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## Chemists and Physicists searching for element 43

**Summary** - As an example of cooperation between Chemists and Physicists, the discovery of the chemical element n° 43 is discussed. Its existence had been foreseen by D.I. Mendeléev (1872) and its nuclear charge quantified by the H.G.J. Moseley (1914). The first systematic attempt to obtain it was carried out by I. Tacke and W. Noddack (1925), by chemical analysis of columbite. In their residue, O. von Berg claimed to have identified, by means of X-ray spectroscopy, a new element they called Masurium. This proved to be a non-discovery, as nobody else could confirm this result.

Whether this was due to the non existence of element 43 in Nature, or to the failure of the process of chemical separation, or to the limits of the physical technique of identification, it is hard to establish to day, eight years after these events.

Quite a different approach was used by the Physicist E. Segrè: with the help of the Chemist C. Perrier the chemical analysis of a molybdenum specimen, taken from the Berkeley 27 inch cyclotron, gave indirect evidences on the chemical identity of the new element (Palermo, 1937). It was then called Technetium, as it was the first element to be made by man in a laboratory.

**Keywords:** Technetium, discovery of the Elements, nuclear fission, X-ray spectroscopy.

### *Introduction*

The identification of chemical elements, their classification according to a general ordering criterion, and the search of the missing ones, in order to complete their roll, can be considered among the fundamental achievements of Chemistry in the XIX century. The discovery of missing elements could be realized, between the end of the XIX and the middle of the XX century, only thanks to a close sharing of knowledge, competences, methods and instruments, independently developed by chemists and physicists. This synergy led to the identification, among others, of the

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element having atomic number 43, but it could be realized only thanks to a deep change in the way Chemists searched for new elements and confirmed their discovery.

In the middle of the XIX century, new elements could be discovered only through chemical procedures. Ores and minerals were dissolved with proper reagents, their components set apart, the rarer ones concentrated up to isolation of the unknown elements, which were then chemically characterized. This process could be improved by the introduction of physical methods, such as emission spectroscopy or radioactivity measurements, that gave strong analytical signals. So Chemists could drive their attention only toward those materials in which these methods had revealed the presence of unknown elements.

Two conditions had to be fulfilled to confirm a claim: the new elements had to be obtained from terrestrial materials (mainly from mines), and they had to be obtained in visible (and weighable) quantities. For instance, Lockyer and Janssen's claim for a new element, identified in the sun, was not accepted from chemists, as they could not grasp it; only several years later it was recognized in gaseous emanations from uranium ores, and finally acknowledged as a true element (Helium) [3].

Strategies for searching new elements were improved by two important contributions from the Russian chemist Dmitri Ivanovic Mendeleév and the English physicist Henry Gwyn-Jeffreys Moseley. The former discovered the *periodicity law*: chemical properties of the elements showed a regular, periodical repetition, as their atomic weight increased. Therefore, he was able, not only to foresee the properties of the element still to be discovered, but also to lead their research toward those minerals containing congener elements, where it was likely that occurred also the unknown ones.

Moseley accurately measured the wavelengths of X-rays emitted from different elements, when they were placed on the anticathode of a cathodic rays tube. He found a clear relationship between these wavelengths and the nuclear charge of the emitting elements. Thus, it was possible to solve an intriguing question of Physics, definitely giving a nuclear charge to each element and, therefore, the number of its electrons. Moreover, the measurement of the wavelength of the X-ray lines proved to be a very sensitive analytical tool that allowed to identify trace elements – known or unknown – in compounds or mixtures. As, according to *Moseley law*, for each element, the value of its nuclear charge allowed to calculate, *a priori*, the wavelength of lines in its X-ray spectrum, from then on, the missing elements could be identified and distinguished from the already known ones.

One of the first chemists to use this analytical method was Georges Urbain, who was looking for the unknown element 72, in some rare earth ores. This element is widely spread in nature, but, owing to its close resemblance to zirconium, it could not have been detected by the usual chemical means. Urbain sent some of his residues to Moseley, who was able to identify the characteristic lines of Erbium, Thulium, Ytterbium and Lutetium, such confirming, in a few days, the results that Urbain had gathered in 20 years of painstaking chemical work [29]. Anyway, he

could not prove Urbain's claim about the presence of element 72. This element was discovered only at the end of 1922 in Zirconium ores, by Dick Coster and Georg von Hevesy: they registered an X-ray spectrum in which lines appeared just at the wavelengths calculated from the atomic number of the searched element [29]. In the same way, element 75 (Rhenium) could be identified by its X-rays spectrum, before it could be obtained in amounts large enough to be chemically characterized.

