

AMS MEASUREMENT OF ^{237}Np AT CIAE

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ABSTRACT. ^{237}Np ($\sim 2.14 \times 10^6$ yr half-life) is potentially applicable in studies on nuclear safeguards and radioactive waste migration. The atomic ratio of $^{237}\text{Np}/\text{U}$ in nature is 10^{-12} or even lower, depending strongly on the integral neutron flux received by the material. As an ultra-sensitive technique, accelerator mass spectrometry (AMS) is the best for measuring ultratrace ^{237}Np . By extracting negative molecular ions NpO^- from the oxide sample using $^{238}\text{UO}^-$ and $^{208}\text{Pb}^{16}\text{O}_2^-$ pilot beams for the simulation of ^{237}Np ion transport, identifying the interference isotopes by high-resolution dedicated injector, electrostatic analyzer, and time of flight (TOF) detector, a method for AMS measurement of ^{237}Np was set up on the HI-13 accelerator at the China Institute of Atomic Energy (CIAE). A sensitivity of $<10^{-11}$ has been achieved for the isotopic ratio $^{237}\text{Np}/^{238}\text{U}$.

INTRODUCTION

Neptunium is the first transuranic element and belongs to the actinide series. Its most long-lived isotope is ^{237}Np , with a half-life of $(2.14 \pm 1) \times 10^6$ yr (Richard 1996). It is principally produced by the following 3 processes: the successive thermal neutron capture on ^{235}U , i.e. $^{235}\text{U}(\text{n},\gamma)(\text{n},\gamma)^{237}\text{U}$ reaction, followed by a β^- decay; high-energy neutron-induced $^{238}\text{U}(\text{n},2\text{n})^{237}\text{U}$ reaction, followed by a β^- decay; and the α -decay of ^{241}Am ($t_{1/2} = 433$ yr), which may be either directly from spent nuclear fuel or accumulated by the β^- decay of ^{241}Pu ($t_{1/2} = 14$ yr).

Most ^{237}Np is a byproduct of nuclear reactors and plutonium production (Dorin and Walter 1997). ^{237}Np is also found in trace amounts in uranium ores due to transmutation reactions ($^{235}\text{U}(\text{n},\gamma)(\text{n},\gamma)^{237}\text{U} \xrightarrow{\beta^-} ^{237}\text{Np}$ and $^{238}\text{U}(\text{n},2\text{n})^{237}\text{U} \xrightarrow{\beta^-} ^{237}\text{Np}$) (Hammond 2004). The $^{237}\text{Np}/^{238}\text{U}$ atomic ratio in nature is expected to be 10^{-12} or even lower (Peppard et al. 1952; Myers and Lindner 1971; Zhang 1978), but it may be significantly higher in high-grade uranium ore (Zhang 1978), depending strongly on the integral neutron flux received by the material. The low ^{237}Np present in the environment means that it has been of less immediate concern to humans than the other transuranium elements, Pu and Am, and it has therefore been studied to a lesser extent (Keith-Roach et al. 2001). However, the study of Np in the environment is now of increasing interest because of its relatively high mobility, its ingrowth in the environment, and the timescales involved. Therefore, ^{237}Np is potentially applicable in studies on nuclear safeguards and radioactive waste migration (Kim et al. 1989). However, to meet these applications, work is needed to get an overview on the distribution of both anthropogenic and natural ^{237}Np in the environment.

Methods previously employed to measure ^{237}Np include α -decay counting (Peppard et al. 1952), isotopic dilution mass spectrometer (IDMS) (Myers and Lindner 1971), inductively coupled plasma mass spectrometry (ICP-MS) (Sabine and Dietze 1999), and accelerator mass spectrometry (AMS) (Fifield et al. 1997; Keith-Roach et al. 2001). Peppard et al. (1952) used the decay counting method to determine ^{237}Np in natural pitchblende, with a maximum value of $(1.8 \pm 0.4) \times 10^{-11}$ for $^{237}\text{Np}/^{238}\text{U}$. However, it is difficult to measure typical environmental levels with the decay counting method. AMS completely suppresses molecular ion species, and its detection limit can be several orders of magnitude below that of the conventional mass spectrometric methods. As an ultra-sensitive technique, AMS is the best choice for measuring ultratrace ^{237}Np . This article details a method

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for AMS measurement of ^{237}Np developed on the HI-13 accelerator at the China Institute of Atomic Energy (CIAE).

