

## ACCELERATOR MASS SPECTROMETRY ANALYSIS OF $^{237}\text{Np}$ IN ENVIRONMENTAL SAMPLES

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**ABSTRACT.** To determine the  $^{237}\text{Np}$  concentration originating from global fallout in the environment, samples were collected from Guangxi, south of China, and measured by accelerator mass spectrometry (AMS) at CIRCE. Serial standard samples and environment samples were prepared and measured using  $^{242}\text{Pu}$  as a tracer. The result indicates that the detection limit of  $^{237}\text{Np}$  as low as  $10^{-15}$  g can be obtained. The concentration of  $^{237}\text{Np}$  in the environmental samples is less than 49.09 pg/kg (i.e. 1.280 mBq/kg), and the most probable value of  $^{237}\text{Np}$  is approximately 20 pg/kg (i.e. 0.53 mBq/kg).

**KEYWORDS:** accelerator mass spectrometry, environmental sample, neptunium.

### INTRODUCTION

Neptunium is the first transuranic element discovered and it belongs to the actinide series. Neptunium metal is silvery and tarnishes when exposed to air. The element normally exhibits five oxidation states, ranging from +3 to +7. Np is present in the environment as a result of atmospheric nuclear weapons testing in the 1950s and early 1960s, from releases from nuclear fuel reprocessing facilities, and nuclear accidents such as Chernobyl. There are 22 isotopes of neptunium which are known today, the most long-lived isotope being  $^{237}\text{Np}$ , with a half-life of  $2.14 \times 10^6$  yr.  $^{237}\text{Np}$  is a byproduct of nuclear reactor operation and plutonium production. It is mainly produced by the following three processes: the successive thermal neutron capture on  $^{235}\text{U}$ , followed by a beta decay, i.e.  $^{235}\text{U}(n,\gamma)^{236}\text{U}(n,\gamma)^{237}\text{U}(\beta)^{237}\text{Np}$ ; high-energy neutron-induced  $^{238}\text{U}(n,2n)^{237}\text{U}$  reaction, followed by a beta decay; directly by alpha decay of  $^{241}\text{Am}$  ( $T_{1/2} = 432.7$  yr). It has been estimated that during the period between 1945 and 1980, about 40 TBq of  $^{237}\text{Np}$  were released into the environment (Beasley et al. 1998). The activity inventory of  $^{237}\text{Np}$  is orders of magnitude lower in the environment compared to  $^{239+240}\text{Pu}$  or  $^{241}\text{Am}$ . Determination of  $^{237}\text{Np}$  is rather complicated, because of its very low specific activity and lack of suitable yield tracer such as high purity  $^{236}\text{Np}$ . Due to the low  $^{237}\text{Np}$  concentration present in the environment, previous studies concerned samples contaminated by other sources. Here we focused on the region only affected by the global fallout, which is located in Guangxi, south of China.

Methods previously employed to determine  $^{237}\text{Np}$  include alpha spectroscopy, neutron activation analysis, inductively coupled plasma mass spectrometry, thermal ionization mass spectrometry, accelerator mass spectrometry, and other mass spectrometry. Alpha spectroscopy is capable of producing good results with lower limits of detection but requires tedious chemical separations and long counting times. The greatest advantage of alpha spectroscopy is the relatively low cost of equipment. On the other hand, for the

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detection of  $^{237}\text{Np}$ , alpha counting is unable to identify the alpha particles emitted by  $^{234}\text{U}$  and  $^{230}\text{Th}$ , due to the small energy differences. In recent years, ICP-MS has become one of the most powerful methods for the determination of ultra-trace levels of  $^{237}\text{Np}$  in many kinds of samples such as environmental, biological samples, and uranium fuels. However, abundance sensitivity is limited by molecular interferences, such as  $^{235}\text{UH}_2^-$ . A detection limit of 0.02 pg/mL with a conventional quadrupole ICP-MS (Muramatsu et al. 2001) and as low as fg/mL or fg/g with SF-ICP-MS could be achieved for actinides (Becker 2003; Varga et al. 2007).