So, thanks to the instrumental (physical) methods of analysis all the elements that have isotopes stable enough to have survived till now in earthly ores could be identified. To discover the others, which – simply – *do not exist in Nature*, it was necessary to change the approach and to create them in laboratory. This could be realized by using the same procedures and instruments developed by Physicists to study nuclear reactions, especially the artificial ones; these were induced, for instance, by bombarding stable nuclei with the proper bullets, such as protons, neutrons, deuterons and alpha particles. In this way, physicists succeeded in transmuting elements, and chemists had to develop procedures to separate and identify the products of such reactions.

The long search process which led to the discovery of element 43 clearly shows the efficiency of the two different research strategies: using the chemical procedure of enrichment, separation and identification, despite the help of the most sensitive analytical methods, resulted in the *non-discovery* of Masurium; on the other side, starting from its creation in the laboratory, traditional methods of chemical analysis allowed to confirm the *discovery* of Technetium.

#### *The non-discovery*

The first systematic attempt to identify element 43 was started in the twenties [28], together with that of element 75, by two German chemists, Ida Eva Tacke and Walter Noddack, which eventually got married, working at the Physikalisch-Technischen Reichsanstalt (Imperial Physico-Chemical Research Office), a government laboratory in Berlin [7a].

Their research strategy developed along the following steps:

- 1) foresee the physical, chemical and geochemical properties of the element, on the basis of periodicity law;
- 2) select minerals in which it could likely be found;
- 3) chemically treat these minerals, to separate main constituents and known elements, and to obtain a residue enriched in the element to be found;
- 4) test the chemical behaviour of the residue to exclude it could contain any known element;
- 5) confirm the identification through two key steps:
  - a) obtain a pure sample or a salt of the element;
  - b) determine its atomic weight.
- 6) alternatively, indirect proofs of its presence, could be obtained by means of suitable physical signals, such as the lines in its emission spectrum, or the nature and intensity of its radioactive emissions, or the lines of its roentgenogram.

Point 1 had the aim to develop the better analytical procedure to isolate elements 43 and 75, from those showing similar physical and chemical behaviour, and to find a precise method to identify them.

Table 1. Expected physical and chemical properties of element 43 [25a]

<p>V</p> <p>a.w. 51 sp.gr. 5.6 M.P. 2100° V<sub>2</sub>O<sub>5</sub> M.P. 660°C Vol. above 1200°C brown yellow</p>	<p>Cr</p> <p>a.w. 52 sp.gr. 6.7 M.P. 1800° CrO<sub>3</sub> M.P. 196°C Vol. above 200°C dark red</p>	<p>Mn</p> <p>a.w. 55 sp.gr. 7.3 M.P. 1500° Mn<sub>2</sub>O<sub>7</sub> M.P. -25°C Vol. above 4°C violet red</p>	<p>Fe</p> <p>a.w. 56 sp.gr. 7.9 M.P. 1800° FeO<sub>4</sub> unknown</p>
<p>Nb</p> <p>a.w. 94 sp.gr. 8.4 M.P. 2000° Nb<sub>2</sub>O<sub>5</sub> M.P. - Vol. - white</p>	<p>Mo</p> <p>a.w. 96 sp.gr. 10.2 M.P. 2650° MoO<sub>3</sub> M.P. 791°C Vol. above 500°C white</p>	<p>43</p> <p>a.w. 98-99 sp.gr. 11.5 M.P. 2300° X<sub>2</sub>O<sub>7</sub> M.P. 350°C Vol. above 250°C light yellow - pink</p>	<p>Ru</p> <p>a.w. 102 sp.gr. 12.3 M.P. 2400° RuO<sub>4</sub> M.P. 22,5°C boils above 100°C orange</p>
<p>Ta</p> <p>a.w. 182 sp.gr. 16.6 M.P. 3100° Ta<sub>2</sub>O<sub>5</sub> M.P. - Vol. - white</p>	<p>W</p> <p>a.w. 184 sp.gr. 19.1 M.P. 3600° WO<sub>3</sub> M.P. 1800°C Vol. above 1300°C yellow</p>	<p>75</p> <p>a.w. 187-188 sp.gr. 21 M.P. 3300° X<sub>2</sub>O<sub>7</sub> M.P. 600°C Vol. above 400°C white</p>	<p>Os</p> <p>a.w. 191 sp.gr. 22.5 M.P. 2800° OsO<sub>4</sub> M.P. 55°C boils above 100°C white</p>

Expected chemical properties of element 43 are summarized in table 1, compared with those of its neighbours. As it had to be placed in the empty space under manganese, Mendeleév had proposed to call it *ekamanganese* [13]. It should show a maximum valence of 7, and to give an oxide having formula M<sub>2</sub>O<sub>7</sub> and a relatively low volatility, compared with that of its neighbours in the periodic table [25, 15].