EXPERIMENTAL

Producing a beam of ^{237}Np ($\sim\text{nA}$) with which to tune the system is out of the question because of the practical, radiological, and safety consequences of keeping ^{237}Np in mg quantities. Fifield et al. (1997) showed that the ionization efficiency of neptunium is 1.5 times that of uranium, based on extracting monoxide-negative molecular ions. A method for AMS measurement of ^{236}U was previously developed at the HI-13 accelerator at (CIAE) (Wang et al. 2010a) based on the extraction of UO^- . Similarly, ^{237}Np can be measured by AMS at CIAE by extracting the molecular ions NpO^- .

As a proof of principle for measurement of ^{237}Np by AMS, we measured the ^{237}Np in a purified uranium-ore sample to develop the method and to test the system at CIAE, while avoiding the complicated chemical separation of Np from U. To satisfy the requirements for AMS measurement of heavy isotopes (e.g. ^{182}Hf , ^{236}U , ^{237}Np) at CIAE, a high-resolution dedicated injector for AMS was set up in 2007 (Tuo et al. 2010), as shown in Figure 1. A mass resolution of 800 can be achieved as demonstrated by scanning of the ion beams from a uranium sample (Figure 2). At the settings for ions with a mass of 253 amu (appropriate for $^{237}\text{Np}^{16}\text{O}^-$), a number of isobaric ions, such as $^{235}\text{UH}^{17}\text{O}^-$, $^{235}\text{UH}_2^{16}\text{O}^-$, $^{238}\text{UH}^{14}\text{N}^-$, etc, interfere. Since no long-lived atomic isobar for ^{237}Np exists, the challenge is to identify the ^{237}Np ions of interest from isotopic backgrounds of ^{238}U and ^{235}U . (^{236}U is not a problem because it is a rare isotope like ^{237}Np .) Fortunately, most ^{238}U and ^{235}U can be resolved from ^{237}Np with the new dedicated AMS injector, as shown in Figure 2.

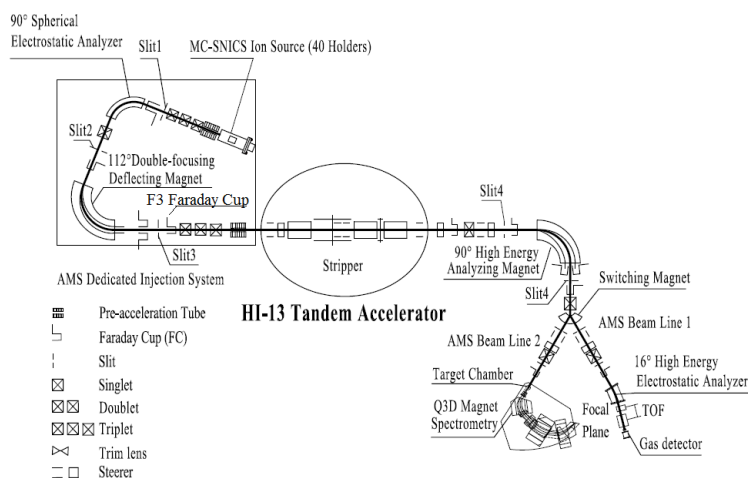


Figure 1 Schematic diagram of the accelerator mass spectrometer based on the HI-13 accelerator at CIAE

The ^{236}U AMS measurement was carried out on AMS beam line 1, as shown in Figure 1. On the CIAE AMS high-energy side, the beam was analyzed by a 90° post-analyzing magnet (maximal mass-energy product of 200 MeV amu) and a 17° electrostatic deflector. For $^{237}\text{Np}^{11+}$ ions, the maximum usable terminal voltage was 7.210 MV, which corresponds to a final energy of 86.172 MeV. At this terminal voltage, the theoretical charge-state fraction is about 13%, calculated with the semi-empirical formula of Sayer (1977). In the terminal of the HI-13 tandem accelerator, a $3\text{-}\mu\text{g}\text{-cm}^{-2}$ thick carbon foil was used as a stripper. In order to clip the isotope background from ^{238}U and ^{235}U

