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A new, ohmic-heating based thermal ionization cavity source for mass spectrometry

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ABSTRACT

We present a new, ohmic-heating based, thermal ionization cavity source for mass spectrometry. We employ independent control of ionization and evaporation to keep sample in the evaporator while increasing the temperature of the ionizer. The 'cold end' phenomenon is eliminated by using optimized blade-shaped connection electrode. We simulated the processes of ionization and transition in the ion source using SIMION program based on Monte Carlo method and obtained spatial and kinetic energy distribution data for the atoms and ions at the outlet of the ionizer. We demonstrate considerable improvements in the extraction and transmission efficiency of the ion optics system. The total efficiencies achieved for uranium were 0.5–2% and the estimated ionization efficiencies - 3–7%. For plutonium, these values were 4–9% and 20–60%, respectively.

1. Introduction

Precise measurements of isotope ratios in trace level actinide samples are becoming increasingly important in many fields, such as fingerprinting of nuclear material [1], trace element analysis in environmental and biological samples [2,3] or forensic examination of swipe samples [4,5]. These are challenging applications: accurate isotope ratio measurements might be required for samples containing less than 1 ng of uranium or 1 pg of plutonium. Many improvements in the sensitivity of mass spectrometry methods have been introduced: Efurd et al. [6] developed a surface ionization–diffusion-type ionization source with a rhenium filament plated with platinum, capable of detecting 10^5 atoms of neptunium. Dirk Schaumlöffel's system [7], based on nano-volume flow injection (FI) and inductively coupled plasma double-focusing sector field mass spectrometry (ICP-SFMS), had the absolute detection limits of 9.1×10^{-17} g (~230,000 ^{238}U atoms) and 1.5×10^{-17} g (~38 000 ^{242}Pu atoms). The new Thermo Scientific NEPTUNE Plus with 'Jet Interface' option offers unparalleled MC-ICP-MS sensitivity, with analyte utilization of about 4% reported for uranium [8].

In the early 1970s, Beyer et al. [9] and Johnson et al. [10] found that the efficiency of hot cavity system was much higher than the value obtained using Saha-Langmuir equation in their isotope separation studies. Since then, Thermal Ionization Cavity (TIC) has been widely used as the ion source in large scale on-line isotope separation systems [11–13] and the mechanisms of TIC ionization were extensively studied [14–18]. Cesario et al. [19] used the TIC as the ion source for mass spectrometry in early 1980s. A TIC ion source consisting of a sample rod and a rhenium tube was developed, and better ion yields (0.02–0.143% per atom) for 40–300 ng of uranium were obtained. Duan et al. [20,21] designed and assembled a TIC source with a quadrupole mass spectrometer, achieving ion source efficiencies of ~8% (U) and ~8.3% (Pu). Wayne et al. [22,23] adapted the Duan's TIC source to couple with a TOF (time of flight) mass analyzer, obtaining the efficiency of 1–3% (Th). Riciputi et al. [24] used High Efficiency Cavity Source (HECS), interfaced to a Finnigan MAT 262 Mass Spectrometer, and achieved average ionization efficiency of 5% for uranium and 7% for plutonium. Bürger et al. [25,26] assembled a HECS on the sample wheel of a ThermoFisher 'Triton' multi-collector TIMS, to be employed in trace analyses, but the total efficiency (~0.02% for U and ~1% for Pu) was not as high as expected.

Due to the simplicity of electron bombardment, all the TIC ion sources mentioned above used the heating method. While using this method, both Wayne [23] and Duan [21] found multiply charged ions; these ions should not be produced by surface ionization – they might have appeared as a result of electron bombardment or some other factors. In this article, we introduce a new TIC ion source with direct ohmic heating to achieve low background

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Table 1
Arrangement of five ion collectors.

