

Recent progress in AMS measurement of ^{182}Hf at the CIAE*

LI Zhen-Yu(李振宇)¹ HE Ming(何明)¹ DONG Ke-Jun(董克君)¹ HE Guo-Zhu(贺国珠)¹
 LI Chao-Li(李朝历)¹ HE Xian-Wen(何贤文)^{1,2} ZHANG Wei(张伟)^{1,2} HU Hao(胡豪)¹
 ZHENG Guo-Wen(郑国文)¹ LI Heng(李恒)^{1,2} WU Shao-Yong(武绍勇)¹
 YUAN Jian(袁坚)¹ JIANG Shan(姜山)^{1;1)}

¹ China Institute of Atomic Energy, Beijing 102413, China

² College of Physics Science and Technology, Guangxi University, Nanning 530004, China

Abstract: In order to improve the accuracy of accelerator mass spectrometry (AMS) measurement for $^{182}\text{Hf}/^{180}\text{Hf}$, a series of measurements have been taken in the AMS laboratory at the China Institute of Atomic Energy (CIAE). The major ones include the instantaneous monitoring of $^{180}\text{HfF}_5^-$ current, testing the stability of transmission, the alternate measurements of an unknown sample and standard, and the origin identification and minimization of background ^{182}W . The experimental details and the improvement in the measurement accuracy, as well as some useful suggestions for better satisfying the requirements of certain practical applications, are presented in this paper.

Key words: ^{182}Hf , AMS, ^{182}W , alternate measurement, suppression factor

PACS: 06.20.Dk, 07.75.+h, 29.25.-t **DOI:** 10.1088/1674-1137/36/11/020

1 Introduction

^{182}Hf with a half life of (8.90 ± 0.09) million years is an ideal candidate for an indicator of a possible supernova explosion in the vicinity of the solar system within the last several million years. This may be accomplished by finding measurable traces of live ^{182}Hf on Earth [1]. Also, ^{182}Hf is a long-lived radionuclide of particular interest as one of the most suitable neutron flux monitors for nuclear environment engineering. Accelerator mass spectrometry (AMS) is one of the most promising methods to detect minute amounts of ^{182}Hf . Successful measurement of ultratrace ^{182}Hf with AMS can offer important experience for the mea-

surements of other heavy nuclides and demonstrate the potential of AMS in the search for super heavy nuclides.

AMS measurement of ^{182}Hf was first reported by Vockenhuber et al. [1]. At the Vienna Environmental Research Accelerator (VERA). The reported detection limit for $^{182}\text{Hf}/^{180}\text{Hf}$ was 1.0×10^{-11} [1, 2]. Follow-up studies on this topic include the methods of isobar suppression [2] and the assessment of ^{182}Hf AMS measurements [3]. AMS measurement of ^{182}Hf was first developed at the China Institute of Atomic Energy (CIAE) with the HI-13 AMS systems in 2006 [4, 5]. Since then, a series of measures have been taken to improve the sensitivity at the CIAE [5–8].

Table 1. Typical performances for AMS measurements of ^{182}Hf at the CIAE.

year	typical $^{180}\text{HfF}_5^-$ current/nA	extraction efficiency	transmission	overall efficiency	typical ^{182}W count rate, s^{-1}	sensitivity of $^{182}\text{Hf}/^{180}\text{Hf}$
2006	48	3.4×10^{-3}	1.97×10^{-4}	6.7×10^{-7}	4/1800	2.2×10^{-10} [5]
2008	80	7.7×10^{-3}	2.14×10^{-4}	1.65×10^{-6}	7/3830	5.0×10^{-11} [7]
2009	150	—	6.41×10^{-4}	—	—	—
2010	117	—	0.96×10^{-3}	—	6/600	1.0×10^{-11} [8]

Received 13 January 2012

* Supported by National Natural Science Foundation of China (10705054)

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

©2012 Chinese Physical Society and the Institute of High Energy Physics of the Chinese Academy of Sciences and the Institute of Modern Physics of the Chinese Academy of Sciences and IOP Publishing Ltd

Up to now, the sensitivity of about 1.0×10^{-11} for $^{182}\text{Hf}/^{180}\text{Hf}$ has been achieved [8]. Table 1 lists some typical performance indices in different years. However, for the samples with $^{182}\text{Hf}/^{180}\text{Hf}$ isotopic ratio in the order of 10^{-10} , the measurement accuracy is unable to satisfy the requirements of certain practical applications at the moment. Presented in this paper is the recent progress made at the AMS Lab of CIAE in an effort to improve the quality for AMS measurements of ^{182}Hf at $^{182}\text{Hf}/\text{Hf}$ level of 10^{-10} .

