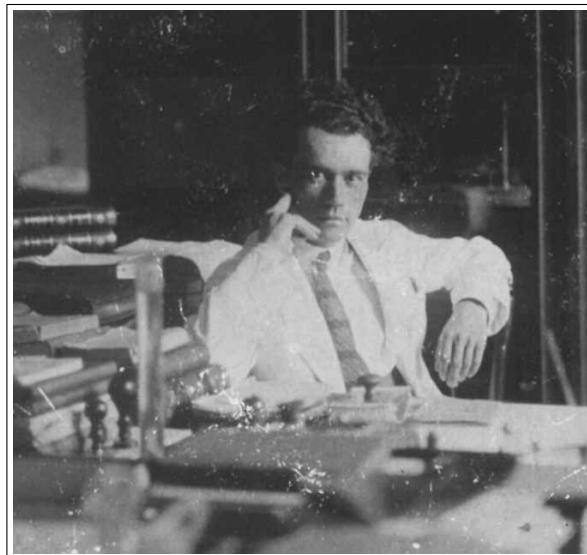


Figure 1. Horia Hulubei

1926, Hulubei returned to France to work for Nobel laureate Jean Baptiste Perrin (1870-1942). There they built a new X-ray laboratory at the Sorbonne (now University Paris VI). In 1928, Yvette Cauchois (1908-1999), who had recently graduated from the Sorbonne, began working in the same group (Fig. 2). As part of her 1933 doctoral thesis work, she constructed a new X-ray spectrograph. The instrument incorporated a curved crystal for splitting the high energy X-rays into a spectrum, which was then recorded on a photographic plate (20). This curved-crystal arrangement greatly improved the resolution of heavy-element spectra and reduced the energy losses in the spectrometer. The unique arrangement was later called the Cauchois spectrometer. The Cauchois arrangement allowed significantly weaker spectra to be studied, and Hulubei and Cauchois first used it to examine noble gases, which had previously eluded X-ray characterization. The Cauchois arrangement is still used for studying the hard X-ray and gamma regions.

In 1925 Rutherford and Wooster had demonstrated that a radioactive isotope of lead, then known as radium B (^{214}Pb), when not excited by an external source of electrons, produced the X-ray spectrum of bismuth (21). According to Rutherford, the X-ray emission occurs because the spontaneous transformation of ^{214}Pb into ^{214}Bi causes “a reorganisation of the external electrons,” which is a similar effect to bombarding the sample with electrons. Rutherford and Wooster were able to show that ^{214}Bi produced the observed X-rays, not the parent isotope. With their improved spectrometer, Hulubei and Cauchois hoped to locate the emission lines of elements like eka-iodine that might be produced during the radioactive decay of radon, which resides in the adjacent slot of the periodic table.

Rather than follow the standard method of exciting a sample placed on the anode of a cathode ray tube, Hulubei and Cauchois placed a radon sample tube in the spectrometer and measured the characteristic X-rays produced when radon daughter elements formed via radioactive decay. In 1934 they described a study in a paper entitled “Nouvelle technique dans la spectrographie cristalline des rayons γ ” (New techniques in the crystal spectrography with gamma rays) (22). In this article, which Perrin



Figure 2. Yvette Cauchois

presented in October, 1934, Hulubei and Cauchois described the multi-line spectra obtained from a ~150-250 mCi (millicurie) sample of radon after 12 hours of exposure. Although eka-iodine is not mentioned in the paper, Hulubei would later cite this publication as the first time they saw its spectral lines. In 1936, Hulubei and Cauchois reported observing a line at 151 X-units (or siegbahn, a unit equal to $\sim 1.0021 \times 10^{-13}$ meters) where the $K_{\alpha 1}$ line for eka-iodine should appear (23-26). These results convinced Hulubei that they might indeed be able to identify more elements produced during the decay of radon. Shortly after publication of the results, their work was delayed

partly due to a temporary lack of radon sources. The rationale for finding eka-iodine in a tube filled with ^{222}Rn was based on nuclear decay to ^{218}Po , which had long been known to α -decay to ^{214}Pb , but the β -decay to eka-iodine was uncertain. Hulubei also considered ^{222}Rn β -decaying to ^{222}Fr , which might α -decay to ^{218}Po .

