

# Developments in accelerator mass spectrometry (AMS) method for $^{182}\text{Hf}^*$

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**Abstract** The present detection limit for  $^{182}\text{Hf}$  at CIAE HI-13 AMS systems could not satisfy various applications (e. g. detection of a nearby supernovae signal). Therefore, techniques were developed in this work to improve the AMS measurement of  $^{182}\text{Hf}$  mainly on building a new injector and using a method that based on solid-phase reaction for the preparation of  $\text{HfF}_4$  samples from  $\text{HfO}_2$ . The experimental results show that mass resolution of the injector can reached 630, and the  $\text{F}^-/\text{O}^-$  and beam current of  $^{180}\text{HfF}_5^-$  for  $\text{HfF}_4$  samples produced by dry method is about 2—3 times and 1.5 times of that by previously method, respectively.

**Key words**  $^{182}\text{Hf}$ , accelerator mass spectrometry (AMS),  $\text{HfF}_4$ , injector, solid-phase reaction

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## 1 Introduction

Long-lived radionuclide  $^{182}\text{Hf}$  with half-lives of  $8.90\pm 0.09\text{Ma}$ <sup>[1]</sup> is of particular interest in both geo-physical and astrophysical studies.  $^{182}\text{Hf}$  also plays an important role for the understanding of nucleosynthesis of heavy elements in stellar environments. Furthermore,  $^{182}\text{Hf}$  is a radionuclide of particular interest for nuclear engineering.

The first Accelerator Mass Spectrometry (AMS) measurement of  $^{182}\text{Hf}$  was carried out by Christof Vockenhuber at VERA<sup>[1–3]</sup>. HI-13 AMS system at China Institute of Atomic Energy (CIAE) has reported the obtained results of  $^{182}\text{Hf}$  with a detection limit of  $2.2\times 10^{-10}$  for  $^{182}\text{Hf}/^{180}\text{Hf}$  ratio<sup>[4]</sup>. It could not fully meet the detection sensitivity required for applications, such as attempts of searching for live  $^{182}\text{Hf}$  from a recent nearby supernova. The main chal-

lenge for improving the detection limit for  $^{182}\text{Hf}$  is how to suppress the  $^{182}\text{W}$ .

Christof Vockenhuber et al.<sup>[5]</sup> using the  $\Delta\text{TOF}$  detection technique at the Munich MP Tandem accelerator (TV = 14 MV) to improving detection limit. While S. Winkler et al.<sup>[6, 7]</sup> explored projectile X-ray emission method together with a solid passive absorber followed by a measurement of the residual energy at ANU 14UD tandem in Canberra Australia. But for the accelerator of HI-13 AMS, the maximum energy of  $^{182}\text{Hf}$  can only reach about 80 MeV, which isn't high enough to separate  $^{182}\text{W}$  from  $^{182}\text{Hf}$  in gas detectors. Therefore, other techniques, such as the improvement of the injector, chemical separation of  $^{182}\text{W}$ , higher the intensity of beam have been used to suppress the interference of  $^{182}\text{W}$  at low-energy side. The preliminary progresses in the improvements of the injector and the preparation of samples by solid-

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phase reactions at CIAE HI-13 AMS systems were reported in this paper.

## 2 Establishment of the dedicated injector and the measurement of the mass resolution

The mass resolution of the original injector at HI-13 AMS systems was 80, it could not satisfy accurate measurement of  $^{182}\text{W}$  and other heavy radionuclides. Therefore, a dedicated injector composed by a  $90^\circ$  spherical electrostatic analyzer and a  $112^\circ$  dual focus magnetic analyzer was set up. During measurement of mass resolution, 5 mg samples was mixed with silver powder (mass ratio 1:1), then pressed firmly into Al-target holders with a 40 position. After baked under  $120^\circ\text{C}$  for a few hours, the target tray was loaded into the MC-SNICS ion source. When image point slit of the magnetic analyzer was set to  $\pm 1$  mm, we obtained the relationship of negative ion current and field of injector magnet (shown in Figs. 1 and 2).