2 Experiments and result

2.1 Instantaneous monitoring of $^{180}\text{HfF}_5^-$ current

For dedicated AMS facilities, the sequential injection (the so-called fast cycling option [9]) of the ion beams for a high abundance reference isotope and that of the ultratrace isotope of interest is generally employed. In that case, the strength of injection magnetic field is fixed. By switching the pre-acceleration voltage, sequential injection can be achieved quickly, the effect of fluctuations in the ion source output minimized and the measurement accuracy guaranteed. For the AMS facility based on the HI-13 tandem accelerator at the CIAE, however, the sequential injection has to be achieved by alternatively exchanging the strength of the injection magnetic field, while the pre-acceleration voltage is fixed. So, with a certain value of magnetic strength, only one kind of isotope (either the abundant isotope or the ultratrace one) can be measured online. For the ultratrace isotope of interest (^{182}Hf in this case), a relatively long measuring time is required in order to obtain good counting statistics. During this time, the fluctuations in the ion source output for the high abundance reference isotope ($^{180}\text{HfF}_5^-$ in this case) are very common and, unfortunately, unable to be monitored. The measurement accuracy is therefore largely influenced. In order to solve this problem, a technique for instantaneously monitoring the beam current of the high abundance reference isotope ($^{180}\text{HfF}_5^-$ current) has recently been developed at the CIAE. It is based on

simultaneous measurements of the ^{182}Hf count rate with a detector at the end of the AMS beam line and the stable Hf isotope current in an off-axis Faraday cup at the image plane of the injection magnet at the low energy side. The detailed descriptions can be found in Ref. [10].

In order to verify the contribution of this technique to the improvement on the measurement accuracy of $^{182}\text{Hf}/^{180}\text{Hf}$, laboratory standard samples with $^{182}\text{Hf}/^{180}\text{Hf}$ isotopic ratio of 10^{-10} level were measured. As shown in Table 2, by using this instantaneous monitoring technique the relative deviation (between the measured value and the standard one) is 9%, compared to 24.6% with the traditional sequential injection method. The total relative uncertainties are 15.7% and 33.0% for instantaneous monitoring and sequential injection method, respectively. An improvement in measurement accuracy is evident.

2.2 Stability test of transmission

Although the technique of simultaneous monitoring of the $^{180}\text{HfF}_5^-$ current reduces the relative uncertainty and relative deviation effectively, the deviation between the measured value and the standard one is still quite large, which may be caused mainly by the fluctuation of transmission. So, it is necessary to test the stability of the system. In this experiment, two ^{182}Hf standard samples were used to monitor the system fluctuation. By sequentially measuring these two samples, the system variation was obtained. As shown in Figs. 1 and 2, the variation of the measured value with time was much larger for the standard sample with $^{182}\text{Hf}/^{180}\text{Hf}$ of 10^{-10} level than that of 10^{-9} level. However, as shown in Fig. 2, the measured value for the 10^{-10} sample varies monotonously within a typical measuring time (from 1000 s to 2500 s for instance). If the variation is assumed to be linear, the fluctuation can be removed by continuous interchange measurements between standard and unknown samples (the so-called alternate measurement) within this period. Thus the feasibility of an alternate measurement for ^{182}Hf needs to be tested by experiments.