Point 2 was fulfilled estimating the geological abundance of element 43: it was known that, in the earth crust, each element having an odd atomic number was from 10 to 20 times rarer than the following one in the periodic table. As reported in table 2, the Noddacks estimated for element 43 a relative abundance of 10<sup>-13</sup>. So, element 43 (and 75 too) was extremely rare and it would not form specific ores, since in that case it would have been already discovered [28]. Moreover, as it happened previously for zirconium and hafnium and for molybdenum and tungsten, it was likely that elements 43 and 75 could be found in the same ore: so the Noddacks were convinced that the discovery of one element would lead to the discover of the other [28].

Table 2. Abundance of the elements in the earth crust [25].

Sc	Ti 2·10 <sup>-3</sup>	V 3·10 <sup>-5</sup>	Cr 3·10 <sup>-5</sup>	Mn 7·10 <sup>-4</sup>	Fe 5·10 <sup>-2</sup>	Co 3·10 <sup>-6</sup>	Ni 3·10 <sup>-5</sup>	Cu 1·10 <sup>-7</sup>	Zn 1·10 <sup>-6</sup>	Ga 1·10 <sup>-9</sup>	Ge	As 1·10 <sup>-6</sup>
Y 2·10 <sup>-6</sup>	Zr 6·10 <sup>-5</sup>	Nb 1·10 <sup>-7</sup>	Mo 1·10 <sup>-7</sup>	43 ~10 <sup>-13</sup>	Ru 2·10 <sup>-12</sup>	Rh 1·10 <sup>-11</sup>	Pd 1·10 <sup>-11</sup>	Ag 1·10 <sup>-8</sup>	Cd 1·10 <sup>-8</sup>	In 1·10 <sup>-9</sup>	Sn 7·10 <sup>-6</sup>	Sb 1·10 <sup>-8</sup>
La 6·10 <sup>-7</sup>	Hf 6·10 <sup>-6</sup>	Ta 5·10 <sup>-7</sup>	W 5·10 <sup>-7</sup>	75 1·10 <sup>-12</sup>	Os 2·10 <sup>-11</sup>	Ir 2·10 <sup>-11</sup>	Pt 1·10 <sup>-9</sup>	Au 1·10 <sup>-9</sup>	Hg 1·10 <sup>-9</sup>	Tl 4·10 <sup>-9</sup>	Pb 4·10 <sup>-7</sup>	Bi 1·10 <sup>-9</sup>
	Th 7·10 <sup>-8</sup>		U 7·10 <sup>-6</sup>									

Table 3. The associated appearance of the elements [25]

<b>I</b>	<b>Sc</b>	<b>Ti</b>	<b>V</b>	<b>Cr</b>	<b>Mn</b>	<b>Fe</b>	<b>Co</b>	<b>Ni</b>	<b>Cu</b>	<b>Zn</b>	<b>Ga</b>	<b>Ge</b>	<b>As</b>
<b>II</b>	<b>Y</b>	<b>Zr</b>	<b>Nb</b>	<b>Mo</b>	-	<b>Ru</b>	<b>Rh</b>	<b>Pd</b>	<b>Ag</b>	<b>Cd</b>	<b>In</b>	<b>Sn</b>	<b>Sb</b>
<b>III</b>	<b>La</b>	<b>Hf</b>	<b>Ta</b>	<b>W</b>	-	<b>Os</b>	<b>Ir</b>	<b>Pt</b>	<b>Au</b>	<b>Hg</b>	<b>Tl</b>	<b>Pb</b>	<b>Bi</b>
<b>IV</b>		<b>Th</b>		<b>U</b>									



Columbite



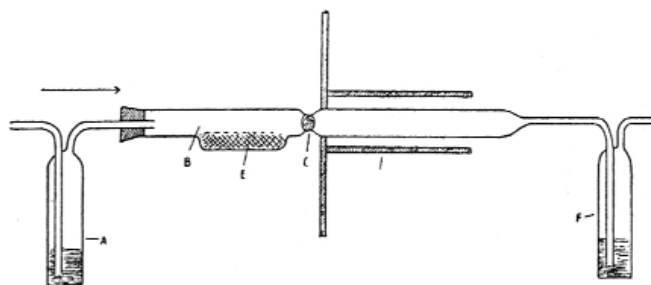
platinum ore



both

According to its presumed chemical and geochemical properties, deduced from those of its horizontal neighbours, they thought that the most promising ores should be platinum ores or columbite, which, as reported in table 3, contain the oxides of several transitional elements of the second and third row [15]. After this preliminary examination, the Noddacks were able to know exactly what, where and how to look for [28].

