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Science in Radiation Education: The new chemical element Nihonium and an old one Nipponium

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Abstract

To enhance the radiation literacy of general public, it seems important to make them interested not only in medical and engineering application of radiation, but also in advancement of basic science associated with radiation. The present author deals with science histories of finding new chemical elements "Nihonuim" and "Nipponium" , as well as production and application of tecnnetium with emphasis laid on the short-lived radionuclide ^{99m}Tc ($T_{1/2}$ = 6 h) used for medical diagnoses worldwide.

In 2016, the International Union of Pure and Applied Chemistry (IUPAC) officially announced that the element 113 was named "Nihonium" with its symbol "Nh". This new chemical element was synthesized with a linear accelerator in RIKEN, Japan by Professor Kosuke Morita and his colleagues in 2007 and then named after the Japanese country name Nihon. Japan is sometimes called "Nippon" in Japanese. In the past, there was a chemical element "Nipponium" (Np) with its atomic number 43 named by Japanese Professor Masataka Ogawa. He claimed the discovery of the element 43 in natural ore in 1908. Unfortunately, however, his discovery was not confirmed by the following experiments, and the name nipponium has disappered from the table of chemical elements. At present, the element 43 is called technetium (Tc), the first manmade element found by C. Perrier and E. Segré in 1937.

1. Introduction

In January 2019, United Nations Educational, Scientific and Cultural Organization (UNESCO) launched the International Year of the Periodic Table of Chemical Elements 2019 (IYPT 2019), celebrating the 150th anniversary of its creation by Russian scientist Dimitry Ivanovich Mendeleev, who proposed it in his lecture at the annual meeting of Russian Chemical Society on June 3, 1869. The program of Opening Ceremony of the IYPT 2019 held on January 29 in Paris included a presentation of "Hand-made elements" by Professor Yuri Oganesian; the lateset synthesized element-118 was named "Oganeson" in honor of his exclusive contribution to the research field of superheavy elements (SHE), extending the periodic table of chemical elements.

At the time when the International Union of Pure and Applied Chemistry (IUPAC) officially announced the name Oganeson (Og) for the element 118 on June 8, 2016, other 3 names of new elements such as "Nihonium" with its symbol "Nh" for the element 113, Moskovium (Mc) for 115 and Tennessine (Ts) for 117 were included in the press release. Nihonium was synthesized in RIKEN (Institute of Physical and Chemical Research), Wako, Japan by Professor Kosuke Morita (**Fig. 1**) and his colleagues in 2004.

The name Nihonium comes from Japanese country name "Nihon". Japan has the other country name "Nippon" and we might remind an old name "Nipponium (Np)" that was named for the element 43 in 1908

by Japanese professor Masataka Ogawa. The brief histories of research on both Nihonium and Nipponium are described in this paper.

Fig. 1 Prof. Dr. K. Morita, Kyusyu Univ./RIKEN

Althought the name "Nipponium" has disappeared, the element sitting in the 43rd place in the modern periodic table of chemical elements is technetium (Tc) that is the first man-made chemical element and all of 19 isotopes of which are radioactive. The present paper also deals with the production and utilization of Tc, with emphasis laid on the short-lived radionuclide ^{99m}Tc which is used for medical diagnoses worldwide.

2. Nihonium and Nipponium

In the early mornig on Decemver 31, 2015, Professor Morita receved an e-mail from the IUPAC informing that the naming right for the element 113 was given to his research group of RIKEN. But behind this goal, there were hard and long-time competions between the Japanese group and the Russia-US joint research team comprised of the Flerov Laboratory of Nuclear Reactions (FLNR) and the Lawrence Livermore National Laboratory (LLNL).

