Discovery of Radium

Discovery of radium is a glorious chapter in the history of science, representing the triumph of human spirit. It was made against several odds – insufficient funds, and lack of laboratory space and proper equipment. Since radium was present in minute quantities in the ore, extracting it was more difficult than looking for a needle in the haystack.

Becquerel had already established that uranium rays could discharge an electroscope. Initially, Marie's assignment was to measure the power of ionization of these rays. Unlike Roentgen and Becquerel who used photographic plates and fluorescent screens to study these rays, Marie employed a different technique, which contributed, enormously to her success. She set up an ionization chamber coupled to an electrometer and a piezoelectric quartz balance designed by her husband, Pierre Curie and his brother. The experimental procedure consisted of spreading a thin layer of uranium salt on one of the plates of the ionization chamber and measuring the ionization current by applying a suitable voltage across the other plate (see *Figure* in the inside back cover). She found that for a given amount of active material, the current increased with the plate separation and voltage, attaining saturation at 100 volts. Under optimal conditions, she made quantitative measurements of the ionization power of uranium rays. Her measurements showed that the ionization current was proportional to the quantity of uranium in the ore. Then she discovered some thing more fundamental: that, unlike phosphorescence, uranium rays were not affected by the chemical state of the uranium salt or physical factors such as temperature, ambient lighting, etc. Further on, she made another surprising observation that not just uranium but thorium also emitted similar rays (this was independently discovered, around the same time, by a German physicist G C Schmidt). This suggested to her that the spontaneous emission of radiation by these elements is an 'atomic' phenomenon and she gave the name 'radioactivity'. We now know that radioactivity is a 'nuclear' phenomenon. However, the existence of the atomic nucleus was unknown at that time. Later, radium was to play a big role in the development of such concepts.

After examining all the compounds available to her for radioactivity, Marie Curie turned her attention to the minerals. This was a turning point, for, this led her to radium. Of the fifteen minerals investigated, she found that those containing uranium and thorium were radioactive, which by itself was not surprising. However, what was surprising was that the radioactivity in those minerals was much more than expected based on their uranium or thorium content. For example, the radioactivity of pitchblende, the uranium ore, was four times more than expected. After repeating her measurements to confirm those findings, she speculated that pitchblende may contain, in addition to uranium, one or more elements, yet unknown, but radioactive. Since the composition of pitchblende was reasonably well known at that time, no new element could have escaped the attention of the chemists unless present in extremely minute quantities. In that case, she reasoned that the unknown element(s) has to be highly radioactive.

The next step was to determine the identity of the new element(s). At this stage, Pierre Curie joined his wife to double their efforts to isolate the new element. In the words of their daughter Eve Curie "they began prospecting patiently, using a method of chemical research invented by themselves, based on radioactivity: they separated all elements in pitchblende by ordinary chemical analysis and measured the radioactivity of the bodies thus obtained. By successive elimination, they saw the 'abnormal' radioactivity take refuge in certain parts of the ore. The radioactivity was concentrated principally in two different chemical fractions of pitchblende. For Pierre and Marie Curie it indicated the existence of two new elements instead of one". They analyzed one of these fractions and discovered a new element, which was similar to bismuth in its analytical properties. They called it 'polonium', after Marie Curie's beloved homeland – Poland.

After a brief holiday, in September 1898, they were "back to the damp work rooms and dull minerals". They subjected the other sample to a series of chemical separation methods including fractionation. This yielded a new radioactive substance, which co-precipitated with barium sulphate. What was the identity of this new compound? Although it was similar to barium in its chemical properties, its chloride was less soluble in water than barium chloride. Using this property, they further enriched the sample to 900 times the radioactivity of an equal amount of uranium, but could go no further, since the quantity of the material was too small to handle. Spectroscopic analysis showed a new line at 3814.7 Å confirming the existence of a new element. Writing to the French Academy of Sciences on December 26, 1898, they stated "the new radioactive substance contains a new element to which we propose to give the name *Radium*". The radioactivity of radium was enormous – a million times more than that of uranium. However, physicists and chemists of that time were not prepared to accept the existence of a new element unless it was available in pure form and its atomic weight determined.

There were many problems in undertaking the extraction of sufficient quantity of radium for physical and chemical analyses. Firstly, it required tons of pitchblende to be processed. Pitchblende, the ore containing 60 per cent uranium was very expensive. They could not afford to buy that in tons. Alternatively, they decided to obtain the residual ore from which uranium was already extracted for they believed that the new radioactive substances would still be present in the residue. The Austrian Government, which owned a mine obliged to supply a ton of the residue free of cost.

