The quest for AMS of $^{182}$Hf – why poor gas gives pure beams

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Abstract. The long-lived radioisotope $^{182}$Hf (T$_{1/2}$ = 8.9 Ma) is of high astrophysical interest as its potential abundance in environmental archives would provide insight into recent r-process nucleosynthesis in the vicinity of our solar system. Despite substantial efforts, it could not be measured at natural abundances with conventional AMS so far due to strong isobaric interference from stable $^{182}$W. Equally important is an increase in ion source efficiency for the anions of interest.

The new Ion Laser InterAction Mass Spectrometry (ILIAMS) technique at VERA tackles the problem of elemental selectivity in AMS with a novel approach. It achieves near-complete suppression of isobar contaminants via selective laser photodetachment of decelerated anion beams in a gas-filled radio-frequency quadrupole (RFQ) ion cooler. The technique exploits differences in electron affinities (EA) within elemental or molecular isobaric systems neutralizing anions with EAs smaller than the photon energy. Alternatively, these differences in EA can also facilitate anion separation via chemical reactions with the buffer gas.

We present first results with this approach on AMS-detection of $^{182}$Hf. With He + O$_2$ mixtures as buffer gas in the RFQ, suppression of $^{182}$WF$_5^-$ vs $^{180}$HfF$_5^-$ by > 10$^5$ has been demonstrated. Mass analysis of the ejected anion beam identified the formation of oxyfluorides as an important reaction channel. The overall Hf-detection efficiency at VERA presently is 1.4 % and the W-corrected blank value is $^{182}$Hf/$^{180}$Hf = (3.4 ± 2.1) × 10$^{-14}$. In addition, a survey of different sample materials for highest negative ion yields of HfF$_5^-$ with Cs-sputtering has been conducted.

1 Introduction

Accelerator mass spectrometry (AMS) commonly is the most sensitive technique for the detection of long-lived isotopes, reaching down to the attogram/gram abundance range. Over recent years, it has subsequently been employed in the search for signatures from recent nucleosynthesis in the vicinity of the solar system and corresponding signals of $^{244}$Fe and $^{244}$Pu have been identified in terrestrial and lunar archives [1,5]. The observed scarcity of $^{244}$Pu has fueled the discussion about the astrophysical site of the rapid neutron-capture process (r-process) in favor of neutron star mergers [3]. Currently, this is the only experimentally confirmed r-process production site following gravitational wave detection GW170817 [5] and spectroscopic observation of the associated kilonova SSS17a (e.g. [7]). However, unexplained discrepancies with astronomical observations remain and suggest further sites and possibly multiple r-process components (see [3] for a recent review).

An important anchor point in this puzzle is $^{182}$Hf with a half life of T$_{1/2}$ = (8.90 ± 0.09) Ma [12]. As is the case for $^{60}$Fe and $^{244}$Pu, there is no natural production of $^{182}$Hf on Earth and all of the primordial contribution has long since decayed away. Thus, any $^{182}$Hf detected must stem from recent nucleosynthesis. Since $^{182}$Hf is in the middle-mass region of the r-process nucleides, it could potentially be produced in different scenarios to those for $^{244}$Pu. Based on various yield- and elemental-ratio-calculations for possible $^{182}$Hf production scenarios [10–13], the estimated $^{182}$Hf/$^{180}$Hf signal intensity is at most a few times 10$^{-13}$, but could even be one to three orders of magnitude lower depending on the Hf incorporation efficiencies and stable Hf content in the archives.

The challenge in AMS-detection of $^{182}$Hf at these low abundances is interference from the ubiquitous stable isobar $^{182}$W. This quest started at the 3-MV-Vienna Environmental Research Accelerator (VERA) in 2002 [14]. It soon turned out that extraction of HfF$_5^-$ from a HfF$_2$ sample matrix provided a W-suppression > 10$^3$, but no further separation could be achieved with subsequent AMS-filters or single ion detectors [15]. The resulting detection limit was roughly $^{182}$Hf/$^{180}$Hf = 1 × 10$^{-11}$, but very susceptible to the W-content of the sputter matrix and the ion source materials [15,16]. The high mass of the isotbars and their relatively low AZ/Z complicate isobar separation by conventional means like differences in energy loss characteristics or gas-filled-magnets [17]. Despite some progress with innovative detector concepts [18], no better detection limits have yet been achieved at larger tandem facilities [19]. A novel approach at VERA making use of differ-

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enances in electron affinities (EAs) between the isobars may, however, allow us to reach the required sensitivity.

