

THE LABORATORY NOTEBOOKS OF PIERRE AND MARIE CURIE AND THE DISCOVERY OF POLONIUM AND RADIUM

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1 Introduction

It is an exceptional and moving privilege to remember at this historical place [Jáchymov] the centenary events which announced the rise of radiochemistry and conducted inexorably to the nuclear era of mankind. In the account of the early history of radioactivity Sankt Joachimsthal, now Jáchymov, is intimately related to Pierre and Marie Curie who one hundred years ago discovered polonium and radium in a sample of Joachimsthal pitchblende.

In 1897 Maria Skłodowska, who had married Pierre Curie in 1895, concluded her studies at the Sorbonne in Paris and was thinking of a subject for a thesis. The X rays were still a topical question but had lost the charm of novelty. On the other hand, the uranic rays discovered in 1896 by Henri Becquerel raised a puzzling problem. The uranium salts appeared to maintain an undiminished ability to blacken a photographic plate over months. The law of energy conservation was solidly established since 50 years. What was the origin of this inexhaustible energy which apparently violated the Carnot principle, the first principle of thermodynamics, which states that energy can be transformed, but can never been created nor destroyed? Pierre Curie, a renowned physicist for his work on magnetism and crystal symmetry, had a presentiment that the phenomenon was quite extraordinary and helped his wife in the decision. Marie Curie, in the biography of Pierre published in 1923, confirmed: *we felt the investigation of the phenomenon very attractive, so much the more the topic was quite new and required no bibliographical research* [1].

A small laboratory was offered to the couple at the Parisian School for Physics and Chemistry. Pierre Curie was already involved in a work on crystal growth and had opened a laboratory diary on the 16 of September 1897. The writing of Marie Curie appears in the notebook on December 16, 1897. This day is the beginning of her work on uranic rays, first alone, later joined by Pierre Curie, which will lead within one year to the discoveries of two radioelements, prelude to two Nobel prizes.

In this lecture the work of Pierre and Marie Curie along the famous year 1898 will be reconstituted. Two sources of information are available: three laboratory notebooks kept at the French National Library and three publications in the *Comptes Rendus de l'Académie des sciences*, the weekly reports of the Academy of Sciences. The dates are not always indicated in the notebooks, however the progress of the work can be established by cross-checking with the publications. During the first months Marie Curie writes practically alone, comments by Pierre are limited to a few words. Subjective remarks are exceptional; on February 6, Marie Curie registers with anger the temperature in the laboratory: 6.25°C followed by 10 exclamation marks. It is an evidence of the miserable working conditions.

The chronology and the connection of the documents are shown in Table 1. The three months covered in the first notebook are mostly used for setting up the equipment.

The second diary ends with the discovery of polonium. The last notebook begins after an interruption of 4 months; six weeks later the third publication announces the discovery of radium. The inscriptions are pursued more or less regularly until mid-1900 with further important findings such as the phenomenon of induced activity. Afterwards the notes are more sporadic. Marie Curie consecrated most of her work to the isolation of a macroscopic amount of pure radium chloride for the determination of the atomic weight of the radioelement; the correct value 225.9 appears in the last page of the diary.

Table 1. Chronology of the documents related to the work of Pierre and Marie Curie during 1898.

Notebook	Publication
16 December 1897 – 18 March 1898	
18 March 1898 – 16 July 1898	12 April 1898 [2], 18 July 1898 [3]
11 November 1898 – 28 March 1902	26 December 1898 [4]

With the sole notebooks it would be difficult to reconstitute the content of the publications. Probably the authors prepared drafts which have disappeared; it is likely that at several occasions results have been reported on sheets rather than in the diaries. In fact, the publications contain information which cannot be found in the laboratory notebooks and reciprocally observations registered in the diaries have not been included in the publications.

2 The strategy

At the end of 1897 all knowledge on uranic rays was contained in the nine Becquerel publications in the *Comptes Rendus*, mostly during the first semester of 1896. After an initial excitement, the interest of scientists in the new rays faded rapidly. One reason was the proliferation of false or doubtful observations of the emission of radiations similar to uranic rays by a variety of substances including glow worms. One can say that the topic was moribund when Marie Curie entered the scenery.

