

Measurements of ^{79}Se with AMS based on extracting molecular negative ions^{*}

WANG Wei(王伟)^{1;1)} LI Chao-Li(李朝历)² HE Ming(何明)¹
WU Shao-Yong(武绍勇)¹ JIANG Shan(姜山)^{1;2)}

1 (Department of Nuclear Physics, China Institute of Atomic Energy, Beijing 102413, China)

2 (Physical Science and Engineering Technology Department, Guangxi university, Nanning 530004, China)

Abstract A new method for measuring selenium-79 with AMS, which is based on extracting molecular negative ions, is described in this paper. According to the experimental results, the extraction ion form SeO_2^- could depress the interference of Bromine-79 as much as 5 order levels, that is to say, the background of ^{79}Br can be deducted to $^{79}\text{Br}/\text{Se} \approx 10^{-10}$. By the way, the chemical form of sample and preparation flow was also developed. Finally, three ^{79}Se AMS calibration standard samples with theoretical $^{79}\text{Se}/\text{Se}$ ratios of 5.06×10^{-7} , 6.87×10^{-8} , 5.40×10^{-10} were obtained and the method of ^{79}Se measurement was set up, which actualized transmission and detection of ^{79}Se . By using our Bragg curve detector, the two isobars ^{79}Br and ^{79}Se could be partly identified to a certain extent and ^{79}Se can be identified from ^{79}Br about 1 order level. AMS measurements of the three calibration standard samples above were performed and good linearity was obtained. The sensitivity of the measurement is $(5.16 \pm 1.80) \times 10^{-11}$.

Key words ^{79}Se , accelerator mass spectrometry (AMS), extraction form, molecular negative ions, isobar, Bragg curve detector

PACS 27.50.+e, 29.30.-h, 82.80.Ms

1 Introduction

Selenium-79 is a long-lived radioactive fission product with a half-life of $(2.80 \pm 0.36) \times 10^5$ years^[1]. It is one of the interesting radio nuclides in radioisotope applications and management of nuclear waste repositories. Recently, owing to the uncertainty of selenium-79 half-life for long time^[2] and its potential migration ability from the repository to the environment, this nuclide is being paid more and more attention. Furthermore, selenium is an essential trace element to animals and plants and related with lots of human disease such as cancer, hepatitis, diabetes, even AIDS^[3-7]. ^{79}Se can be used as biological tracer

in life science. Due to the widely application of ^{79}Se in environmental science and biomedicine, the method for quantitation of trace ^{79}Se is very significant.

During recent years, there were many national and international works on selenium-79: first in the site of half-life determination, $(4.80 \pm 0.36) \times 10^5$ years was acquired by Yu Runlan at China institute of atomic energy (CIAE) with radiochemical method in 1995^[8]; while $(2.80 \pm 0.36) \times 10^5$ years was acquired by He Ming at CIAE with accelerator mass spectrometry in 2002^[1, 9]; in 2007, Philippe etc. in France developed a new chemical disposal procedure and obtain a new value of $(3.77 \pm 0.19) \times 10^5$ years with ICP-MS^[10], while Zhang Shengdong etc. at CIAE adopt the same

Received 8 July 2008

* Supported by National Natural Science Foundation of China (10490158)

1) E-mail: weiking@yahoo.cn

2) E-mail: jiangs@ciae.ac.cn

method but derived the value of $(4.61 \pm 0.19) \times 10^5$ years^[11]. Second in the site of environmental analysis, Dewberry in Savannah River Technology Center at Westinghouse U.S.A measured the content of ⁷⁹Se in Savannah River Site high level waste tank fission product waste with the method of liquid scintillation β -decay counting^[12]; Jerome in France determined selenium-79 in solutions of fission products after pre-treatment by ion exchange chromatography and ETV-ICP-MS^[13]; while Sandrine who also came from France developed the ⁷⁹Se radiochemical separation method^[14, 15]. In addition, G. Rugel of Munich Technology University (MTU) at Germany measured the (n, γ) cross sections at stellar energies for ⁷⁸Se so as to assess the temperature of the stellar and the neutron density by comparing isotope abundance ratio^[16].