2 Isobar suppression in the ILIAMS setup

2.1 Setup and Electron Affinities

The Ion Laser InterAction Mass Spectrometry (ILIAMS) setup is the central part of a new injector at the VERA facility dedicated to element selective filtering by laser photodetachment; a recent description of the layout is given in [26]. It consists of a cesium sputter ion source followed by a 90° bending magnet and the ILIAMS radiofrequency quadrupole ion cooler, a 1 m long linear ion guide based on a 2D Paul trap, where electrostatically-slowed anions gently collide with He buffer gas and reach almost thermal energies resulting in transit times of several ms [21]. Inside the ion cooler, the ion beam is co-linearly overlapped with an intense cw- or quasi-cw laser beam. All anions with EAs smaller than the photon energy are thereby efficiently neutralized while anions with EAs larger than the photon energy remain unaffected. This novel technique works extraordinarily well and provides isobar suppression factors of 10^5 and 10^12 for ³⁶S⁻ vs ³⁵Cl⁻ and ⁵⁶MgO²⁻ vs ⁶⁰AlO²⁻, respectively [20, 22].

For Hf, optical filtering has not been implemented so far since no experimental data for the EAs of HfF₅⁻ and WF₅⁻ exist. Theoretical calculations suggest that EAs are suitable and lie in the UV, with calculated vertical detachment energies of 3.9 eV for WF₅⁻ and 8.8 eV for HfF₅⁻ [23]. The only experimental anchor point so far is the finding that the detachment cross section of WF₅⁻ is a factor of 100 higher than that of HfF₅⁻ with a 266 nm laser (photon energy 4.66 eV) [24].

2.2 Gas reaction studies

Differences in electronic structure of anions can also be exploited in anion-gas reactions at eV energies and O₂ was found particularly well suited for HfF₅⁻-WF₅⁻ separation, providing an isobar suppression of at least 10⁵ in an earlier study [25]. While the exact reaction channel remained elusive, Zhao et al. [25] argued that HfF₅⁻, being a superhalogen anion, is extraordinarily stable and, thus, highly immune to electron charge transfer reactions, collisional detachment and association or transformation of molecules at eV energies.

Similar experiments have now been conducted at ILIAMS using gas mixtures of He+O₂ and He+CCl₂F₂. The respective buffer gases were volumetrically premixed in a 12 liter gas bottle. For each buffer gas, the system was first tuned for optimum ¹⁸⁰HfF₅⁻ transmission at 0.20 mbar pressure at the buffer gas inlet and then the pressure was varied while measuring the respective ion species as ¹⁸⁰HfF₅⁻ and ¹⁸²W⁻ in a Faraday cup or an ionization chamber detector on the high-energy side of VERA (Fig. 1). Sputter targets contained HfF₂+PbF₂+Ag (1:1:1 by weight), and the ion source produced typically 50–300 nA of ¹⁸⁰HfF₅⁻ (from either material) and 100–500 pA of ¹⁸²WF₅⁻, respectively.

While ¹⁸⁰HfF₅⁻ transmissions are almost identical for pure He and He+O₂ (30:1), the amount of ¹⁸²WF₅⁻ transmitted through He+O₂ (30:1) is a factor of 10⁵ lower compared to pure He. Accounting for the total ILIAMS transmission of 35% for ¹⁸⁰HfF₅⁻ (cf. [24]), this translates into an isobar suppression of 3x10⁵.