How undertake the subject chosen for Marie's thesis? One approach could be the search for substances sharing the peculiar property of uranium and its compounds. This seemed to be a logical process. It is clearly expressed in the introduction of Marie Curie's first publication [2]: *I have searched if substances other than uranium compounds render air conducting for electricity*. This last precision implicitly refers to the method used for the measurement of the radiation.

The photographic plate by which radioactivity was discovered was a primitive and merely qualitative radiation detector. On the other hand, the ionization of air could be used for a quantitative determination of the action of rays and thus the intensity of their emission. However, a convenient measurement of very small intensities had still to be imagined.

At this point the genius of Pierre Curie was decisive. In 1880, Pierre Curie together with his brother Jacques had discovered piezoelectricity. This is the production of electric charges when a pressure is applied to hemihedral crystals like quartz. Pierre Curie invented a device based on this phenomenon which is the key of the prodigious discoveries of the Curies (Fig. 1).

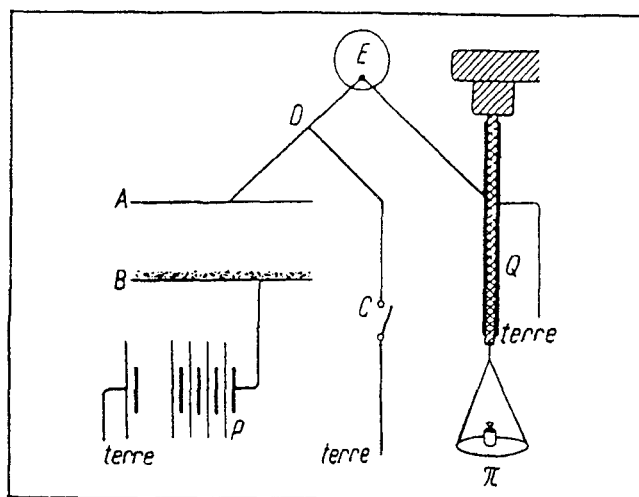


Fig. 1. Scheme of the device used for the measurement of the ionization current. AB ionization chamber. CD connection to ground. E quadrant electrometer. Q piezoelectric quartz. π weight [5].

The apparatus consists of two metallic electrodes between which an electric field is applied. One plate is loaded with a powder of the material to be tested. The uranic rays produce electric charges in the air and a ionization current flows between the electrodes. The charges in the chamber are compensated by opposite charges obtained by applying a weight to a leaf of piezoelectric quartz. The compensation is controlled by a quadrant electrometer. The charges produced by the quartz are calculated from the weight applied and from the time during which the weight is applied. Eventually the ionization current can be calculated. For the first time the emission of uranic rays could be quantified on the basis of the current produced by the rays under controlled conditions.

The setting of the equipment was painful and fills 50 pages in the notebook. Humidity in the uncomfortable laboratory was the source of numerous difficulties. The handling of the device required considerable skill but Marie Curie now had an invaluable tool for routine measurements (Fig. 2).

3 Marie Curie's first publication

The first publication on the 12 of April with the title *Radiations emitted by uranium and thorium* is signed Marie Skłodowska Curie [2]. Pierre Curie without whom the work would not have been possible is not associated as author. Two months before, Marie Curie had started the systematic search for compounds which may impart electric conductivity to air. She tested all samples at hand or borrowed from various collections. By courtesy of Henri Becquerel, she had access to the rich collection of minerals assembled by Professor Lacroix at the Museum of National History, the place where Becquerel had discovered radioactivity. There she found among other minerals pitchblende of various origins, in particular from Joachimsthal.

