



Developing a detection method of environmental ^{244}Pu

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Abstract

The long-lived radionuclide ^{244}Pu ($t_{1/2} = 80.8 \pm 1.0$ Ma) is a candidate for the detection as a live remnant of close-lying and relatively recent supernovae in geological records on the earth. We will present the development of an AMS method for measuring ^{244}Pu at the low abundance levels which are expected for natural ^{244}Pu . For artificial samples prepared from chemically pure reagents a sensitivity of more than 3×10^{-6} counts in detector per atom in sputter target was achieved. For true sediment samples the detector background induced by chemical impurities and possible cross contamination from high level standards were identified as the present limitations.

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1. Introduction

The possibility to detect a radioisotopic signal of a recent, nearby supernova in terrestrial geological archives [1] and the detection of live ^{60}Fe in deep sea sediments [2] has spawned a search for

other potentially supernova-related isotopes [3–6]. Considering the half-life of ^{244}Pu (80.8 ± 1.0 Ma) we can hope for enough accumulation in the interstellar matter (ISM) so that ISM swept up by a supernova shock front will yield a detectable signal. On the other hand the half-life is short enough that there is no primordial background. Additionally, there is a contribution to ^{244}Pu abundance on the earth from atomic bomb tests.

We have started to develop an AMS method to measure ^{244}Pu from these sources at the Vienna Environmental Research Accelerator (VERA).

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2. AMS technique for Pu measurement

Recently, the VERA system was upgraded for AMS measurements of heavy isotopes. Details of these modifications are described in Ref. [5].

For measurements of plutonium isotopes, we inject PuO^- and select the 5+ charge state which is the lowest our analyzer magnet can bend at a terminal voltage of 3 MV [5]. The beam line is tuned using ^{238}U pilot beams. We scale to the plutonium isotopes by changing the voltage of the injector magnet chamber, the accelerator terminal, and the high-energy electrostatic analyzer (ESA). Since Pu is present only in trace amounts in the sputter targets, there are no beam currents suited to trace the source output. Slow sequencing is done between the Pu isotopes by modified versions of existing computer scripts [7]. A few 100 s are measured on each isotope and ~ 30 s are spent on switching. For particle identification we use a time-of-flight (TOF) spectrometer combined with an ionization chamber [8].

3. Dilution series

The raw material for the dilution series was a high purity ^{242}Pu tracer solution (US Department of Energy, Environmental Measurements Laboratory), and a solution of ^{244}Pu (Argonne National Laboratory) which contains a small fraction of ^{242}Pu also. The α -activity of the ^{242}Pu solution was determined independently [9] to be 2.83 mBq/ μl , which corresponds to 4.80×10^{10} ^{242}Pu atoms per μl . A 30 μl aliquot of this solution was diluted with 2 M nitric acid to 10 ml in order to have a ^{242}Pu stock of appropriate concentration. The concen-

tration of the ^{244}Pu material is 0.33 ng/ml or 8.14×10^{11} ^{244}Pu atoms per ml. A stock of 5 ml was prepared from 500 μl of this standard by dilution with 2 M nitric acid. The target materials (Table 1) were prepared by co-precipitation with $\text{Fe}(\text{OH})_3$, followed by combustion in air and Fe powder was added as binder.

Three alternating measurements (150 s each) on ^{242}Pu and ^{244}Pu were performed on each target before proceeding to the next, which allowed one to check for the time development of the target performance. During the first turn of the target wheel each target showed a steep increase of the count rate and this turn is therefore not included in the mean value. Within each of the following turns the count rate still increased with time (see Fig. 1). As ^{242}Pu and ^{244}Pu were not measured simultaneously this increase of target performance requires a trend correction of the isotopic ratio of $^{244}\text{Pu}/^{242}\text{Pu}$.

As can be seen in Fig. 2, there is a linear dependency between the nominal and the measured isotopic ratios. This indicates that a measurement relative to a standard material would yield uncertainties of about 5%. Given the nominal plutonium concentrations of the dilution material the measured isotope ratios are only $\sim 2/3$ of the expected values.

