ACCELERATOR MASS SPECTROMETRY FOR LONG-LIVED HEAVY ION ^{236}U AT CIAE*

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Abstract

^{236}U is a long-lived radioactive isotope with a half-life of 2.342(3) $\times 10^7$ a, which produced principally by thermal neutron capture on ^{235}U. ^{236}U is potentially applied in geological research and nuclear safeguards. Accelerator mass spectrometry (AMS) is presently the most sensitive technique for the measurement of ^{236}U. A method for AMS measurement of long-lived heavy ion ^{236}U was developed at CIAE with the set up the AMS dedicated injector and the newly proposed $^{208}Pb^{16}O_2^-$ molecular ions for the simulation of ^{236}U ion transport. A sensitivity of lower than 10^{-10} has been achieved for isotopic ratio ^{236}U/^{238}U in present work.

INTRODUCTION

^{236}U is a long-lived radioactive isotope with a half-life of 2.342(3) $\times 10^7$ a, mainly produced by the thermal neutron induced ^{235}U(n,γ) ^{236}U reaction. The isotopic ratio of ^{236}U/^{238}U in nature is about 10^{-14}, depending strongly on the integral thermal neutron flux received by the material. This makes ^{236}U usable as an integrating neutron monitor over the last 100 million years [1], and potentially applicable in geological research [2]. The isotopic ratio of ^{236}U/^{238}U could also be used as a "fingerprint" for indicating the presence of neutron-irradiated uranium usually originated from nuclear activities [3].

Recently, several efforts have been made to measure ^{236}U in environmental samples using techniques based on mass spectrometry such as high-resolution inductively coupled plasma spectrometry (HR-ICPMS), thermal ionization mass spectrometry (TIMS) and accelerator mass spectrometry (AMS). However, detection limits with conventional mass spectroscopy for ^{236}U/^{238}U are ~10^{-10}, leading to errors larger than 50% for uranium ore samples [4, 5]. Therefore the measurement of natural ^{236}U is difficult or even impossible without AMS. AMS offers significant advantages over conventional mass spectroscopic methods in high sensitivity, smaller sample size, relatively free from isomer and molecular-ion interferences, and shorter measurement time. AMS measurement of actinides was presented firstly by IsoTrace facility X.L. Zhao *et al.* of Toronto group [6], in which the ^{236}U/^{238}U is lower than 5×10^{-10} in a natural uranium ore from Cigar Lake deposit in Canada. The natural ^{236}U/^{238}U has also been measured by several other groups, such as: VERA [7], ANU [8], LLNL [9], ANSTO [10], Munich [11], ETH [12] and Israel Weizmann Institute [13].

In this paper, a method for AMS measurement of long-lived heavy ion ^{236}U developed on the HI-13 Accelerator at China Institute of Atomic Energy (CIAE) is reported. The unique features include establishing of the AMS dedicated injector and the newly proposed $^{208}Pb^{16}O_2^-$ molecular ions for the simulation of ^{236}U ion transport.

THE AMS DEDICATED INJECTOR

There is a general rule in AMS that a high mass resolution analyzer is needed to separate the neighboring interference and a high energy resolution analyzer is required to clip the tail of the high energy. The original injector setup at CIAE [14] with the mass resolution of $M/\Delta M$ ~220, could not satisfy the requirement for AMS measurement of heavy isotopes (e.g., ^{236}U, ^{182}Hf, ^{151}Sm). Therefore, a high resolution dedicated injector for AMS was developed, as shown in Fig. 1. The new injector adopts achromatic technique, which consists of a 90º electrostatic analyzer (ESA) and a 112º double-focusing analyzing magnet (MA). A triplet electric quadruple lens and a single electric quadruple lens were mounted at the entrance and the exit of the ESA beam line, respectively, for ions focusing. This spherical 90º ESA with 750 mm radius, has maximum electric field strength of 4 kV/cm and provides both horizontal and vertical focusing. The 112º double-focusing MA with a bending radius of 800 mm, has a maximum magnetic field of 1.3 T.