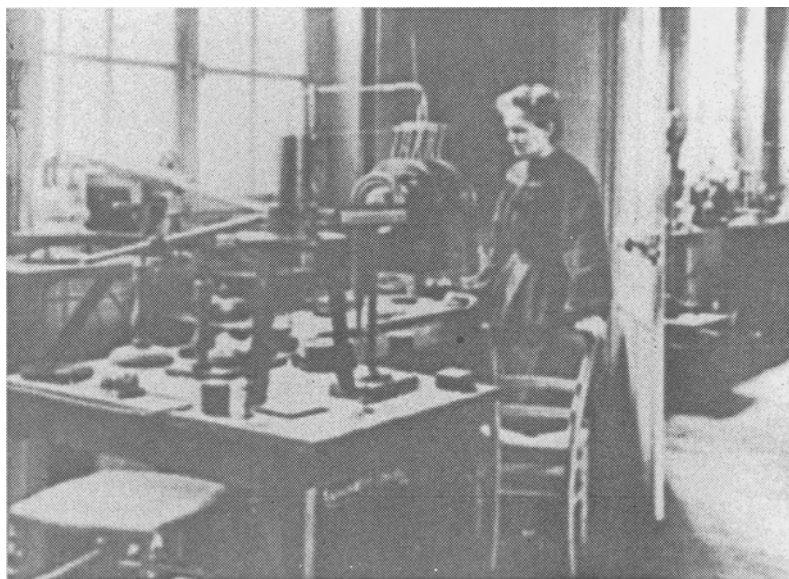


Fig. 2. Marie Curie in the laboratory and a view of the equipment.

On February 18, she performed the first measurement of a pitchblende which was about twice as active as metallic uranium (Fig. 3). For each compound the weight in grams applied to the quartz and the compensation time in seconds are registered. For sake of comparison of activities the ratio weight over time (designated i in the notebook) was convenient. The ionization current itself is calculated from the characteristics of the quartz and appears only in the publication. Metallic uranium prepared by Henri Moissan in 1896 by reduction of uranium oxide in the electric furnace which he had invented, was used as a reference for quantifying the relative strength of radioactive substances.

The intensity observed for pitchblende was quite unexpected since no uranium containing substance ought to be more active than the metal. It was not commented in the notebook, but numerous tests of the equipment which followed immediately show that Marie Curie was extremely preoccupied by the finding. Further significant results are shown in Table 2.

Table 2. A selection of substances measured by Marie Curie [2].

Sample	Intensity (pA)
metallic uranium (Moissan)	24
thorium oxide	53
potassium fluoxytantalate	2
Joachimsthal pitchblende	83
Johanngeorgenstadt pitchblende	67
natural chalcocite	52

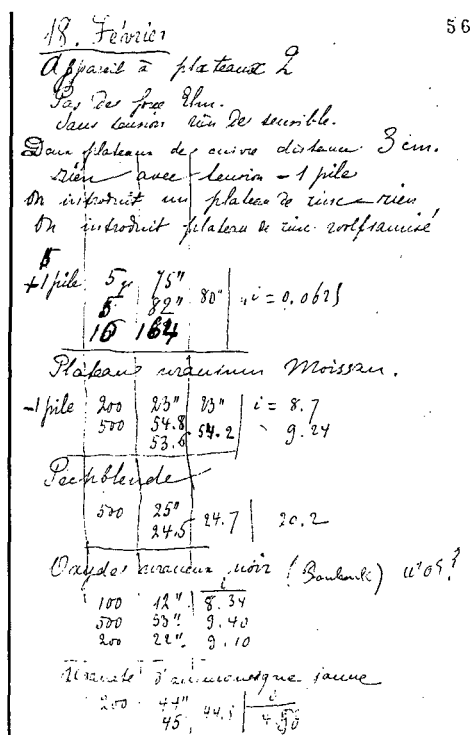


Fig. 3. Marie Curie's first measurement of pitchblende on February 18, 1898. The compensation of charges produced in the chamber required a weight of 500 g applied during 24.7 s.

It had been found earlier by Becquerel and confirmed by Marie Curie that the emission of rays was specific property of uranium atoms, independent of the chemical combination of the element. Accordingly the excess of activity of certain minerals had an unequivocal origin which Marie Curie stated in following terms: *This fact is quite remarkable and suggests that these minerals may contain an element much more active than uranium itself.*

Evidence in favour of this hypothesis was rapidly proven since Marie Curie knew how to prepare artificial chalcocite: *I have prepared chalcocite by the Debray method with pure products; this artificial chalcocite 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 uranium.