Prior to the escalation of hostilities, prompted by Germany’s invasion of Poland in September, 1939, Hulubei and Cauchois had reported observing X-ray wavelengths for three spectral lines of eka-iodine, $K_{\alpha 1}$, $L_{\alpha 1}$, and $L_{\beta 1}$ (Table 2), which closely correlated with Moseley’s predicted positions (27). They used the technique they described in 1934, but started looking for new elements in the spectra and repeated the experiments with the spectrometer from Cauchois’ thesis research that had a 40-cm radius curved mica crystal reflecting on the mica 201 plane. In addition the length of the exposure was increased to 24 hours to reveal more spectral lines. The radiation emitted by the radon source included lines of Po—and apparently 85—on the top part of the plate. The emission lines of Pb, Bi, and Po also were produced in the X-ray tube and appeared on the bottom of the plate; these lines were used as an internal standard (28).

Although Hulubei’s and Cauchois’ work would soon be disrupted by the war, Manuel Valadares (1904-1982), who was a student at the Sorbonne with Cauchois, performed some related studies on X-ray spectra of ^{222}Rn at the University of Lisbon in Portugal (29). Valadares had the advantage of a stronger source than his predecessors—600 mCi instead of ~ 100 -200 mCi. Because

he worked in a slightly more limited wavelength range (700-1200 X-units, about 70-120 pm), he could not see the $K_{\alpha 1}$ line. He published his results in 1941, noting that they were suggestive of eka-iodine (30). During the war there was often little communication between scientists, and Hulubei only learned of Valadares' work when he visited Portugal in 1942.

Investigating α -Particles in an Occupied Country

In 1938 Germany annexed Austria, forcing many prominent Austrian scientists to flee the country; however, physicists Berta Karlik and Traude Bernert remained in Vienna to work at the Institute for Radium Research. Karlik (1904-1990) had obtained her Ph.D. from the University of Vienna in 1928; Bernert began working as a volunteer at the institute in the early 1940s (31). In early 1942, Karlik and Bernert (Fig. 3) reported detection of α particles in samples of ^{222}Rn , which they attributed to ^{218}Po because the energies they observed were in agreement with those predicted by the Geiger-Nuttall Rule, about 5.53 cm (32, 33). Karlik and Bernert, who began their studies during the war, were unaware of the creation of artificial eka-iodine in Berkeley when they published their first reports. They demonstrated that measurements of α -particles from ^{222}Rn by the Swiss physicist Walter Minder (1905-1992) and Alice Leigh-Smith, attributed to eka-iodine (34, 35), were likely in error because of contamination.

In 1943 and 1944 Karlik and Bernert, unaware of the ongoing work outside of German territory, were convinced they had identified an isotope of a new element (36-40). They next attempted to detect it in the radioactive decay of ^{220}Rn and ^{219}Rn . It was not until their later papers that they became aware of the Berkeley work (41). Nonetheless, the identification of eka-iodine within the natural decay series was a major goal, independent of the Berkeley group's synthesis of the element. Karlik and Bernert continued studying the formation of element 85 in the decay series, showing that the β -branching of radon to element 87, then α -decaying to 85, was at least a million times less common than α -decay of radon (40).



Figure 3. Berta Karlik (right) and Traude Bernert.

Geopolitics, Scientific Discovery, Resolution, and Nomenclature

All of the investigators involved in the search for eka-iodine were impacted by world politics and war. Segré, who previously isolated element 43 with Carlo Perrier from cyclotron-exposed molybdenum (42), was forced to leave Italy because of anti-Semitic government policies and move permanently to Berkeley. Despite leaving his homeland, Segré was fortunate to join the LBL, which was at the vanguard of nuclear chemistry in the 1940s. When Germany invaded France in 1940, Perrin, Hulubei's mentor and supporter, also was forced to leave France for the United States. In contrast, Cauchois, Hulubei, Karlick, and Bernert all remained in Europe. While Cauchois stayed in Paris during the occupation, Hulubei returned to the University of Bucharest, where he was named rector in 1941. Unfortunately, Hulubei's return to Romania created political problems for him in the immediate postwar years (19). After the Soviet Union occupation of Romania, Hulubei's earlier advancement at the University of Bucharest while Romania was a German ally led to accusations that he supported the Germany-allied Romanian government during the war. The intervention of French Nobel Laureate Jean-Frédéric Joliot-Curie was needed to clear his name (43).