The content of selenium-79 in radioactive wastes and biological trace samples is very low, while the half-life of ⁷⁹Se is very long, so the radioactivity of the sample is very weak. Because interference from molecular ions and isobar is very strong, it is difficult to carry out ultra-sensitive measurement of ⁷⁹Se by β -decay counting, neutron activation analysis as well as traditional mass spectrometry method. Accelerator mass spectrometry (AMS) turns out to be the optimal choice for that purpose, but some difficulty in the background interference from bromine-79 was still found. So far, there are only two laboratories, namely CIAE and MTU where selenium-79 was measured by AMS. The former identified these two isobars by detecting the X-ray of projectile particles^[18], the latter made use of gas filled magnet and gas ionization chamber detector^[16], the sensitivity turned out to be 3×10^{-9} and 2×10^{-10} respectively. This work will describe the preparation flow of the selenium-79 standard samples and the AMS method based on extracting the SeO_2^- molecular negative ions.

2 Preparation of ⁷⁹Se standard samples

There are two effective ways to obtain ⁷⁹Se, one way is ⁷⁹Se separation from high level fission product waste, and the other way is reactor neutron irradiation on ⁷⁸Se by (n, γ) reaction. The latter method was adopted in this work. ⁷⁹Se was produced by ir-

radiating 50 mg selenium, enriched in ⁷⁸Se to 57%, on the heavy water research reactor at CIAE for about 458 hours in 2000. The average thermal-neutron flux density was $\Phi = 5.5 \times 10^{13} / (\text{s} \cdot \text{cm}^2)$. The content of ⁷⁹Se after irradiation is calculated to be $^{79}\text{Se}/\text{Se} = (4.68 \pm 0.73) \times 10^{-5}$ by the software ORIGEN. After a cooling period of about 7 years, the sample was used to prepare different ratios of ⁷⁹Se/Se through the following procedure: first, 21.6 mg of the sample was dissolved in 3 ml of 6 M concentrated HNO_3 solution which was heated by 95°C water bath, then the solution was diluted with deionization water to 100 mL; Second, the different ratios of ⁷⁹Se/Se liquor were confected with high-pure selenium dioxide (bought from Alfa Aesar Company with 99.999% purity) as the isotopic diluents. These levels of ⁷⁹Se/Se liquor were used for preparing series of standard samples of ⁷⁹Se. In this work, three standard samples with ⁷⁹Se/Se ratios of 5.06×10^{-7} , 6.87×10^{-8} , and 5.40×10^{-10} were confected in order to measure the actual samples with the abundance ratio from 10^{-7} to 10^{-10} .

In the measurement of heavy nuclei ($Z > 20$) with AMS, chemical form of the sample and ion form of the extracted negative ions have great effect on the quality of the beam current and suppressive ability of the isobar interference. It was derived from this work that extracting SeO_2^- from selenium dioxide compound can greatly depress the isobar bromine-79 as much as 5 orders before accelerated. Accordingly, samples should be made into selenium dioxide and the sample is purer, the beam current is stronger, the interference from the isobar bromine-79 is weaker. The chemical procedure mainly contained two steps for sample preparation including distilling and dehydrating. Attentions need to be paid to two aspects: first, because selenium dioxide can be easily reduced to red selenium substance by tiny organic microsomes in the warm and wet atmosphere, the drying temperature shouldn't be too high (about 110—120°C); Second, because the solidified selenous acid has serious effect on quality of beam current, the period of dehydrate time should be long enough in order to convert selenous acid to selenium dioxide as fully as possible. All the samples, including actual samples and standard samples need to be prepared into selenium dioxide powder.