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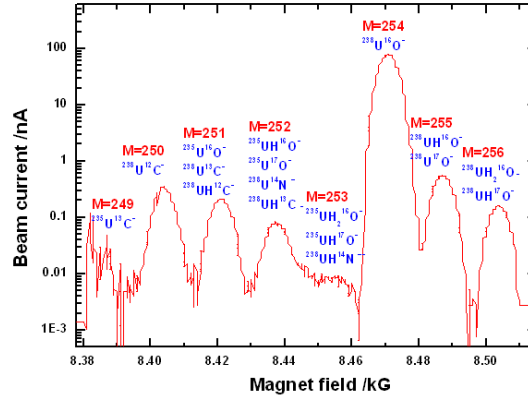


Figure 2 Scan spectrum of the AMS dedicated injector with a U_3O_8 sample.

as much as possible, the object slit and the image slit of the 90° post-analyzing magnet were set to ± 1.9 and ± 1.3 mm, respectively. The image slit of the AMS electrostatic deflector was set to $3\text{ mm} \times 10\text{ mm}$ for clipping the tails of $^{235}\text{U}^{11+}$ and $^{238}\text{U}^{11+}$ ions. The combination of the analyzing magnet and ESA achieved an energy resolution (dE/E) of better than 0.2%. As a consequence of scattering and Coulomb explosion of these very heavy ions in the stripper foil, together with the restrictions imposed by the slit settings, the measured transmission efficiency from the F3 Faraday cup (low-energy side) to the detector system was only about 9×10^{-4} for $^{238}\text{U}^{11+}$ (Wang 2010).

The beam $^{238}\text{UO}^-$ is the best pilot beam for $^{237}\text{NpO}^-$ because the mass of ^{238}U is close to ^{237}Np . However, the $^{238}\text{U}^{11+}$ beam current on the high-energy beam line is not large enough for tuning. Since the beam current is only 20–100 nA of $^{238}\text{U}^{16}\text{O}^-$ injected into the accelerator, the current of $^{238}\text{U}^{11+}$ is only 0.2–1.0 nA. Tuning of the accelerator then proceeded in 2 steps by using $^{208}\text{Pb}^{16}\text{O}_2^-$ and $^{238}\text{UO}^-$ pilot beams, respectively. First, in order to optimize the accelerator parameters, a $^{208}\text{Pb}^{10+}$ beam ($^{208}\text{Pb}^{16}\text{O}_2^- \sim 300\text{ nA}$) at a terminal voltage of 7.458 MV ($^{208}\text{Pb}^{10+}$ has the same momentum as $^{237}\text{Np}^{11+}$ at a terminal voltage of 7.210 MV) was used to define the beam transport from the low-energy system to the image of the analyzing magnet. Second, a $^{238}\text{U}^{11+}$ beam at a terminal voltage of 7.180 MV ($^{238}\text{U}^{11+}$ has the same momentum as $^{237}\text{Np}^{11+}$ at a terminal voltage of 7.210 MV) was used to set up the $^{237}\text{Np}^{11+}$ transport from the image of the analyzing magnet to the AMS beam line, while keeping all the parameters unchanged that were already optimized in the first step. The 2-step tuning method for optimizing the ^{237}Np beam transport makes the adjustment much easier. This poor beam transmission limits the efficiency of ^{237}Np measurements. In the future, we intend to investigate other methods to improve the overall transmission.

The energy difference between the background ions and the ^{237}Np ions of interest is very small, about 0.8% for ^{235}U , and about 0.4% for ^{236}U , ^{238}U . The order of magnitude of the ratio $^{237}\text{Np}/^{238}\text{U}$ in our natural sample is similar to the $^{236}\text{U}/^{238}\text{U}$ ratio (see below), so the ^{236}U is most likely not a significant background in the ^{237}Np measurement. However, ^{238}U and ^{235}U constitute $\sim 99.3\%$ and 0.7% of natural uranium, respectively, and hence are inevitably the main background in the ^{237}Np measurement. For the detectors available at our laboratory, only the time-of-flight (TOF) detector has sufficient resolution to distinguish ^{237}Np from the nuclides ^{238}U and ^{235}U . Table 1 shows the time of flight for the flight path of 1.8 m length for 11+ ions of different masses with the same magnetic rigidity.

Table 1 Time of flight for a flight path of 1.8 m and 11+ ions of different masses with the same magnetic rigidity.