In a 1944 article, Hulubei reported the April destruction of his laboratory from an American bombardment, but also provided a detailed summary of his X-ray studies and other researchers' work on eka-iodine (44). In the summary of his work with Cauchois, combined with Valadares' studies, Hulubei described six lines attributable to element 85, believed to be formed by the β -decay of ^{218}Po that appeared exactly where theory predicted (Table 2). He believed Karlik's work on α particles provided the strong corroborating evidence. In his review, Hulubei suggested the name dor for the new halogen, presumably derived from the Romanian word for "longing," as in longing for peace. He dedicated the work to Perrin, who died in exile in the United States two years earlier. Hulubei was writing in French, which does not include the "-ine" suffix, so the name presumably would have become dorine in English. The name

Table 2: X-ray Spectral Lines for Element 85 Observed by Hulubei, Cauchois, and Valadares

Spectral Line ^{a,b}	Observed (x units)	Observation Accuracy ^c	Observed (eV)	Calculated Value (eV) ^d	Possible Interferences ^e
K _{α1}	151	0.33%	81935.8	81520.0	-
L _{α1}	1082.6	0.05%	11428.3	11426.8	-
L _{β1}	892	0.06%	13870.3	13876.0	Pt
L _{β3}	917	0.05%	13492.2	13474.4	Br
L _{β4}	880	0.06%	14059.5	14058.4	-
L _{β5}	875	0.06%	14139.8	14164.4	Hg, Sr

- a. Valadares' line designations are based on extrapolations from the Bearden compilation (69).
- b. Hulubei and Cauchois reported the K_{α1} line in 1936 (23, 24), and additionally the L_{α1} and L_{β1} lines in 1939 (27). The other 3 lines were reported by Valadares in 1941 (30).
- c. The error in the original data is based on Hulubei and Cauchois' reported ± 0.5 X-units. Note that the error is larger for shorter wavelengths.
- d. K_{α1}, L_{α1}, L_{α1} are calculated values from (69). The last 3 lines were extrapolated because values are not listed for these lines. We calculated the values by obtaining a linear fit to the reported values for Pb, Bi, and Po, and extrapolating a value for element 85. Interpolation would require using Po and Th, which may be less accurate than the extrapolation because of the large gap between values.
- e. Interferences are lines of other elements, which would fall within the reported experimental error. Interferences would be more likely in studies using an external X-ray source and not when observing X-rays created by radioactive decay processes.

dor is also significant because it signaled a shift away from nationalistic names of elements, which had been popular since the late 1800s. The names of elements discovered since Mendeleev's predictions were rife with nationalistic pride: (e.g. gallium, germanium, rhenium, polonium, lutecium, and hafnium).

When World War II ended in Europe in 1945, questions began to emerge in the chemistry community about new elements. Some of the discoveries associated with the Manhattan Project, such as the indisputable existence of plutonium and other transuranium elements, presented the questions: were man-made elements comparable to classical elements, and was synthesizing an element equivalent to discovering an element in nature? The debate on these questions was particularly relevant to the question of discovery priority and the eventual sanctioning of a name for eka-iodine.

At a 1946 conference in Nice, Hulubei presented a summary of his work on element 85 as well as the work of others (45). When the paper was published the following year, Hulubei included a detailed discussion on the detection limits of the technique he and Cauchois had employed. He claimed that they could detect as few as 1,000-10,000 atoms of element 85, based on their experience with detecting ²¹⁴Bi in a matrix produced from ²²²Rn. He contrasted their ability to do such sensitive qualitative detection with quantitative analysis techniques that required $\sim 2.5 \times 10^{11}$ atoms of heavy ele-

ments to reach the sensitivity limits of standard cathode ray tube X-ray techniques.