It was a stupendous task. The couple divided the job between themselves – Pierre to study the properties of radium and Marie, the harder task of developing chemical methods to extract salts of pure radium. The first stage of operation consisted of extracting radium with barium in the form of sulphates. Then the sulphates were converted to chlorides and fractionally crystallized from water. Each step yielded crystals richer in radium (see Flow chart for details). By repeating the process a great number of times, Marie Curie was able to isolate about 100 milligram of pure radium chloride from a ton of pitchblende residue! It was a dull white powder, which could easily be mistaken to the ubiquitous common salt. She determined the atomic weight of radium as 225.9, close for the current value of 226.02.

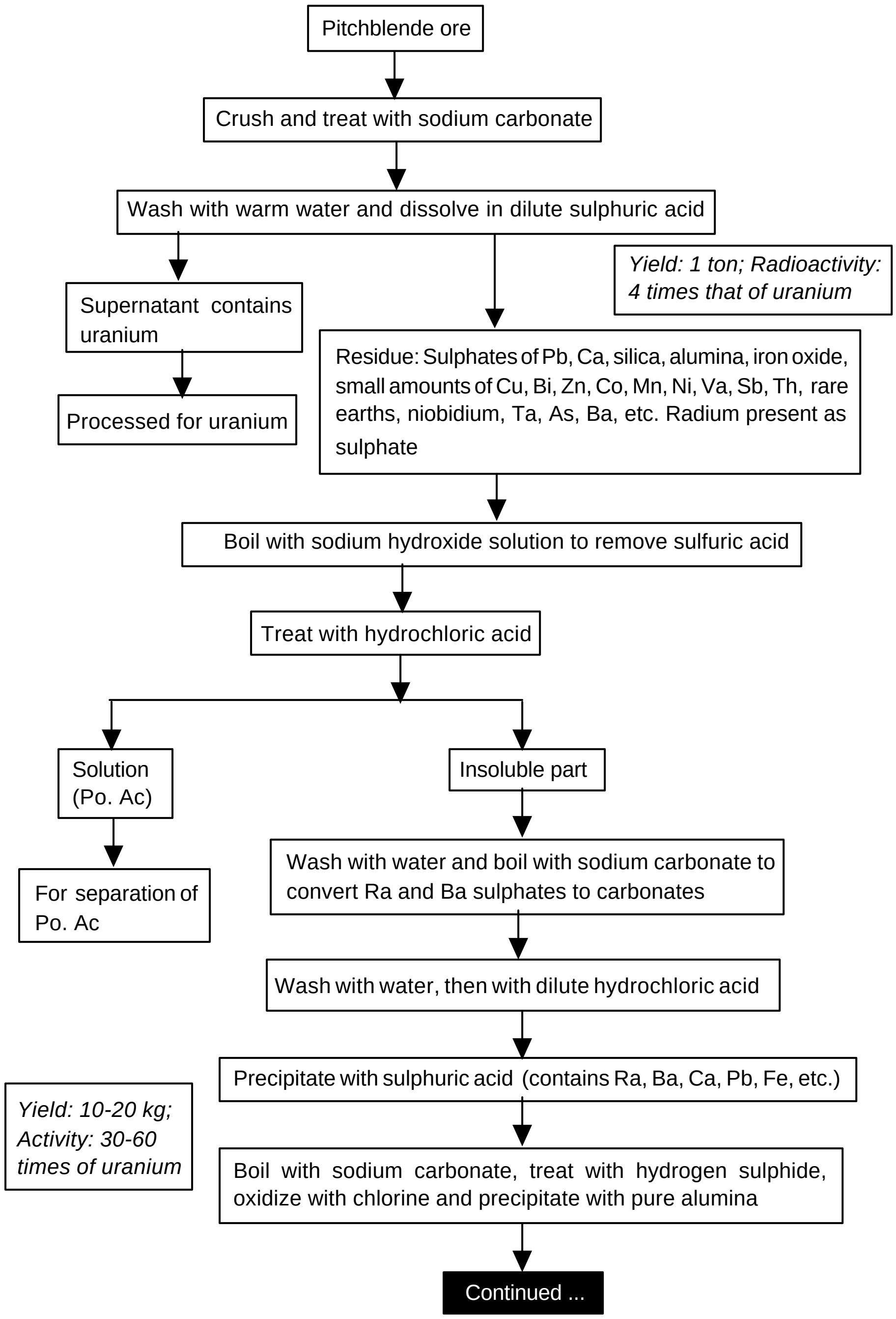
In the following years radium became the most important source of radioactivity. The tremendous amount of energy spontaneously pouring out of radium and other radioactive elements greatly puzzled the scientists of that time. What was the source of this energy? To answer this question Rutherford, Soddy, Geiger, Marsden and others carried out some fundamental experiments. In the process, they unlocked some of the profound secrets of nature and laid the foundations of nuclear physics. In the hands of medical men, radium symbolized the gift of science to the suffering humanity. It became a tool to cure the dreaded cancer.