Table 2. Comparison between measurement accuracies obtained by using the instantaneous monitoring technique and the sequential injection method.

monitoring method	standard value of $^{182}\text{Hf}/^{180}\text{Hf}$	measured value of $^{182}\text{Hf}/^{180}\text{Hf}$	relative uncertainty(%)	relative deviation(%)
instantaneous (this work)	1.33×10^{-10}	$(1.21 \pm 0.19) \times 10^{-10}$	15.7	9.0
sequential injection [11]	3.45×10^{-10}	$(2.60 \pm 0.86) \times 10^{-10}$	33.0	24.6

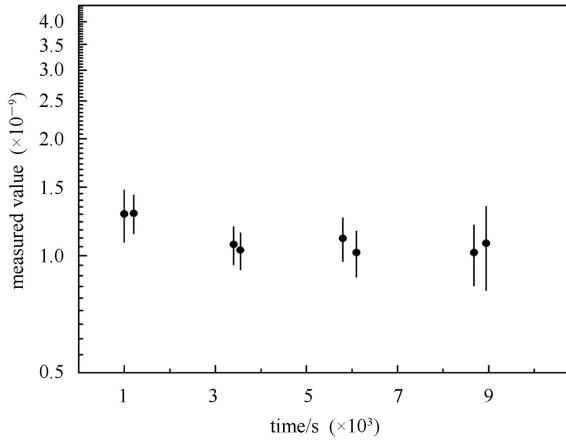


Fig. 1. The variation of measured $^{182}\text{Hf}/^{180}\text{Hf}$ value (for a standard sample with $^{182}\text{Hf}/^{180}\text{Hf}$ of 1.28×10^{-9}).

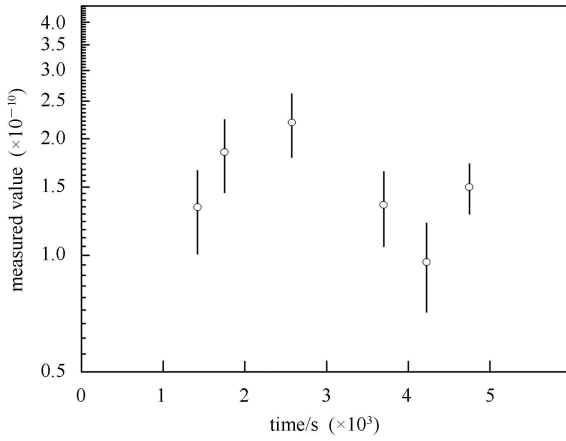


Fig. 2. The variation of measured $^{182}\text{Hf}/^{180}\text{Hf}$ value (for a standard sample with $^{182}\text{Hf}/^{180}\text{Hf}$ of 1.33×10^{-10}).

In this experiment, 4 groups of measurements were performed independently. In each measurement group, the standard and simulated samples were measured in the order of standard-simulated-standard

(we named it the ‘sandwich monitoring’ technique as shown in Table 3), then the beam line was adjusted to its optimization for the next group. A measuring time of about 500 s was used for each sample and 1600 s for each group in total. The experimental data are listed in Table 3. According to

$$T = \frac{n}{\frac{I \times 10^{-9}}{1.6 \times 10^{-19}} \cdot R_0}, \quad (1)$$

the transmission for standard samples can be derived, where T and R_0 denote the transmission and true value of $^{182}\text{Hf}/^{180}\text{Hf}$ for standard samples, respectively. I represents the $^{180}\text{HfF}_5^-$ current with unit nA and n is the count rate of ^{182}M (^{182}Hf in this case). It should be noticed here that ^{182}W is ignored because the aim in this experiment is just to test the feasibility of the alternate measurement method. Because the linear variation of transmission is assumed, the transmission for simulated samples T' can be obtained by

$$T' = \frac{T_1 + T_2}{2}, \quad (2)$$

T_1 and T_2 denote the transmission for standard samples on both sides of the simulated one. Finally, the value of $^{182}\text{Hf}/^{180}\text{Hf}$ for simulated samples can be calculated by

$$R = \frac{n}{\frac{I \times 10^{-9}}{1.6 \times 10^{-19}} \cdot T'}. \quad (3)$$

As shown in Table 3, the true value of $^{182}\text{Hf}/^{180}\text{Hf}$ for simulated samples is 1.33×10^{-10} , the same as that of the standard one and the calculated result is $(1.36 \pm 0.11) \times 10^{-10}$, average value of 4 calculated ones. The relative deviation and uncertainty are 2.1% and 8.1%, respectively. This result is obviously better