Friedrich Adolph Paneth (1887-1958), a respected Austrian chemist working in the United Kingdom after being forced to leave Austria, helped establish a new order in chemical nomenclature. In the early 20th century, many isotopes were given element-like names, and statements were often encountered stating that two "elements" were chemically inseparable. This practice was gradually abandoned, but the chemistry world was now confronted with the existence of man-made elements. On January 4, 1947, Paneth published an editorial on the process of naming new elements in *Nature* (46). In the article he described a procedure for deciding the names of elements in situations where more than one name had been proposed. He suggested that the first group to characterize the element reproducibly should be granted naming privileges. So masurium, the originally suggested name for element 43, was dismissed because of irreproducibility. Paneth insisted Segrè and Perrier were the rightful discoverers of element 43, and that the discovery of element 85 should be credited to the LBL group. He invited those groups and the group that found element 61 to propose names. In response to Paneth's request, a letter was published in the same issue of *Nature* proposing the name astatine for element 85, from the Greek word for unstable astatos ($\alpha\sigma\tau\alpha\tau\omega\varsigma$) (47). Unlike earlier reports of discovery, the LBL group had not suggested a name for the element in their previous papers because they were cognizant of

the failed alabamine claim. The lingering prominence of alabamine made them hesitant to suggest a name until the discovery was accepted (48).

Paneth noted that after the Berkeley group produced element 85 in the cyclotron in 1940, Karlik and Bernert showed that it exists in natural sources (46). He went on to state that “former claims were open to grave objections and were experimentally disproved by very careful work by the Vienna physicists.” Although Paneth did not identify the specific former claims, those of Minder and Leigh-Smith were the only ones that Karlik and Bernert had disproved since they measured α particles and not X-rays in their studies (49). They had pointed out errors in Minder’s work, but they had not reported any issues with Hulubei’s and Cauchois’ studies. Paneth had worked at Vienna before leaving Austria, and his polite words regarding Karlik and Bernert, who stayed behind, may have been due to his knowledge that Karlik strongly disliked German war policies. Paneth did not have a personal knowledge of Hulubei and Cauchois politics, so their residency and advancement in occupied Europe may have influenced his judgment. Paneth was influential in the discovery disputes with other elements (50). He supported fellow Austrian Auer von Welsbach’s claim to have first obtained element 71 over Georges Urbain’s claim, although today Urbain and von Welsbach are given credit for its discovery simultaneously. Lutetium, a modification of Urbain’s suggestion, is the adopted name.

The statement that his work was disproved coupled with the simultaneous publication of a proposed name upset Hulubei. His 1946 presentation was not published yet, but he arranged to have a short appendix added before publication (45). In the appendix he indicated the oversight and politely attributed Paneth’s omission of his X-ray work on element 85 to the difficulties caused by the war, a diplomatic statement since both Karlik and the Berkeley researchers cited Hulubei and Cauchois. He noted that Karlik had not refuted his work “contrary to what one would think after reading the exposé of Mr. Paneth.” Hulubei and Cauchois appeared to have been slighted unjustly since Karlik had not conducted any X-ray studies, but Paneth’s phrasing and lack of citations made it appear that Hulubei and Cauchois’ work was definitively erroneous. Shortly after Paneth and Hulubei’s papers were published, Karlik suggested in a summary paper that Hulubei and Cauchois’ work was insufficient, due to the small amount of element 85 in their sample. Karlik estimated 6×10^{-16} g, or $\sim 1,670,000$ atoms in Hulubei’s samples and suggested the possibility of interferences in the X-ray data (51); however she only

cited one paper, and the criticism seems to be based on the detection limits of traditional cathode ray tube X-ray spectrometry, not the technique pioneered by Rutherford and Wooster (21). In 1949 at its meeting in Amsterdam, the International Union of Chemistry sanctioned the name astatine for element 85 (52). Paneth, who was the committee’s chair, was able to convince the committee to adopt his previously outlined nomenclature practices. Statements released after the meeting detailed that certain names had been chosen over others; for instance, that the name astatine was preferred over alabamine, but none of the other suggested names for element 85 was mentioned.