In a first attempt, by treating 80 g of platinum ore, they obtained only trace amounts of the presumed element 43. So, they used 1 Kg of the cheaper Norwegian columbite. In both cases, the samples were treated by chemical enrichment procedures to concentrate the searched elements in a small fraction of the original sample. After the elimination of the main constituents, they obtained about 20 mg of a residue containing different oxides, which were separated by sublimation under an oxygen flow, into the hot quartz tube reported in figure 1. The less volatile oxide settled as small white needle shaped crystals; as the chemical tests excluded the presence of any known element, the Noddacks supposed it was the oxide of a yet unknown one, likely belonging to the Manganese group [25].



Apparecchio per il trattamento del minerale di platino.

Figure 1. Apparatus for treatment of the enriched sample [25a].

### *The help from Physics*

The amount of oxide collected (about one milligram) could not be converted into the pure element and was indeed too small to allow an accurate wet analysis, in order to chemically confirm the discovery. So, they had to turn to instrumental analysis: optical spectroscopy proved to be unsuitable, owing to the difficulty to identify the faint lines of a new element, between several (even thousands) lines of already known elements.

X-ray spectroscopy displayed an higher sensitivity: so, they joined Otto Carl von Berg, an X-ray specialist, who had the competence and instruments at the Physikalisches Laboratorium des Wernerwerks M der Siemens & Halskhe A. - G. [7b].

The residue for X-ray analysis was obtained by melting columbite with sodium nitrate and caustic soda, treating the solution, obtained by leaching the fuse, with  $H_2S$  [25]. Sulphides were then converted into metals and exposed to cathodic bombardment. The way the X-ray spectrum was registered and interpreted is a crucial point in the discussion following their claim of the discovery, confirming how important physical techniques were in these true chemical investigations. For that reason it is important to treat it in details. As the wavelength of the emitted X rays depends on the applied voltage, they selected it, in order to excite either the K spectrum of element 43 ( $\lambda \approx 0,6 \text{ \AA}$ ) or the L spectrum of element 75 ( $\lambda \approx 1,4 \text{ \AA}$ ). As already pointed out, X-ray analysis allows a qualitative identification through the wavelengths of the lines in the spectrum, and a quantitative determination of the elements, through their intensity. The wavelengths of lines  $K_{\alpha 1}$ ,  $K_{\alpha 2}$  and  $K_{\beta 1}$  for element 43 and lines  $L_{\alpha 1}$ ,  $L_{\alpha 2}$ ,  $L_{\beta 1}$  and  $L_{\beta 2}$  for element 75 are reported in table 4. In the following, only the spectrum of the former will be discussed [5].

The majority of spectra showed the most intense line related to the transition  $K_{\alpha 1}$ , and in some case also lines  $K_{\alpha 2}$  e  $K_{\beta 1}$ ; without giving quantitative data, the Noddacks stated that these transitions showed the correct relative intensities. A picture of the original plate representing this spectrum was reported only in the minutes of a session of the Prussian Academy of Sciences [17], where the first

Table 4. Wavelengths in Å of the measured lines of elements 43 and 75.

	43			75				
wavelengths	$K_{\alpha 1}$	$K_{\alpha 2}$	$K_{\beta 1}$	$L_{\alpha 1}$	$L_{\alpha 2}$	$L_{\beta 1}$	$L_{\beta 2}$	$L_{\beta 3}$
measured	0.672	0.675	0.601	1.4299	1.4407	1.235	1.2048	1.216
calculated	0.6734	0.6779	0.6000	1.4306	1.4406	1.2355	1.2041	1.2169