Japanes group produced 3 atoms of the element 113 in 8 years from 2004 to 2012 by bombarding $^{70}_{30}Zn^{n+}$ ions on $^{209}_{83}Bi$ targets,

$$^{209}_{83}Bi + {}^{70}_{30}Zn \rightarrow {}^{278}_{113}Nh + n, \qquad (1)$$

by means of a linear accelerator "RILAC" in RIKEN, Wako, Japan.[1,2] Before their first production of the element 113 on July 23, 2004, the Russia-US joint research team found the element 113 in the α-decay chain of the element 115 (^{288}Mc) produced by bombarding $^{48}_{20}Ca^{n+}$ ions on $^{243}_{95}Am$ targets,

$$^{243}_{95}Am + {}^{48}_{20}Ca \rightarrow {}^{288}_{115}Mc + 3n \qquad (2a)$$

$$^{288}_{115}Mc \rightarrow {}^{284}133 + \alpha, \qquad (2b)$$

using the U-300 cyclotron in FLNR. [3] Furthermore, they found more than a few tens of aotms of the element 113 in their successive experimnents thereafter.

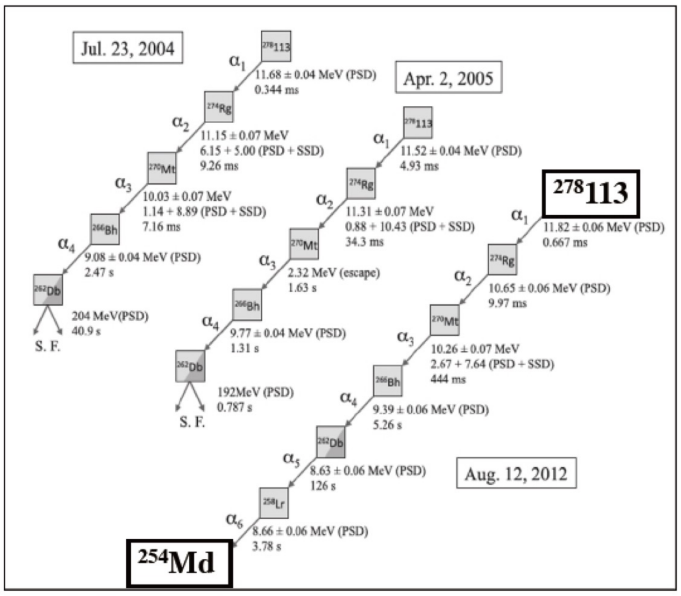


Fig. 2 Observed decay chain in the present work together with previously observed chains.

In these situations, it seemed hard for Morita's group to grab the naming right for the element 113, but Morita's group had a luck to insist the naming right. They detected memdelevium-254 (^{245}Md) in the α-decay chain of the element 113 of the third atom appeared in the experiment on August 12, 2012 (**Fig. 2**).[2] This detection was the essential evidence for supporting the existence of the new element 113, because ^{254}Md was a well known transuranium nuclide with half-life of 10 min, while the

Fig. 3 Prof. Masataka OGAWA
(1865-1930)
First Chair of Inorganic Chemistry, Tohoku Imperial University

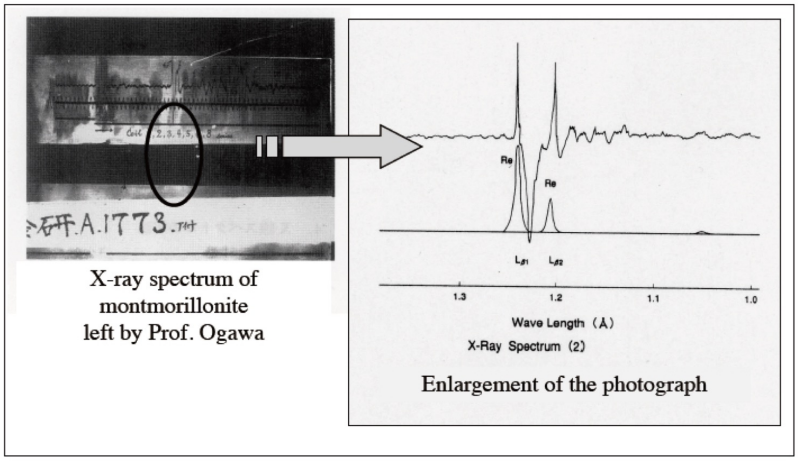
Russia-US joint team was not successful enough in obtaining the clear evidence for confirming their findings.

Consulting with his colleagues in RIKEN, Morita eventually decided to propose the name "Nihonium" for the new element 113, and the name and its symbol Nh were officially announced by the IUPAC through pressrelease on June 8, 2016.