After the apparent resolution of element 85’s discovery, Hulubei went on to a distinguished career and helped to rebuild the post-war Romanian physics community. In 1949 the Institute of Physics of the Romanian Academy was established, Hulubei being named its first director. In 1956 the Institute was split, and Hulubei led the Institute of Atomic Physics until 1968. In 1996 the Institute of Physics and Nuclear Engineering (IFIN) was renamed the Horia Hulubei Institute of Physics and Nuclear Engineering (IFIN-HH), 24 years after his death. Cauchois remained active in the X-ray spectroscopy field throughout her career. From 1953 until her retirement in 1978, she directed the Laboratoire de Chemie Physique at the Sorbonne. She received numerous awards for her work during her career. Karlik also had a successful career in Austria, where she worked at the University of Vienna the rest of her life, leading the Radium Institute for almost 30 years. The Austrian Academy of Sciences awarded her its Haltinger prize in 1947 for discovering element 85 in the natural decay series, and in 1967 the Erwin Schrödinger Prize, partly for her work on element 85. She became the first female member of the Austrian Academy of Science in 1973. After leaving Berkeley, Dale Corson joined the faculty of Cornell University as a professor of physics and later served as the president and chancellor of the university. After working on the Manhattan Project in the 1940s, Emilio Segrè became a professor of physics at the University of California, Berkeley, where he remained until 1972. He returned to Italy in 1974 as professor of nuclear physics at the University of Rome, where he had started his career 40 years previously.

Epilogue: Ambiguity of Discovery

Corson, MacKenzie, and Segrè are recognized as the first to prove the existence of astatine, but can the early element hunters like Hulubei and Cauchois claim some

credit for the discovery of the element before 1940? Although the X-ray determination of elements was popular early in the 20th century, the minute quantities of the new elements produced in particle accelerators, nuclear reactors, and small tubes of radon gas during and after World War II were not amenable to detection with this technique. The studies conducted on astatine after the war utilized almost exclusively the characteristic α -particle radiations of the common artificial isotope ^{211}At , a variation on the technique of Karlik and the Berkeley group. Although Hulubei had claimed his technique could detect as few as 1,000–10,000 atoms of astatine and that he had ^{218}At , Paneth's unilateral dismissal of competing discoveries discouraged further inquiries.

From the reported activity of the Hulubei and Cauchois samples, a ^{222}Rn source would produce ^{218}Po with a half-life of 3.11 min, and ^{218}Po rapidly decays to ^{218}At or ^{214}Pb . Only 0.0202 % of the ^{218}Po decays into ^{218}At , which has a half-life of less than 2 seconds. So, within a few minutes of obtaining a sample of ^{222}Rn , steady-state conditions, with stable concentrations of ^{218}At and ^{218}Po , are reached. Hulubei and Cauchois had a ^{222}Rn sample with 200 mCi activity, which corresponds to 7.4×10^9 becquerels (^{222}Rn decays per second) or 7.4×10^9 ^{218}Po atoms produced each second. After ^{218}Po enters steady-state, a 0.0202 % conversion to ^{218}At corresponds to 1,500,000 astatine atoms being produced each second. With a 2-second half-life, ~3 million astatine atoms would be present at any one time. Standard cathode ray tube X-ray studies, requiring at the time at least 0.1 nanogram of sample material, meant the amount of astatine in the sample tube was below the detection limit. Hulubei and Cauchois, however, relied on the radiation from the decaying atoms, so the instantaneous astatine concentration is not important, but rather the total number formed during the measurement. Over a one-hour spectrum, about 5.25 billion astatine atoms would briefly appear and then decay away in Hulubei and Cauchois' sample, emitting their characteristic X-rays before vanishing, a number far above Hulubei's claimed limit of detection. Additionally, they were able to see clearly the L_{α_7} line of polonium, which has approximately a 500-fold lower transition probability than the observed astatine L_{α_1} and L_{β_1} lines, suggesting that the astatine lines would be visible to Hulubei and Cauchois (28). These numbers would be approximately tripled in Valadares' samples, because he had a 600 mCi ^{222}Rn source.

