1937: Palermo. The discovery of technetium

Aurelio Agliolo Gallitto - Department of Physics and Chemistry; University of Palermo - aurelio.agliologallitto@unipa.it
Ileana Chinnici - INAF, Osservatorio Astronomico di Palermo - ileana.chinnici@inaf.it
Roberto Zingales - Department of Physics and Chemistry; University of Palermo - roberto.zingales@unipa.it

Abstract: In 1937, at the University of Palermo, Segrè and Perrier extracted, from an irradiated molybdenum plate, minute amounts of an unknown chemical element, with atomic number 43, the only element ever discovered in Italy. It was named technetium, after the Greek word for "artificial", as it can hardly be found in nature, but only produced in laboratory, through nuclear reactions. We hereby describe Segrè and Perrier work, providing an account of the scientific environment of the University of Palermo in the 1930s.

Keywords: radioactivity, cyclotron, chemical elements.

1. Introduction

The chemical element having atomic number 43 was identified, for the first time, in Palermo, in 1937. This resulted from the close collaboration between physicists, whose instrumentation produced isotopes of that element, and chemists, whose experimental skill provided the indirect, although unquestionable, evidence of its existence.

The story of the hypotheses and experiments that led Emilio Gino Segrè (1905-1989) and Carlo Perrier (1886-1948) to this result has already been told (Gambaro 1987), (Segrè 1995), (Zingales 2005). We will hereby mainly try to also reconstruct the academic scientific milieu in which it was realized, at the University of Palermo, in those years.

2. Chemistry at Palermo University in the Thirties

When Segrè arrived in Palermo as full professor of Physics (fall 1935), Giuseppe Oddo (1865-1954) had just retired by age. For almost 20 years, Oddo had been professor of General Chemistry and Director of the same Institute. His scientific work had spanned across several fields of Chemistry: in particular, he had investigated the industrial exploitation of the mining resources of Sicily (mainly sulphur and potassium salts). On

the theoretical side, he had developed the so called "rule of 4" (better known as Oddo-Harkins rule), the concept of mesoidria, which anticipated the hydrogen bond theory, and investigated the possibility to obtain compounds of the heavier noble gases.

From November 1935, in his academic position, he was succeeded by Emanuele Oliveri Mandalà (1882-1971), his former assistant in Palermo, and then professor of Pharmaceutical Chemistry in Siena and Messina, who had been also Chancellor of the Messina University from 1932 to 1935.

Anyway, Segrè seemed not to have contacs with his chemist colleague at the Science Faculty, possibly because of the fact that Oliveri sympathized for the ruling Fascist Party. In 1936, Segrè become a member of the Pharmacy Faculty too, which included other two chemists: Carlo Perrier and Francesco Angelico (1873-1949), the latter a pharmaceutical chemist of international fame. Segrè particularly appreciated Perrier, whom he described as "a pleasant man, a true gentleman, loyal to Giolitti and anti-fascist". Segrè struck up a fruitful friendship with him, also because Perrier "well knew classic mineralogy and analytical chemistry" (Segrè 1995).

Perrier had got his degree in Chemistry at Turin University in 1908; after that, he had worked with Michele Fileti (1851-1914) and attended the Zurich Polytechnic. Later, he became assistant professor of Pharmaceutical and Toxicological Chemistry in Naples, where studied physical chemistry, investigating natural substances, radioactivity and helium presence in rocks. After becoming acquainted with Ferruccio Zambonini (1880-1932), Perrier developed an interest in mineralogy, becoming his assistant at Turin University. He then became Director of the Chemical Petrographic Institute of the Geological Survey in Rome, and, once obtained the qualification as university teacher, he became Professor of Mineralogy in Messina and in Palermo, as well as Director of the related Institute, and, after the death of Michele La Rosa (1880-1933), also suceeded him as Director of the Institute of Physics.

3. Physics at Palermo University in the Thirties

La Rosa had been Professor of Physics for almost 20 years, succeeding his father-in-law Damiano Macaluso (1845-1932). His research was mostly oriented toward electromagnetic effects; he proposed an electronic theory of metals, that met the criticism of Orso Mario Corbino (1876-1937). La Rosa is especially known for his opposition to some postulates of relativity, for instance that light speed should be the same in whatever reference system. Through a photometric study of double and variable stars and novae, he attempted to confirm the ballistic theory of light of Walter Ritz (1878-1909). Although initially in disagreement, he proved more favourable toward quantum and wave mechanics, in his last years (Chinnici 2015). La Rosa was Dean of the Science Faculty, and, from 1932 to 1935, Chancellor of the University of Palermo.