The energy resolution of the electrostatic deflector is $\frac{E}{\Delta E}=\frac{D\rho}{S_2-MS_1}$. The Mass resolution of the analyzing magnet is $\frac{M}{\Delta M}=\frac{D\rho}{S_2-MS_1}$, where $D\rho$ is coefficient of chromatic dispersion (3000 for ESA, 3360 for MA), M (-1 for ESA, -1.14 for MA) is the coefficient of magnification, S_2 and S_1 are the slits of object and image, respectively. The new injector system was tested by using the sample material of HfO_2. When the ESA's slits (Slit 1) and MA's object slits (Slit 2) are fully open, the image point slit (Slit 3) of MA is 1 mm, the mass resolution of the injector system is about 430. If the Slit 2 and Slit 3 are respectively set at ±2.5 mm and ±1 mm, the

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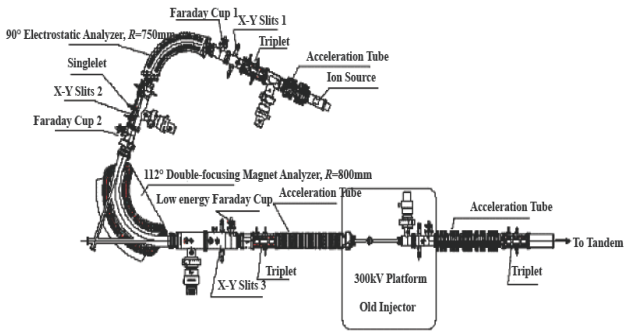

Figure 1: The Layout out the improved Injector System.

mass resolution can be increased to 630, which leads to a decrease of beam current only by 5%, compared with the beam current of slits completely opened up. If the Slit 2 and Slit3 are respectively set at ±1 and ±1 mm, the mass resolution can be increased to ~1100, but the beam transmission efficiency will decrease by 40%. When the Silt 1 is set at ±5 mm, the $^{238}U^{11+}$ count rate is 10 times lower than that when the Slit 1 is fully open. The overall transmission efficiency is very low in our AMS system based on our experimental experience, especially for heavy ions, due to the long beam line of the AMS system. During the ^{236}U AMS measurement, the slit 1, slit 2 and slit 3 were set at ±5, ±2.5 and ±1 mm, respectively. The mass resolution is about 400.

The negative ions are pre-accelerated to the maximum injection energy E_{inj} = 120 keV. During the heavy ion ^{236}U measurement, we found that the pre-accelerated voltage must be higher than 90 kV to clip the tails from ^{235}U and ^{238}U. Because the interactions of the ions of interest with residual gas in the accelerator tubes may change the charge state and movement direction, and lead to the unwanted transmission of interfering ions with either the wrong mass or the wrong energy. This is a small effect, but the $^{236}U/^{238}U$ is also very small and the effect ultimately becomes the main background in the detection. If the pre-accelerated voltage is lower than 90 kV, the transmission efficiency, and in turn the measurement sensitivity will be very low. During the ^{236}U AMS measurement, 100 kV pre-accelerated voltage is chosen and the vacuum is better than 10^{-6} Pa.

AMS MEASUREMENT

Production and Analysis of Negative Ions

In order to optimize the source performance for ^{236}U measurement, experiments on extracting multiform negative ^{238}U-containing molecular ions (including UO_X^-, UC_x^-, UF_x^-) and different conductor powders (Nb, Al and Ag) were carried out. Considering the overall efficiency (including the yield and transmission of the negative ions of interest), UO^- was found to be the most suitable form of ions to be extracted from the target. As an proximate measure of ionization efficiency, a sample consisting of U_3O_8 Nb=1:1 by weight was measured. The ionization efficiency, calculated from the integrated uranium oxide beam, was at least 0.1%.