At about the same time, on the 26 of February, Marie Curie discovered the radioactivity of thorium. This was a matter of chance since the compound appears at random in the midst of other substances such as lanthanum nitrate, titanitic acid, zirconium oxide. (Fig. 4). One may notice that Moissan uranium is measured repeatedly in order to check the correct working of the equipment. Thorium oxide was found to be even more active than uranium (Table 2). We know that uranium was in equilibrium with its first two descendants while thorium was closer to complete equilibrium with all daughters.

62

Oxyde d'yttrium rien
 Oxyde de cerium donne très faible
 - 1 pile 5 gr - 50" } 58 $i = 0.086$
 + 1 pile 5 gr - 67" }
 mouillé donne aussi quelque chose
 Uranium Moissan
 500 gr - 51"
 Terre de la capsule (Oxyde de thorium pur)
 + 1 pile 500 gr - 58.6 } 58.5 $i = 9.5$
 - 1 pile 500 gr - 58.2 }
 Plomb zinc frais. Rien de régulier
 Acétate de lanthane et ammonium
 rien de certain
 Acide titanique
 rien de certain
 Oxyde de zirconium
 rien de certain
 Mine de platine rien

Fig. 4. Discovery of thorium radioactivity on February 26, 1898. *Terre de la capsule* is pure Th oxide. Ce exhibits a very feeble activity probably due to traces of Th. For other compounds Marie Curie reports *nothing certain*.

However, the discovery of the radioactivity of thorium was not a premiere. Two months before Marie Curie's paper the German physicist Gerhardt Schmidt at Erlangen had published that thorium and its compounds blacken a photographic plate [6]. Marie Curie could not be aware of this work, but when Schmidt read Marie Curie's paper, he hastened to announce in the *Comptes Rendus* [7] that *he* was the discoverer of the radioactivity of thorium.

Interestingly enough, Marie Curie reported a feeble activity for two potassium salts and she was probably the first to record without knowing it the activity of ^{40}K . She also proceeded to the first systematic investigation of the absorption and self-absorption of uranic and thoracic rays.

A strange observation registered in the notebook is not mentioned in the publication. Marie Curie found that the activity of thorium oxide decreased when a stream of air was flown through the ionization chamber and afterwards it increased again during a few minutes. It is the same observation, but more salient, which led Rutherford to postulate a few months later the emission of a radioactive gas by thorium oxide. Thus one can think that Marie Curie was on the verge to make the same discovery. But she was probably much more intrigued by the activity of pitchblende. If she had concentrated her investigation on the erratic behaviour of thorium, perhaps the orientation of her work would have been fully changed.

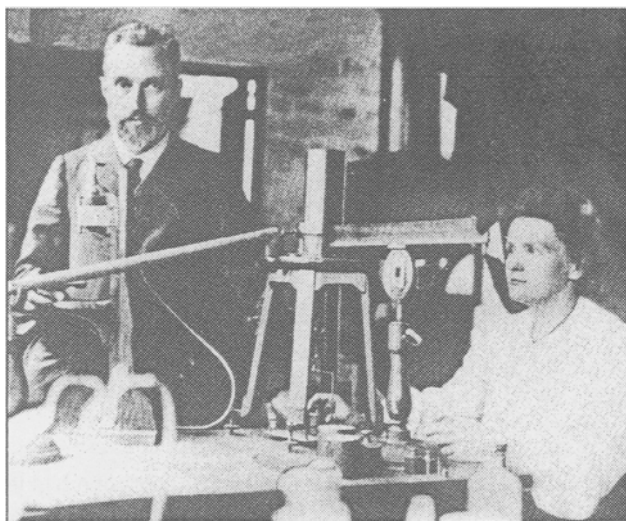


Fig. 5. Marie Curie proceeds to the measurement of a radioactive sample. With the right hand she lifts progressively the weight applied to the quartz; in the left hand she holds the chronometer.

The sum of results acquired in two months is prodigious. The search of the element more active than uranium was now a matter of highest priority and urgency. Pierre Curie fascinated by Marie's findings abandoned his own research projects and joined his wife in the adventure (Fig. 5).