To find the source of this deviation, the material “Pu300” was prepared anew from the stock solutions. During a new beam time, it was measured in comparison to one unused “Pu300” target left over from the first preparation. The isotopic ratios obtained in the second beam time for the two preparations agree within counting statistics, proving the reproducibility of the precipitation procedure. However, the results for the same

Table 1
The materials of the dilution series and their ^{242}Pu and ^{244}Pu content

Sputter material label	Nominal ^{242}Pu (atoms)	Nominal ^{244}Pu (atoms)	Nominal $^{244}\text{Pu}/^{242}\text{Pu}$ ratio	Nominal ratio to “Pu300”
Pu300	4.35×10^{10}	2.44×10^{10}	0.561	1.000
Pu100	4.33×10^{10}	8.14×10^9	0.188	0.335
Pu30	4.32×10^{10}	2.44×10^9	0.0565	0.101
Pu0	4.32×10^{10}	0	0	0.000

The ^{244}Pu spike solution gives a small contribution to the amount of ^{242}Pu .

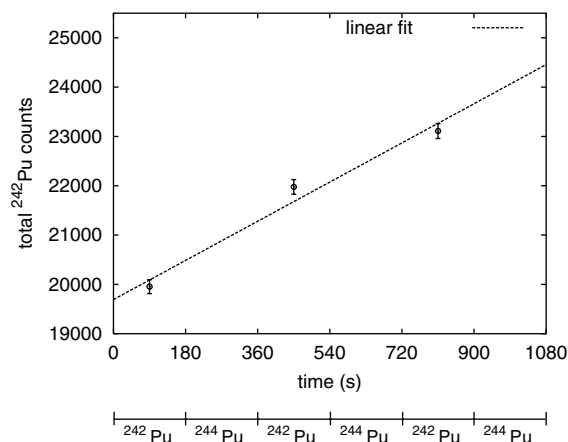


Fig. 1. Development of the ^{242}Pu count rate within each period of sputtering, summed for all materials containing ^{242}Pu . The first data point is the sum for the first time intervals from 0 to 180 s, the second point is the sum from 360 to 540 s, and the third point is the sum from 720 to 900 s. ^{244}Pu was measured in the time intervals in between. The target performance shows an increase during the sputter intervals.

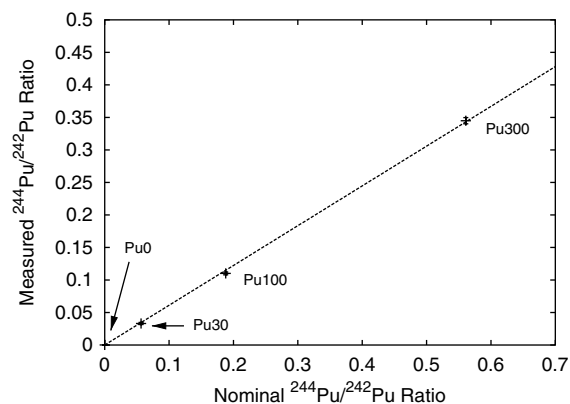


Fig. 2. The dilution series. The measured isotope ratios are compared to the nominal values.

material in the two separate beam times do not agree. The $^{244}\text{Pu}/^{242}\text{Pu}$ ratios measured for “Pu300” in the first and in the second beam time are 0.3840 ± 0.0051 and 0.3449 ± 0.0048 , respectively. The deviation is a measure of the reproducibility of the AMS measurement, emphasizing the need for a reliable reference standard which would allow to remove the uncertainty resulting from different machine setup conditions.

4. Reproduction of a known isotopic ratio

To find out whether the discrepancy of the nominal and measured isotopic ratios lies in the AMS measurement or in the chemical target preparation, we tried to reproduce an independently measured ratio. For the ^{244}Pu spike solution from ANL a value of $^{242}\text{Pu}/^{244}\text{Pu} = 1.12 \times 10^{-2}$ was determined by α -spectrometry. For sputter targets without addition of the ^{242}Pu spike, the $^{242}\text{Pu}/^{244}\text{Pu}$ ratio measured with AMS was 1.12×10^{-2} with a statistical uncertainty of 0.09×10^{-2} . The agreement between the measured and nominal values let us conclude that the measured values represent the true isotopic ratios of the sputter targets, and the problem in the dilution series is either in the initial spike solutions or in the chemical sample preparation.