At the settings for ions with a mass of -252 (aiming at $^{236}U^{16}O^-$) to be injected into the accelerator, all kinds of ions with mass number of -252, such as $^{235}U^{17}O^-$, $^{235}U^{16}OH^-$, $^{238}U^{14}N^-$, $^{238}U^{12}CH_2^-$, etc, will be accompanied. Of these ions, $^{235}U^{17}O^-$ is unavoidable. For heavy ion ^{236}U AMS measurement, the isobar problem is not expected to occur, the problem is how to identify the interest ^{236}U ions from isotope background ^{238}U and ^{235}U.

Acceleration and Transmission

The measurement of ^{236}U was performed with a 13-MV tandem accelerator (HI-13) mass spectrometer at CIAE [14]. On the high-energy side, the beam was analyzed by a 90° post-analyzing magnet (maximal 200 MeV·amu) and a 17° AMS ESA. For $^{236}U^{11+}$ ions, the maximum usable terminal voltage was 7.800 MV, which corresponds to a final energy of 93.2 MeV, with a charge state fraction of about 14%. In the terminal of the HI-13 tandem accelerator, a 7 μg cm^{-2} thick carbon foil was used as a stripper. At the high-energy side, $^{236}U^{11+}$ ions were analyzed.

At the beginning of our work, the ^{236}U beam transport was simulated with the sample material of UO_2 and extracting ions of $^{238}U^{16}O^-$. Due to the small beam current (20-100 nA) and the significant scattering induced by the carbon foil and Coulomb explosion, the beam current in high-energy side was too small to be tuned for beam transport simulation. In order to tune the accelerator, the transportation simulation was divided into two steps by using $^{238}UO_2$ and $^{208}Pb^{16}O_2$ pilot beams, respectively. Firstly, in order to optimize the accelerator parameters, a $^{238}U^{11+}$ beam (7.773 MV) was used to simulate the beam transport from lower energy system to the image of the post-analyzing magnet. Secondly, a $^{208}Pb^{10+}$ (8.034 MV) ion beam (~300 nA) was used to simulate the $^{236}U^{11+}$ transport from the image of post-analyzing magnet to the AMS detection system, while keeping all the parameters already optimized in the first step unchanged. The experiment showed that the two-step simulation method for the optimization of ^{236}U beam transportation makes the adjustment much easier.

The overall particle transmission between the image of the injection magnet (mass 254) and the detection system ($^{238}U^{11+}$) is about 8×10^{-4}.

Detector System

The energy difference between the background ^{238}U and ^{235}U ions and the interested ion ^{236}U is only 0.8% and 0.4%, respectively. Only the time of flight (TOF) detector has sufficient resolution to distinguish the isotopes ^{238}U and ^{235}U from ^{236}U. The TOF system consists of a time "start" detector micro-channel plate (MCP) and a time "stop" detector gold-silicon surface barrier detector (SBD), separated by a flight path of 1.8 m. A 7 μg cm^{-2} carbon foil was employed to the "start" detector to produce the secondary electrons, which were then reflected by an electrostatic mirror, collected and multiplied by MCP. In order to minimize the scattering when the 93 MeV heavy ions $^{236}U^{11+}$ pass through the

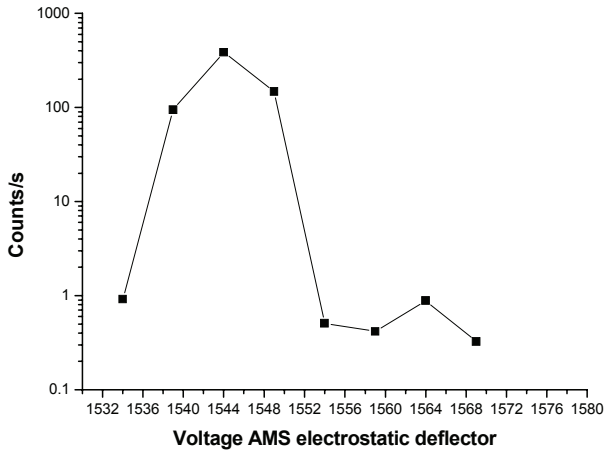

Figure 2: The scan spectrum of the AMS electrostatic deflector.