4 The discovery of polonium

The second publication, this time signed by Pierre and Marie Curie, is based on experiments performed from April 9 to July 16. The title *On a new substance, radioactive, contained in pitchblende* [3] is eloquent for two reasons. It announces that the search for the element much more active than uranium was successful and the word *radioactive* appears for the first time.

It is noteworthy that research on uranic rays now turned from physics to chemistry. The obstacles were immense: separate and identify a substance whose chemical properties were completely unknown. The couple was helped by Gustave Bémont, an analytical chemist at the Parisian School for Physics and Chemistry. The collaboration with Bémont lasted for 6 months.

On the other hand, the hypothetical element could be followed by its radioactivity. Marie Curie stated in the biography of Pierre: *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* [1]. This sentence announces the beginning of radiochemistry. Marie Curie added that radioactivity acts like a specific analytical reagent with a high sensitivity but she could not imagine that the limit of sensitivity was a few atoms.

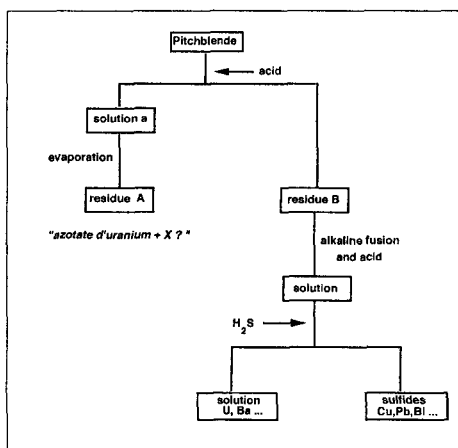


Fig. 6. Simplified scheme of the first acidic treatments of pitchblende.

Pierre Curie more inclined to physics undertook the analysis of pitchblende by sublimation. Already in the first trial it was found that a very small amount of substance about 10 times as active than uranium could be obtained and this method was pursued in parallel with the chemical analysis.

The first treatment began on April 14, whereby 100 g of Joachimsthal pitchblende was ground and attacked by nitric acid (Fig. 6). The acidic solution as well as the insoluble residue were both active which could mean that each fraction contained a different radioactive substance or that a single one was distributed between the two phases. The authors were excessively optimistic in thinking that this first step could already be significant. Pierre Curie measured immediately the absorption spectrum of the solution and found a weak band non existent in uranyl nitrate. He underlined this result which in his mind was a first indication of the presence of a new element. On her side, Marie Curie evaporated the solution, measured the activity and noted *uranium azotate + X*. She also thought that the mysterious element could be hidden in this fraction.

But it was still a long way to the success. From the notebooks it appears that the authors followed simultaneously several strategies. The residue was fused with potassium carbonate and afterwards dissolved in acid. The treatment of the solution with H_2S was a significant step since the precipitate of sulfides was active, as well as the residual solution which contained uranium.

The activity contained in the sulfides was insoluble in ammonium sulfide and thus could be separated from As and Sb (Fig. 7). It became clear that X was associated with Pb, Cu and Bi. In the meanwhile Pierre Curie had separated by fractional sublimation a substance 100 times as active as uranium. Now a dilemma had to be lifted: is the substance insoluble in ammonium sulfide identical with that obtained by sublimation? Does a known element share both properties? During a whole week all possible elements and their compounds were tested: arsenic, iodine, sulfur, natural sulfides and many others. None was active.

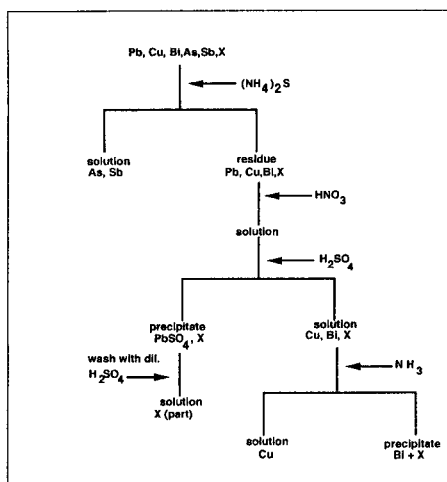


Fig. 7. Principle of the treatment of the precipitate of sulfides.