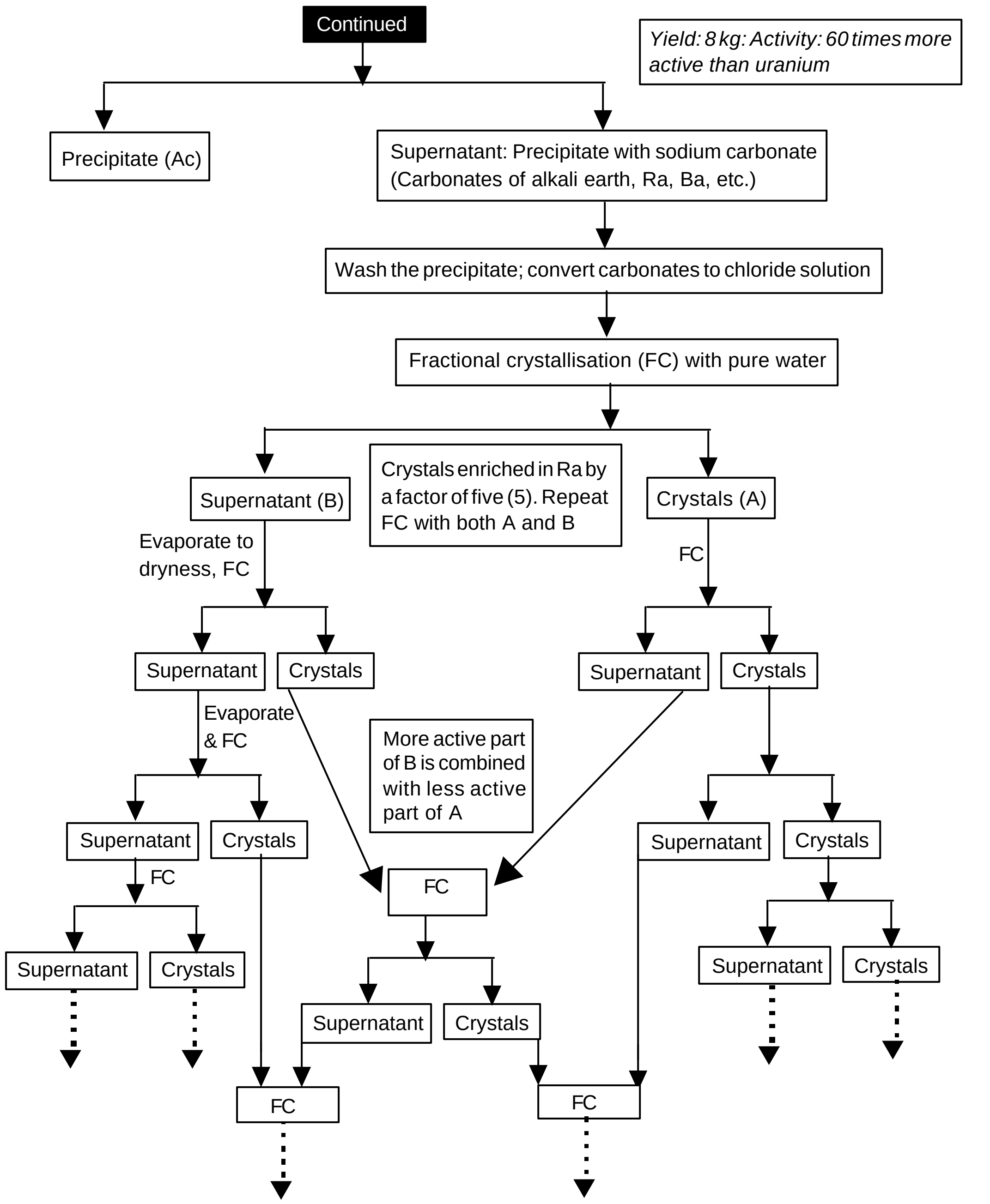
M S S Murthy

B-104, Terrace Garden Apartments, 2nd Main Road, BSK IIIrd Stage, Bangalore-560 085, India.

Flow Chart of the Major Steps in the Separation and Purification of Radium from Pitchblende

(Based on Procedure described in Marie Curie's Thesis)





– FC continued for 6 stages; – Activity of the most soluble fraction decreases each time, when it becomes negligible, it is discarded; – At some stage the most active crystals are withdrawn from further FC and pooled; – Final yield was nearly 100 mg of pure radium chloride; – Activity nearly 2×10^6 times that of equal weight of uranium.