Ion	Energy (MeV)	Flight time, t (ns)	Δt (ns)
$^{235}\text{U}^{11+}$	86.114	213.116	1.814
$^{236}\text{U}^{11+}$	86.143	214.023	0.907
$^{237}\text{Np}^{11+}$	86.172	214.930	
$^{238}\text{U}^{11+}$	86.201	215.837	0.907

The TOF system in CIAE-AMS consists of a microchannel plate (MCP, “start” detector) and a silicon surface barrier detector (SBD, as a “stop” detector) with a gold front contact. The length of the flight path is 1.8 m, as shown in Figure 3. A 7- $\mu\text{g}\cdot\text{cm}^{-2}$ carbon foil (with a diameter of 30 mm) was employed in the start detector to produce the secondary electrons, which were then reflected by an electrostatic mirror, collected and multiplied by the MCP. The stop detector SBD also provides the measurement of the ion’s energy for discrimination against lighter-mass and hence lower-energy ions of the same mass/charge ratio that pass both the analyzing magnet and ESA. The time resolution of the original setup as determined for ^{236}U measurements was ~ 670 ps, which resulted in a sensitivity of $\sim 5 \times 10^{-10}$ for $^{236}\text{U}/^{238}\text{U}$ (Wang et al. 2010a). To achieve higher sensitivity for both ^{236}U and ^{237}Np , the time resolution of the TOF must be improved. Thus, several steps were adopted to improve the time resolution:

1. To minimize the scattering when the heavy ions $^{237}\text{Np}^{11+}$ pass through the “start” detector, a carbon foil supported by a copper mesh was designed with a transparency of 97%, instead of the original copper mesh ($\sim 90\%$ transparency). The TOF 7- $\mu\text{g}\cdot\text{cm}^{-2}$ carbon foil is larger than thinner foils, such as the ultra-thin diamond-like carbon foil (DLC foils, 0.6 $\mu\text{g}\cdot\text{cm}^{-2}$) (Liechtenstein et al. 1999). However, these thinner carbon foils are not available with the large 30-mm diameter required by our assembly.
2. Optimization of the MCP assembly. The electrons stripped from the carbon foil have an energy of several eV with a large scattering angle. In order to get a good time resolution, electrons should have approximately the same energy and the same direction for the velocity during the free flight area (after acceleration). A high field near the foil helps to shorten the time when the electrons are slow and travel on erratic tracks. Thus, the electrons must be accelerated properly to minimize the spread in angle and energy. Figure 3 also shows the deflection parabola of the electrons in the electrostatic mirror. All the electrons emitted from the carbon foil have the same flight time to the MCP detector due to the properties of the electrostatic mirror. The time spent in the electrostatic mirror Δt could be expressed as (Hu 1993):

$$\Delta t = 2d_2 \sqrt{\frac{m_e}{e}} \sqrt{\frac{V_{acc}}{V_{mirr}}} \quad (1)$$

where e and m_e are the charge and mass of the electron; d_2 is the distance between the 2 electrostatic grids forming the electron mirror; V_{acc} is the potential difference between the carbon foil and the electron acceleration grid; and V_{mirr} is the potential difference between the 2 grids of the electrostatic mirror. Therefore, the flight time Δt is dependent on d_2 , V_{acc} , and V_{mirr} . The shorter the Δt , the better the resolution because the Δt spread (variation of Δt) is less. The detection efficiency of the MCP also depends on V_{acc} . If $V_{acc} < 600$ V, the detection efficiency is less than 40%. If $V_{acc} > 750$ V, the detection efficiency is $\sim 60\%$ (Hu 1993). In the original setup, $d_1 = 8$ mm, $d_2 = 8$ mm, $V_{acc} = 500$, and $V_{mirr} = 1200$ V, where d_1 is the distance between carbon foil and acceleration grid. Hence, the acceleration and reflection electric fields are ~ 62.5 V/mm

proportional to the ratio of atomic mass), for $^{237}\text{Np}^{11+}$. The ^{237}Np standard sample 1 (1.50×10^{-9}) was then used to validate the settings. In the $^{237}\text{Np}/^{238}\text{U}$ ratio measurement, the ^{238}U was measured with the F3 Faraday cup, while ^{237}Np was recorded with the TOF.