Among his pupils, we must remember Antonio Sellerio (1885-1973), later Professor of Theoretical Physics at the Engineering Faculty, getting involved in Philosophy of Science, and Cosimo Cannata, private docent of Experimental Physics. A hidden but

important role in the life of the Institute was also played, from 1889 to 1939, by technician Giovanni Battista Russo, whom Segrè judged "skilled and eager" (Segrè 1995).

La Rosa died on July the 6th 1933; in those years, physics was undergoing a period of renewal and strong evolution, both of its research themes and instrumentation. In 1932, James Chadwick (1891-1974) had discovered neutron, and in 1934 Irène Curie (1897-1956) and her husband Frédéric Joliot (1900-1958) artificial radioactivity. In Rome, Enrico Fermi (1901-1954) and his collaborators were turning from atomic to nuclear physics; Fermi had discovered that neutrons could be more efficient than alpha particles, as bullets to induce nuclear reactions. Several new radioactive isotopes were obtained, and slow neutrons discovered; these latter ones, moving at a speed close to that of thermal agitation, were very efficient in producing nuclear reactions (Segrè 1960).

4. The Chair of Physics at Palermo University

In this scenario, Segrè was appointed Professor of Physics in Palermo, also thanks to the presence of Fermi within the examining board. Meaningfully, the other members of the board scarcely appreciated the importance of Segrè's contribution to investigations on radioactivity. In their final relation, only a few lines are devoted to this:

> Segrè scientific production essentially concerns spectroscopy and artificial radioactivity. […] Regarding artificial radioactivity, he has very efficiently worked with Fermi, and his activity has particularly been devoted to chemical problems (Segrè 1995, p. 138).

Segrè was aware that the Chair was an acknowledgment to his scientific and didactic activity, but he suffered to leave the stimulating environment of via Panisperna, where he had benefited from excellent intellectual and experimental resources. He knew that in Palermo he would have found nothing but an empty new building, to be furnished and organized, and he felt "very much like a missionary leaving Rome for his first mission" (Segrè 1960). Nevertheless, he realized this was an opportunity to create a modern school of physics in Palermo, to be compared to the one in Rome, and decided to work hard and maximise local resources.

5. Organizing the Institute

Segrè arrived in Palermo soon after the moving of the Institute from its first building at the Theatins' complex (via Maqueda) to a new one, located at the ground and first floors of via Archirafi 36. There he found "very large rooms, waste space, and instruments and tools of the previous century or missing at all" (Segrè 1995). Among his collaborators, Giuseppe Petrucci, a mid-aged assistant, which Segrè judged "not reformable", and the aged abovementioned technician, Russo. Among his very few students

(eight in the years 1935/6 and 1936/7), Mariano Santangelo (1908-1970), who later became his assistant, and Ginetta Barresi "an unusual person, most intelligent, accustomed to use her brain, with deep Sicilian roots, sincerely religious, learned in Catholic doctrine, and, in many respects, ahead of time" (Segrè 1995). To expand his team, Segrè obtained that Bernardo Nestore Cacciapuoti (1913-1979) and Manlio Mandò (1912-1989), former students of the Scuola Normale of Pisa, were appointed his assistants in Palermo.

In regard to his experimental activities, he built a hood for chemical operations, and restored the glassware and laboratory equipment, possibly dating back to the times of illustrious chemist Stanislao Cannizzaro (1826-1910), what Segrè judged to be auspicious. To measure radioactivity, he asked Russo to build a standard ionization chamber and bought a Perucca-type electrometer (fig. 1); electrometers were called by somebody "*Signum Romanum*", the Roman sign, as Fermi's pupils had left them everywhere they had been (Segrè 1960). Segrè was thus ready to begin studies on artificial radioactivity in Palermo, despite the lack of radioactive sources, and funds to buy them.

Shortly after his move to Palermo, on February the 2nd 1936, he married in Florence Elfriede Spiro. Initially, the new wed set up in Palermo at the Excelsior Hotel, in the smart via Libertà, later moved to a new built apartment, in the near piazza Francesco Crispi, in front of Monastero delle Croci and Giardino Inglese (Segrè 1995).

