Paper presented at the 9th international Conference on Accelerator Mass Spectrometry (AMS-9), 9-13 September 2002, Nagoya, Japan, submitted to the Proceedings, Nucl. Inst. Meth. Phys. Res. B.

^{182}Hf, a new isotope for AMS

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Abstract

The neutron-rich isotope ^{182}Hf with its half-life of 9±2 million years [1] was alive in the early solar system and has been used to study the early development of the Earth and the Moon through isotopic anomalies of its stable decay product ^{182}W. In addition, ^{182}Hf may also complement a few other radionuclides in the million-year half-life range to trace relatively recent stellar events with high neutron fluxes in the vicinity of the Earth. This may be accomplished by finding measurable traces of live ^{182}Hf in suitable terrestrial archives. With accelerator mass spectrometry (AMS) it should be possible to detect minute amounts of ^{182}Hf. We will show that the main interference for the detection, the stable isobar ^{182}W, can be significantly reduced by using HfF_5^- ions. The AMS detection method of ^{182}Hf and first results from Hafnium control rods of a recently retired research reactor are presented, which encourage us to search for naturally produced traces of ^{182}Hf on Earth.

1. The half-life of ^{182}Hf

^{182}Hf is a long-lived radionuclide of particular interest for the early history of the solar system. Its half-life of about 9 million years is apparently long enough to survive the time interval between production through stellar nucleosynthesis and the formation of the solar system. However, it can clearly not survive the 4.6 billion years of the solar system. Therefore it is an extinct radionuclide and can only be detected by an isotopic anomaly of its stable daughter product ^{182}W. This ^{182}Hf – ^{182}W system forms a very powerful chronometer for the timing of the formation of various early objects of the solar system [2–4]. In recent years many measurements have been performed, after the new detection method of MC-ICPMS (Multi Collector Inductively Coupled Plasma Mass Spectrometry, starting around 1995) made it possible to measure tungsten isotopes at the desired precision level [5]. However, the half-life of ^{182}Hf was measured only in connection with its discovery in neutron irradiated hafnium samples more than 40 years ago [6, 7, 1]. The accepted value of 9±2 million years has the largest uncertainty among important chronometers. Although this uncertainty does not influence relative chronometry, an improvement of the absolute time scale is desirable. We are currently in the process of performing a new half-life measurement using sample material prepared by Helmer and Reich some 40 years ago, which led to the discovery of the 30-year isomer in ^{178}Hf [8, 9].

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2. ^{182}Hf as a possible supernova signal

^{182}Hf is a typical r-process nuclide, but it can also be produced by the so-called “fast” s-process in massive stars [10]. During a supernova explosion a certain amount of this radionuclide should be injected into the surrounding interstellar medium. If such an event took place in the vicinity of the Earth within a few half-lives, a signal should be detectable in appropriate archives. The use of radionuclides with half-lives in the range of 10^5 to 10^9 years as signatures of nearby supernovae was proposed by [11]. A strong indication for such an event was found by the detection of ^{60}Fe ($t_{1/2}$ = 1.6 million years) in ferromanganese (Fe-Mn) crusts [12, 13]. Live ^{182}Hf, as well as ^{244}Pu (81 million years) [14–16], are other possible candidates and could support the results from ^{60}Fe data. The fact, that all primordial produced ^{182}Hf had already decayed, together with supernovae as the only known production source in nature, makes ^{182}Hf an ideal candidate for an indicator of a possible supernova in the vicinity of the Earth within the last 100 million years.