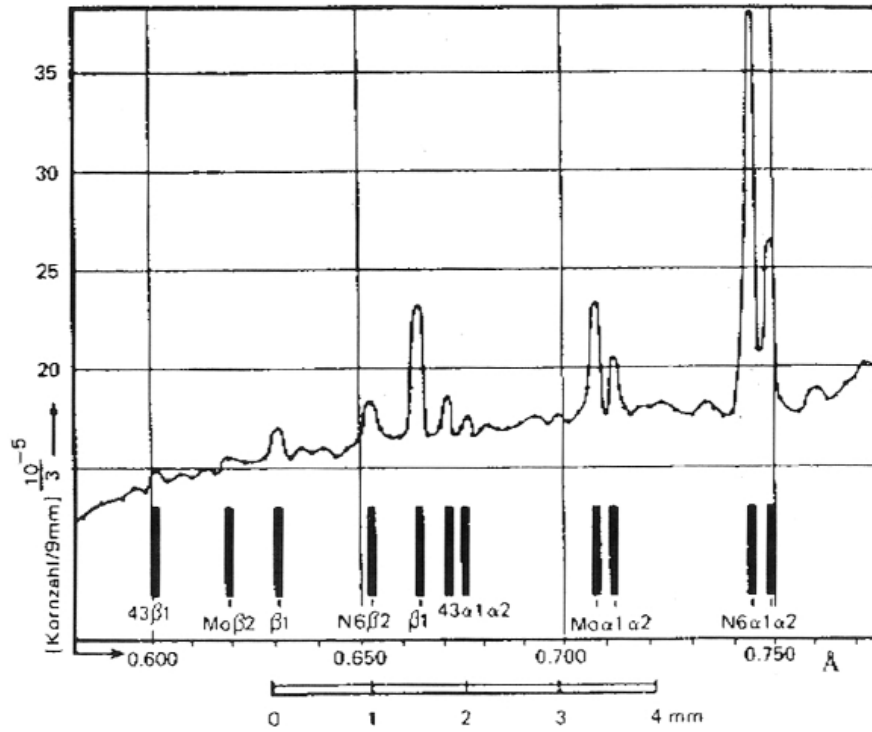


Figure 2. X-ray spectrum resulting from grain counting [4].

announcement of the discovery was given by Walther Nernst, the 11<sup>th</sup> of June 1925. The picture was reproduced later on [26], but as the authors themselves acknowledge, the  $K_{\alpha 2}$  and  $K_{\beta 1}$  lines can hardly be recognized [8]. In a subsequent paper [4], Berg described in details his measurements, giving the X-ray spectrum resulting from grain counting (figure 2), which is easier to read than the corresponding dark photographic plate, with the lines of element 43 emerging above the background fluctuations.

Although these lines corresponded, with a good approximation, to those cal-

culated for element 43, the authors took into account also the possibility of interferences from other elements. Only the second order  $K_{\alpha 2}$  line of Neodimium is very close to the  $K_{\alpha 1}$  line of element 43, but no first order line of this element could be observed and its presence in the sample could be excluded on a chemical basis. They therefore considered definitive the physical evidences supporting the identification of element 43, and proposed for it the name of Masurium, after the Masurian district (the German eastern border, to day in Poland), from where Walter Noddack's family originated.

Anyway, the Noddacks were not yet satisfied with their results, as they believed that the only way to definitely prove the existence of Masurium was to produce weighable amounts of it [28]. In fact, as the claim was based on the result of physical determinations, chemists accurately checked it with their own criteria: no one was able to confirm their experimental results, nor to isolate appreciable amounts of the element. Many chemists, and among them the influential analytical chemist Wilhelm Prandtl, casted doubt on the correctness of their assignment of X-ray lines, suggesting that Zinc and Tungsten spectral lines could have led them to wrong conclusions [9]. Prandtl also had some doubts on the Rhenium discovery, which was instead confirmed by Heyrowsky, by means of polarography, and the Noddack, which were able to produce weighable amounts, patenting the process to obtain the pure element [16] (in the '30s, about 120 Kg of Rhenium, the less abundant element on the earth crust, had been produced [28]).

The Noddacks' claim for Masurium discovery was definitely rejected after that, in 1934, Josef Mattauch stated [11] that stable isobar pairs cannot exist if they differ of only one charge unit. As Molybdenum and Ruthenium, its closest neighbours in the periodic table, have stable isotopes showing all the possible mass values for element 43, Mattauch's selection rule definitively ruled out the possibility of Masurium's existence on the earth's crust. Accordingly, when, in the fifties, all of the isotopes of element 43, laying in the beta-stability valley, had been identified, none of them showed a half-life long enough for survival since the formation of the earth's crust [8].

The experimental failures and the proved impossibility to find Masurium in ores and minerals concurred to the Noddacks' scientific discredit, as they had reported a physically unfeasible result. So it became superfluous to question its reliability and the correctness of Noddacks' spectra interpretation: it was simply *impossible* that they could have identified element 43. They, apparently, did not carry out further research to improve the method to isolate Masurium, also because all their work was devoted to produce weighable amounts of Rhenium, to overcome questions about its discovery [28]. However, they never doubted that Masurium was a *natural* element, present in the earth's crust, even if at a concentration so low to be undetectable with the chemical and physical methods of analysis at their disposition [28]. For a few years chemists retained the name of Masurium to indicate element 43: still in 1953, it was reported in a spread treatise of inorganic chemistry [12].