3 Measurements of ^{79}Se with AMS based on extracting molecular negative ions experiment on beam currents extraction

In AMS measurement, negative ions are extracted from ion source and transported to accelerator. In the ion source, atomic ion and molecular ions can be selected according to different requirements. For ^{79}Se measurement, the ideal ion form is the beam current for Se is strong, but for Br is weak. In the previous work, Se^- was extracted from CdSe compounds during all the studies of measuring ^{79}Se via AMS. The beam current of this extracted ion form was very strong, but $^{79}\text{Br}^-$ was also very strong. Consequently, atomic ion is not the suitable selection.

With the purpose of depressing ^{79}Br interference, experiments on extracting multiform of molecular negative ions were carried out. Three kinds of molecular negative ions of Se (SeC_2^- , SeO^- , SeO_2^-), correspondingly, the same ion form of bromine (BrC_2^- , BrO^- , BrO_2^-) were tested. The results are shown in Table 1. It was found that SeO^- or SeO_2^- molecular negative ion might be the suitable choice.

Table 1. Data on extracting molecular negative ion beam current (SeC_2^- , BrC_2^- , SeO^- , BrO^- , SeO_2^- , BrO_2^-).

chemical form of sample	molecular proportion	extracted ion and beam current value/nA
CdSe+C+Ag	1:2:1	$^{80}\text{SeC}_2^-$ 46.3
CdSe+C+Ag	1:3:1	$^{80}\text{SeC}_2^-$ 27
AgBr+C+Ag	1:2:1	$^{81}\text{BrC}_2^-$ 0.7
SeO ₂ +Ag	1:1	$^{80}\text{SeO}^-$ 290
SeO ₂ +Ag	1:1	$^{80}\text{SeO}_2^-$ 270
AgBr+MgO+Ag	1:2:1	$^{81}\text{BrO}^-$ 1
AgBr+MgO+Ag	1:2:1	$^{81}\text{BrO}_2^-$ <0.1

4 Experiment on background exploration

In order to check the ability for suppressing the ^{79}Br interference in case of extracting the SeO^- or SeO_2^- , the ^{79}Br background were measured with our AMS system by using a SeO_2 commercial blank sample. Selenium dioxide powder along with silver powder with the mass ratio of 1:1 was pressed into the standard NEC aluminum target holder. SeO_2^- nega-

tive ions were extracted from the MC-SNICS (Multi-Cathode Source of Negative Ion by Cesium Sputtering) cesium sputter source. $^{79}\text{BrO}_2^-$ ions were selected by an injection magnet and injected into the accelerator. The charge state of 9^+ was selected by analyzing magnet after ^{79}Br was stripped by a carbon foil. The accelerator terminal voltage was chosen at 8.2 MV owing to the limitation of an electrostatic analyzer in our AMS system. Before this, $^{80}\text{SeO}_2^-$ was extracted and injected into accelerator and $^{80}\text{Se}^{9+}$ was used to simulate the transmission of ^{79}Br for the whole AMS system. Afterwards, the particle entered into Bragg curve detector filled with 90 mbar P10 gas. The beam current of $^{80}\text{SeO}_2^-$ was measured by faraday cup in the image point of the injection magnet, while ^{79}Se counts were recorded by the detector. The results are shown in Table 2. The background of ^{79}Br by extracting Se^- is also listed in Table 2.

Table 2. The ^{79}Br background levels by extracting SeO^- and SeO_2^- molecular negative ions.

chemical form	mass ratio	ion form extracted	beam current/nA	$^{79}\text{Br}/\text{Se}$
SeO ₂ +Ag	1:1	SeO^-	230	3.95×10^{-9}
SeO ₂ +Ag	1:1	SeO_2^-	95	1.16×10^{-11}
SeO ₂ +Ag	1:1	Se^-	1530	2.63×10^{-6}

The results proved that extracting SeO^- and SeO_2^- can greatly suppress ^{79}Br interference and extracting SeO_2^- was better than extracting SeO^- . Consequently, SeO_2^- molecular negative ion was determined as the final extracted ion form.