Figure 1. Ion intensities of ¹⁸⁰HfF₅⁻ and ¹⁸²WF₅⁻ transmitted through the ILIAMS cooler as a function of buffer gas pressure for various gases. The respective ion species were measured as ¹⁸⁰HfF³⁺ and ¹⁸²W⁴⁺ in a Faraday cup or an ionization chamber detector on the high-energy side of VERA. Plotted intensities are corrected for the effective charge state yield of 20% (including accelerator transmission). Lines between symbols are to guide the eye.
mass scans of the anion beam extracted from the ILIAMS ion cooler operated with di
(100:1), the in-
(70%)
2.5 ml HF (48%
180
(10:1) is
leaking into the electrostatic de- and acceleration areas
mass was observed. Whether the fluorine atoms
, albeit with lower
, but a
with He
182
182
182
182
administration by 10:1) produce the same
. The amount of transmitted
(30:1) does not yield any transmitted W-
(30:1). This yet un-
tributed to the formation of
WF
5
irradiated W. Basic steps are:
3.) BaHfF
6
3.) Addition of 1 mg natural Hf as solution;
1.) Dissolving W in 2 ml HNO
3
(99.9%) or reference materials from earlier campaigns
15, 16. In parallel, a sample preparation procedure
has been developed to allow
3
Hf analysis from neutron-
irradiated W. Basic steps are:
1.) Dissolving W in 2 ml HNO
3
(70%)/ 2.5 ml HF (48%;
drop-by-drop; cooling);
2.) Addition of 1 mg natural Hf as solution;
3.) BaHfF
5
precipitation by 0.5 ml saturated Ba(NO
3
2
solution
27);
4.) Dissolving in HNO
3
(~35%) saturated with H
3
BO
3
27;
Figure 3. Cumulative negative ion yield of HfF$_{5}^-$ as a function of sputter time for targets filled with powders of HfF$_4$, Ag and PbF$_2$ mixed in three different weight ratios. Ions were collected as 180HfF$_{5}^-$ in a Faraday cup. Three sputter targets of each sample material were measured.

The ion exchange described in [28, 29] has been further optimized for higher Hf-yield using inductively coupled plasma mass spectrometry (ICP-MS). A sufficient decontamination factor of $>10^5$ could be reached with chemical yields of 91-100%, thus making the production of a 1–2 mg HfF$_2$-target with a W-content of $<10 \mu g/g$ starting from a 1 g W matrix feasible. The use of Suprapur® chemicals has proven necessary as otherwise remaining W traces clearly originate from chemical products and consumables. Variants of this procedure will be applied for environmental samples in future studies. All HfF$_4$ materials for chemistry tests have been mixed (1:3 by weight) with PbF$_2$ (Alfa Aesar Puratronic$^\text{TM}$, >99.997% purity) and pressed in Cu cathodes; future samples will be additionally mixed with Ag for more stable sputter rates. Single BaHfF$_6$ precipitation yields $\sim 10^4$ as decontamination factor, which is not sufficient in most cases. Furthermore, BaHfF$_6$, a sputter material suggested by [19], was found to quickly poison the ionizer and the current output from the source dropped by at least a factor of 100 within a few minutes of sputtering.

3.2 AMS detection efficiency

As for any low-level AMS measurement, the overall detection efficiency of $^{182}$Hf is a crucial parameter and highest losses generally occur in the production of negative ions in the Cs sputter ion source. Therefore, a study of the HfF$_{5}^-$ ionization yield with different admixing ratios of PbF$_2$ powder to the final sputter matrix was conducted.

Batches of sputter targets containing known amounts of typically 1–4 mg HfF$_4$ were prepared and sputtered to exhaustion while collecting the $^{180}$HfF$_{5}^-$ current in the Faraday cup right after the first bending magnet (Fig. 3). Of the three mixtures tested, the best HfF$_{5}^-$ yields are achieved with highest PbF$_2$ admixture, i.e. HfF$_4$ + Ag + PbF$_2$ 1:1:3 by weight. Within the first two hours of sputtering, 2% of the sample material was turned into HfF$_{5}^-$, peaking at finally about 6%. On the other hand, increasing the proportion of PbF$_2$ results in higher WF$_{5}^-$ formation from the target material, as demonstrated in [10]. The study here was conducted with ultrapure commercial HfF$_4$ and in first tests, no enhanced WF$_{5}^-$ content in the anion beam was observed (cf. [23]). For real environmental samples with a slightly elevated W-content, it might however be necessary to determine the optimum PbF$_2$ mixing ratio as a trade-off between high HfF$_{5}^-$ and still strong WF$_{5}^-$ suppression in the ion source. For these reasons, an ionization yield of only 2% achievable with low admixture (1:1) of PbF$_2$ is assumed for the considerations below.