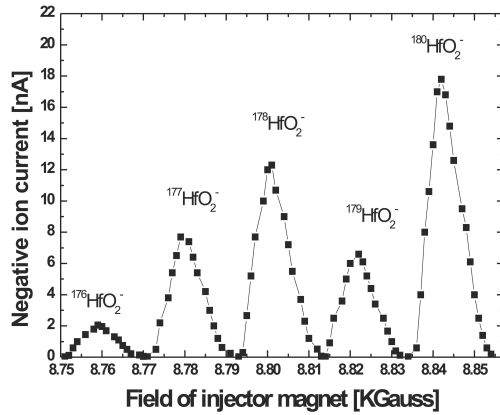


Fig. 1. Injector mass scan of  $\text{HfO}_2$ .

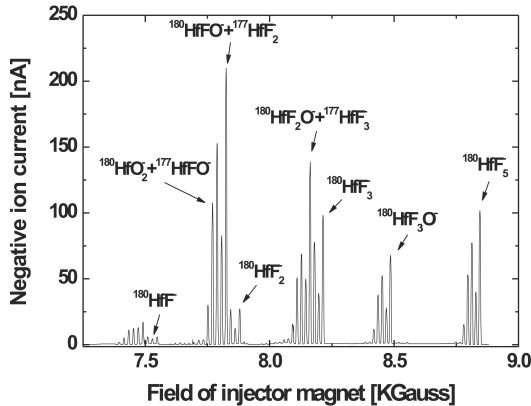


Fig. 2. Injector mass scan of  $\text{HfF}_4$  sample.

We can see from Fig. 1, mass resolution of the injector can reach 430 by scanning of  $\text{HfO}_2$  sample when the object point slit of the magnetic analyzer was widely opened and image point slit was set to  $\pm 1$  mm. If the object point and image point slit were set to  $\pm 2.5$  mm and  $\pm 1$  mm respectively, as shown in Fig. 2, the mass resolution of the injector can reach 630.

The beam intensity and efficiency of transmission were shown in Table 1 for different object point slits with the object point slit fixed at  $\pm 1$  mm. It's shown that the efficiency of transmission was 100% when the object point slit was wider than  $\pm 2$  mm. While efficiency of transmission lowed to 95.8%, 87.5% and 61% respectively when the object point slit was set to  $\pm 1$ ,  $\pm 0.5$  and  $\pm 0.25$  mm correspondingly.

Table 1. The dependence of beam intensity on object point slit.

slit/mm	beam/nA	$\eta(\%)$	slit/mm	beam/nA	$\eta(\%)$
1	7.7	17.7	5	43.0	99.3
1.5	12.6	29	6	43.3	99.8
2	25.6	59	7	43.3	99.8
3	32.0	73.7	8	43.4	100
4	39.3	91	9	43.4	100

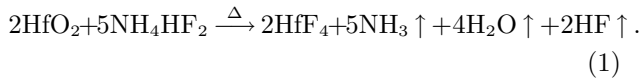
## 3 Preparation of $\text{HfF}_4$ samples by solid-phase

### 3.1 Background and principles

In the experimental, the dependence of beam intensity on oxygen content in the samples was obtained. The results suggest us that negative ion current of  $^{180}\text{HfF}_5^-$  is reduced if high values oxygen are present. Although, a  $^{182}\text{W}$  suppression of about 6000<sup>[2]</sup> can be achieved by using  $\text{HfF}_5^-$  ions, if a large amount of oxygen exists in the samples, ions such as  $\text{WF}_4^{18}\text{OH}^-$  can be easily formed and the high suppression of  $^{182}\text{W}$  can not be achieved. Thus, it requires the samples to be made in pure  $\text{HfF}_4$  form.