Thus the activity insoluble in ammonium sulfide was that of a new element mixed with Cu, Pb and Bi. These three elements could be easily separated and eventually most of the activity remained with Bi. The authors could not find an accurate wet method for the separation of the radioactive substance from Bi. A partial concentration was obtained by precipitation with water: the first fractions are the more active.

Suddenly on July 13, without further comment, the symbol Po appears in the notebook (Fig. 8). Pierre Curie proceeds to the sublimation of about 1g of a mixture of Bi, Pb and the supposed new element Po, 12 times more active than uranium. In this historical page he describes the colour of fractions separated while Marie Curie measures the activities; the highest is that of a *fragment black, yellow orange, considerably black* 400 times more active than U. This success was the result of the joint efforts of both scientists since Pierre Curie's sublimation method was applied to Marie Curie's sulfides (Fig. 9).

The second notebook ends on July 16 with a final test for activity on a large variety of compounds. This was a last precaution before the discovery of a new element could be claimed with confidence. Two days later the discovery of polonium is announced, however cautiously: ... *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.*

Prior to polonium, four elements were given names referring to countries: germanium, ruthenium, gallium and scandium. But the designation of polonium had a provocative significance since as a state Poland had disappeared in 1795, being parcelled out between Prussia, Russia and the Austrian Empire. Francium, the last discovered natural radioelement, was found in 1939 by Marguerite Perey, a former laboratory assistant of Marie Curie.

13, juillet sublimation de la
distillation de sulfures Volant 12 p. 100
sulf. B. 100 et 10 0°/4

150° sulfures
matière jaunâtre, goudronneuse
et. avec beaucoup

220° au dessus sulfures
noirâtre brun. 10 avec
Vine au jaune sur place

370° Vine au noir sur place

650°

774° 780° ? on laisse refroidir

morcen orange et jaune
200 — 20"

morcen noir, jaune rouge, pas mal noir
1000 — 10.5
— 11"

morcen rouge, jaune, un peu noir
800 — 15.5

morcen avec un petit peu de noir
200 — 12"

Fig. 8. The symbol Po appears in the notebook on July 13, 1898.

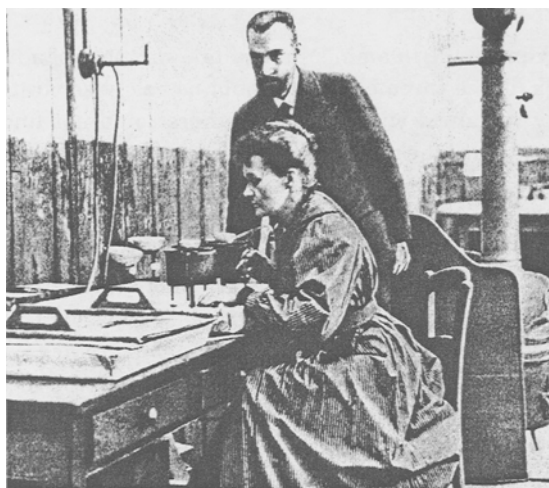


Fig. 9. Pierre and Marie Curie at the laboratory bench.

For the first time in the history of chemistry the existence of an invisible element was claimed which could be identified solely on the basis of its emission of uranic rays. In the 19th century 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, the leading spectroscopist of the time, could not distinguish any new characteristic line in the most active sample of bismuth sulfide. The authors admitted *this fact does not favour the idea of the existence of a new metal*. However, Demarcay indicated that the absence of specific rays does not prove absolutely that the sample contains only bismuth, since spectral analysis is not very sensitive for heavy elements.

The amount of Po in 100 g of pitchblende was at the most a few ng, well below the sensitivity of the spectrometer. A few spectral lines of Po will be detected 12 years later on a sample of a tenth of mg extracted by Marie Curie and André Debierne from several tons of residues of Joachimsthal pitchblende.

One may wonder if the announcement of the discovery was premature. The excess of activity of pitchblende revealed in Marie Curie's first paper was a scoop which would undoubtedly incite other scientists to search for the origin of the phenomenon. Marie Curie had already missed the priority of the radioactivity of thorium and another mischance should be avoided.