Channel	Location of collector	Type of collector	Movablility
H_2	After magnetic sector	Faraday	Yes
H_1	After magnetic sector	SEM	Yes
A	After M–E double focus	Faraday or SEM	No
L_1	After magnetic sector	SEM	Yes
L_2	After magnetic sector	Faraday	Yes

values. The ionization efficiencies, background and the effect of drift voltage are evaluated and discussed.

2. Equipment and experiments

2.1. Magnetic sector mass spectrometer

The mass spectrometer used in our experiments has a magnetic sector similar to MAT-261 (deflection radius 23 mm), with mass resolution of around 500 (in the mass range of U, Pu). Five configurable ion collectors are installed (Table 1 shows the arrangement of ion collectors). The instrument's background counting rate at the central channel (A) is about 0.02–0.1 cps; we use a low noise SEM (ETP AF150) and a special ion-electron transfer and deflection unit. The abundance sensitivity of the mass spectrometer is about 2×10^{-7} (test at $m/z = 238 \pm 1$). The source slit's size is $4\,\text{mm} \times 0.2\,\text{mm}$, and the slit of ion collector is 0.6 mm wide.

A new sample wheel was designed and manufactured using copper covered with TiN, and special parts for heat dissipation and a high current interface were added. 13 TIC ion sources can be installed on the sample wheel. Fig. 1 shows the new sample wheel with a TIC ion source fitted.

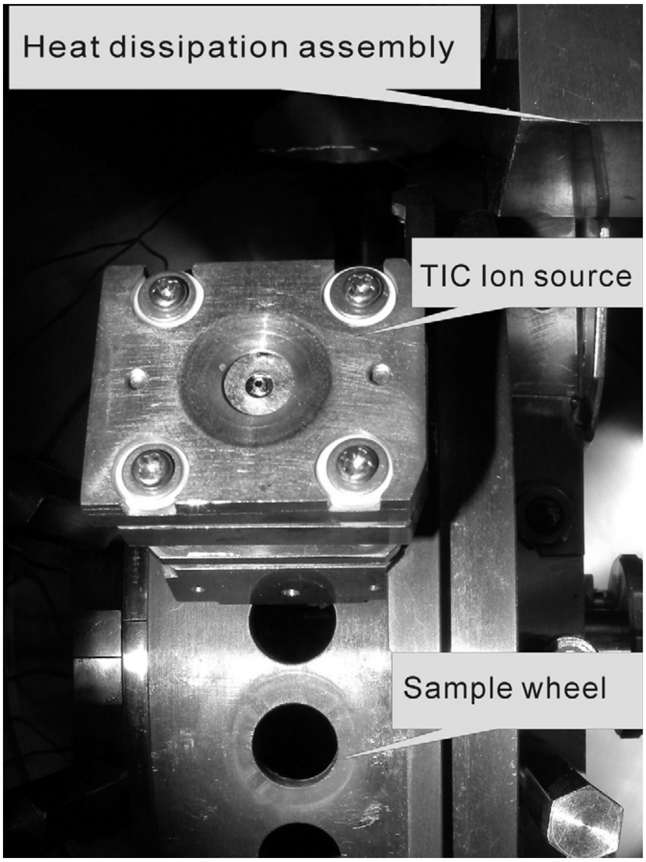

Fig. 1. Sample wheel and heat dissipation assembly with a TIC ion source.