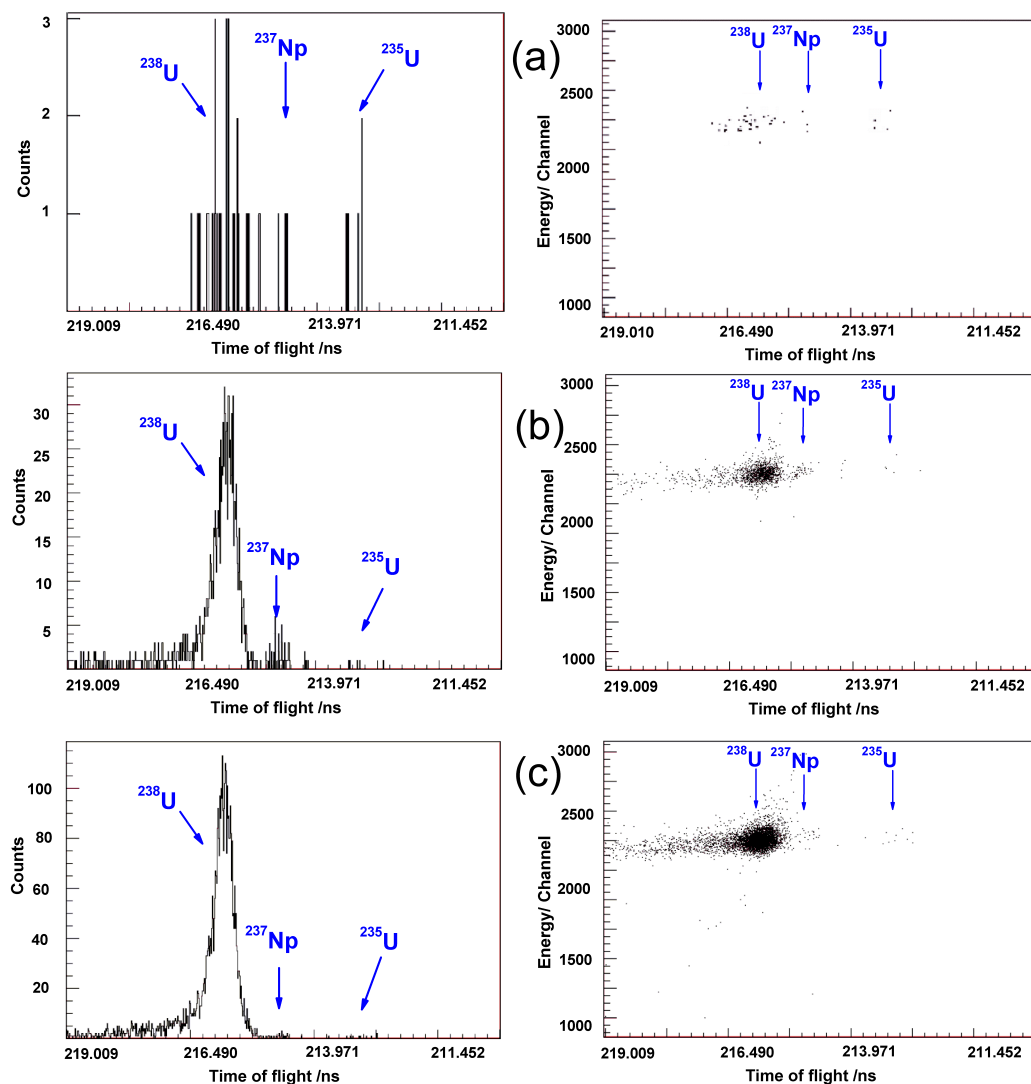


Figure 4 TOF spectra (left) and 2-dimensional spectra of TOF vs. energy (right) samples: (a) a natural uranium sample with a $^{237}\text{Np}/^{238}\text{U}$ ratio of $(5.09 \pm 2.10) \times 10^{-11}$; (b) standard sample 1, with a $^{237}\text{Np}/^{238}\text{U}$ ratio of $(1.50 \pm 0.05) \times 10^{-9}$; (c) standard sample 2, with a $^{237}\text{Np}/^{238}\text{U}$ ratio of $(5.55 \pm 0.15) \times 10^{-10}$.