Because of the lack of molecular isobars, AMS is the most sensitive detection technique for  $^{237}\text{Np}$  (down to  $10^5$  atom/sample, ca. 0.001  $\mu\text{Bq}$ ) and has the highest abundance sensitivity. However, very few  $^{237}\text{Np}$  measurements have been reported by AMS. Environmental samples such as mud, water and sediment were analyzed by AMS at the Australian National University (Fifield et al. 1997; Keith-Roach et al. 2001). It was estimated that sensitivity by AMS is ca.  $10^5$  atoms ( $4 \times 10^{-17}$  g) of  $^{237}\text{Np}$ . A method for AMS measurement of  $^{237}\text{Np}$  was set up at the China Institute of Atomic Energy, and a sensitivity less than  $10^{-11}$  has been achieved for the isotopic ratio  $^{237}\text{Np}/^{238}\text{U}$  (Wang et al. 2013). More details about analytical techniques and sample preparation for determination of  $^{237}\text{Np}$  are reviewed in Thakur and Mulholland (2012). The aim of this work is to determine activity concentration of  $^{237}\text{Np}$  in surface soil samples collected from Guangxi, south of China.

## EXPERIMENTAL

### Sample Preparation

Surface soil and sediment samples were collected at 4 locations in 2012–2016 (Table 1). At each location, approximately 500 g (dry weight) of soil was collected at 0–10 cm depth. These locations have been used for monitoring various radionuclides (e.g.,  $^{137}\text{Cs}$ ) in the environment. Preliminary gamma spectrometry results for  $^{137}\text{Cs}$  are listed in Table 1. In total, 17 samples were selected, of which 15 were analyzed for  $^{237}\text{Np}$ . Twelve samples were collected from 3 different monitoring locations, the other 5 samples were collected from the region near the newly built nuclear power plant (Figure 1).

The radiochemical procedure used in this study for the preparation of  $^{237}\text{Np}$  use a modification of the method for ICP-MS (Kim et al. 2004). The flow chart of the analytical procedure for the determination of  $^{237}\text{Np}$  in environmental samples is shown in Figure 1. After baking at 500°C for 2 hr, about 10 g of sample was weighed and placed into a Teflon beaker. Consequently, 3 pg of  $^{242}\text{Pu}$  (i.e.  $10^{10}$  atoms) as tracer was added and mixed with the sample for radiochemical separation.

Samples were dissolved using 50 mL concentrated  $\text{HNO}_3$  on a hot plate at 200°C for 4 hr to mix plutonium into solution, filtered and then vaporized to approximately 1 mL. The resulting solution was dissolved by adding concentrated  $\text{HNO}_3$ , then adjusted to acidity of 5 M  $\text{HNO}_3$  by adding de-ionized water and then filtered. Ascorbic acid was added to the solution and allowed to stand for 1 hr to carry out the redox reaction. Separation and purification of  $^{237}\text{Np}$  was achieved with anion-exchange chromatography using TEVA resins. In the first purification stage, the prepared sample solution was loaded into a preconditioned 2-mL TEVA column with 0.5 M HCl. Then, the column was washed with 13 mL 5 M  $\text{HNO}_3$  followed by 7 mL 9 M HCl and 10 mL 1 M  $\text{HNO}_3$  to remove uranium and thorium. After that, neptunium and plutonium were eluted with 0.5 M HCl. The eluant was transferred to a 10-mL centrifuge tube, and then 0.5 mL  $\text{Al}(\text{NO}_3)_3$  solution

Table 1  $^{137}\text{Cs}$  and  $^{237}\text{Np}$  radioactivity in collected sample from Guangxi, China.