Anyway, they kept scientifically active for a long time: for instance, Ida Noddack was the first to have doubts [18] on the possibility that Fermi and coworkers in Rome had actually produced elements 93 and 94, by neutron bombardment of Uranium. Her criticism was based on the lack of a chemical proof of the presence of these species; on the contrary, she suggested that Fermi had obtained smaller fragments in a process that was later called *fission*.

### *The discovery*

Despite the painstaking attempts of chemists, element 43 was finally discovered from the Italian physicist Gino Emilio Segrè, one of the Fermi's pupils, who succeeded because he was able to find the mine where the element could be found. Really, Segrè was not involved in the purely chemical project of discovering new elements, but he was instead carrying out a typically physical investigation on radioactivity, both natural and artificial.

In 1935, he had been appointed full professor of Physics at the University of Palermo. There, to his great disappointment, he found an Institute lacking of any equipment suitable for experiments in modern Physics [24a], for instance, those on artificial radioactivity he had started in Rome with the Fermi's team. Nevertheless, he could buy a Perucca electrometer and get a home made ionization chamber. What he lacked in was a source of radioactivity, to produce particle beams to bombard atomic nuclei, in order to obtain heavier ones and to realize transmutation of the elements.

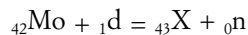
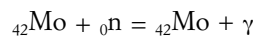
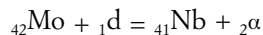
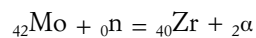
In the summer of 1936, on suggestion of Otto Stern, he visited the Radiation Laboratory in Berkeley, to see at work the 27 inch cyclotron there built by Ernest Lawrence. Segrè was well aware that, in this powerful device, neutrons could produce an artificial radioactivity that was much stronger than the natural one. During this visit, an apparently trifling event happened, that would have changed the course of the history of element 43. Segrè noticed that worn out pieces of the cyclotron that laid down useless on the floor had been damaged by the long lasting bombardment they underwent, and therefore showed a strong radioactivity, whose origin nobody cared for, as Lawrence was more interested in increasing the efficiency and the power of his machines, than to use them for nuclear physics investigations [24b].

Lawrence allowed Segrè to take away some copper and brass scraps from the D electrodes of the cyclotron, in order to study in Palermo long term radioactivity. Back home, lacking the required chemical competence to separate and analyze radioactive components of the irradiated samples, Segrè looked for the help of the chemist Carlo Perrier, working in the same building where the Physics Institute was located [30]. They found that the most abundant radioactive component was  $^{32}\text{P}$ , and employed it for some biological experiments together with the physiologist Camillo Artom [2]. This could have been the beginning of a close and useful coop-

eration between scientists of different education, but the anti-Semitic policy of the Italian government spread out this team and wasted its potentiality.

On January the 6<sup>th</sup> 1937, Segrè received by mail, from his friend Lorenzo Emo Capodilista, working at Berkeley, a small Molybdenum plate that had been the target of the cyclotron for a long time. Segrè faced the investigation on the origin and nature of this radioactivity from two different points of view, the chemical and the physical one. The chemical investigation had the aim to ascertain which element (or elements) caused the long period radioactivity. A preliminary qualitative analysis of the plate had shown the presence of  $^{32}\text{P}$ , which contaminated every substance which had been bombarded in the Berkeley cyclotron. Anyway, radioactivity of the irradiated Molybdenum showed [20] characteristics quite different from those of  $^{32}\text{P}$ .

Moreover, Segrè noticed that the opposite sides of the plate showed different amounts of radioactivity. He argued that it had been originated from bombardment of charged particles (deuterons), then strongly slowed down from Molybdenum. So he decided to gently attack only the most radioactive surface, to bring in solution and concentrate the products of (d,n) e (d,p) reactions. According to the kind of particles which could hit Molybdenum inside the cyclotron, the only possible nuclear reactions were [14]:



One of the products was an element likely present in extremely low amounts and whose chemical properties were still unknown. So Perrier had to use all his chemical skill to manage the problem. First of all, he proved that radioactive isotopes of Zirconium and Molybdenum were absent and therefore could not be responsible for the observed radioactivity. Then he started a process of chemical separation of the components of the radioactive solution.<sup>1</sup> After each separation, only the radioactive fraction was further analyzed, while the discarded fractions were almost inactive. After Molybdenum Removal, Rhenium and Manganese were added as carriers for element 43, because of their supposed chemical similarity. Manganese was recovered, but it did not show any radioactivity. Finally, Rhenium was quantitatively distilled at 180°C in a current of moist gaseous hydrochloric acid; as the solution remained radioactive, Perrier and Segrè inferred it should contain the element 43, formed from the deuterons bombardment of Molybdenum into the cyclotron.