"start" detector, the carbon foil supported by a copper mesh was designed with a transparency of 95%. The SBD detector is also used as energy detector for mass/charge discrimination, since the nuclide of interest (^{236}U) has an energy gain different from that of interfering isotopes (isobars) in the acceleration process. The detector efficiency was measured to be about 50%.

In order to get a good time resolution of the TOF, the threshold and constant fraction delay were set carefully to optimize the CFD584 (constant fraction discrimination). The length of the 50Ω-coaxial cable in CFD584 for constant-fraction shaping delay was calculated according to the formula $L = \frac{t_{d(Ext)}}{\lambda} \approx \frac{1.1t_r - 0.7}{\lambda}$ ($\lambda = 5\ ns$, delay time of 1m 50 Ω-coaxial cable; t_r is the rise time). The bias voltage for the "stop" detector SBD was set carefully too. When the bias voltage is 300 V, the time resolution (FWHM) is about 790 ps for 93 MeV $^{236}U^{11+}$, and the energy resolution is 4.7%. When it is increased to 600 V, the time and energy resolutions are ~670 ps and 4.2%, respectively, as shown in Fig. 5(a). As can be seen from Table1, this resolution is sufficient to separate ^{236}U from ^{238}U of the same magnetic rigidity, but still needs further improvement for the separation of ^{235}U.

Table 1: Flight Times over a 1.8 m Flight Path for 11+ Uranium Ions of different Masses with the same Magnetic Rigidity

Ion	Energy (MeV)	Flight time, *T* (ns)	Δ*T* (ns)
$^{235}U^{11+}$	93.167	205.34	0.88
$^{236}U^{11+}$	93.198	206.22	
$^{238}U^{11+}$	93.261	207.97	1.75

Calibration and Cross-Checks

The 17°AMS ESA with 360 mm radius, and the maximal voltage (±200 kV) result in an energy/charge state ratio of E/q = 10.7 MeV for $^{236}U^{11+}$. The vacuum is about 10^{-5} Pa to reduce charge changing and scattering of the ions inside the ESA. At the beginning of ^{236}U measurement, the AMS ESA was used to scan the spectrum from ^{238}U to ^{235}U to monitor the beam transport and locate the would-be ^{236}U candidate events. A scan spectrum of the AMS electrostatic deflector is depicted in Fig. 2. The isotopes were counted directly with SBD. The image slit of the AMS electrostatic deflector was set to 4 mm×7mm for clipping the tails of $^{235}U^{11+}$ and $^{238}U^{11+}$ ions. An energy resolution ($\Delta E/E$) of better than 0.4% was achieved. A dilute ^{236}U standard (10^{-8}) was then used to validate the above calibration, as shown in Fig. 3(a).

RESULTS

Fig. 3 shows two-dimensional spectra of TOF vs energy and TOF spectra for a natural uranium ore sample and a ^{236}U dilution standard sample. Taking the advantages of the high terminal voltage of HI-13 accelerator and the relatively small energy straggling of the flying ions, a TOF resolution (FWHM) of about 670 ps has been obtained. However, the rise time of the "stop" SBD detector (bias voltage at 300 V is about 20 ns) and the quality and the thickness of the MCP foils are still the limiting factors for further improvement of TOP resolution. The total transmission of uranium ions at 93.2 MeV from the "start" MCP to the SBD was measured to be ~45%, resulting from the angular spread of the heavy-ion beam after the TOF carbon foils and the shadow of the wire grids.