The overall detection efficiency determines the amount of sediment which must be processed for a measurement of ^{244}Pu from ISM fallout. For our type of ion source (MC-SNICS) a conservative estimate of the PuO^- ionization yield of 0.3% is given in [10]. For the uranium pilot beam, we observe a charge state yield of 3% for the 5+ state, and it should be about the same for plutonium. With a measured efficiency of 20% for the TOF/Bragg detector system, this leads to an expected total efficiency of 1.8×10^{-5} . From the counts obtained and the number of atoms in the sputter targets it is possible to obtain an experimental lower limit to the efficiency. For the measured ten cathodes of the dilution series containing a total of $\sim 4.3 \times 10^{10}$ atoms ^{242}Pu about $\sim 6.9 \times 10^4$ were detected. As the measurement times for ^{244}Pu and ^{242}Pu were equal, $\sim 1.4 \times 10^5$ counts of ^{242}Pu could have been measured during the total time. (In a ^{244}Pu measurement on environmental samples, the major part of the measurement time would be spent on ^{244}Pu and not on the ^{242}Pu spike.) This gives an efficiency of $\sim 3 \times 10^{-6}$ in this measurement. Since the material in the cathodes was not sputtered completely this is only a lower limit. It compares favorably with the expected theoretical efficiency of 1.8×10^{-5} . Considering the increased stripping yield for heavy ions on O_2 [8] another gain of about 2 can be expected in efficiency. The reduction of the isotope switching time is a goal for future development.

5. Sediment samples

A first test with sediment samples has been performed. Despite the fact that there was not enough sample material available to expect any ^{244}Pu counts, the problems associated with preparation from natural sediments (as opposed to precipitation from high purity solutions) could be studied.

The two ^{242}Pu spike targets (“Pu0”) in this beam time showed a total of five counts in the ^{244}Pu region (Fig. 3(a)). As the content of ^{244}Pu is not specified for the ^{242}Pu spike material, this may reflect the true isotopic content of the spike. Another possible explanation is cross contamination in the preparation or in the ion source originating from the “Pu300” targets used as internal standards.

The spectra of the three sediment samples measured also show events in the ^{244}Pu window. For one (“SedI-Bi3”) a spectrum is shown in Fig. 3(b). This sample contains plutonium extracted from a sea sediment in the Mediterranean at 700 m depth, from a layer 20–40 mm below the surface. No counts are expected, so also for those targets cross contamination is the most likely explanation. Therefore, for the third beam time, we prepared reference targets containing much less plutonium atoms per target (a factor of $\sim 10^2$ less). No count of ^{244}Pu was observed on the ^{242}Pu spike targets in a combined total of 2 h of measurement.

Until the origin of the background (3×10^{-4} cts/s) is unambiguously identified, it imposes a detection limit. Therefore, assuming a sputter rate of 1 mg/h for $\text{Fe}_2\text{O}_3 + \text{Fe}$, at least 1 true count per mg target material is required. Considering the total detection efficiency this corresponds to $\sim 3 \times 10^5$ atoms ^{244}Pu per mg $\text{Fe}_2\text{O}_3 + \text{Fe}$.

Whereas detector pulse pile-up can be ruled out at the observed low background count rates for the previous samples, an aliquot of the Japanese deep ocean sediment sample “92SAD01” [11] (the major part was already measured at the Koffler 14UD Pelletron tandem accelerator, Weizmann Institute, Rehovot, Israel, see [3]), showed $\sim 10^{-2}$ cts/s in the ^{244}Pu region (Fig. 3(c)). Remarkable is a background of 50 cts/s with TOF and energy corre-