Based on the measured ^{60}Fe signal in Fe-Mn crust [12, 13] we can make a rough estimation of the expected ^{182}Hf signal. The solar system initial values for the ^{60}Fe/^{56}Fe isotope ratio is $4\text{x}10^{-9}$ [17] and for ^{182}Hf/^{180}Hf = $1.0\text{x}10^{-4}$ [18, 19]. The abundance of the stable reference isotopes in the solar system is $8.25\text{x}10^5$ ^{56}Fe atoms/10^6 Si and 0.0541 ^{180}Hf atoms/10^6 Si [20]. This gives ^{182}Hf/^{60}Fe ~$2\text{x}10^{-3}$, which is an upper limit for this ratio produced by a single supernova. Typical concentrations of Fe in Fe-Mn crusts are around 20%, whereas the Hf concentration is in the order of 5 ppm [21]. The measured ^{60}Fe/^{56}Fe signal is $2\text{x}10^{-15}$ for an event 3 Myr ago [12, 13]. Assuming no fractionation between ^{182}Hf and ^{60}Fe during ejection, transport to the Earth and uptake into the Fe-Mn crust, we can estimate an isotope ratio for ^{182}Hf/^{180}Hf of ~$4\text{x}10^{-13}$ from the above information. After a decay correction of 3 Myr, we obtain a ^{182}Hf/^{180}Hf ratio of ~$1\text{x}10^{-12}$. This rather optimistic estimation can be wrong by orders of magnitude because of very simplified assumptions. According to [10] the stellar production mechanisms for ^{182}Hf and ^{60}Fe are different and can therefore lead to uncorrelated isotope signatures. Hence, measured signals from several radionuclides produced in one supernova event may help to better understand production mechanism in explosive nucleosynthesis.

One advantage of ^{182}Hf compared to ^{60}Fe is the possibility to detected signals from supernova events much longer ago because of the longer half-life.

3. First AMS measurement of ^{182}Hf

The two prerequisites for AMS measurements of ^{182}Hf are high mass resolution (because of the stable neighboring isotopes) and isobar separation (because of the stable and common isobar ^{182}W). The upgraded VERA facility provides sufficient mass resolution for heavy isotopes demonstrated in ^{236}U and ^{244}Pu measurements [22, 23, 16].

However, the low energy of 12 – 20 MeV available at VERA does not allow isobar separation in the final detector system. In order to suppress ^{182}W relative to ^{182}Hf, the different negative ion formation probabilities in the ion source are used. Hafnium does not form negative atomic ions very well because of its very low electron affinity (~0 eV). We tried commercially available hafnium hydride and hafnium fluoride, for which a tungsten suppression is expected [24]. In table 1 the current of $^{180}\text{Hf}^-$ and the resulting detection limit for ^{182}Hf is shown for the individual hydrides and fluorides. A ^{182}W suppression of about 6000 can be achieved using HfF_5^- ions, which results in a detection limit of about 10^{-11} for the isotope ratio ^{182}Hf/^{180}Hf.

For the first ^{182}Hf measurement with AMS we used material from Hafnium control rods of a recently retired nuclear research reactor at the Austrian Research Center Seibersdorf/Austria. With an average neutron flux of ~2x10^{12} neutrons cm^{-2} s^{-1} and 15 years of operation, an isotopic ratio of ^{182}Hf/^{180}Hf of ~5x10^{-6} can be estimated from double neutron capture on ^{180}Hf (Fig. 1).

3.1. Sample material and chemical preparation

The reactor was shut down in July 1999. Even after a cool down period of 3 years the control rods showed high activity. A remotely controlled hydraulic device was used to cut off several pieces with a total weight of ~15 g. The dose rate at the surface was measured to be about 10 mSv/h with ^{182}Ta ($t_{1/2}$ = 114 days) being the main activity, which had been produced by neutron capture on stable ^{181}Ta during reactor operation.

The pieces were cleaned in an ultrasonic bath with a NaOH-solution and HNO_3 conc. in order to remove all remnants from storage and the cutting procedure. A sample of 1.19446 g was dissolved in 2 ml 40% HF suprapur (Merck) and diluted with 40 ml aqua destillata. Under these conditions Ta forms heptafluorotantalat-ions $[TaF_7]^{2-}$ which can be removed easily by liquid-liquid extraction with tributyl-phosphate (TBP) in n-heptane. Each step of the procedure was checked by γ-spectrometry. Two times, 1 ml of hydrofluoric acid was added to improve the extraction efficiency. The sample's initial ^{182}Ta activity of nearly 20 MBq was reduced to 387 Bq. The purified Hf solution was isotope diluted to several different isotopic ratios using commercial HfF_4 without ^{182}Hf. Finally HfF_4 was precipitated and dried. The sample material was mixed with silver powder. A few mg were pressed into Al-target holders of the 40 position MC-SNICS source of VERA [23].