Sample number	Sample type	Sampling year	Latitude	Longitude	$^{137}\text{Cs}$ activity Bq/kg	$^{237}\text{Np}$ activity mBq/kg
G13	Soil	2013	24°37'18.8"N	111°34'1.9"E	5.40	0.489 ± 0.097
G14	Soil	2014	24°37'18.8"N	111°34'1.9"E	5.01	0.361 ± 0.078
G15	Soil	2015	24°37'18.8"N	111°34'1.9"E	4.50	0.425 ± 0.085
G16	Soil	2016	24°37'18.8"N	111°34'1.9"E	4.55	0
B13	Soil	2013	23°29'35.9"N	111°20'18.6"E	0.38	—
B14	Soil	2014	23°29'35.9"N	111°20'18.6"E	0.42	0.223 ± 0.065
B15	Soil	2015	23°29'35.9"N	111°20'18.6"E	1.07	0.526 ± 0.112
B16	Soil	2016	23°29'35.9"N	111°20'18.6"E	1.06	0.179 ± 0.054
J13	Soil	2013	24°41'32.3"N	108°3'43.6"E	4.09	0.533 ± 0.106
J14	Soil	2014	24°41'32.3"N	108°3'43.6"E	6.04	0
J15	Soil	2015	24°41'32.3"N	108°3'43.6"E	6.06	1.280 ± 0.195
J16	Soil	2016	24°41'32.3"N	108°3'43.6"E	6.72	0.787 ± 0.156
3	Soil	2012	21°40'56.0"N	108°27'43.0"E	5.39	1.080 ± 0.213
23	Soil	2012	21°43'39.0"N	108°27'40.0"E	4.06	0.525 ± 0.104
25	Soil	2012	21°44'59.0"N	108°30'38.0"E	3.84	0.499 ± 0.104
51	Sediment	2012	21°48'17.7"N	108°33'55.1"E	1.37	0.371 ± 0.075
52	Sediment	2012	21°46'48.4"N	108°31'7.7"E	5.94	—

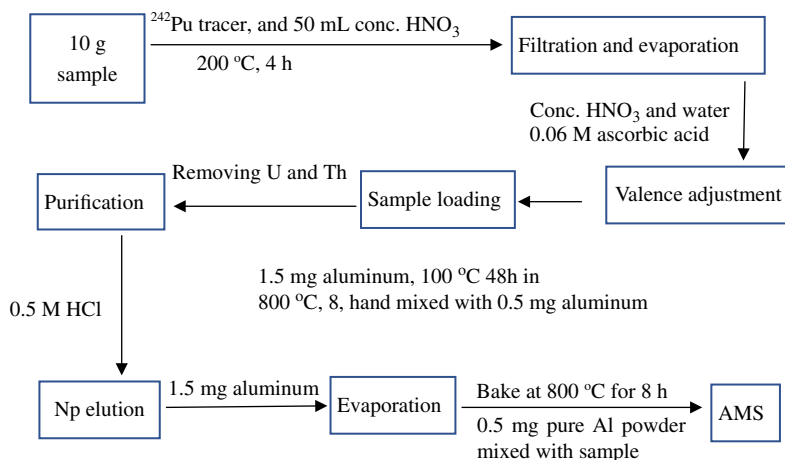


Figure 1 Flow chart of the analytical procedure for the determination of  $^{237}\text{Np}$  in environmental samples.

equivalent to 1.5 mg aluminum was added. The centrifuge tube was heated at 100°C for 48 hr. What remained was weighted and then transferred to a quartz crucible followed by 8 hr of baking at 800°C. The resulting sample was crushed in an agate mortar and mixed with 0.5 mg aluminum powder. The mixture was pressed into an aluminum sample holder for AMS measurement. Serial standard samples quantified using the isotopic dilution technique with  $^{242}\text{Pu}$  and  $^{237}\text{Np}$  as tracers, and chemical blank samples were prepared. The standard samples were prepared by dilution of the standard solutions of  $^{237}\text{Np}$  (NIST 4341a standard reference material,  $152.3 \pm 1.4$  Bq/g) and  $^{242}\text{Pu}$  (NIST 4334I standard reference material,  $26.77 \pm 0.18$  Bq/g). Three dilution series samples including single  $^{237}\text{Np}$ , single  $^{242}\text{Pu}$  and mixture of  $^{237}\text{Np}$  and  $^{242}\text{Pu}$  were made following the preparation procedure described above. To test the reliability and repeatability of the treatment procedure, several batches of standard samples were prepared during different time periods. Two uranium samples were used for tuning the AMS system, and two chemical procedural blanks were prepared to check the detection limit.

