Henri Becquerel demonstrated that this radiation, unlike phosphorescence, did not depend on an external source of energy but seemed to arise spontaneously from uranium itself. Influenced by these two important discoveries, Marie Curie decided to look into uranium rays as a possible field of research for a thesis. Marie used an innovative technique to investigate samples. Fifteen years earlier, Pierre Curie and Pierre Curie’s brother had developed a version of the electrometer, a sensitive device for measuring electric charge. Using Pierre Curie's electrometer, Marie Curie discovered that uranium rays caused the air around a sample to conduct electricity. Using this technique, Marie Curie's first result was the finding that the activity of the uranium compounds depended only on the quantity of uranium present. Marie Curie hypothesized that the radiation was not the outcome of some interaction of molecules but must come from the atom itself. This hypothesis was an important step in disproving the assumption that atoms were indivisible.

In 1897, Marie Curie's daughter Irène was born. To support Marie Curie’s family, Marie Curie began teaching at the École Normale Supérieure. The Curies did not have a dedicated laboratory; most of their research was carried out in a converted shed next to ESPCI. The shed, formerly a medical school dissecting room, was poorly ventilated and not even waterproof. The Curies were unaware of the deleterious effects of radiation exposure attendant on their continued unprotected work with radioactive substances. ESPCI did not sponsor Marie Curie's research, but Marie Curie would receive subsidies from metallurgical and mining companies and from various organizations and governments.

Marie Curie's systematic studies included two uranium minerals, pitchblende and torbernite (also known as chalcolite). Marie Curie’s electrometer showed that pitchblende was four times as active as uranium itself, and chalcolite twice as active. Marie Curie concluded that, if Marie Curie’s earlier results relating the quantity of uranium to its activity were correct, then these two minerals must contain small quantities of another substance that was far more active than uranium. Marie Curie began a systematic search for additional substances that emit radiation, and by 1898 Marie Curie discovered that the element thorium was also radioactive. Pierre Curie was increasingly intrigued by Marie Curie's work. By mid-1898 Peirre Curie was so invested in it that Pierre Curie decided to drop Pierre Curie’s work on crystals and to join Marie Curie.

The research idea, writes Reid, was Marie Curie's own; no one helped Marie Curie formulate it, and although Marie Curie took it to Pierre Curie for Pierre Curie’s opinion Marie Curie clearly established Marie Curie’s ownership of it. Marie Curie later recorded the fact twice in Marie Curie’s biography of Marie Curie’s husband to ensure there was no chance whatever of any ambiguity. It is likely that already at this early stage of Marie Curie’s career Marie Curie realized that many scientists would find it difficult to believe that a woman could be capable of the original work in which Marie Curie e was involved.

Pierre, Irène, and Marie Curie, ca. 1902

Marie Curie was acutely aware of the importance of promptly publishing Marie Curie’s discoveries and thus establishing Marie Curie’s priority. Had not Henri Becquerel, two years earlier, presented Henri Becquerel’s discovery to the Académie des Sciences the day after Henri Becquerel made it, credit for the discovery of radioactivity (and even a Nobel Prize), would instead have gone to Silvanus Thompson. Marie Curie chose the same rapid means of publication. Marie Curie’s paper, giving a brief and simple account of Marie Curie’s work, was presented for Marie Curie to the Académie on 12 April 1898 by Marie Curie’s former professor, Gabriel Lippmann. Even so, just as Silvanus Thompson had been beaten by Henri Becquerel, so Marie Curie was beaten in the race to tell of Marie Curie’s discovery that thorium gives off rays in the same way as uranium; two months earlier, Gerhard Carl Schmidt had published his own finding in Berlin.

At that time, no one else in the world of physics had noticed what Marie Curie recorded in a sentence of her paper, describing how much greater were the activities of pitchblende and chalcolite than uranium itself: "The fact is very remarkable, and leads to the belief that these minerals may contain an element which is much more active than uranium." Marie Curie later would recall how she felt "a passionate desire to verify this hypothesis as rapidly as possible." On 14 April 1898, the Curies optimistically weighed out a 100-gram sample of pitchblende and ground it with a pestle and mortar. Marie Curie and Pierre Curie did not realize at the time that what Marie Curie and Pierre Curie were searching for was present in such minute quantities that Marie Curie and Pierre Curie would eventually have to process tonnes of the ore.

In July 1898, Marie Curie and Pierre Curie published a joint paper announcing the existence of an element they named "polonium," in honour of her native Poland, which would for another twenty years remain partitioned among three empires (Russian, Austrian, and Prussian). On 26 December 1898, the Curies announced the existence of a second element, which they named "radium," from the Latin word for "ray." In the course of Marie Curie and Pierre Curie’s research, the Curies also coined the word "radioactivity."

Pierre and Marie Curie, c. 1903

To prove their discoveries beyond any doubt, Marie Curie and Pierre Curie sought to isolate polonium and radium in pure form. Pitchblende is a complex mineral; the chemical separation of its constituents was an arduous task. The discovery of polonium had been relatively easy; chemically it resembles the element bismuth, and polonium was the only bismuth-like substance in the ore. Radium, however, was more elusive; it is closely related chemically to barium, and pitchblende contains both elements. By 1898 the Curies had obtained traces of radium, but appreciable quantities, uncontaminated with barium, were still beyond reach.