Hafnium is always accompanied by Zirconium in the range of several percent, because of the nearly identical chemistry. A content of 1.7% for the control rod and 0.2% for the dilution material HfF_4 was included in the calculations.

3.2. ^{182}Hf measurement and correction for tungsten isotopes

The VERA beamline was tuned by maximizing the $^{180}HfF_5^-$ current for the injector and the $^{180}Hf^{4+}$ current for the analyzer [23]. The ^{182}Hf ions were detected by an energy and time-of-flight (TOF) measurement described in [23] (Fig. 2a).

In addition to ^{182}Hf the stable Tungsten isotopes were measured (Fig. 2b-d), to allow for an accurate subtraction of the ^{182}W contribution to the mass 182 events. During the long neutron irradiation of the sample material the natural isotopic composition of tungsten (^{182}W : ^{183}W : ^{184}W : ^{186}W = 26.3 : 14.3 : 30.6 : 28.6) changed significantly (Fig. 3).

Calculations were performed by solving the differential equations of production (neutron capture and radioactive ingrowth) and decrease (radioactive decay and burn up) of the Hafnium-Tantalum-Tungsten system (Fig. 1). The main production path for ^{182}W and ^{183}W is the decay of ^{181}Hf (42.4 days) to stable ^{181}Ta leading to ^{182}Ta and ^{183}Ta by neutron capture. Finally ^{182}Ta decays to ^{182}W while ^{183}Ta (5.1 days) decays to ^{183}W. Varying of the initial W concentration in the calculations from 0 – 10 ppm and of the Ta concentration from 0 – 100 ppm showed only a variation of 10 – 20% of the final amount of ^{182}W and ^{183}W, whereas the ^{184}W and ^{186}W amounts remain almost unchanged. From the measured ^{183}W/^{186}W~30 a initial W content of ~1 ppm can be calculated. This agrees with the analysis of Hafnium material used for the control rods, which gave a Tungsten content of <10 ppm and a Tantalum content of <100 ppm.

From the mass 182 events the ^{182}W contribution can be subtracted, which is calculated from the ^{183}W measurement and the expected ^{182}W/^{183}W ratio for each material. The corrected data show a good relative precision in a dilution series measurement (Fig. 4). For the ^{182}Hf/^{180}Hf isotopic ratio of the irradiated Hf control rod we get $(3.9\pm0.2)\times10^{-6}$, which agrees well with the estimated value above.

3.3. Overall efficiency

Investigations were performed to increase the overall efficiency. There are three limiting factors: the sputter and ionization yield for the HfF_5^- ions, the stripping yield from HfF_5^- to Hf^{4+} and the detector efficiency (measured counts in the detector relative to the current measured in the analyzing Faraday cup).

The sputter and ionization yield was measured with a target of known sample mass. The current for the whole lifetime of the target was collected and the amount of extracted $^{180}HfF_5^-$ ions was calculated. This results in a yield of ~1% for HfF_5^- ions in our source.

The stripping yield depends strongly on the stripper gas used. Using Oxygen (O_2) as stripper gas instead of the usually used Argon (Ar) the maximal stripping yield is increased by a factor of more than 2 and lies around 6%.

An attenuated beam was used to measure $^{180}Hf^{4+}$ as a current of several pico ampere in the analyzing Faraday cup and ^{174}Hf as counts in the detector. From the known ratio we can calculate the detector efficiency, which, depending on the detector setup, lies around 20%.

In sum the overall efficiency for ^{182}Hf measurements with our setup is $\sim1\times10^{-4}$.