More realistically the notebooks show that in their experimental conditions the authors had reached the extreme limit of concentration of Po in Bi. After each fractional precipitation the amount of material become smaller and in any case they could not have obtained a sample with an activity much higher than 400 times that of uranium and 130 times that of pitchblende. Hence there was no reason to delay the publication.

The isolation of Po from U had been accomplished although the authors were unaware of the relationship between the two elements. They considered the whole material as a mixture. They knew nothing at the time of radioactive decay. In this sense it was a matter of chance since the isolation was performed in a short time with respect to the 140 days half- life of Po. It was only 4 years later that the Curies noticed with astonishment and great perplexity that Po was progressively disappearing.

Moreover they could not imagine that they were dealing with trace amounts of the new element. By simple reasoning the new substance must obviously be present in very small amount since it had not yet been found. However, it was not evident that this amount was below the limit of any chemical means of detection.

The assignment of Po in the periodic table does not seem to have preoccupied the discoverers. Po was concentrated in the Bi fraction. This affinity led Marie Curie to consider that the two elements had similar properties. In fact, Po is an homologue of tellurium and the neighbour of Bi in the periodic table. The confusion is readily explained since Po was coprecipitated at trace concentrations with Bi sulfide and hydroxide.

The publication ended the short story of polonium for several years. The Curies were still preoccupied with the authenticity of the element and with honesty they did not hide their doubts. In 1899 they observed the phenomenon of induced radioactivity and Marie Curie raised the question: *is Po which exhibits the spectral lines of Bi really a new element or simply Bi activated by the radium contained in pitchblende?* Still in 1902 the authors noted *Po is a kind of active Bi; it has not yet been proven that it contains a new element.*

5 The discovery of radium

Since the first chemical treatment the Curies suspected the presence of two new elements in pitchblende. A clue to this hypothesis was the distribution of the activity between several fractions (Fig. 6). The authors focused their attention on the sulfides first because it seemed easier to search for the activity concentrated in a solid.

The 4 months interruption in the notebooks from July to November has been the subject of several interpretations. During the summer the couple rented a farm in central France. Eve Labouisse-Curie in the biography of her mother points out *everyday they discussed about the new metal, polonium and the other one which was still to be discovered. In September they returned to their humid workshop and resumed their investigations with a renewed enthusiasm* [8]. On his side, Robert Reid suggested that both had to take a rest because of a strange and intense tiredness and repeated faintings which might have been the first signs of radiation sickness [9].

Surprisingly in the last diary the writing of Marie Curie is absent from November 17 to December 18, precisely the time during which the proofs for the existence of a second radioelement were accumulated.

The title of the third publication which is co-authored by Gustave Bémont is identical to that of the second paper with addition of a single word: *On a new "strongly" radioactive substance contained in pitchblende* [4]. In the first sentence the authors remember that they had extracted from pitchblende a radioactive substance which may *perhaps* be considered as a new element. Again one notices the caution: the authors were still reluctant to assert officially the existence of polonium. But in the intimacy of the laboratory the doubt is lifted: in the third notebook the word polonium appears frequently.

The chemical behaviour of the second radioactive substance was strikingly different from that of polonium: it did not precipitate by hydrogen sulfide nor by ammonium sulfide: on the other hand it coprecipitated with barium carbonate and sulfate. While Bi was the carrier of Po, Ba was the carrier of the new radioactive substance. The spectra of radioactive barium showed the characteristic pattern of pure barium.

Once it was sure that the radioactivity was contained in barium it remained to prove that it was not barium, but a new element. This important demonstration was based on three tests. First, Marie Curie verified that natural barium is not radioactive and contains no radioactive substance. She undertook a fractional crystallisation of 50 kg of commercial barium chloride until a final amount of 10 g was obtained. The residue showed no activity within the limit of sensitivity of the detector which means that the activity was less than one hundredth of that of uranium.