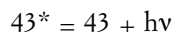
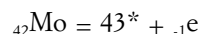
These results were presented by Nicola Parravano at a meeting of the Royal

<sup>1</sup> A flow diagram of this process is reported in [30].

Accademia Nazionale dei Lincei [21], on June, the 4<sup>th</sup> 1937, and later published in the Journal of Chemical Physics [20]. Despite the widespread enthusiasm arisen in Italy after this communication, Segrè and Perrier delayed the claim for the discovery of a new element. This hesitation was due, not only to the extremely small amount (about  $10^{-10}$  g) of element produced, but also to the fact that they were not sure of their priority.

The research could not be further carried out in Italy, as, in the summer of 1938, Segrè left forever his country, to escape the consequences of Italian racial laws. Before leaving Palermo, together with Bernardo Nestore Cacciapuoti, he found out that residues from the analysis of the Molybdenum plate showed three different decay periods of, respectively, 90, 50 and 80 days [6].

In the USA, Lawrence allowed him to work at the Radiation Laboratory, investigating the physical properties of radioactive species. There, together with Glenn Seaborg, a Gilbert N. Lewis' pupil, succeeded in separating an isotope of element 43, that showed two isomeric states. The excited isomer decayed to the stable one, by a mechanism of internal conversion of the gamma rays, ejecting a K electron that could be revealed by a magnetic spectrograph. It was also possible to observe an X-ray emission and to measure its wavelength with a spectrograph: it was identified, without doubts, as the  $K_{\alpha}$  line of element 43. The measured radioactive decays could be explained, according to the following transformations:



where the asterisk indicates the excited nuclear state. As Segrè was proud to remark, this was the first time that the X-ray line of a new element, artificially synthesized, had been directly observed [23].

So, in 1939, it was widely known that all the identified isotopes of element 43 had extremely short half lives, in agreement with Paneth's selection rule. This was the definitive proof that Noddacks' claim was not correct. Rhenium had been successfully discovered using traditional (chemical) methods of investigation, while, at the same time, traditional methods failed to separate Masurium. The Noddacks failed to realize that time had changed and that this event marked the end of a research tradition [22].

Nature was unfair with them, hiding the element they were searching; instead, Nature had to be substituted by a device, the cyclotron, that was able to create the missing elements. Not by chance, most of the transuranic elements have then been produced by using such a device, as shown in table 5. At the end of World War II, it was the Uranium pile to overcome the cyclotron's performance regarding the capability to transmute elements, as it could produce a much greater amount of neutrons and therefore of synthetic elements [19].

These considerations and the production of an X-ray spectrum of the element 43 cancelled all the doubts that Segrè had about his priority in the discovery of this element.

Table 5. Transuranic elements produced by bombardment into the cyclotron.

Element	Bullet	Target	Discoverer	Year	Name
93	Neutron	U	Mc Millan, Abelson	1940	Neptunium
94	Deuteron	U <sub>3</sub> O <sub>8</sub>	Seaborg et al.	1941	Plutonium
95	Neutron	Pu	Ghiorso et al.	1945	Americium
96	Alpha	Pu	James and Morgan	1944	Curium
97	Alpha	Am	Thompson et al.	1949	Berkelium
98	Alpha	Cm	Ghiorso, Seaborg et al.	1950	Californium
101	Alpha	Es	Seaborg et al.	1955	Mendelevium
102	<sup>13</sup> C	Cm	Ghiorso et al.	1957	Nobelium
103	B	Cf	Ghiorso et al.	1961	Laurentium

The possible creation of new elements forced chemists to change their ideas about them and to acknowledge as such also those that could not be found in Nature. In 1946, the Austrian chemist Friedrich Paneth complained that a full citizenship was denied to elements that had been artificially produced only in invisible amounts, and were unstable and usually not present on the earth. On the other hand, very considerable amounts of natural elements have always existed, also if they belong to the radioactive families and are only represented from short life isotopes.

In order to acknowledge the same dignity to artificial elements, he stated [19] the rules to accept names and symbols for the newly discovered ones:

- 1) The right to name an element should go to the first one who gives definite proof of the existence of one of its isotopes;
- 2) In deciding the priority of the discovery, there should be no discrimination between naturally occurring and artificially produced isotopes;
- 3) If a claim of such a discovery has been previously accepted, but is refused in further research, the name given should be deleted and replaced by one chosen by the real discoverer.

Element 43 is well suited to represent this change of strategy, in each of these points.

As a consequence of the proved incorrectness of Noddacks' claim, Paneth invited Perrier and Segrè to give a name to element 43. Instead of complying with nationalistic feelings, suggesting names as Trinacrium (from the ancient one of Sicily), they preferred to give emphasis to the new process which had led to the production of the element. So they proposed the name of Technetium, from the Greek word *technetos*, that means made by art, artificial, to underline the fact that it was produced in laboratory, by Molybdenum neutronic bombardment.