Usually a liquid-phase reaction was used to prepare fluorides (as we called “wet-method”). The main defect of wet-method is the long fluoride process, which could introduce a lot of impurities especially the high content of oxygen caused by the dehydration in the last part of fluoride. In order to reduce oxygen we improved the method of preparation  $\text{HfF}_4$  by a solid-phase reaction using  $\text{NH}_4\text{HF}_2$  instead of

the common liquid-phase reaction. The principle of reaction can be expressed in formula:



### 3.2 Reagents and equipment of solid-phase reaction

Several reagents are used in the experiment, such as hafnium dioxide ( $\text{HfO}_2$ ), hydrogen fluoride ammonium ( $\text{NH}_4\text{HF}_2$ ), ultra-pure water, BV-III-class: nitrate, MOS-class: hydrochloric acid and hydrofluoric acid. In addition, an agate mortar should be prepared to grind the sample. Our solid-phase reaction

equipment is shown in Fig. 3.

### 3.3 Preparation of sample by solid-phase reaction

Materials of reaction vessels, proportion of  $\text{NH}_4\text{HF}_2$  and escaped temperature of ammonium as well as the reaction time of the solid-phase reaction were studied in this work. PTFE vessel was finally chosen because of its high recovery rate, the small introduction of the pollution as well as good experimental results of AMS. The results show that the excessive rate of  $\text{NH}_4\text{HF}_2$  with about 500% could result in the largest beam intensity, and thus be chosen in solid-phase reaction.

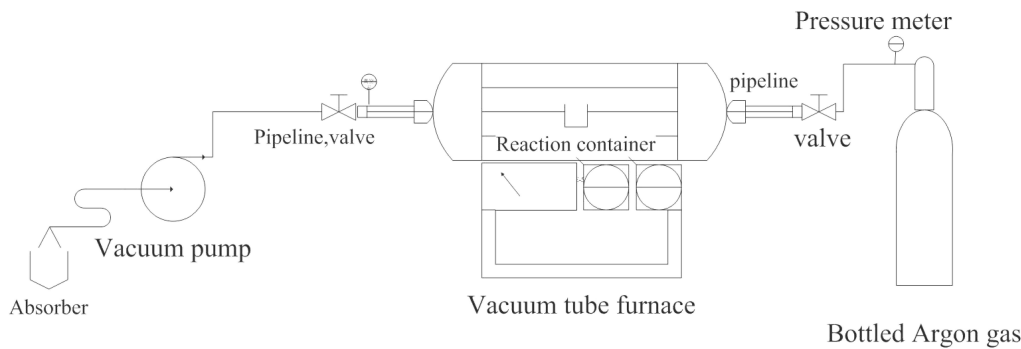


Fig. 3. Schematic of solid-phase reaction equipment.

The processes of sample prepare by solid-phase reaction as follows:

- 1) Vessel cleaning: the furnace tube, small PTFE cups and bracket are cleaned and dried.
- 2) Weighing: weigh a certain quantity of  $\text{HfO}_2$  powder and 500% excess of  $\text{NH}_4\text{HF}_2$ .
- 3) Charging: mix  $\text{HfO}_2$  and  $\text{NH}_4\text{HF}_2$  fully in the weighing paper. After grinded gently in the agate mortar, the mixtures are put into the vacuum furnace.
- 4) Fluoridation: seals the vacuum furnace and start mechanical pump. After pulling vacuum, argon gas is filled. Repeat the "gas bath" three times then fill a small amount of argon gas into the vacuum furnace. Next, closes the valve of the ends, stops pumps, elevates temperature to  $200^\circ$ , keep the degree for 4 h.
- 5) Escapes of the ammonium: 4 h later, pulls vacuum and then passes the argon slowly, maintains the system in the slow air bleed condition and rises the temperature to  $250^\circ$ , separates excessive  $\text{NH}_4\text{HF}_2$  and side reaction product  $\text{NH}_4\text{F}$  to outdoor, keeps

$250^\circ$  temperature condition for 2 h, then stops heating and temperature decrease.