### The AMS Technique

The  $^{237}\text{Np}$  measurements were performed at the AMS facility at the Center for Isotopic Research on Cultural and Environmental Heritage (CIRCE) in Caserta, Italy. Detailed information of the main elements of CIRCE AMS has been provided previously (Terrasi et al. 2007; De Cesare et al. 2010; Guan et al. 2017). The process of  $^{237}\text{Np}$  AMS measurement is similar to that of  $^{236}\text{U}$ , plutonium and other actinide measurements. An initial pilot beam of  $^{238}\text{U}^{16}\text{O}^-$  at a terminal voltage of 2.680 MV was used for tuning purposes and transmission measurement because the intensity of  $^{237}\text{Np}$  is not large enough to obtain measurable current, neither in standard samples nor environmental samples. Scaling the optimizing parameters for  $^{238}\text{U}$ , the operating parameters for  $^{237}\text{Np}$  and  $^{242}\text{Pu}$  are calculated: all magnetic fields are kept constant and electric and magnetic rigidities of the various beams are matched using the bouncer voltage applied to the injection magnet vacuum chamber, the terminal voltage and electrostatic analyzer voltage. Table 2 summarizes the operating parameters for the various actinides measured with CIRCE AMS

Table 2 The AMS operating parameters for transmission of  $^{242}\text{Pu}$  and  $^{237}\text{Np}$ .

Ions	Injected ions	Bouncer voltage/kV	Charge state	Terminal voltage/MV	ESA/kV
$^{237}\text{Np}$	$^{237}\text{Np}^{16}\text{O}^-$	2.206	5+	2.641	38.160
$^{238}\text{U}$	$^{238}\text{U}^{16}\text{O}^-$	2.000	5+	2.630	37.999
$^{242}\text{Pu}$	$^{242}\text{Pu}^{16}\text{O}^-$	1.192	5+	2.586	37.370

facility. Negative  $\text{NpO}^-$  and  $\text{PuO}^-$  ions are extracted by sputtering the sample with a  $\text{Cs}^+$  beam in a commercial ion source (40 samples, MC-SNICS, NEC). These ions are pre-accelerated to 50 kV and passed through a high-resolution injection system including an electrostatic analyzer and an injector magnet. Cycling between  $^{242}\text{Pu}$  and  $^{237}\text{Np}$  was done by fast changing the bouncer voltage on the injection magnet, terminal voltage and the voltage of high energy electrostatic analyzer. Sequential injection into the accelerator was set 100 s for  $^{242}\text{Pu}^{16}\text{O}^-$  and  $^{237}\text{Np}^{16}\text{O}^-$ . The durations of injection of  $^{237}\text{Np}$  and  $^{242}\text{Pu}$  is 20 s. Samples are typically counted for 100 s at both mass 242 ( $^{242}\text{Pu}$ ) and mass 237 ( $^{237}\text{Np}$ ) for 3 times, always ending with a  $^{242}\text{Pu}$  measurement. Standards of known amounts of  $^{237}\text{Np}$  and  $^{242}\text{Pu}$  in aluminum oxide were run periodically to give the relative counting efficiencies for Np and Pu, allowing quantitative measurement of the amount of Np in each sample.