Table 3. Alternate measurements between standard and simulated samples.

order	sample	count rate of ^{182}Hf	average $^{180}\text{HfF}_5^-$ current/nA	standard value (R_0)	calculated transmission(T)	calculated transmission(T')	calculated value(R)
1	standard	0.085 ± 0.021	116.26	1.33×10^{-10}	$(9.29 \pm 2.25) \times 10^{-4}$		
	simulated	0.044 ± 0.009	43.33	1.33×10^{-10}		$(12.30 \pm 1.82) \times 10^{-4}$	$(1.39 \pm 0.30) \times 10^{-10}$
2	standard	0.058 ± 0.011	47.91	1.33×10^{-10}	$(15.40 \pm 2.86) \times 10^{-4}$		
	simulated	0.038 ± 0.006	52.47	1.33×10^{-10}	$(6.72 \pm 1.73) \times 10^{-4}$	$(9.00 \pm 1.25) \times 10^{-4}$	$(1.36 \pm 0.22) \times 10^{-10}$
3	standard	0.039 ± 0.006	43.94	1.33×10^{-10}	$(11.30 \pm 1.81) \times 10^{-4}$		
	simulated	0.040 ± 0.006	43.16	1.33×10^{-10}	$(7.76 \pm 1.47) \times 10^{-4}$	$(10.70 \pm 1.31) \times 10^{-4}$	$(1.47 \pm 0.23) \times 10^{-10}$
4	standard	0.039 ± 0.006	36.49	1.33×10^{-10}	$(13.60 \pm 2.17) \times 10^{-4}$		
	simulated	0.026 ± 0.007	36.13	1.33×10^{-10}	$(9.14 \pm 2.54) \times 10^{-4}$	$(14.20 \pm 1.90) \times 10^{-4}$	$(1.21 \pm 0.20) \times 10^{-10}$
	standard	0.047 ± 0.007	30.89	1.33×10^{-10}	$(19.30 \pm 2.82) \times 10^{-4}$		

than the single measurement mentioned in Section 2.1. Thus the alternate measurement is feasible for improving the measurement accuracy.

However, the uncertainty and deviation are still too large to satisfy real applications. There are two main reasons. One is the low counting statistics. The other is that the variation of system is not strictly monotone within a 1600 s measuring time interval. A shorter measuring time will lead to more linear variation during a standard-sample-standard measuring cycle and get higher measurement accuracy. To maintain sufficient count rate statistics for ^{182}W with a shorter counting time, the only way is to increase the $^{180}\text{HfF}_5^-$ current. Recently, the conical collector used previously in ion sources has just been replaced by a spherical one, which may bring about an increase in extraction efficiency by about 3 times. In addition, the wheel of the sample holder can now be rotated both clockwise and counterclockwise, which makes the measurements of a series of samples/standard efficient and flexible.

2.3 The origin of ^{182}W

In the measurement of ^{182}W with AMS, the interference of isobar ^{182}W is almost an irresolvable problem. So far, there has been no way to separate ^{182}W totally from the ^{182}Hf events. During the measurement procedure, the stable tungsten isotope of ^{183}W was also measured by tuning the beam line to its operation parameters at our laboratory. The net ^{182}Hf events can be obtained by subtracting the ^{182}W contribution, being estimated by a measured $^{182}\text{W}/^{183}\text{W}$ ratio in ^{182}Hf free samples (blank samples) and ^{183}W events, from the total events of mass $A=182$. This is named the isotopic deduction method. Generally, the deduction method of ^{182}W depends on the origin of tungsten directly. In our former calculations [8], tungsten is usually considered to come mainly from samples. Recently, Forstner and co-authors pointed out that a substantial part of ^{182}W background may come from the ion source [3]. If ^{182}W mainly comes from the ion source, the ^{182}W count rate measured by the detector should be irrelevant to $^{180}\text{HfF}_5^-$ current, and the ^{182}W events should be deducted just as count rate. Otherwise, the count rate should be normalized by the corresponding off-axis current. So, it is necessary to test the origin of ^{182}W in experiments. In this work, all of the useful data for blank samples were collected to investigate this problem. As shown in Fig. 3, the preliminary result shows that the ^{182}W count rate is almost constant with the increase of $^{180}\text{HfF}_5^-$ current. This implies that the tungsten

mainly comes from the ion source.