The transmission of $^{180}$HfF$_{5}^-$ through the ion cooler is 35% at an injected current of 200 nA. In contrast to e.g. Cl, where the cooler transmission is limited by the total charge limit of the RFQ ion guide [20], losses of HfF$_{5}^-$ are mostly caused by the large emittance of the ion beam from the ion source. The intense F$^-$ current from the sample on the order of 50 $\mu$A blows up the size of the entire ion beam between the source and first mass-separation in the magnet. Therefore, even the mass-separated ion beam becomes too large to fit through the 3 mm entrance aperture of the ion cooler. Subsequently, this issue cannot be overcome by attenuation of the stable reference isotope beam but would require a redesign of the cooler injection optics, which is yet beyond our scope. In addition, around $\sim 30-35\%$ of the HfF$_{5}^-$ beam is lost in collisional detachment with O$_2$, leaking into the injection and extraction area of the cooler.

The tandem accelerator is operated at 2.4 MV with He as stripper gas providing an effective 3+ charge state yield of 20%. The resulting 8.8 MeV $^{182}$Hf$^{3+}$ ion beam is directed without losses into a split anode ionization chamber with a 10×10 mm$^2$ large, 100 nm thick silicon nitride entrance window. Since no W isobar separation is achieved within the ionization chamber, virtually all events fall within the wide ROI of the 3+ charge state, thus, the detector efficiency is close to 100%. Stable $^{180}$Hf$^{3+}$ is measured in the Faraday cup following the analyzing magnet.

The performance is summarized in Table 1 and results in an overall Hf detection efficiency of $>1.4\%$. Assuming that at least 30 events need to be collected in

| Table 1. Summary of Hf detection efficiency |
|---------------------------------------------|
| negative ion yield                          | $>2\%$ |
| ILIAMS cooler transm. He+O$_2$ at 200 nA     | 35%    |
| low-energy transport efficiency             | 100%   |
| accelerator transm. and 3+ charge state yield| 20%    |
| high-energy transport efficiency            | 100%   |
| ionization chamber efficiency               | 100%   |
| overall detection efficiency                | $>1.4\%$ |

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the detector for an unambiguous $^{182}\text{Hf}$ signal identification, we presently require $2.2 \times 10^4$ $^{182}\text{Hf}$ atoms in the sputter sample. In a 1 mg Hf sample, this corresponds to an implied theoretical abundance sensitivity level of $^{182}\text{Hf}/\text{Hf} = 1.8 \times 10^{-14}$ if isobaric interferences can effectively be fully suppressed.

### 3.3 Results of first AMS measurements

First AMS measurements were conducted on a set of inhouse reference materials also employed in [16] with nominal ratios of $^{182}\text{Hf}/^{180}\text{Hf} = 5.59 \times 10^{-10}$ (now labeled Vienna-Hf-10) and $^{182}\text{Hf}/^{180}\text{Hf} = 5.88 \times 10^{-11}$ (Vienna-Hf-11) and blank material from commercial HF$_3$ (Alfa Aesar). Very recent measurements suggest that both reference materials might in fact have $(2.0 \pm 0.2)$-times higher ratios and certainly require thorough remeasurement and cross-calibration in the very near future. For the following evaluation, the above nominal values were used. Hence, all measured Hf-ratios may require scaling by this factor once the proper isotopic ratios of these materials have been determined.