4. Summary

With the dilution series measurement we were able to show that we can measure ^{182}Hf/^{180}Hf ratios down to 10^{-11}. However, the detection limit depends on the Tungsten content in the sample material. If we know the ^{182}W/W ratio, we can correct the results for the mass 182 fraction by measuring the other stable Tungsten isotopes. Although the desired measurement limit is not reached at the moment, a search for live ^{182}Hf from a recent nearby supernova should be attempted. In addition, the simulations and measurements done in this work help us to understand the artificial production of ^{182}Hf, which is necessary for an accurate half-life measurement.

Acknowledgment

We thank Joerg Casta from the Austrian Research Centers Seibersdorf/Austria for the supply of the Hafnium control rods of the ASTRA research reactor, and Martin Suter from the PSI/ETH AMS facility in Zurich for useful suggestions concerning the use of different stripper gasses. We acknowledge the effort of Irshad Ahmad from Argonne National Laboratory to locate the ^{182}Hf sample for the planned half-life measurement.

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Tables

Table 1 Different negative ions investigated for their ^{182}W suppression

Ion species	Sample Material	typical $^{180}Hf^{4+}$ current [nA]*)	typical ^{182}W count rate [s^{-1}]	^{182}W suppression**)	$^{182}Hf/^{180}Hf$ detection limit
Hf^-	HfH_2+Ag, 1:1	0.004	141	~0.02	~10^{-4}
HfH^-	HfH_2+Ag, 1:1	0.06	454	0.1	3x10^{-5}
HfH_2^-	HfH_2+Ag, 1:1	0.33	76	3	8x10^{-7}
HfH_3^-	HfH_2+Ag, 1:1	0.35	55	4	5x10^{-7}
HfH_4^-	HfH_2+Ag, 1:1	0.07	11	4	5x10^{-7}
HfH_5^-	HfH_2+Ag, 1:1	0.31	2	100	2x10^{-8}
Hf^-	HfF_4+Ag, 1:1	0.02	1800	0.0002	3x10^{-4}
HfF_2^-	HfF_4+Ag, 1:1	0.03	1	5	1x10^{-8}
HfF_3^-	HfF_4+Ag, 1:1	35	2	250	2x10^{-10}
HfF_5^-	HfF_4+Ag, 1:1	80	0.2	6000	1x10^{-11}

*) The transmission ($^{180}Hf^{4+}/^{180}HfH_x^-$) for the hydrides was around 3% because Ar was used as stripper gas, whereas for the fluorides a transmission of 6% was achieved with O_2 as stripper gas. The fluorides were measured with the ion source optimized for high output.

**) The ^{182}W suppression is the relative formation probability of the various negative Hafnium ions (measured as $^{180}Hf^{4+}$ current) divided by the relative formation probability of the various negative Tungsten ions (measured as ^{182}W count rate in the detector).