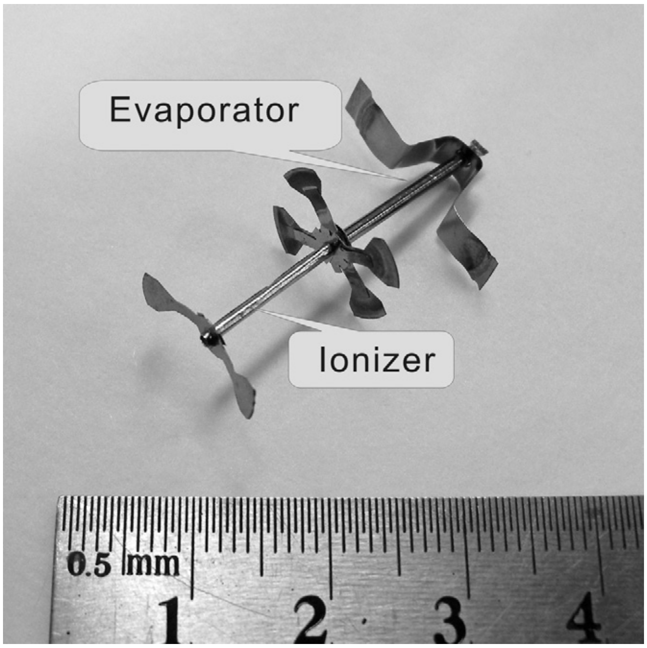

Fig. 2. Ionizer and evaporator with the blade-shaped connection electrodes.

2.2. TIC ion source

The main parts of TIC ion source are an ionizer and evaporator. We chose zone-refined rhenium and tantalum foil to enhance the ionization efficiency and to reduce the ion source background. The rhenium foil forms a tube with outer diameter ~1 mm, inner diameter ~0.5 mm and the length of 12.5 mm. Tantalum foil is shaped into a tube with outer diameter ~1.2 mm and inner diameter ~1.0 mm. The ionizer (rhenium tube) is inserted into the evaporator (tantalum tube) to avoid the atom loss. The bottom of evaporator is sealed with a piece of graphite. Graphite does not sinter with tantalum at the working temperature; the bottom of the evaporator can be opened easily for sample changing.

We designed blade-shaped connection electrodes to maintain evenly distributed high temperature in the ionizer and avoid the formation of 'cold end' and 'hot point' regions. The lower ionization probability and the higher combination probability at the 'cold end' inside the ionizer might reduce the efficiency substantially. While using ohmic heating method, the faster evaporation of rhenium at the 'hot point' can bring it into a positive feedback (fewer cross-sections at the 'hot point' lead to higher resistance, causing temperature increase and even faster evaporation). This phenomenon could considerably shorten the working life of an ion source. Fig. 2 shows our ionizer and evaporator with the blade-shaped connection electrodes.

We used multi-layer heat shields to enhance the temperature and block off the spray of evaporated material which might affect the vacuum levels and insulation in the system.

2.3. Sample loading

The samples used in our experiments were aliquots of natural uranium or other elements dissolved in nitric acid.

In the past, various sample loading methods were developed to increase the efficiency of ribbon type ion source [6,27,28]. We chose a traditional sample loading method to be used in this study [29]. To minimize the effect of impurities, we preheated the newly designed TIC ion source to its working temperature, in vacuum, for at least 30 min. For U sample loading, the sample was placed on a