RESULTS AND DISCUSSION

Figure 4 shows 2-dimensional spectra of TOF vs. energy and TOF spectra for a natural uranium sample and 2 ^{237}Np initial standard samples. There are more ^{238}U counts in Figure 4b (standard sample 1) and Figure 4c (standard sample 2), compared to Figure 4a (natural sample). The reason may be that ethyl cyanoacrylate ($\text{C}_6\text{H}_7\text{NO}_2$) tape was used to stick the uranium sample and Co monitor

foils together during neutron irradiation for standard samples. The main component element of the ethyl cyanoacrylate is N, which could form $^{238}\text{UH}^{14}\text{N}^-$ in the ion source and result in this interference. Although the samples had been dissolved in 4M HNO_3 and baked in a furnace at 800 °C for at least 2 hr, the ethyl cyanoacrylate is hard to eliminate completely. Figure 5 shows a scan spectra of an irradiated sample (standard sample 1) from the dedicated injector. The peak of $M = 253$ is higher compared to the one for the not-irradiated sample in Figure 1. However, taking advantage of the high-resolution dedicated injector, the high-time-resolution TOF (500 ps) and the high terminal voltage of the HI-13 accelerator, the ^{237}Np ions of interest can be distinguished from the background ions. Laboratory standard sample 1 ($^{237}\text{Np}/^{238}\text{U} = (1.50 \pm 0.05) \times 10^{-9}$) was used for normalization. The natural uranium sample is derived from high-grade ore from the Inner Mongolia Autonomous Region of China, purchased by CIAE. The uranium was extracted from the ore with a commercial liquid-phase method (Xu 1994). The $^{236}\text{U}/^{238}\text{U}$ of this sample is 7.80×10^{-11} (Wang 2010). The samples were mixed with Nb powder (U:Nb = 1:1) for the AMS sample. The $^{237}\text{Np}/^{238}\text{U}$ atom ratio for this natural uranium sample measured in the present work is $(5.09 \pm 2.10) \times 10^{-11}$.

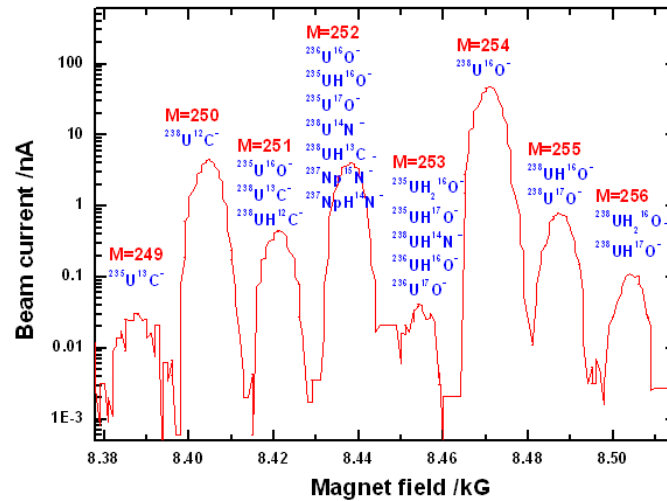


Figure 5 Scan spectra of an irradiated U_3O_8 sample (standard sample 1) by the AMS dedicated injector.

The relative uncertainty in the AMS measurements is about 41%, including the statistical uncertainty, the reproducibility of the measurement (4 runs, 6 counts), and a systematic contribution from the measurement relative to reference materials (284 counts). The main contribution to the uncertainties is the poor counting statistics due to the small number of ^{237}Np atoms recorded in the detector.

CONCLUSIONS

A primary method for measuring ^{237}Np was set up at CIAE, and a sensitivity of $\sim 10^{-11}$ for $^{237}\text{Np}/^{238}\text{U}$ in a uranium sample has been achieved in the present work. Although the natural uranium was extracted from the ore by the commercial liquid-phase method, no specific chemical processing for the uranium ore was used to remove Np. The ^{237}Np AMS measurement result shows that the $^{237}\text{Np}/^{238}\text{U}$ ratio of this natural uranium sample should be higher than 5×10^{-11} . Peppard et al. (1952) gave a maximum value of $(1.8 \pm 0.4) \times 10^{-11}$ for $^{237}\text{Np}/^{238}\text{U}$ in a natural pitchblende. Myers and Lindner (1971) reported a natural abundance of ^{237}Np in Katanga pitchblende with $\sim 2 \times 10^{-12}$ for $^{237}\text{Np}/^{238}\text{U}$,

using IDMS. It is possible that our result is higher than those mentioned above because our original ore is a high-grade uranium ore. However, there are no further details regarding this original ore for use in additional research.