As a very important point it was possible to concentrate the radioactive substance by fractional crystallisation of barium chloride. This was based on the high solubility of the salt in water and its insolubility in alcohol. The aqueous solution of radioactive barium was treated with alcohol and the first portions of the solid were much more active than the remaining solution. The operation was repeated until the activity of barium chloride was 900 times that of uranium. At this point the authors had to cease the concentration because the amount of material was too small. They insist that this limit was provisional: *it is foreseeable that the activity would still have much increased if it would have been possible to pursue the concentration.*

The third and last argument was decisive. Demarcay found in the spectrum of the radioactive barium chloride several lines which could not be assigned to any known element [10]. The intensity of the most intense new line increased with the radioactivity of the substance, from very weak with the first sample up to notable for the sample 900 times more active than uranium. Of course, the lines of barium were the strongest but the authors noted with great satisfaction that the main line of the new

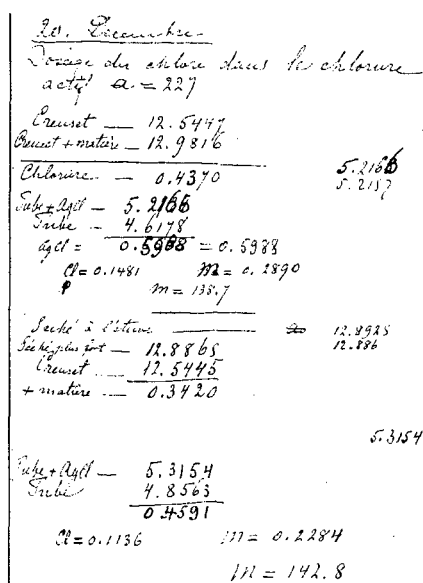


Fig. 10. Marie Curie's first determination of the atomic weight of radium.

substance was more intense than the weak lines of barium. Finally they write: *we think this is a very serious reason to attribute the new line to the radioactive 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.*

Besides the spectroscopic analysis, a second official proof for the existence of radium was the measurement of the atomic weight. Marie Curie proceeded to the determination using the classical method based on the precipitation of silver chloride from radioactive barium chloride. The procedure was tested with pure BaCl_2 : the atomic weight of barium was found between 137 and 139. On December 20 – this date is that of the last entry in the notebook before the publication – Marie Curie obtained a first value of 142.8 for the atomic weight of the radioactive metal on a 437 mg sample of radiferous barium, 227 times more active than uranium (Fig. 10). This value was slightly higher than that of barium but still within limits of errors. Obviously the amount of radium was too small to change the apparent atomic weight of barium.

When the Curies ran out of material they were aware that vast amounts of pitchblende would be necessary in order to prepare visible quantities of radium. They could not afford the purchase of this expensive material. But they supposed correctly that the residues of the ore after extraction of uranium should contain the new elements Po and Ra. They also thought that the residues had no commercial value. In a foot note of the publication the authors thank Professor Suess of the University of Vienna for his intervention with the Austrian government proprietor of the Joachimsthal mines. The Curies were offered free of charge 100 kg of residues and the authors acknowledged *this will greatly facilitate our research*.

With the foregoing discovery of Po, the authors 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 Po; it is a true chemical analogue of barium, from which it can be separated and it could be readily assigned to its correct position in the periodic table.

Probably in order to mark the difference with polonium the authors indicated in the title of the publication that the new element is *strongly* radioactive. Their radium was 900 times more active than uranium but polonium only 400 times. They commented: *our preparation contains very likely a high proportion of barium; nevertheless the radio-activity is considerable; the radioactivity of pure radium must be enormous*. Of course it could not be imagined that for an equal amount of substance polonium is 4000 times more active than radium.

At the end of this memorable year 1898 radiochemistry was born and 4 radioelements were known: U, Th, Po and Ra. However, despite of these prodigious discoveries, practically nothing was known about radioactivity itself.

It was found that Po and Ra excite the fluorescence of a screen of barium platino-cyanide. This observation led the authors to conclude the publication of the discovery of radium in stating: *a source of light which requires no energy can thus be obtained in contradiction, at least apparently, with the principle of Carnot*. It is precisely this puzzle which had prompted Marie Curie to investigate the emission of uranic rays.

Acknowledgement

Madame H elene Langevin is gratefully acknowledged for providing a copy of the notebooks of Pierre and Marie Curie.

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