Corson, MacKenzie, and Segrè definitively produced synthetic astatine in 1940 and were able to perform chemical tests on the element, something that Hulubei

and Cauchois could not claim. Hulubei recognized this deficiency in his work, which perhaps explains his lack of significant protests after 1947. There were numerous erroneous element discoveries based on X-ray studies in the 20th century, where lines were observed in the correct positions but the element was not present. Without a very high precision spectrometer, nearby lines of other elements may masquerade as the searched-for element. Hulubei and Cauchois encountered this issue in their studies of element 87 (53); yet their observed lines for element 85 were actually fairly interference-free (Table 2). Unlike other flawed studies with X-ray spectroscopy, Hulubei and Cauchois indisputably had astatine in their samples. The only uncertainty is whether their instrument was sensitive enough to distinguish the spectral lines of element 85.

The criteria for discovering an element have changed with technology. Old techniques have been replaced with new ones, but occasionally the trends reverse. In the early 20th century an X-ray spectrum was necessary to convince the scientific community a new element had been found; but for Hulubei's and Cauchois' work, it was deemed insufficient because they lacked chemical proof. By the 1940s, α -particle studies were necessary to verify the discovery of radioactive elements. Karlik and others provided these measurements for naturally occurring astatine, as did several other investigators, but as the quest for new elements reached past Z=100, some felt α -particle studies were no longer enough (54). Throughout history, the only constant for being credited with element discovery has been the ability to convince your scientific peers of your success. In some eras, Hulubei's and Cauchois' work might have been accepted, but at the time they reported their data their methods were not accepted widely. Convincing scientific peers of an experiment's validity is often easier with an influential scientist as an advocate. Although Hulubei and Cauchois were respected in the scientific community, Nobelist Jean Baptiste Perrin, who was the most ardent supporter of their claim of discovering element 85, had died in 1942.

There were three defendable "discoveries" of element 85. The first may have occurred in 1934 or 1939 when Hulubei and Cauchois reported X-ray emission lines corresponding to element 85 in a sample that contained ^{218}At . The second came in 1940, when the Berkeley group produced ^{211}At in a cyclotron, and chemically characterized their newly created element and detected its characteristic α particles. The third occurred in 1942, when Karlik and Bernert detected the characteristic α

particles of naturally occurring ^{218}At . At various times in history, any of these groups might have been regarded as the discoverers.

Hulubei, Cauchois, Valadares, Karlik, and Bernert all published their work on element 85 in non-English journals, which may account for their lack of familiarity to English readers. To complicate matters, the mis-translation into English by several reviewers of astatine chemistry of some of the early European articles led to perpetuation of erroneous analysis of the research (55-57). In most modern English-language sources, Corson, Segrè, and MacKenzie are credited exclusively as the discoverers of astatine. German language texts tend to credit both the LBL group with discovery and mention that Karlik found astatine in natural sources in 1942. Authors from France and Eastern Europe often recognize the contributions of Hulubei and Cauchois to the discovery of element 85. Unfortunately, this inconsistency detracts from the contributions these scientists made not only to the search for missing elements, but also to other areas. This ambiguity has also led to an occasional misconception that astatine is a completely artificial element. Neither natural nor artificial astatine is available in substantial quantities; all studies must be done on minuscule amounts of the element. Whether Hulubei and Cauchois were able to detect the X-ray radiation from the astatine formed, and whether that detection, without chemical characterization, constituted ‘discovery’ as Hulubei believed, is an interesting question that can be left to debate if and when the experiments are ever revisited.

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- of sodium hydroxide. The sodium salt did not evaporate on heating, nor was it changed by addition of sulfuric acid and heating; however, adding hydrobromic or hydriodic acid caused the formation of a volatile substance (assumed to be element 85), and the sodium salt could be converted to sodium sulfate by addition of sulfuric acid (to the acid-treated material). De used the stoichiometry of sulfate metathesis to determination the approximate atomic mass for element 85 (211).
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