During the measurements, the ILIAMS cooler was operated at 0.30 mbar He+O$_2$ (30:1) buffer gas pressure. Sample spectra from the split anode ionization chamber are shown in Fig. 4. Measured $^{160}\text{Hf}^+$-currents were typically 30 – 40 nA. Since $^{182}\text{Hf}^+$ and $^{182}\text{W}^+$ cannot be distinguished in the ionization chamber, the amount of $^{182}\text{W}^+$ is monitored via separately counting $^{183}\text{W}^+$ and subsequent correction for the $^{182}\text{W}$-contribution to the m=182 signal [15]. The $^{182}\text{W}^{183}\text{W}$ seen by the detector is experimentally determined on samples contaminated with W on purpose at the 1000 µg/g level and was 2.43 ± 0.21 for the first measurement in comparison to the natural ratio of 1.85. Different masses are injected sequentially by adjusting the field of the ILIAMS bending magnet, the voltage of the insulated chamber of the injection magnet before the accelerator and the accelerator terminal voltage with switching times of ~3 s. Each run consists of four sequences for determination of the stable reference isotope currents in 5 s and in between 3 pairs of counting sequences for masses $182$ ($\sim 150$ s) and $183$ (variable, here ~150 s). The system ran automatically and unattended for three days.

Final results normalized to the Vienna-Hf-10 reference material are plotted in Fig. 5. The reproducibility for the Vienna-Hf-11 material is better than 5% and in agreement with its nominal value. After correction of the W-induced background, the average blank value is $^{182}\text{Hf}/^{180}\text{Hf} = (3.4 \pm 2.1) \times 10^{-14}$. The upper limit translates into a present detection limit of $^{182}\text{Hf}/\text{Hf} \approx 6 \times 10^{-14}$, which

![Figure 4. Detector spectra of runs on Vienna-Hf-11 reference material with a nominal ratio of $^{182}\text{Hf}/^{180}\text{Hf} = 5.88 \times 10^{-11}$ and a blank material containing no $^{182}\text{Hf}$. Red events were collected with the system tuned for mass 182 (i.e. $^{182}\text{Hf}^+$ and $^{182}\text{W}^+$), blue events for mass 183 (only $^{182}\text{W}^+$ and m/q ambiguities). The acquisition time was 455 s in all cases. There is a strong surplus of m=182-events on the reference material.](image1)

![Figure 5. AMS measurement results for samples with Vienna-Hf-10 and Vienna-Hf-11 reference materials with nominal ratios of $^{182}\text{Hf}/^{180}\text{Hf} = 5.59 \times 10^{-10}$ and $^{182}\text{Hf}/^{180}\text{Hf} = 5.88 \times 10^{-11}$, respectively, as well as blank material from commercial HF$_3$ containing no $^{182}\text{Hf}$. All results have been normalized to the Vienna-Hf-10 reference material. Filled symbols indicate that PbF$_2$ was admixed to the sample matrix by weight 1:1 to HF$_3$, open symbols indicate no addition of PbF$_2$. Each datapoint is the average of one sputter target over multiple runs.](image2)
is at least a 170-fold improvement compared to previous work [16][19]. Interestingly, no statistically significant difference in W-induced background has been observed between targets with admixture of PbF₂ and the one without. This is rather surprising considering the strong dependence of the WF⁵/HF⁵ ratio on F-availability in the sputter matrix observed in Ref. [16]. In our view, it indicates that for commercial HfF₄ a significant part of the W in the ion beam extracted from these samples does not originate from the sputter matrix itself (in agreement with findings in Ref. [16]), but further investigations are certainly necessary. Cross contamination and memory effects in the ion source have not been observed above this background so far.

4 Conclusions and Outlook

Significant progress has been achieved in AMS of ¹⁸²Hf by using reactive gases in an RFQ ion cooler and the mechanisms underlying the W-suppression have been studied. Despite an improvement in sensitivity by more than two orders of magnitude compared to previous work, estimations suggest that the detection of live nucleosynthesis signals remains still challenging and can presently only be expected for the high-¹⁸²Hf/Hf-signal scenarios. The EAs of molecular anions are promising to implement optical filtering by means of a suitable laser in the near future. This should provide the missing one to two orders of magnitude in isobar suppression required to reach the sensitivity deemed necessary for low-signal scenarios. Within the next months, the ILIAMS setup will be used to determine the ¹⁸⁶W(n,n'⁰)¹⁸²Hf cross section on samples irradiated with MeV neutrons, where ¹⁸²Hf/Hf-ratios of at least 2×10⁻¹² are expected.