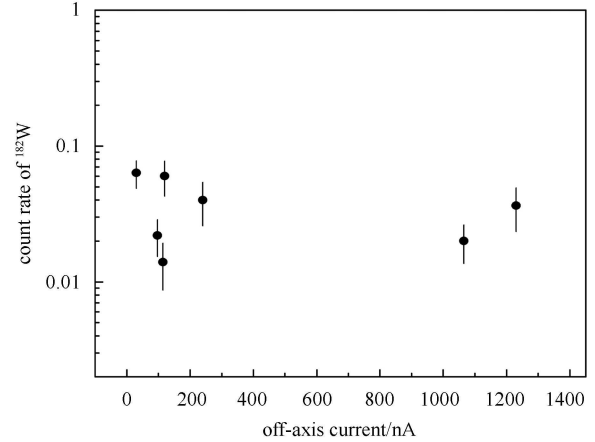


Fig. 3. ^{182}W count rate (N/T) vs. off-axis current (I) for blank samples.

2.4 Suppression factor of ^{182}W

Suppression factor of ^{182}W is an important index in the measurement of ^{182}Hf . This factor is defined as the value of $^{182}\text{W}/^{180}\text{Hf}$ in blank samples divided by the measured value of $^{182}\text{W}/^{180}\text{Hf}$ using the AMS method. In order to satisfy a certain requirement of measurement sensitivity, the upper limit of the tungsten component in the measured samples should be estimated with the suppression factor of ^{182}W , which is important to the chemical preparation of measured samples [12]. Research indicates that by choosing the fitted chemical form as the target material and extraction ions in an ion source, the ^{182}W is suppressed largely. In Ref. [1], a ^{182}W suppression of about 6000 can be achieved using HfF_5^- ions. Later, a ^{182}W suppression of about 36000 [3] was reported at the same laboratory. In their work, however, the ^{182}W suppression is just a relative factor which is different from the definition here. So far, there have been no reports about the suppression factor of ^{182}W . In our work, the blank samples were measured by using the inductively coupled plasma mass spectrometry (ICP-MS) method and the suppression factors were calculated, where the ratio of $^{182}\text{W}/^{180}\text{Hf}$ about 1.0×10^{-11} with the AMS method for blank samples is used. Table 4 lists the data in detail. It is shown that the suppression factor of ^{182}W is greater than 10^8 . Thus, the suppression factor was obtained firstly in experiments. However, it is worth noting that in the experiment, the value of $^{182}\text{W}/^{180}\text{Hf}$ with the AMS method is obtained by formula (3), where the counts of ^{180}Hf are relevant to $^{180}\text{HfF}_5^-$ current. Because the ^{182}W count rate is irrelevant to $^{180}\text{HfF}_5^-$ currents as mentioned in Section 2.3, the suppression factor has a negative correlation with the $^{180}\text{HfF}_5^-$ currents. The

Table 4. Suppression factor of ^{182}W is calculated using the values measured by ICP-MS.

sample (powder)	weight of powder/mg	volume of solution/mL	measured component of w with ICP-MS/(mg·L ⁻¹)	component of W (wt%)	calculated $^{182}\text{W}/^{180}\text{Hf}$	suppression factor
NH_4HF_2	81.4	50	0.022	0.001	—	—
HfO_2 (99.9%)	83.4	100	1.508	0.181	1.36×10^{-3}	—
HfF_4^*	121.0	100	1.939	0.160	1.20×10^{-3}	1.20×10^8
HfF_4 (commercial)	111.3	100	2.335	0.210	1.58×10^{-3}	1.58×10^8

HfF_4^* was obtained by multiphase synthesis [13] from NH_4HF_2 and HfO_2 .

measured value of $^{182}\text{W}/^{180}\text{Hf}$ with AMS at the CIAE listed in Table 1 is usually the typical one (the best one). So, the suppression factor listed in Table 4 is actually the best one.