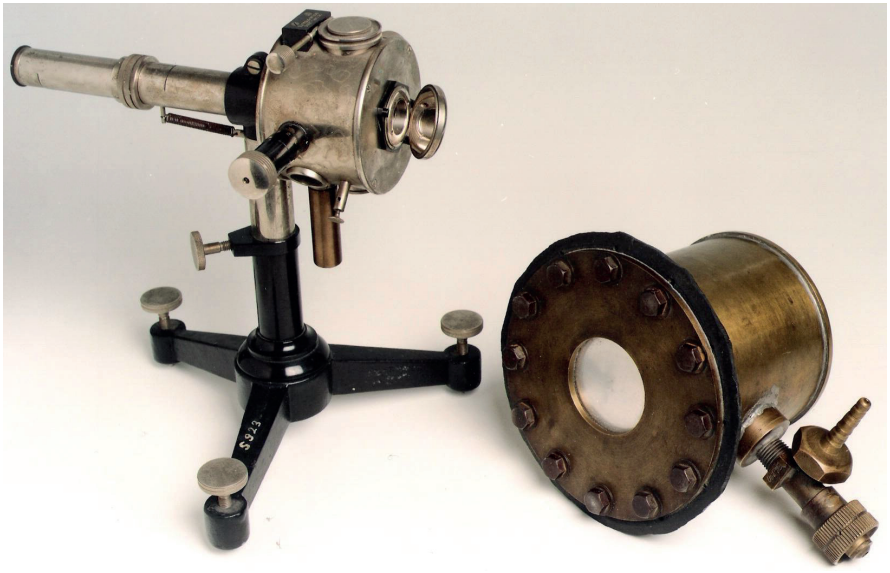

Fig. 1. Ionization chamber and Perucca-type electrometer displayed at the Department of Physics and Chemistry, in the historical building of via Archirafi 36, Palermo (Italy).

6. The cyclotron

At the end of the lecture course and examination session, in the summer 1936, Segrè and his wife set sail to the States. After a short stay in New York, where they visited Columbia University, they moved to Berkeley, as suggested by Otto Stern (1888-1969), at whose laboratory in Hamburg Segré had worked in previous years. At Berkeley, Ernst Orlando Lawrence (1901-1958) had built a 27-inch cyclotron, to obtain a relatively high amount of radioactive isotopes.

Fermi had unsuccessfully tried to build one in Roma too; therefore, he and Segrè were very interested to have first-hand information on the functioning and performance of this instrument. At Berkeley, Segrè got acquainted with Lawrence and his associates: Edwin McMillan (1907-1991), Don Cooksey (1892-1977), Franz Kurie (1907-1972) and Philip Abelson (1913-2004). He met Lorenzo Emo Capodilista (1909-1973), a former student of Bruno Rossi (1905-1993) and Gilberto Bernardini (1906-1995) from Florence.

Segrè was strongly impressed by the cyclotron, especially from the great amount of radioactivity it was able to produce, and assumed he would succeed, with careful work, in finding some new long-lived isotopes, in the targets of the instrument. He therefore obtained some worn out brass D electrodes and other pieces of the cyclotron from Lawrence in order to study them in Palermo. The choice of these pieces would reveal very lucky.

7. Physiological studies using ^{32}P

Back in Palermo, he soon started to work in his new laboratory, using the previously collected instruments, to separate different radioactivities with the usual radiochemical methods. To achieve this, he asked Perrier for help: their Institutes were hosted in the same building, and both of them belonged to the Science and Pharmacy Faculties. Also the physiologist Camillo Artom (1893-1970) belonged to the latter Faculty.

When Perrier succeeded in extracting a large amount of radioactive ^{32}P (phosphorus) from the brass electrodes, Segrè stated to involve Artom in further investigations. He explained him the utility of radioactive tracers (relatively unusual for the time), convincing him to use them in his studies on phospholipids metabolism, offering him both the isotopes and the technical support to measure radioactivity. Artom immediately understood details and potentialities of this new technique, and planned interesting and fruitful applications. In a short time, their cooperation produced excellent results: thanks to Segrè and Artom's enthusiasm and scientific far-sightedness, a multidisciplinary research group was born in Palermo. Beside Perrier, also Santangelo and Artom's assistant Gaetano Sarzana joined the group, working on innovative themes, of international reputation. Unfortunately, their activity was suddenly shut down by the new anti-Semitic politics of the Italian Government, which dispersed and wasted this potentiality.