Japan is called "Nihon" or "Nippon" in Japanese. The name "Nihonium" comes from Nihon. It should be noticed here that the name "Nipponium" (Np) was once used for the element 43, which Professor Masataka Ogawa (**Fig. 3**) of Tohoku Imperial University, Sendai, Japan claimed its discovery in natural ore "Thorianite" in 1908, while he stayed in Professor Ramsay's Laboratory in University College, London. He reported the finding in English journal *Chemical News*.[4,5] Unfortunately, however, his discovery was not confirmed by the following experiments because the element 43 did not occur naturally, and the name nipponium has disappered from the table of chemical elements. At present, we know that the element 43 is called technetium (Tc), the first artificially synthesized element found in a molybdenum plate — parts of experimental equipmet exposed to deuteron beam from the cyclotron in California University, Berkeley, US — by C. Perrier and E. Segré in 1937 (Fig. 5). [6] The symbol Np is now used for neptunium of transuranium elememt with the atomic number of 93.

Althoug Ogawa was not successful in confirming his discovey of a new element, his work on nipponium should be respected because the element he discovered might be the elemnt 75, the rhenium discovered by W. Noddack and I. Tacke in 1925, [7] more than 17 years after the Ogawa's paper in 1908. This possibility was revealed by K. Yoshihara, Professor Emeritus of Tohoku University in 2003.[8] Tracing the footprint of Ogaeas's work in Sendai, Yoshihara found an Ogawa's mistake in calculation of the atomic weight of nipponium. Ogawa gave the atomic weight 100.6 to nipponium by considering that the material he analyzed was chloride ($NpCl_2$), and then he placed the new element in a 43rd box of the periodic table. Yoshihara recalculated its atomic weight by assuming that it should be oxychloride ($NpOCl_4$). In the latter case the atomic weight becomes 185.2, that is very close to 186.2 of rhenium (Re) at present.[9]

Furthermore, Yoshihara foud an important glass plate in his relics. That is an X-ray spectrophotogram of montmorillonite ores which Ogawa used in his experiments to confirm the existence of nipponium in Sendai. Surprisingly, the two peaks in the X-ray spectrum (shown in Fig. 4) fitted just to that of characteristric lines $L_{\beta 1}$ and $L_{\beta 2}$ of rehenium (Re).[10,11] The fact indicates that Ogawa likely discovered the element 75 for the first time, and if he placed his element not in the 43rd but 75th box both of which were vacant in the periodic table at that time, "Nipponium (Np)" might still remain even in the modern periodic table of chemical elements.



X-ray spectrum of montmorillonite left by Prof. Ogawa

Enlargement of the photograph

Fig. 4 Ogawa likely discovered Element 75 (Re).

3. Production and utilization of technetium, the first man-made chemical element

Technetium does not occur naturally, because all of 19 isotopes of Tc are radioactive and even ^{98}Tc ($T_{1/2}$ = 4.8 × 10^6 y) with the longest lifetime has disappeared in the past 4.6 billion years after the birth of the earth; though we can find trace amounts of ^{99}Tc ($T_{1/2}$ = 2.1 × 10^5 y) in uranimun ores such as pitchblende, produced by spontaneous fission of ^{238}U; i.e., 4 ng of ^{99}Tc in 1 kg of U. In the past decases, in addition, a few hundred tons of radioactive ^{99}Tc—a daughter nuclide of ^{99}Mo produced by nuclear fission of ^{235}U—have been piled up in spent nuclear fuel of nuclear power stations around the world, as well as in nuclear fuel reprocessing plants in specific countries.

- A radioactive, silvery metal that does not occur naturally.
- The first artificially synthesized element (hence its name).
- Deuteron bombardment on Mo metal:

^{96,97}Mo(d,xn)^{97m}Tc ($T_{1/2}$ = 91 d)
→ ^{97}Tc ($T_{1/2}$ = 2.6×10^6 y)
[x=1,2]

Emilio G. Segrè (1905-1989)
University of California, Berkeley, US
Nobel Prize in Physics for discovery of antiproton (1959).