Table 2 shows the suppression factors for ^{235}U and ^{238}U and transmission efficiencies of ^{236}U in various AMS components. The new AMS dedicated Injector has a very high suppression factor when the slit 1, slit 2 and slit 3 are set at ±5, ±2.5 and ±1 mm (about 10^8 for both ^{238}U and^{235}U). The total suppression factors for ^{238}U and ^{235}U is about 10^{14} and 10^{10}, respectively. ^{235}U is hard to be separated from ^{236}U, due to the small differences in energy and time of flight.

Table 2: The Rejection Power for neighboring Isotopes ^{235}U, ^{238}U and Transmission Efficiency of ^{236}U in the various AMS Components

Components	^{238}U rejection	^{235}U rejection	^{236}U transmission efficiency
Injector system	~10^8	~10^8	~0.9
Accelerator			~0.3
Post-analyzing magnet			~0.8
Electrostatic deflector	~10^3	~10^1	~0.8
TOF dectector	~10^3	~10^1	~0.4
Total	~10^{14}	~10^{10}	~8×10^{-4} (Q=11+)

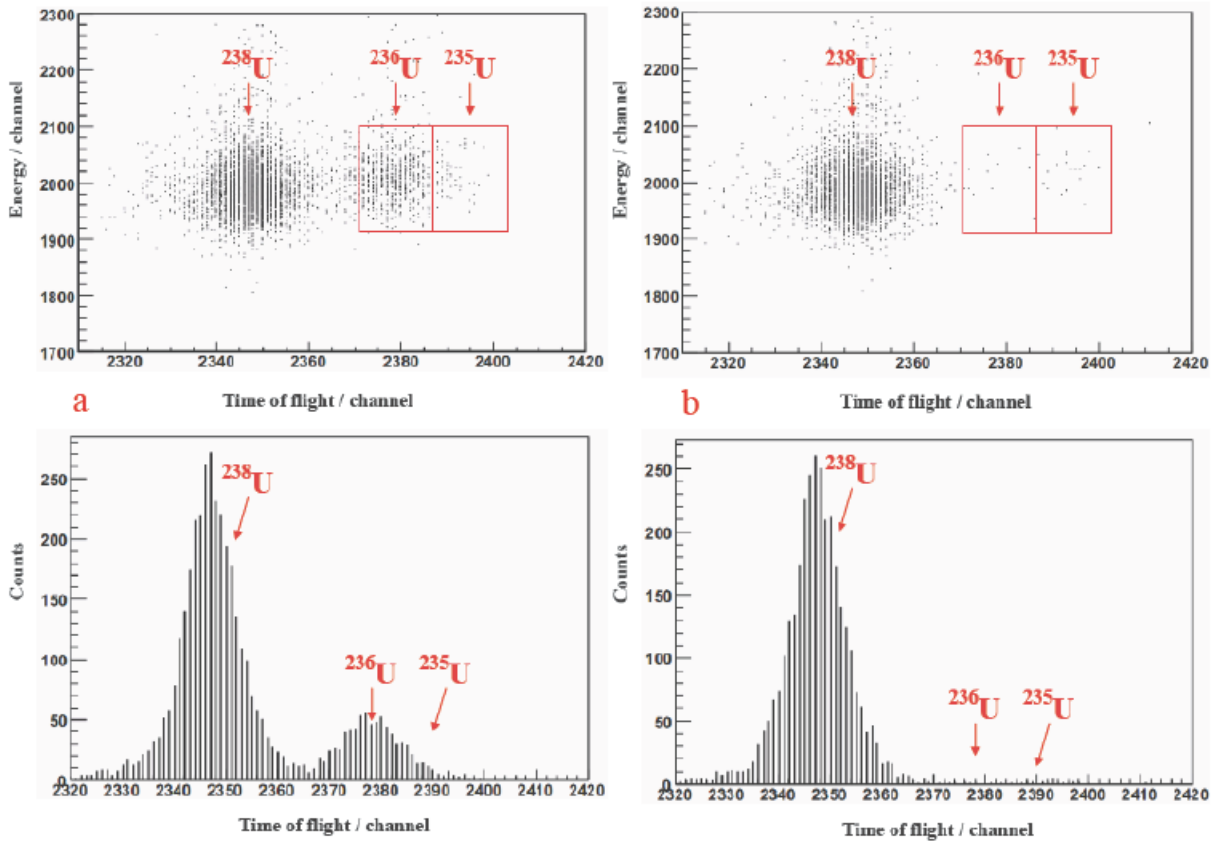

Figure 3: Example of a full-width figure showing the distribution of problems commonly encountered during paper processing. This figure is labeled with a multi-line caption which has to be justified, rather than centred.

Table 2 shows that the overall particle transmission between the image of the injection magnet and the detection system is about 8×10^{-4}, lower than those of most other AMS facilities. The transmission efficiency is especially low inside the accelerator which is about 30%, mainly due to the small diameter (8 mm) and long gas tube (1 m) of the gas stripper tube that is not suitable for the beam optics design. Besides, the carbon foil stripper used in our measurement system would increase the yield for high charge-states (high energy) ions, and deteriorate the beam quality (larger divergence and wider energy distribution) due to Coulomb explosion in the foil, especially for heavy ion $^{236}U^{11+}$.

Table 3: Results of $^{236}U/^{238}U$ ratios for Uranium Ore Sample

Sample	$^{236}U:^{238}U$ ratio
Sample 1[a]	$(2.710\pm0.008)\times10^{-5}$
Sample 2[b]	$(4.6\pm0.4)\times10^{-8}$
Sample 3	$(4.8\pm0.7)\times10^{-10}$