### $^{237}\text{Np}$ Measurement Results

The reliability of the  $^{237}\text{Np}$  results was verified by the linearity and reproducibility of the results. Four batches, with 3 standard samples for each batch with the concentration of  $^{237}\text{Np}$  from 0.3 to 30 pg were measured (Figure 2). The counts in Figure 2 are the average value of three cycles, and the values on a 95% confidence level ( $2\sigma$ ). In our experiment, the  $^{237}\text{Np}$  counts in 4 batches within 100 s for 30 pg samples varied from 250 to 650. The uncertainty of  $^{237}\text{Np}$  are less than 10%, 15%, and 25% for 30 pg, 3 pg, and 0.3 pg  $^{237}\text{Np}$ , respectively. A good linearity is observed for each batch for  $^{237}\text{Np}$  counts recorded by the final gas ionization chamber versus the  $^{237}\text{Np}$  concentration. The count rates of samples taken in different batches fluctuated greatly, indicating a variability of the sample preparation process. Sometimes, the chemical yield is not strictly constant and even varied by three times, as it has been reported in the earlier  $^{237}\text{Np}$  preparations (La Rosa et al. 2005). The specific research on this fluctuation reason, such as chemical yield and/or experimental operation skills will be undertaken in the near future. In fact, the chemical yield can be confirmed by alpha spectroscopy or HPGe detector, but this needs a large amount of  $^{237}\text{Np}$  and  $^{242}\text{Pu}$  standard material. We did not carry out this step. ICP-MS is an ideal choice to determine the chemical yields, we will also investigate this method in the future. Figure 3 shows the gated  $^{242}\text{Pu}$  counts measured by the ionization chamber vs sputter time for seven environmental samples. For the first half hour of the experiments, counts of  $^{242}\text{Pu}$  in each sample are relatively stable. In order to estimate the maximum sputter time, all the cathodes were weighted before and after experiment: the results indicated that only a part (about 30–50%) material in the cathode was consumed.

A batch of standard samples containing known amounts of  $^{242}\text{Pu}$  and  $^{237}\text{Np}$  dispersed in aluminum oxide was prepared for determining relative negative ion formation probabilities of  $\text{PuO}^-$  and  $\text{NpO}^-$  by AMS. Ratios of abundance of the isotope of interest (e.g.  $^{237}\text{Np}$  and  $^{242}\text{Pu}$ ) to aluminum were approximately  $10^{-8}$ . The standards were run periodically to give the relative negative ion formation probabilities for Np and Pu, allowing quantitative

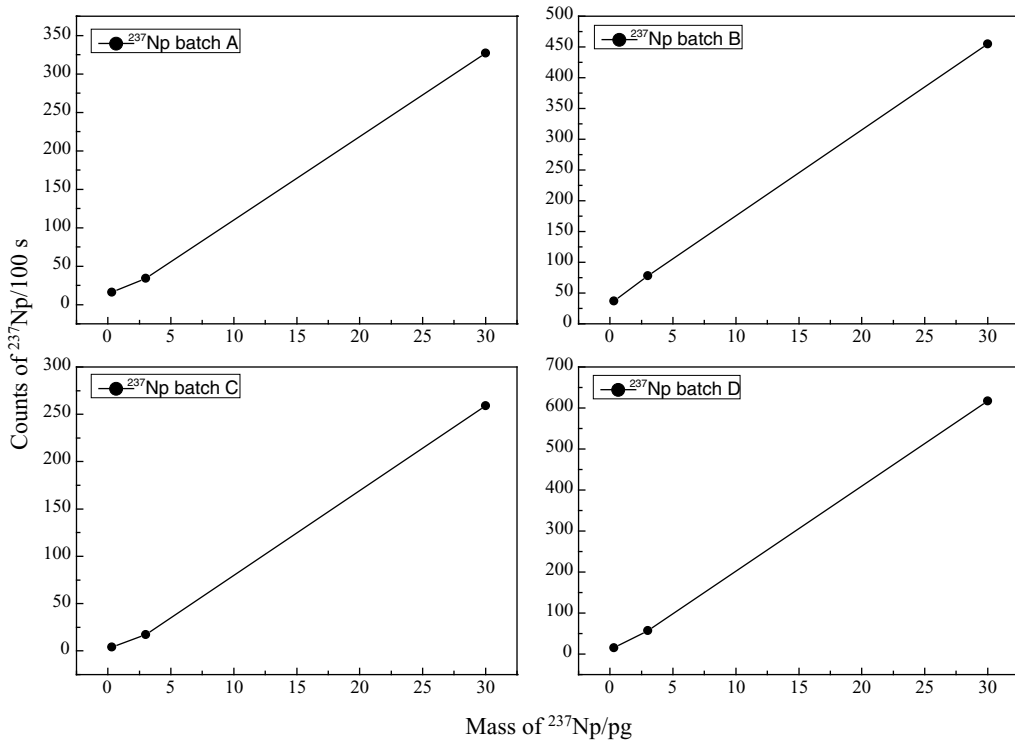


Figure 2 Linearity of the AMS measurements for  $^{237}\text{Np}$  with 4 batches of standard samples.