If the ^{237}Np were to be chemically extracted from the natural uranium sample, there would have been negligible U isotopic background. Sensitivity and precision are, however, presently limited by the low transmission efficiency through the large accelerator. Using thinner carbon foils (such as diamond-like carbon foils) as a stripper in the accelerator would increase the transmission efficiency. Nevertheless, the present level of sensitivity is sufficient for ^{237}Np applications in the areas of nuclear safeguards and radioactive waste migration.

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REFERENCES

- Dorin NP, Walter G. 1997. *Experimental Techniques in Nuclear Physics*. Berlin: Walter de Gruyter.
- Fifield LK, Clacher AP, Morris K, King SJ, Cresswell RG, Day JP, Livens FR. 1997. Accelerator mass spectrometry of the planetary elements. *Nuclear Instruments and Methods in Physics Research B* 123(1–4): 400–4.
- Hammond CR. 2004. The elements. In: *Handbook of Chemistry and Physics*. 81st edition. London: CRC Press.
- Hu XM. 1993. A time-of-flight detector based on a micro-channel plate [Master's thesis]. Beijing: Institute of Modern Physics.
- Keith-Roach MJ, Day JP, Fifield LK, Livens FR. 2001. Measurement of Np in environmental water samples by accelerator mass spectrometry. *Analyst* 126(1):58–61.
- Kim CK, Takaku A, Yamamoto M, Kawamura H, Shiraishi K, Igarashi Y, Igarashi S, Takayama H, Ikeda N. 1989. Determination of ^{237}Np in environmental samples using inductively coupled plasma mass spectrometry. *Journal of Radioanalytical and Nuclear Chemistry* 132(1):131–7.
- Liechtenstein VK, Ivkova TM, Olshanski ED, Baranov AM, Repnow R, Hellborg R, Weller RA, Wirth HL. 1999. Preparation and comparative testing of advanced diamond-like carbon foils for tandem accelerators and time-of-flight spectrometers. *Nuclear Instruments and Methods in Physics Research A* 438(1): 79–85.
- Myers WA, Lindner M. 1971. Precise determination of the natural abundance of ^{237}Np and ^{239}Pu in Katanga pitchblende. *Journal of Inorganic and Nuclear Chemistry* 33(10):3233–8.
- Peppard DF, Mason GW, Gray PR, Mech JF. 1952. Occurrence of the (4n+1) series in nature. *Journal of the American Chemical Society* 74(23):6081–4.
- Richard BF. 1996. *Table of Isotopes*. CD-ROM edition.
- Sabine BJ, Dietze HJ. 1999. Application of double-focusing sector field ICP mass spectrometry with shielded torch using different nebulizers for ultratrace and precise isotope analysis of long-lived radionuclides. *Journal of Analytical Atomic Spectrometry* 14(9):1493–500.
- Sayer RO. 1977. Semi-empirical formulas for heavy-ion stripping data. *Revue de Physique Appliquée* 12: 1543–6.
- Tuo F, Ruan X, He M, Wu S, Wang W, Hu Y, Bao Y, Ouyang Y, You Q, Dou Y, He G, Jiang S. 2010. Improvement on AMS measurement method for ^{182}Hf . *Nuclear Instruments and Methods in Physics Research B* 268(7):776–8.
- Wang XG. 2010. Measurement of $^{238}\text{U}(n,3n)^{236}\text{U}$ cross-section induced by 14 MeV neutrons with AMS [PhD dissertation]. Beijing: China Institute of Atomic Energy.
- Wang XG, Jiang S, He M, Dong KJ, Wang W, Li C, He GZ, Li S, Gong J, Lu LY, Wu SY. 2010a. ^{236}U measurement with accelerator mass spectrometry at CIAE. *Nuclear Instruments and Methods in Physics Research B* 268(13):2295–9.
- Wang XG, Jiang S, Dong KJ, He M, He GZ, Li CL, Li SZ, Gong J, Lu LY. 2010b. Development of laboratory standards for AMS measurement of ^{237}Np . *Nuclear Instruments and Methods in Physics Research B* 268(11):1949–53.
- Xu HJ. 1994. *Chemical Conversion Technology of Uranium*. Beijing: Atomic Energy Publishing Company.
- Zhang XX. 1978. *Neptunium Analytical Chemistry*. Beijing: Atomic Energy Publishing Company.