7. A molybdenum plate

On February 1937, Lawrence sent Segrè a letter containing a molybdenum plate that had been part of the cyclotron deflector. Segrè immediately suspected that it could contain isotopes of the element having atomic number 43, one of the very few still missing elements of the Periodic Table. This element was quite unknown. In 1925, two German chemists, Ida Tacke (1896-1978) and her husband Walter Noddack (1893-1960), had claimed its discovery in a columbite sample, giving it the name "masurium" (Tacke 1925). This element was never obtained again, and many chemists suspected the Noddacks had been deluded and their claim was not correct. Moreover, the Mattauch rule excluded its presence in natural ores.

Segrè argued that, as the molybdenum plate (atomic number 42) had been bombarded with neutrons and deuterons, beside the isotopes of molybdenum, zirconium and niobium, one or more isotopes of element 43 could likely have been produced, through a (d, n) or (d, p) reaction, followed by a beta decay. To confirm the presence of the unknown element, it should be proved that the strong surface radioactivity of the plate was not due to any other known element; moreover, as many radioactive and chemical properties of the new element as possible should be determined.

Once again Segrè sought the help of Perrier, who had a better expertise and experience in analytical chemistry; together they started to collect evidence in favour of the presence of element 43 in the bombarded plate. Their strategy to solve the problem consisted in:

1. Using Mendeleév periodicity criteria to foresee chemical properties of the searched element;
2. Applying Marie Curie's procedure to separate and identify it with radiochemical methods, also considering that a macroscopic sample could behave quite differently from its trace amounts.

Perrier procedure was a striking, but not unusual, examples of what chemists do everyday: to inductively infer, from their experiments, what others are unable to see. Eventually, brought apart all possible interferences in non-active fractions, the radioactivity extracted from the molybdenum plate could be attributed to nothing else than element 43, even if in extremely small amounts, likely 10^{-10} grams or less. In Segrè comments, "all this work was very fun, and of obvious importance" (Segrè 1995).

8. The element 43

As the work proceeded, Segrè and Perrier discovered several interesting properties of this element, the first artificially obtained, thus confirming its similarity with its congener manganese. This investigation was completed in a short time, and the results were presented from fellow Nicola Parravano (1883 -1938) to the Royal National Academy of Lincei, on June the 4th 1937; they were later published in the Proceedings of the

Academy, and, in English, in the Journal of Physical Chemistry (Perrier, Segrè 1937). Shortly later, together with Cacciapuoti, Segrè identified three isotopes of element 43, with half lives of 90, 50 and 80 days respectively (Cacciapuoti, Segrè 1937).

This discovery drew great interest in the scientific community, and both Fermi and Bohr expressed their appreciation: Segrè was exceedingly pleased for these comments, as they acknowledged the high interest and quality of researches carried out at the Physical Institute of Palermo University. Widespread enthusiasm arose also in non-scientific Italian circles: as the discoverers had the right to name new-found elements, some names were suggested to celebrate fascism or to give fame to Sicily, such as "trinacrium". Anyway, Segrè and Perrier delayed the choice, as they did not share these sentiments; their hesitation was due to the extremely small amount of element obtained, and to their refusal to spark a quarrel on priority. They were well aware of the soundness of their own results and decided to wait for the acknowledgment of the scientific community, and the falsification of Noddack claim: "We believed it was more elegant not to show haste in naming the element" (Segrè 1995).

Although Capodilista frequently sent from Berkeley new fragments of the cyclotron to improve Segrè investigation, short lived isotopes could not be studied, as they decayed during the sea travel to Palermo. Therefore, during 1938 summer holidays, Segrè went back to Berkeley, where he built a simple ionization chamber to carry out investigations *in loco*. There, he also got acquainted with the young chemist Glenn Theodore Seaborg (1912-1999), a former pupil of Gilbert Newton Lewis (1875-1946); Seaborg accepted to work with Segrè. Together they succeeded in separating an isotope of element 43, with a 6-hour half-life. Investigating its electrons and gamma-ray emissions, they concluded these were generated by a transition between two isomeric states. The excited isomer decayed to the stable one, by an internal conversion mechanism, ejecting a K electron that could be revealed by a magnetic spectrograph. From the lines of the X-ray spectrum of this isotope, it was possible, according to Moseley law, to confirm it had atomic number 43.