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References

[1] K. Knie, G. Korschinek, T. Faestermann et al., Phys. Rev. Lett. 93, 171103 (2004).
[2] L. Fimiani, D. L. Cook, T. Faestermann et al., Phys. Rev. Lett. 116, 151104 (2016).
[3] A. Wallner, T. Faestermann, J. Feige et al., Nature Comm. 6, 5956 (2015).
[4] A. Wallner, J. Feige, N. Kinoshiita et al., Nature 532, 69–72 (2016).
[5] D. Koll, G. Korschinek, T. Faestermann et al., Phys. Rev. Lett. 123, 072701 (2019).
[6] B. P. Abbott et al. (LIGO Scientific Coll. and Virgo Coll.), Phys. Rev. Lett. 119, 161101 (2017).
[7] B. P. Abbott, R. Abbott, T. D. Abbott et al., Astrophys. J. Lett. 848, L12 (2017).
[8] J. J. Cowan, Ch. Sneden, J. E. Lawler et al., arXiv 1901.01410 (2019).
[9] C. Vockenhuber, F. Oberli, M. Bichler et al., Phys. Rev. Lett. 93, 0172501 (2004).
[10] M. Lugaro, A. Heger, D. Osnir et al., Science 345, 650–653 (2014).
[11] T. Rauscher, A. Heger, R. D. Hoffman et al., Astrophys. J. 576, 323–348 (2002).
[12] S. Goriely, H.-Th. Janka, Mon. Not. Roy. Astron. Soc. 459, 4174–4182 (2016).
[13] B. J. Fry, B. D. Fields, J. R. Ellis, Astrophys. J. 800, 71 (2015).
[14] C. Vockenhuber, I. Ahmad, R. Golser et al., Int. J. Mass Spec. 223–224, 713–732 (2003).
[15] C. Vockenhuber, M. Bichler, R. Golser et al., Nucl. Instrum. Methods B 223–224, 823–828 (2004).
[16] O. Forstner, H. Gnaser, R. Golser et al., Nucl. Instrum. Methods B 269, 3180–3182 (2011).
[17] H.-A. Synal, Int. J. Mass Spec. 349–350, 192–202 (2013).
[18] C. Vockenhuber, A Bergmaier, T. Faestermann et al., Nucl. Instrum. Methods B 259, 250–255 (2007).
[19] C. Vockenhuber, C. Feldstein, M. Paul et al., New Astron. Rev. 48, 161 – 164 (2004).
[20] M. Martschini, D. Hanstorp, J. Lachner et al., Nucl. Instrum. Methods B 456, 213 – 217 (2019).
[21] M. Martschini, J. Pitters, T. Moreau et al., Int. J. Mass Spec. 415, 9 – 17 (2017).
[22] J. Lachner, C. Marek, M. Martschini et al., Nucl. Instrum. Methods B 456, 163 – 168 (2019).
[23] H. Chen, P. Andersson, A. O. Lindahl et al., Chem. Phys. Lett. 511(4-6), 196 – 200 (2011).
[24] T. Leopold, J. Rohlén, P. Andersson et al., Int. J. Mass Spec. 359, 12 – 18 (2014).
[25] X.-L. Zhao, J. Eliades, A. E. Litherland et al., Rap. Comm. Mass Spec. 27, 2818 – 2822 (2013).
[26] J. A. Eliades, X.-L. Zhao, A. E. Litherland et al., Nucl. Instrum. Methods B 361, 294 – 299 (2015).
[27] E. Merz, Geochim. Cosmochim. Acta 26, 347 – 349 (1962).
[28] M. F. Horan, M. I. Smoliar, R. J. Walker, Geochim. Cosmochim. Acta 62(3), 545 – 554 (1998).
[29] T. Kleine, C. Münker, K. Mezger et al., Nature 418, 952–955 (2002).