Sample 4	$(5.9\pm0.8)\times10^{-10}$

[a] measured with thermal ionisation mass spectrometry, and used for normalization. [b] Sample 2 is diluted from Sample 1, and used for normalization.

The results for $^{236}U/^{238}U$ ratio are shown in Table 3. The $^{236}U/^{238}U$ of Sample 1 is $(2.710\pm0.008)\times10^{-5}$, measured with Thermal Ionization Mass Spectrometry (TIMS). Sample 2 was quantitatively diluted from Sample 1, and used for normalization. Sample 3 and Sample 4 were purchased by CIAE in 1960s. The $^{236}U/^{238}U$ for sample 3 and sample 4 is $(4.8\pm0.7)\times10^{-10}$ and $(5.9\pm0.8)\times10^{-10}$, respectively. The main contribution to the uncertainties is the poor counting statistics due to the small number of ^{236}U atoms recorded in the detector. The sensitivity is lower than 10^{-10} for $^{236}U/^{238}U$ in present work.

SUMMARY

A method for AMS measurement of long-lived heavy ion ^{236}U has been developed at CIAE. Its unique features include the establishing of the AMS dedicated injector and $^{208}Pb^{16}O_2^-$ molecular ions for simulation of ^{236}U transportation. A sensitivity of lower than 10^{-10} for $^{236}U/^{238}U$ has been achieved in present work.

There is still room for further improvement in the AMS measurement of ^{236}U on our AMS system. Firstly, a new TOF system is being considered with two MCPs, one energy detector, and an ultra-thin diamond-like carbon foil [15] (DLC foils) as the entry window. The new TOF system may have a resolution of ~500 ps, sufficient to identify the isotope ^{235}U for ^{236}U AMS measurement. Secondly, a new stripper made of a thinner carbon foil

(such as diamond-like carbon foil) is to be installed in our HI-13 tandem accelerator to increase the transmission efficiency for ^{236}U measurement, so that we can set the AMS dedicated injector at ±1 mm state to increase the mass resolution (~ 1000) for ^{236}U AMS measurement.

The method can also be applied to other long-lived actinide isotopes, such as ^{210}Pb, ^{237}Np, ^{239}Pu, ^{240}Pu, ^{242}Pu and ^{244}Pu.

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