Their spectrum was of a better quality than the one obtained by the Noddacks, and never published on an international journal; Segrè believed that this, together with the short half-lives of the isotopes, provided evidence that the Noddacks could not have extracted element 43 from an ore, simply because it could not exist on the Earth. Half-lives of all its isotopes are so short, compared to the geological times, that, if present at the birth of the Earth, they could not have survived till now (Segrè 1960).

9. Technetium

The closely following burst of World War II slowed or precluded information exchange between scientists, and delayed the solution of some fundamental chemical questions:

1. Should be acknowledged the existence of an element that could not be found in nature, but only produced through spontaneous or induced nuclear reactions?

2. Should be accepted indirect proofs of the existence of such an element, lacking appreciable or measurable amounts of it?

At the end of the war, the question was once again brought to life by Friedrich Adolf Paneth (1887-1958): in a paper published in *Nature*, on January 1947 (Paneth 1947), he answered positively to the above questions, vindicating for these elements the full right to be hosted into the empty places of Periodic Table, according to their atomic numbers, thus putting an end to the discussion about the supposed difference between natural and artificial elements. As a consequence, Paneth proposed to ascribe the discovery of an element to the first who would be able to produce irrefutable proofs of its identification, even if not in an ore. Certain of the incorrectness of the Noddacks' claim, Paneth invited Segrè and Perrier to give a name to element 43, as that of masurium had been illegally attributed.

To recall the artificial origin of element 43, Segrè choose a Greek term, *technetos*, which means artificial. In agreement with Perrier, in a letter to *Nature* (Segrè 1947) he proposed the Latin name *technetium* (symbol Tc), definitively adopted from IUPAC in 1949.

10. A priority dispute

Although they had both tried to verify the reliability of the results, Segrè and Noddacks never gave rise to a public dispute on priority. Nevertheless, in recent years, someone has tried to reassess Noddacks' discovery. The point was: can element 43 be found in terrestrial ores or not? In 1939 Siegfried Flügge (1912-1997) suggested that, in past eras, uranium could have undergone self-sustained nuclear chain reactions, in natural environment, in large deposits such as that in Joachimsthal, Bohemia (Flügge 1939). In 1965 the Japanese nuclear chemist Paul Kazuo Kuroda (1917-2001) calculated the age of such a natural reactor, which indeed was found in 1972 in the Oklo (Gabon) pitchblende mine (Scerri 2013). There, small amounts of technetium were found, likely due to the spontaneous ^{238}U, or neutron induced ^{235}U fission.

As a consequence, the Belgian Physicist Peter van Assche (1988) had tried to rehabilitate the Noddacks, proving element 43 really present in the ores they had analysed. The Noddacks had indeed treated uranium-containing ores too, such as monazite, and pitchblende, but they didn't claim to have found masurium there. Van Assche tried:

1. To evaluate masurium abundance in the ores they analysed (columbite, sperrilite, gadolinite and fergusonite), on the basis of their uranium content;
2. To establish if such a small amount could produce X-rays lines surely detectable, by the best instruments available in 1925.

Starting from the half lives of the isotopes ^{99}Tc and ^{238}U, and from the yield of the uranium spontaneous fission to ^{99}Tc (about 6.3%), and assuming a 5% medium content of

uranium in the analysed ores, van Assche evaluated a relative atomic abundance of about 10^{-13} for technetium.

The second point was harder to verify *a posteriori*, lacking information about the instrument used, and the X-ray plates themselves, because they had been gone destroyed, as Noddack told to Segrè on September 1937 (Segrè 1995). Despite van Assche's attempts to correct the instrument detection limits, that Carl von Berg, the technician who registered the X-ray spectra of Noddacks' residues, had estimated, through the calibration line, as low as 10^{-9}, this value was still too large compared with the estimated masurium content (Herrmann 1989). In conclusion, this and other attempts to rehabilitate Noddacks proved unsuccessful.