Figures

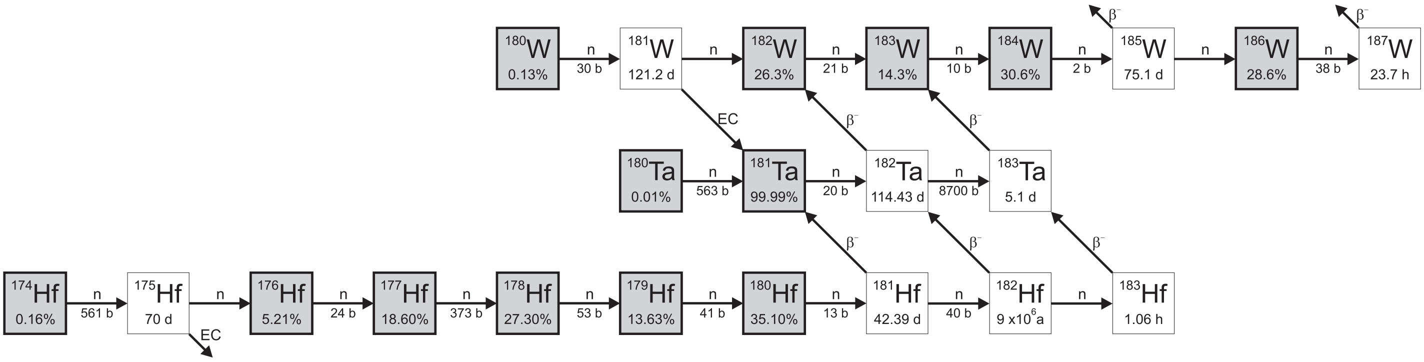

Figure 1: Nuclear chart of the Hafnium, Tantalum and Tungsten isotopes. The natural occurring stable isotopes are shown in the shaded squares with their relative abundance, whereas the radioactive isotopes are shown in open squares with their half-life. The production path under neutron irradiation (cross section for fast neutron capture) and the decay of the radioactive isotopes are shown as arrows. The data are taken from [25].