5 Experiments on serial standard samples measurement

For validating the reliability of selenium-79 isotopic ratio measurement with AMS, series of standard samples were measured on HI-13 tandem AMS system at CIAE. Selenium dioxide along with silver powder with mass ratio of 1:1 were pressed into aluminum cones respectively, and then the target plate into which all the aluminum cones were mounted would be baked at 70°C for 24 hours before it was put into the MC-SNICS ion source. Typical parameters used for the detection of ^{79}Se on HI-13 AMS system are a tandem voltage of 8.4 MV and a charge state of $q=10^+$ owing to the deficient deflection ability. The

particle finally entered into the Bragg curve detector filled with 95 mbar P10 gas. The beam current of $^{80}\text{SeO}_2^-$ which can be converted to the counts of ^{80}Se was measured by faraday cup in the image focus point of the injection magnet, while ^{79}Se counts was derived in the two-dimensional coincidence spectrum of two signals from the detector. It is shown in Fig. 1. The Bragg curve detector was debugged, because the identification of these two isobars needs detector with high-level resolving power^[19]. By using this detector, the counts were recorded efficiently, and bromine-79 can be depressed 10 times after gating other signals strictly by software.

The results of measurement on blank sample and series of standard samples are shown in Table 3. The background level of commercial blank sample is 5.16×10^{-11} , which showed the sensitivity of this method. The alignment chart with theoretical value and measured value as abscissa and ordinate is shown in Fig. 2. The linearity of series standard samples turned out to be great ($R^2=0.99992$), which means that the measurement method is reliable. These results make it clear that the sample with $^{79}\text{Se}/\text{Se}$ value of 5.06×10^{-7} up to 5.40×10^{-10} can be measured exactly.

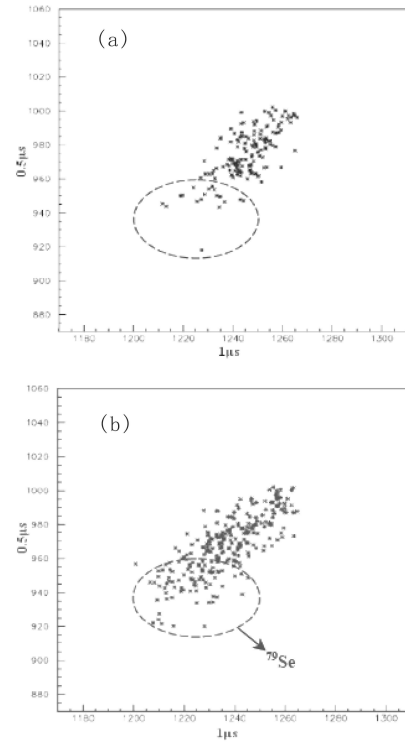


Fig. 1. The measured two-dimensional spectra of blank (a) and $^{79}\text{Se}/\text{Se}=5.40 \times 10^{-10}$ standard sample (b) when the shaping time chose 0.5 and 1 microseconds, the circle area is the ^{79}Se area.

Table 3. Measured AMS $^{79}\text{Se}/\text{Se}$ ratios and calculated $^{79}\text{Se}/\text{Se}$ ratios from serially diluted standards.

samples	$^{79}\text{Se}/\text{Se}$ theoretical value(T)	$^{79}\text{Se}/\text{Se}$ measured value (M)	T/M
blank		$(5.16 \pm 1.80) \times 10^{-11}$	
S3	5.40×10^{-10}	$(6.01 \pm 0.91) \times 10^{-10}$	1.11 ± 0.15
S2	6.87×10^{-8}	$(6.83 \pm 0.54) \times 10^{-8}$	0.99 ± 0.08
S1	5.06×10^{-7}	$(5.06 \pm 0.10) \times 10^{-7}$	1 ± 0.02

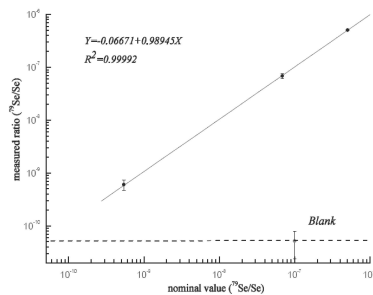


Fig. 2. $^{79}\text{Se}/\text{Se}$ ratios of serially diluted samples analyzed by AMS. The dashed line shows the sensitivity.