Anyway, in the Fifties, astronomers working with Paul Willard Merrill (1887-1961), at Mount Wilson Observatory, identified intense technetium lines in spectra of S-stars (Merrill 1952). As a consequence, the problem of actual existence in nature of element 43 was solved. Though not found on Earth in significant quantities, because of its short half-life, as far as we know, technetium is mostly produced by stellar nucleosynthesis in S-stars and is formed in the star's core by slow neutron capture (s-process). S-stars belong to the class of asymptotic giant branch (AGB), which includes stars of less than 8 solar masses, near to their final evolutionary stage.

In AGB stars there is plenty of C13, and alpha capture onto C13 provides an efficient free neutron source for s-process. AGB stars, having helium and hydrogen burning shells, dredge up heavy elements from the core to the surface. Tc-rich S-stars have undergone third dredge-up (TDU) events, while in Tc-poor S-stars, technetium has completely decayed (Shetye et al. 2018). For this reason, technetium is not observed in all S-star spectra. According to some simulations, a fraction of technetium could be also produced by Type Ia supernovae (Leung, Nomoto 2018). Nature therefore produces technetium, as well as other "exotic" heavy elements, in the various final stages of stellar evolution, in that wonderful forge which is our universe.

References

Cacciapuoti B.N., Segrè E. (1937). "Radioactive Isotopes of Element 43". *Physical Review*, 52, pp. 1252-1253.

Chinnici I. (2015). *La Fisica negli anni trenta: uno sguardo al contesto*. In Workshop *Palermo, 1937. La scoperta del Tecneto*, Università di Palermo, 20-22 October 2015.

Flügge S. (1939). "Kann der Energieinhalt der Atomkerne technisch nutzbar gemacht werden?". *Naturwissenschaften*, 27, pp. 402-410, citato da (Scerri 2013, p. 225).

Gambaro I. (1987). *La scoperta del Tecnezio.* In *Atti dell'VIII Convegno Nazionale di Storia della Fisica*. Napoli: pp. 187-200.

Herrmann G. (1989). "Technetium or masurium – a comment on the history of Element 43". *Nuclear Physics*, A 505, pp. 352-360.

Leung S.C., Nomoto K. (2018). "Explosive Nucleosynthesis in Near-Chandrasekhar-mass White Dwarf Models for Type Ia Supernovae: Dependence on Model Parameters". *The Astrophysical Journal Supplement*, 861 (2), p. 143.

Merrill P.W. (1952). "Spectroscopic Observations of Stars of Class S". *The Astrophysical Journal*, 116, p. 21.

Paneth F. A. (1947). "The making of the missing chemical elements". *Nature*, 159, pp. 8-10.

Perrier C., Segrè E. (1937). "Alcune proprietà chimiche dell'Elemento 43". *Atti della reale Accademia Nazionale dei Lincei*, Serie VI, pp. 723-730; "Some Chemical Properties of Element 43". *Journal of Chemical Physics*, 5, pp. 712-716.

Scerri E. (2013). *The Tale of 7 Elements*. New York: Oxford University Press.

Segrè E. (1947). "Technetium. The Element of Atomic Number 43". *Nature*, 147, p. 24.

Segrè E. (1960). *From atoms to antiprotons. Forty-Seventh Annual Faculty Research Lecture.* March 24, https://oac.cdlib.org/findaid/ark:/13030/c8639vx8/dsc/

Segrè E. (1995). *Autobiografia di un fisico*. Bologna: Il Mulino. See also Segrè E. (1993). *A mind always in motion. The autobiography of Emilio Segré.* Berkeley: University of California Press.

Shetye S., Van Eck S., Jorissen A., Van Winckel H., Siess L., Goriely S., Escorza A., Karinkuzhi D., Plez, B. (2018) "S stars and s-process in the Gaia era. I. Stellar parameters and chemical abundances in a sub-sample of S stars with new MARCS model atmospheres". *Astronomy & Astrophysics*, 620: A148, p 21.

Tacke I. (1925). "Die Eka-Mangane." *Naturwissenschaften*, 13, pp. 567-574.

Van Assche P. (1988) "The ignored discovery of element Z = 43". *Nuclear Physics*, A 480, pp. 205-214.

Zingales R. (2005). "From Masurium to Trinacrium. The troubled story of element 43". *Journal of Chemical Education*, 82, pp. 221-227.