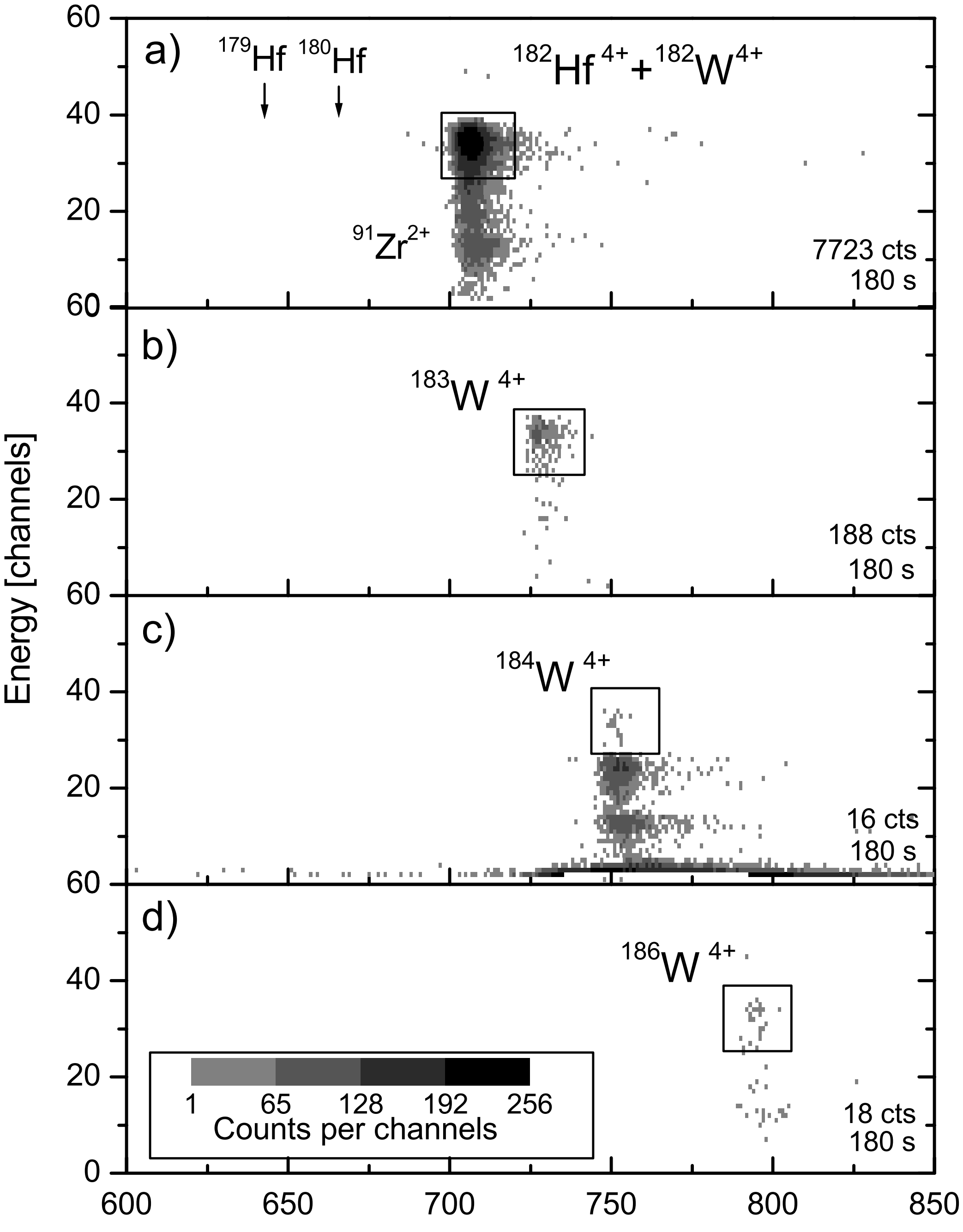

Figure 2: Energy-vs.-TOF spectra of a Hf sample from a reactor control rod diluted 1:100 (180 seconds measurement time, respectively):

a) tuned for mass 182 (^{182}Hf + ^{182}W). No background ions from other Hafnium isotopes reach the detector. The peak with lower energy is ^{91}Zr^{2+}, which can not be suppressed by the ion-optical filters.

b) tuned for ^{183}W.

c) tuned for ^{184}W.

d) tuned for ^{186}W.

The current of ^{180}Hf^{4+} during this measurement was ~1 nA.

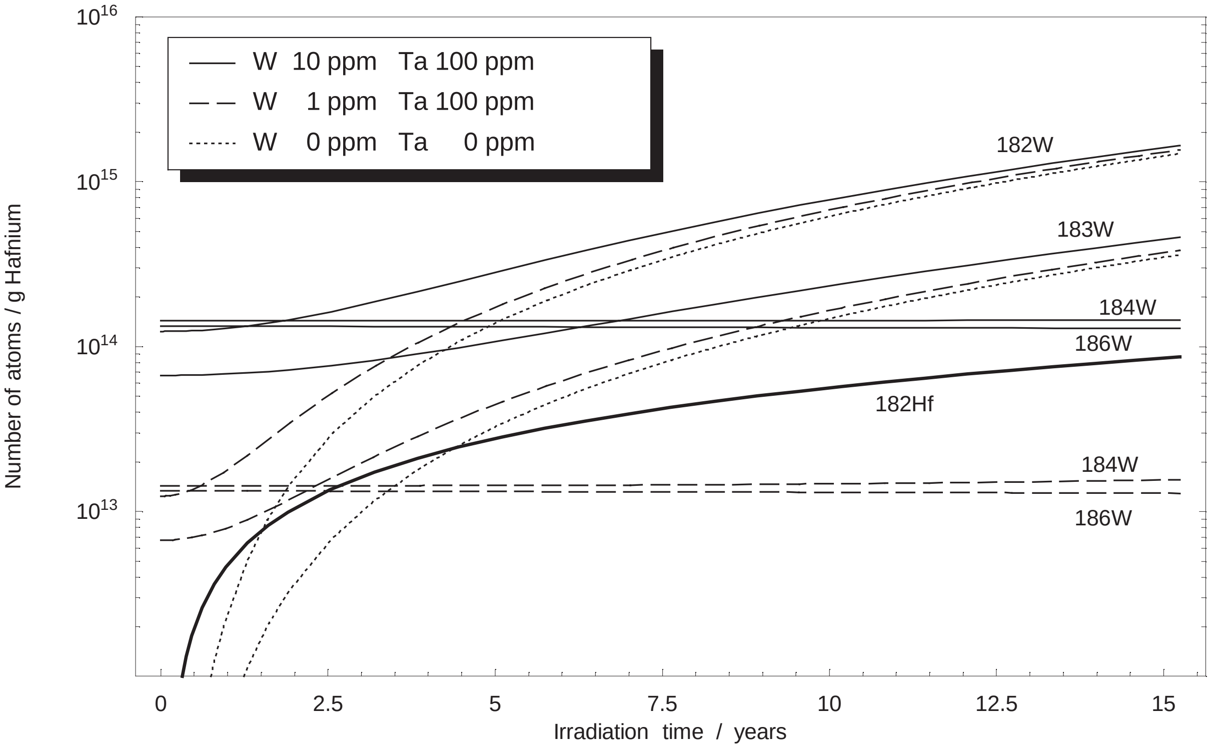

Figure 3: Simulation of the change of ^{182}Hf and the stable Tungsten isotopes under a neutron flux of 2x10^{12} neutrons cm^{-2} s^{-1} for 1g Hafnium. The influence of the final amount of the tungsten isotopes are shown for different initial Tungsten and Tantalum concentrations.