Fig. 5 Discovery of Technetium in Mo metal exposed to deuteron in cyclotron.

Table 1. Useful technetium isotopes and production.

Nuclide ($T_{1/2}$)	Decay	Reaction	Target Materials	Utilization
^{95m}Tc (61 d)	IT	^{93}Nb (α, 2n) ^{95m}Tc	Nb metal	Enviomental tracer
^{99}Mo (66.0 h)	β^-	^{235}U (n,f) FP	UO_2 pellet	^{99m}Tc generator
^{99m}Tc (6.0 h)	IT	^{99}Mo [β^-] ^{99m}Tc	Milking	Medical diagnosis
^{99}Tc (2•10^5 y)	β^-	^{99m}Tc [IT] ^{99}Tc	–	Enviomental tracer

Of useful radioisotopes of Tc listed in **Table 1,** short-lived ^{99m}Tc ($T_{1/2}$ = 6 h) is one of the most essential radioisotopes for medical diagnoses and is most widely used in the world nowadays. This radioisotope is suitable for the single photon emission computed tomography (SPECT) for metastasis, breast and thyroid cancers as well as blood stream tests associated with heart attck and stroke, because of its appropriate characters of emitting radiation described as follows: (1) the γ-ray energy of 0.14 MeV —an single photon emitted — is suitable for detection with high sensitivity, (2) the half-life of 6 hours is appropriate for diagnoses —not too short nor too long, (3) ^{99m}Tc-labeled medicines are easely prepared in hospitals by milking ^{99m}Tc from a ^{99}Mo cow — using a small equipment called a generator — followed by aquick preparation of ^{99m}Tc-labeled medicine by means of a kit supplied from phermceutical companies once a week.

As shown in the decay scheme of ^{99}Mo and ^{99m}Tc in **Fig. 6**, both the nuclides ^{99m}Tc and ^{99}Mo are in the radioactive equilibrium: it takes about 20 h to attain the secular equilivrium after a separation of ^{99m}Tc from ^{99}Mo and then the apparent half-life of daughrer ^{99m}Tc in the generator becomes 66 h (2.7 days) — the same as that of the parent ^{99}Mo. And we can obtain ^{99m}Tc neccessary for SPECT once a day by milking repeatedly through one week at the site of medical use. **Figure 7** shows an example of preparation kits for

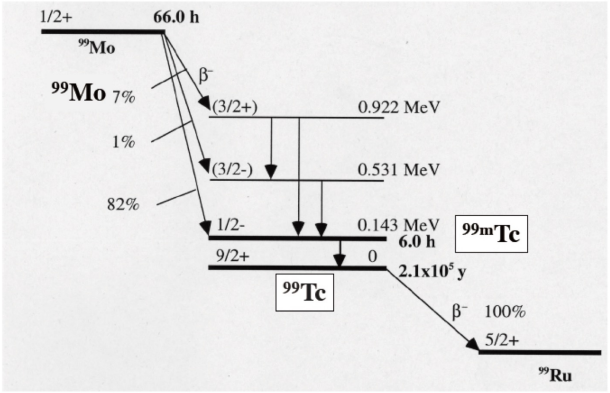


Fig. 6 Decay Scheme of ^{99}Mo-^{99}Tc.

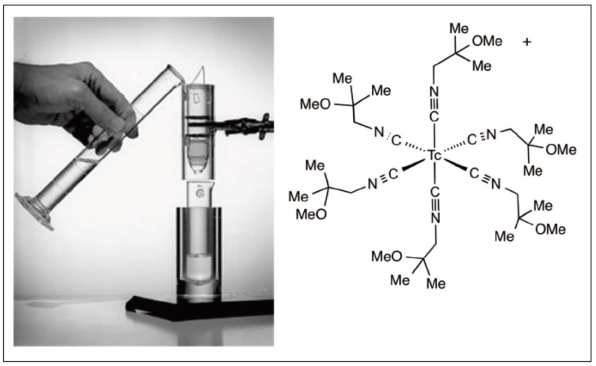


Fig. 7 Technetium-99m generator and sestamibiis-^{99m}Tc ("Cardiolite") used for blood stream test of the heart.