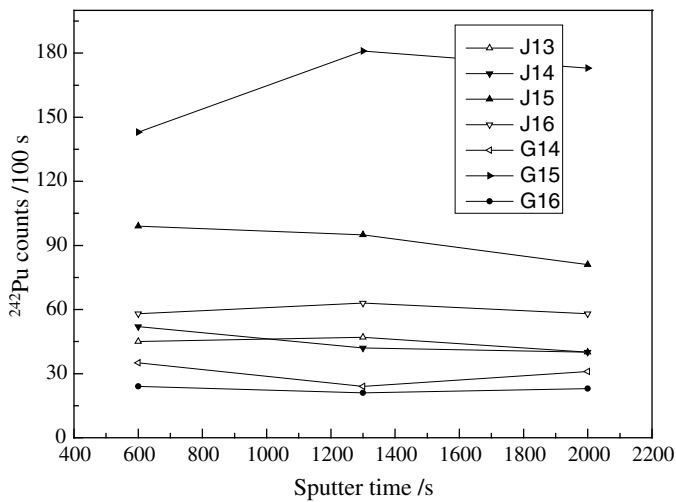


Figure 3  $^{242}\text{Pu}$  gated counts in each 100 s measurement time as a function of sputter time. Each sample was measured for 3 cycles.

measurement of the amount of  $^{237}\text{Np}$  and  $^{242}\text{Pu}$ . In our results, count rates of  $0.170 \pm 0.018$  cps/pg and  $0.061 \pm 0.006$  cps/pg were obtained for  $^{237}\text{Np}$  and  $^{242}\text{Pu}$ , respectively, from several samples. If we assume that  $^{237}\text{Np}$  and  $^{242}\text{Pu}$  have the same chemical yield, then we can get a relative negative ion formation probability of Np/Pu of  $0.353 \pm 0.004$ .

Determination of  $^{237}\text{Np}$  in environmental samples was then carried out: the concentration of  $^{237}\text{Np}$  was normalized to the  $^{242}\text{Pu}$  according to the relative negative ion formation probabilities of Pu and Np. The results are listed in Table 1. The  $^{237}\text{Np}$  concentrations in both samples G16 and J14 are lower than the detection limit, and two samples B13 and 52 were contaminated during sample preparation. In addition to these samples, the activity concentrations of  $^{237}\text{Np}$  in environmental samples collected from Guangxi, which are only affected by the global fallout, varied between  $0.179 \pm 0.054$  and  $1.280 \pm 0.195$  mBq/kg. In all the chemical procedural blank samples and two uranium tuning samples, we could not get any counts of neither  $^{237}\text{Np}$  nor  $^{242}\text{Pu}$  within 500 s.  $^{237}\text{Np}$  activity concentrations in forest litter samples from Poland with pure global fallout were 0.099 mBq/kg and 2.21 mBq/kg (La Rosa et al. 2010). A preliminary comparison between our experiment and Poland, shows that the  $^{237}\text{Np}$  concentrations are of the same order of magnitude.

## CONCLUSIONS

The reliability of the chemical analytical procedure for the determination of  $^{237}\text{Np}$  using  $^{242}\text{Pu}$  as a tracer for  $^{237}\text{Np}$  AMS measurement was demonstrated. Standard samples and environmental samples were prepared and measured, and the linearity and reproducibility of  $^{237}\text{Np}$  was verified (Figure 2). The counts of  $^{242}\text{Pu}$  in each environmental sample are relatively stable in the first half hour (Figure 3). If we assume that  $^{237}\text{Np}$  and  $^{242}\text{Pu}$  have the same chemical recoveries, the relative negative ion formation probability of Np/Pu was found to be  $0.353 \pm 0.004$  in this study, and there is a significant difference between this value and the earlier study (Fifield et al. 1997). According to our preliminary analysis, the difference is more likely caused by binder effects. Different binder materials, such as Nb, Ag, Fe, and Al, will be used to further investigate this issue. Since the sample containing 2 mg of aluminum will run for at least 4000 s, the ultimate sensitivity for  $^{237}\text{Np}$  is estimated be  $1.5 \times 10^{-15}$  g. Due to an insufficient amount of standard material, we did not measure the chemical yield, so we cannot obtain the accuracy result of negative ion formation probability in this study. The average value of  $^{237}\text{Np}$  concentration in the region of interest is about 20 pg/kg (i.e. 0.53 mBq/kg). We observed a very good consistency of  $^{237}\text{Np}$  concentration with pure global fallout from different locations between our experiments and the early report (La Rosa et al. 2010). Improvements in chemical recoveries and choice of the ideal binder material will lead to greater reliability and sensitivity.