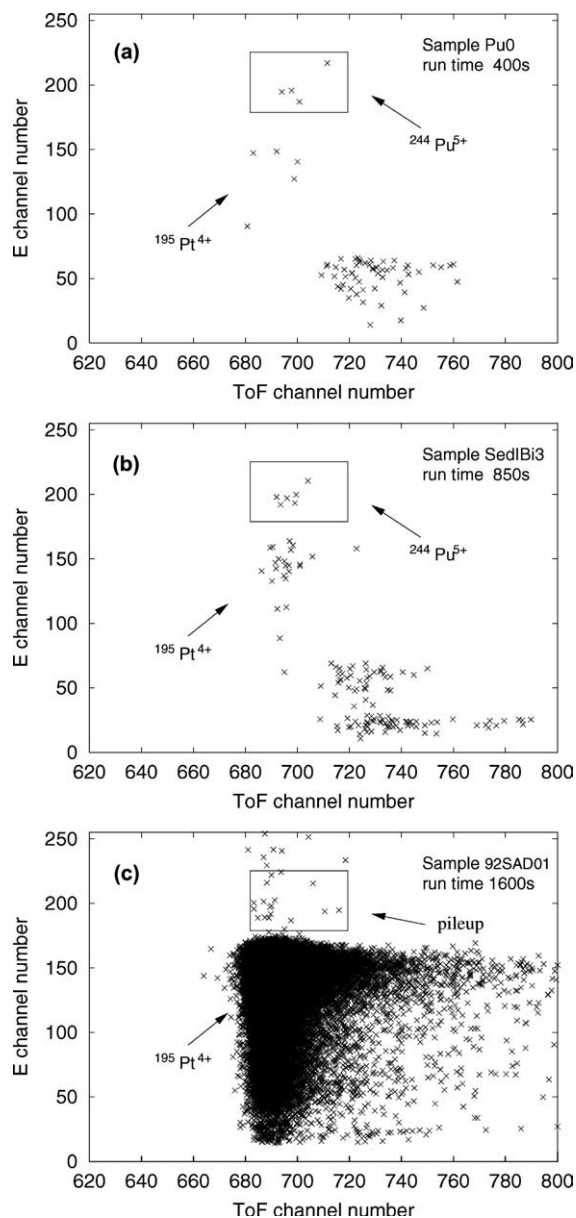


Fig. 3. Spectra of the sediment sample beam time that show the problem of contamination (a) and (b) and detector pulse-pile-up (c). Only runs containing counts in the ^{244}Pu -region were included in these spectra.

sponding to $^{195}\text{Pt}^{4+}$. Detector pulse pile-up from these events is the reason for the background in the ^{244}Pu window. Injector mass spectra revealed that Pt is abundant in these targets. The plutonium of

this sample was electroplated on Pt electrodes in the course of the chemical preparation.

6. An attempt to measure the global nuclear fallout

We recently obtained a Pu sample from Lake Michigan sediments. The sample corresponds to ~ 1 g of sediment and contained 0.377 dpm $^{239+240}\text{Pu}$ ($\sim 7 \times 10^9$ atoms). Taking the abundances measured in the first large scale thermonuclear test explosion [12], up to about 10^7 atoms of ^{244}Pu may be found in the sample. This is clearly within our current detection limit. In contrast to the “92SAD01” sample the Pu Lake Michigan samples were electroplated onto stainless steel disks from an oxalic acid/HCl solution [13,14]. Therefore we hoped that the Pt background would be low enough for a measurement of ^{244}Pu . Unfortunately, also for the sediment sample a high count rate for $^{195}\text{Pt}^{4+}$ was observed preventing a measurement for the time being. At this point, the origin of the platinum is not clear. It may originate from the sediment itself. The platinum anode used in the electroplating procedure is not expected to contribute to the material deposited on the cathode. Further investigations as to the cause of the $^{195}\text{Pt}^{5+}$ background are needed.

7. Conclusions

We were able to reproduce a dilution series of $^{244}\text{Pu}/^{242}\text{Pu}$ isotope ratios. In the course of this measurement an efficiency of at least $\sim 3 \times 10^{-6}$ was achieved. We could show that absolute isotope ratios can be measured by reproducing an independently measured isotopic ratio. For a measurement of ^{244}Pu in the environment, several grams of raw sediment must be processed. However, the expected low count rates ($\sim 1/\text{h}$) make control of cross contamination essential. Electronic pile-up rejection should be sufficient to suppress the background induced by Pt in the sputter targets [15].

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