- 6) Final sample: after the temperature of furnace drop to normal temperature, final sample are removed out. After weighed, samples are deposited in the argon environment.

### 3.4 The measurement of sample

Sample material of  $\text{HfF}_4$  made by solid-phase reaction was pressed firmly into Al-target holders of the 40 position MC-SNICS source. The typical experiment parameter is: Extraction voltage 11 kV, cathode voltage 2.5 kV, cesium pot heating temperature  $150^\circ\text{C}$ , ion source vacuum  $4.0 \times 10^{-5}$  Pa. We have tested 3 kinds of samples: the self-made liquid-phase reaction sample, the commercial sample (Alfa Aesar, USA) and the solid-phase reaction sample were compared. Extracted  $\text{F}^-$  and the  $\text{O}^-$  ion separately, measures their beam intensity with the Faraday cup to obtain  $\text{F}^-$  and  $\text{O}^-$  beam intensity ratio ( $\text{F}^-/\text{O}^-$ ), the results of several measures shows in the Table 2.

Table 2. Comparison of  $F^-/O^-$  in three kind of  $HfF_4$  samples.

material	$F^-/O^-$			
	experiment 1	experiment 2	experiment 3	experiment 4
$HfF_4$ made by liquid-phase reaction	6.2	5.4	5.7	9.5
commercially available $HfF_4$	5.2	7.5	7.8	6.5
$HfF_4$ made by solid-phase reaction	19.1	14.0	10.6	30.5

As can be seen from Table 2,  $F^-/O^-$  of solid-phase reaction samples is 2-3 times of that liquid-phase reaction and commercially available  $HfF_4$ . Also, negative ion current of  $^{180}HfF_5^-$  can reach up to 150 nA (for naturally abundance samples), it is 2 times larger than that of liquid-phase reaction.

#### 4 The measurement of $^{182}Hf$ by AMS after the improvement of the injector

After the establishment of new injector, the transmission efficiency from image point of injector magnet to the low-energy side of the accelerator is 90%. In order to enhance the transmission efficiency, pre-accelerate voltage was set to 110 kV.  $^{180}HfF_5^-$  from  $HfF_4$  were extracted, at the high-energy side,  $^{182}Hf^{9+}$  ions were analyzed. The Faraday cup and the gold-silicon surface barrier detector (SBD) were used to record  $^{180}Hf$  beam intensity and the  $^{182}Hf$  particle spectrum respectively, and then  $n(^{182}Hf)/n(^{180}Hf)$  can be calculated, the detailed measurement principle is shown in reference<sup>[4]</sup>. At present, we got some primary results for  $^{182}Hf/^{180}Hf$  isotope ratios at  $3 \times 10^{-10}$  with transmission efficiency of  $2.68 \times 10^{-4}$ . This result is based on that we just rely on the injector and slits to depress the interference of stable hafnium isotopes, and use naturally abundance samples without any chemical separation of  $^{182}W$ . The background of

isotopes have been depressed a lot compare with the measurements before. We can foresee that by using the Time of Flight (TOF) detector, a measurement of  $^{182}Hf/^{180}Hf$  at the  $10^{-11}$  level may soon be possible.

#### 5 Conclusions and prospects

This work developed the measurement of  $^{182}Hf$  by AMS.  $F^-/O^-$  of solid-phase reaction samples is 2–3 times of that of liquid-phase reaction. The reduction of the oxygen content not only reduces the risk of interference caused by impurities but also increase the beam intensity of  $^{180}HfF_5^-$ , which make it easy to further improve sensitivity of the measurement for  $^{182}Hf$ .

After the establishment of dedicated injector for AMS, mass resolution of the injector can reach 630 when the object point and image point slit is set to  $\pm 2.5$  mm and  $\pm 1$  mm respectively, which effectively reduces the interference of isotope  $^{180}Hf$ . At present, the works of Time of Flight (TOF) detector which suppress interference of isotopes and the works of chemical separation which suppress interference of isobar are continued. Next step we will measure the flow blank samples and rock samples.

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