*The quarrel on primacy*

Quite curiously, no public dispute on primacy arose between the Noddacks and Segrè soon after his claim of identification of element 43. Instead, in recent years, someone has suggested that the Noddacks could have effectively found Masurium in their residues. This originated from the discovery, in the sixties, that, in particular conditions, element 43 can be continuously produced by spontaneous fission of  $^{238}\text{U}$ , or by neutron induced fission of  $^{235}\text{U}$ . As very minute amounts of it were effectively found in pitchblende from Oklo (Gabon) [10], Belgian physicist Pieter van Assche [26] tried to analyze Noddacks' data, to evaluate the possibility that they could have effectively met measurable amounts of element 43, in their uranium containing ores. His arguments were developed mainly along two lines: i) estimate the abundance of element 43 in the analyzed ores (columbite, sperrylite, gadolinite, fergusonite), on the basis of their uranium content; ii) state if the emission lines produced from such a small amount of the element could be beyond any doubt detected by the Berg's spectrograph.

The latter point is the more difficulty to consider *a posteriori*, as available information about the instruments he used is rather scarce and the whole set of roentgenograms recorded by Berg have been irremediably destroyed [24c], as Walter Noddack told Segrè in 1937.

van Assche asserts that the Noddacks found Masurium only in uranium containing ores and not elsewhere, despite they could not be aware of its production by uranium fission. Instead, as observed by Herrmann [8], they analyzed unsuccessfully also monazite and pitchblende, despite their relatively high uranium content.

To estimate the relative atomic abundance of element 43 in an uranium containing ore, one must know the half lives of the isotopes  $^{99}\text{43}$  and  $^{238}\text{U}$  ( $\sim 2,1 \cdot 10^5$  and  $6 \cdot 10^{15}$  years respectively), and the yield of the uranium spontaneous fission to  $^{99}\text{43}$  (about 6,3%). Using these values, van Assche found:

$$C_{43}/C_{\text{U}} = 0,06 \cdot 2,1 \cdot 10^5 / 6 \cdot 10^{15} = 2,1 \cdot 10^{-12}.$$

Assuming a 5% mean uranium content in a mineral of the kind used by the Noddacks, he obtained [26]:  $0,05 \cdot 2,1 \cdot 10^{-12} \approx 10^{-13}$  as atomic abundance; Herrmann corrected this figure to a concentration of  $3 \cdot 10^{-14}$  g of  $^{99}\text{43}$  per gram of mineral.

Such a low quantity poses a further question about the identification limits of the instruments used by Berg in 1925. From calibration experiments, he had stated that, using a sample of at least 1 mg (to produce appreciable lines in the spectrum), his apparatus allowed him to detect a 0,1% content of an element, through its strongest emission line [26]. This means that no spectrographic analysis of diluted components could have been carried out without a previous chemical enrichment of the original ore.

As the Noddacks started with 1 Kg of columbite, they expected that the identification limits of their instrument should have been  $10^{-9}$ , indeed too high to allow the identification of the above estimated content of  $10^{-13}$ . To fit these quantities,

van Assche argued some hazardous hypotheses to lower this limit by three logarithmic unities: these hypotheses have been convincingly confuted by Herrmann, since even in samples containing 5% uranium the amount of element 43 results non weighable and can be detected only by radioactive measurements [7c].

In recent years, John T. Armstrong, a researcher at NIST, using extensive X-ray database and sophisticated spectral analyzer program DTSA, simulated the Noddacks data. The relative intensities of the lines and the peak to background ratio were estimated and compared to Berg's spectrum. The lines he attributed to the new element appear consistent with that of element 43, at a value of at least five times the detection limits, and the mass calculated from the peak to background ratio appeared consistent with the concentration expected in the sample from uranium spontaneous fission [1]. No reference to where this data have been published in details is reported; nevertheless, these ideas have had wide circulation, especially in the web [27].

So, also this attempt to rehabilitate the Noddacks proved to be unsuccessful. Anyway, if they had really found Masurium in their ores, this could have changed the history of Physics, as it would have been the first proof that Uranium spontaneous fission can actually take place in ores.

The most probable cause of their failure was their firm believe that element 43 should be present in nature and that, anyway, Chemists would be able to isolate appreciable amounts of it. They never became aware that the only way to produce it was by nuclear reactions and that, at the state of art of chemistry in the late twenties, successful searching for new elements should turn from chemical analysis of mineral to their laboratory synthesis by means of physical methods of investigation of nuclear reactions.

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