3 Summary and outlook

Although a sensitivity of 1.0×10^{-11} ($^{182}\text{Hf}/^{180}\text{Hf}$) has now been achieved in the measurement of ^{182}Hf at the CIAE, the measurement accuracy for samples with $^{182}\text{Hf}/^{180}\text{Hf}$ of 10^{-10} level is still unable to satisfy the requirements of certain practical applications. The following measures have been taken to solve this problem.

Firstly, a technique of instantaneous monitoring of $^{180}\text{HfF}_5^-$ current on an off-axis Faraday cup has been developed. In order to verify the contribution of this technique to the improvement in the accuracy of $^{182}\text{Hf}/^{180}\text{Hf}$ measurement, laboratory standard samples with a $^{182}\text{Hf}/^{180}\text{Hf}$ isotopic ratio with the level of 10^{-10} were measured, and the result was compared with those by using the traditional sequential injection method. It turns out that a substantial reduction in measurement uncertainty can be achieved.

Secondly, in order to reduce the uncertainty originating from transmission fluctuation, alternate measurements of standard and unknown samples were used. The experimental results show that the measurement accuracy can be largely improved for samples with $^{182}\text{Hf}/\text{Hf}$ of 10^{-10} level by using this ‘sand-

wich monitoring’ technique. After the installation of the new ion source with a spherical collector, it is expected that the $^{180}\text{HfF}_5^-$ current will be increased, measuring time shortened, and transmission fluctuation better overcome by using the ‘sandwich monitoring’ method.

In the case of the origin of ^{182}W in the measurement of ^{182}Hf , the preliminary experimental data indicate that the tungsten mainly comes from the ion source. This result is important for the correct choice of the deduction method of ^{182}W . But the amount of data in this work is insufficient, and more data should be collected later.

Finally, the suppression factor of ^{182}W was first obtained in experiments. It is shown that the suppression factor of ^{182}W is up to 10^8 . This is important for the chemical preparation of measured samples.

In the near future, we will focus on the optimization of alternate measurement between standard and unknown samples and assessment of the deduction method of ^{182}W , so that the measurement accuracy can be improved further.

We wish to thank Ph. D. QIAO Bo-Tao from the Dalian Institute of Chemical Physics, Chinese Academy of Sciences for help in testing samples with ICP-MS, and Professor TIAN Wei-Zhi from the Department of Nuclear Physics, China Institute of Atomic Energy (CIAE) for helpful suggestions, as well as the technical staff at the CIAE for ensuring smooth accelerator operation.

References

- Vockenhuber C, Bichler M, Golser R et al. Nucl. Instrum. Methods B, 2004, **223–224**: 823–828
- Forstner O, Andersson P, Diehl C et al. Nucl. Instrum. Methods B, 2008, **266**: 4565–4568
- Forstner O, Gnaser H, Golser R et al. Nucl. Instrum. Methods B, 2011, **269**: 3180–3182
- QIU J Z, JIANG S, HE M et al. Chinese Physics C, 2007, **31**: 719–723 (in Chinese)
- QIU J Z, JIANG S, HE M et al. Nucl. Instrum. Methods B, 2007, **259**: 246–249
- TUO F, HE M, SHEN H T et al. Chinese Physics C (HEP & NP), 2008, **32**: 201–204
- TUO F, RUAN X D, HE M et al. Nucl. Instrum. Methods B, 2010, **268**: 776–778
- DONG K J, HE M, LI Z Y et al. Chin. Phys. Lett., 2010, **27**: 110701
- Fifield L K. Rep. Prog. Phys., 1999, **62**: 1223
- LI Z Y, HE M, DONG K J et al. Nucl. Sci. Tech., 2012, **23**: 199–202
- YIN X Y, HE M, DONG K J et al. High Energy Physics and Nuclear Physics, 2007, **31**: 978 (in Chinese)
- FAN J L, ZHANG S D, LU J C et al. J. Radioanalytical and Nuclear Chemistry, 2010, **284**: 93
- JIANG T, YANG J, YANG L et al. Acta Chimica Sinica, 2010, **68**: 2211