6 Conclusions and discussion

Three ^{79}Se reference standard samples with $^{79}\text{Se}/\text{Se}$ ratios of 5.06×10^{-7} , 6.87×10^{-8} and $5.40 \times$

10^{-10} were prepared in this work. By experiments on extracting molecular ions of multiform, molecular negative ions of SeO_2^- which could depress background of bromine-79 as much as 5 order levels was determined. In addition, chemical form and preparation flow of the actual samples were also studied. Finally, the method for measuring ^{79}Se by AMS was built up, including transmission of ^{79}Se beam current, detection of ^{79}Se particles, identification of isobars and measurement of one blank sample along with three standard samples. Results showed that good linearity between measured value and theoretical value was obtained and the sensitivity was 5.16×10^{-11} which was better than projectile X-ray method.

References

- 1 HE Ming, JIANG Song-Sheng, JIANG Shan et al. Nucl. Instrum. Methods B, 2002, **194**: 393
- 2 ZHOU Chun-Mei, WU Zhen-Dong. Atomic Energy Science and Technology, 2006, 40-4 (in Chinese)
- 3 LIU Jian-Fu, ZHANG Jin-Jie, ZHANG Yong-Kang. Journal of Jishou University (Nature Science Edition) 1997, 18-3(in Chinese)
- 4 Clark C, Kalkin B, Krongrad A et al. Decreased Incidence of Prostate Cancer With Selenium Supplementation: Results of a Double-Blind Cancer Prevention Trial [J] Br J Urol, 1998, **81**(5): 730—734
- 5 LUSH D T. Preventing Heart Disease and Cancer. What Randomized, Primary-Prevention Studies Show [J]. Postgrad Med, 1999, **106**(5): 143—148
- 6 BAUM M K, Shor-Posner G, LAI S et al. High Risk of HIV-Related Mortality Is Associated With Selenium Deficiency [J]. J Acquir Immune Defic Syndr Hum Retrovirol, 1997, **15**(5): 370—374
- 7 CHEN C Y, ZHOU J Y, XU H B et al. Effect of Selenium Supplementation on Mice Infected With LP-BM5 MuLV, a Murine AIDS Model [J]. Biol. Trace. Element. Res., 1997, **59**(1-3): 187—193
- 8 YU R, GUO J, CUI A et al. J. Radial. Nucl. Chem., 1995, **196**(1): 165
- 9 JIANG Song-Sheng, HE Ming, DIAO Li-Jun et al. Nucl. Instrum. Methods A, 2002, **489**: 195—201
- 10 Philippe B, Philippe C, Gilbert A. Appl. Radiat. Isotopes, 2007, **65**: 355
- 11 REN Tong-Xiang, ZHANG Ji-Long, PAN Jing-Shun. Measurements of ^{79}Se Half Life. et al. CNRCS 2007 (in Chinese)
- 12 Dewberry R A, Leyba J D, Boyce W T, Radial. J. Nucl. Chem., 2000, **245**(3): 491
- 13 Jerome C, Philippe B, Eric B et al. J. Anal. At. Spectrom, 2003, **18**: 702—707
- 14 Sandrine Aguerre, Carole Frechou. Talanta, 2006, **69**: 565—571
- 15 Carol Frechou, Sandrine Aguerre, Jean-Pierre Degros. Talanta, 2007, **72**: 1166—1171
- 16 Rugel G, Dillmann I, Faestermann T et al. Nucl. Instrum. Methods B, 2007, **259**: 683
- 17 JIANG Song-Sheng. Physics, 1985, **14**(8): 481 (in Chinese)
- 18 HE Ming, JIANG Shan, JIANG Song-Sheng et al. Nucl. Instrum. Methods B, 2004, **223—224**: 78
- 19 LI Chao-Li, WANG Wei, HE Ming et al. A Bragg Curve Detector and Its Application in AMS Measurements for Medium-Weight Nuclides (this publication) (in Chinese)