^{99m}Tc-labeled medicine sestamibiis ("Cardiolite") to be used for SPECT imaging of blood stream of the heart in a manner as shown in **Fig. 8**, the nuclear medicine being injected into the paitient's vein.

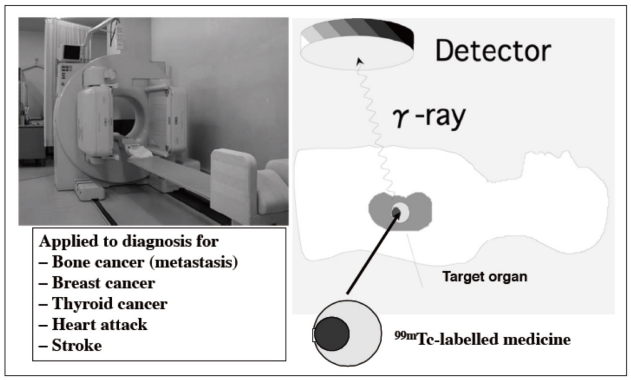


Fig. 8 Single photon emission computed tomography (SPECT) with ^{99m}Tc

Technetium-99m labeled nuclear medicines nowadays are used for 30 million patients or more a year in the world (~500 thousands in Japan), but we have recently a big problem in shortage of the supply. To use ^{99m}Tc for nuclear medicine, we need sufficient amounts of pure ^{99}Mo with high specific activity as a cow for the milking. In principle, the ^{99}Mo nuclide is produced by extraction from the fission products of enriched ^{235}U targets irradiated in nuclear reactors but it is not easy to keep the production technology because of its difficulty in post-irradiation chemical processes—similar to the nuclear fuel reprocessing, albeit small in scale—as well as conditions of nuclear reactor operations. In fact, more than 95% of ^{99}Mo has been produced in such 5 countries as Canada, the Netherland, France, Belgium and South Africa. However, Canada the biggest supplier—more than 30% of share in the world—had problems with aging of nuclear reactors used for the ^{99}Mo production. In fact, the NRU reactor in Chalk River, Canada—operated more than 50 years—shut down for the safety reason in 2007 and 2009, and it gave rise to global crisis in short supply of medical ^{99}Mo.

To overcome these problems raised from the short supply of ^{99}Mo, Japan has changed the strategy of importing ^{99}Mo not only from the above-mentioned 5 coutries but also from Asutralia and Indonesia. But the problem has not yet been solved enough because the amounts of production in the latter two countries are limited. Many medical users in Japan ask to produce ^{99}Mo inland but it is not still attainable, albeit continuing efforts. Actualy early in 1980s in Japan, we have once succeeded in producing ^{99}Mo, in the work of which I myself was engaged while staying in Japan Atomic Energy Instititute (JAERI). Despite the excellent quality of the product with specific activity high enough for medical use, the product was not received by medical users in Japan, unfortunately. The serious problem was a lack of supply for several times a year, due to the periodical suspension of reactor operation—not to meet the user's desire of the regular supply once a week throughout a year from January to December. The actual problem was not in technological difficulty of the production, but in a commercial matter of regular and constant supply of the product.

4. Conclusion

"Nihonium" (Nh) with its atomic number 113 is the chemical element found or produced in Asia for the first time and named after the Japanes county name Nihon of Japan. About 110 years ago, there was a chemical element "Nipponium" with its atomic number 43, named after Nippon of the other Japanese country name of Japan, but the latter has dissapered from the periodic table of chemical elements. The 43rd element in the modern periodic table is technetium (Tc)—the first mann-made chemical element—all the isotopes of which are radioactive and do not occur naturally. Of 19 radionuclides of Tc, the short-lived ^{99m}Tc ($T_{1/2}$ = 6 h) is the most widely used radionuclide around the world for imaging of medical diagnoses. Recently, however, we have problems with shortage in supply due mainly to aging of nuclear reactors used

for the production of ^{99}Mo ($T_{1/2}$ = 66 h), from which ^{99m}Tc is extracted by milking for preparation of ^{99m}Tc-labeled radiomedicine in hospitals.

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