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## REFERENCES

- Beasley TM, Kelley JM, Maiti TC, Bond LA. 1998.  $^{237}\text{Np}/^{239}\text{Pu}$  atom ratios in integrated global fallout: a reassessment of the production of  $^{237}\text{Np}$ . *Journal of Environmental Radioactivity* 38(2):133–146.
- Becker JS. 2003. Mass spectrometry of long-lived radionuclides. *Spectrochimica Acta B* 58(10):1757–1784.
- De Cesare M, Guan Y, Quinto F, Sabbarese C, De Cesare N, D'Onofrio A, Gialanella L, Petraglia A, Roca V, Terrasi F. 2010. Optimization of  $^{236}\text{U}$  AMS at CIRCE. *Radiocarbon* 52(2–3):286–294.
- Fifield LK, Clacher AP, Morris K, King SJ, Cresswell RG, Day JP, Livens FR. 1997. Accelerator mass spectrometry of the planetary elements. *Nuclear Instrument and Methods B* 123(1–4):400–404.
- Guan YJ, Wang HJ, De Cesare M, Terrasi F. 2017. The AMS measurement of  $^{236}\text{U}$  at CIRCE. *Nuclear Science and Techniques* 28(7):98.
- Keith-Roach MJ, Day JP, Fifield LK, Livens FR. 2001. Measurement of  $^{237}\text{Np}$  in environmental water samples by accelerator mass spectrometry. *Analyst* 126(1):58–61.
- Kim CS, Kim CK, Lee KJ. 2004. Simultaneous analysis of  $^{237}\text{Np}$  and Pu isotopes in environmental samples by ICP-SF-MS coupled with automated sequential injection system. *Journal of Analytical Atomic Spectrometry* 19(6):743–750.
- La Rosa J, Gastaud J, Lagan L, Lee S-H, Levy-Palomo I, Povinec P, Wyse E. 2005. Recent developments in the analysis of transuranics (Np, Pu, Am) in seawater. *Journal of Radioanalytical and Nuclear Chemistry* 263(2):427–436.
- La Rosa J, Mietelski JW, Wyse E. 2010. Pilot measurements of  $^{237}\text{Np}$  in forest litter from Poland. *Journal of Radioanalytical and Nuclear Chemistry* 283(2):385–387.
- Muramatsu Y, Yoshida S, Tagami L, Uchida S, Ruhm W. 2001. ICP-MS analysis of environmental plutonium. *Radioactivity in the Environment* 1:63–77.
- Terrasi F, Rogalla D, De Cesare N, D'Onofrio A, Lubritto C, Marzaioli F, Passariello I, Rubino M, Sabbarese C, Casa G, et al. 2007. A new AMS facility in Caserta/Italy. *Nuclear Instruments and Methods B* 259:14–17.
- Thakur P, Mulholland GP. 2012. Determination of  $^{237}\text{Np}$  in environmental and nuclear samples: a review of the analytical method. *Applied Radiation and Isotopes* 70(8):1747–1778.
- Varga Z, Suranyi G, Vajda N, Stefanka Z. 2007. Rapid sequential determination of americium and plutonium in sediment and soil samples by ICP-SFMS and alpha-spectrometry. *Radiochimica Acta* 95(2):81–87.
- Wang X, Jiang S, He M, Dong K, Chen H, He G, Wang W, Wu S, Hu Y. 2013. AMS measurement of  $^{237}\text{Np}$  at CIAE. *Radiocarbon* 55(2):294–301.