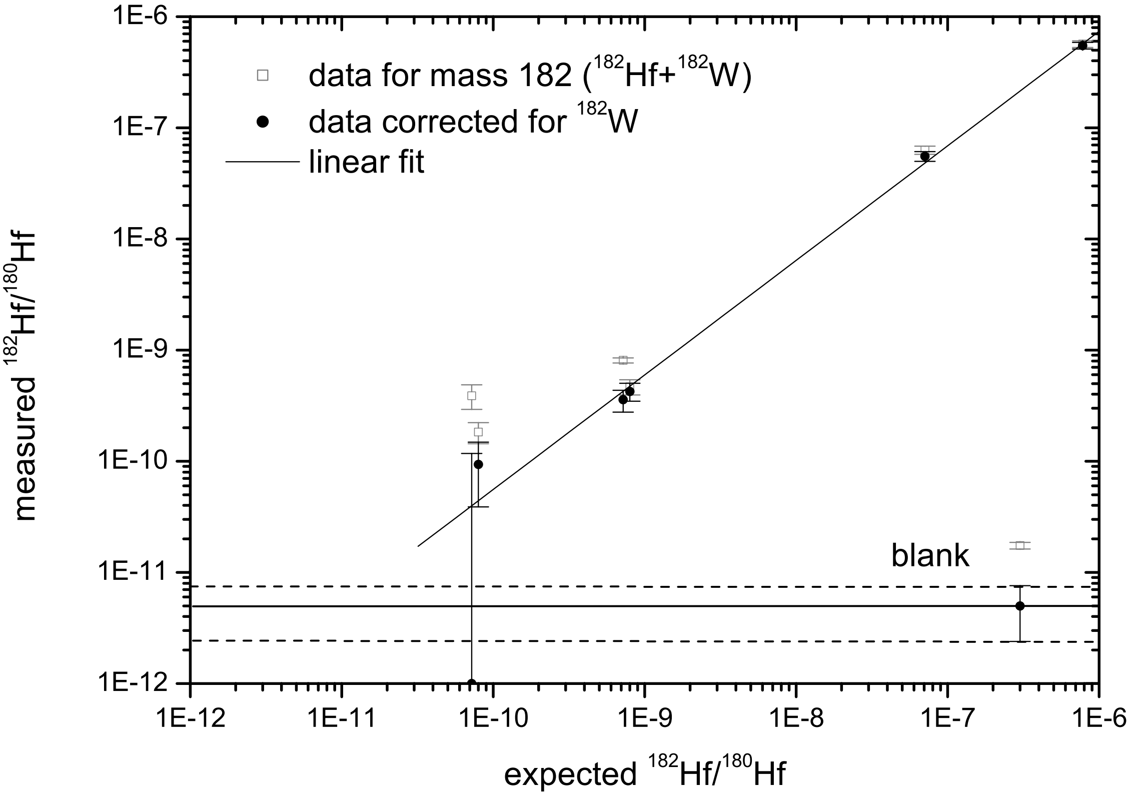

Figure 4: Result of the dilution series measurement (several samples with a measuring time of ~2200 s each). The measured isotopic ratio is plotted against the expected ratio from the calculated dilution. The open circles are the mass 182 fractions containing both ^{182}Hf and ^{182}W. The black squares are the ratios corrected for ^{182}W, which show a good linearity. The ^{182}W correction for the lowest ratio induces a large error because of the limited counting statistics of the ^{183}W measurement.