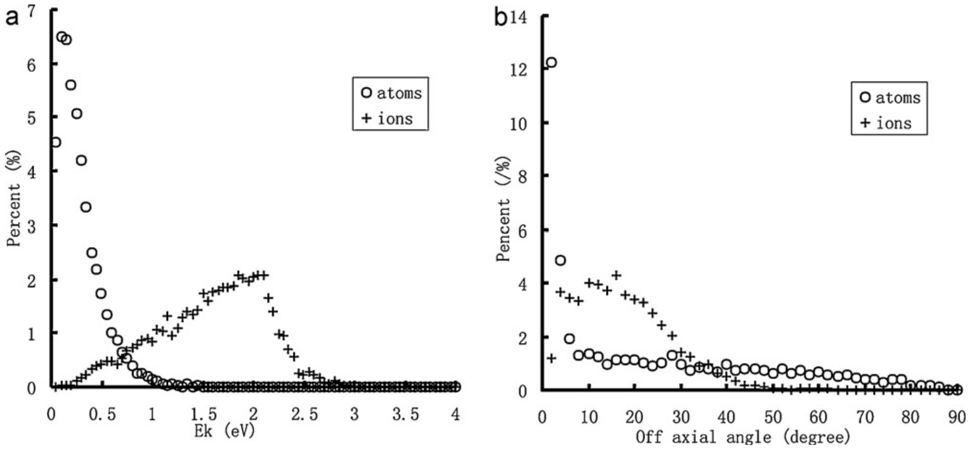

Fig. 3. Statistical graphs for atoms and ions at the outlet of the ionizer. (a) Kinetic energy; (b) off axial angles. Notes: the ion source in simulation has inner radius of 2 mm and length of 20 mm. Ionization probability of one emission is preset as 0.5%. The voltage between the ends of the ionizer is 2 V. Atoms are generated at the bottom randomly. Total atoms (circles) + ions (crosses) in graphs **a(b)** = 100%.

Ta filament pre-baked in vacuum. After drying at 0.5 A, the current of the filament was slowly increased to 1.8 A over approximately 1 min, then further increased to a dull red glow and held for 5–10 s. The filament was cut off the support and put in the evaporator. At the end of this process, the sample was located at the bottom of the evaporator. For other samples tested, similar procedure was carried out, with the temperature adjusted according to their differing chemical properties.

2.4. Simulation of ionization in the ion source

The processes of ionization were simulated using SIMION software to obtain the kinetic/spatial distribution of ions.

In a simplified tube model, the initial velocities of atoms obey the Maxwell distribution and the launch angles (off the normal direction at the starting point of the surface) obey cosine distribution. Atoms are ‘ionized’ with a given probability calculated according to Saha-Langmuir equation, using a given temperature. The ‘ions’ drifting in the ionizer are accelerated by the longitudinal electric field (caused by ohmic heating) and reflected off the wall. The atoms which are not ‘ionized’ fly straight until they reach another point on the wall. Collisions between atoms/ions in the ion source are omitted. The velocity and off-axis angle of each ‘ion’ and atom at the outlet of the ionizer are recorded for statistical analysis.

The statistical graphs shown in Fig. 3 were obtained after a large number of flights in SIMION simulation. For atoms, the kinetic energy is maintained at thermal value, and the off-axial angles are evenly distributed within a large angle range, except for the small angle values. For ions (without extracting electrical field), the kinetic energy increased depending on the voltage between the ends of the ionizer, and the off-axial angles group between 0° and 45°. The ionization multiplication (total ionization efficiency/one emission ionization probability in simulation) is strongly related to the number of atom emissions in the ion source.

2.5. Simulation of ion optics and ion transmission

Based on the simulation of original ion optical system of MAT-261 [30], the TIC ion source simulated in Section 2.4 was assembled virtually in front of the ion optical system. Fig. 4 shows the horizontal cross-section plane of the TIC ion source, the trajectories and the nearby electrodes with the accelerating and focal voltage on.

Some electrodes in the original ion optical system were changed, and the voltage parameters were optimized using the simulation data. Fig. 5 shows the ion beam cross-section in front of the source slit in the simulation (left) and the source slit after several experiments (right). With a good match between the ion optics in the simulation and in the experiment, the transmission efficiency of the ion optic system can be estimated roughly with the aid of simulation [31].

2.6. Control of the ion source

In the ohmic heating method, a current about 40 A is sufficient for ionization, and 20 A is enough for evaporation. The structure of the TIC ion source makes it possible to control actinides’ ionization and evaporation independently. The temperature of ionizer is monitored by the ion current of $^{187}Re^{+}$. 2–3 V signal in Faraday channel (the preamplifier with high value resistance of $1 \times 10^{11}\ \Omega$) means that the temperature of the ionizer should be more than 2300 K. Considering possible evaporation of the rhenium, the ionization current should be gradually reduced to control the temperature.

3. Results and discussions

3.1. The temperature

With a good connection between the ionizer and the connecting electrodes, the working temperature differences (measured by pyrophotometer) between the middle and the end of the ionizer are no more than 100 °C. While using ohmic heated ion source, it is very important to ensure even temperature along the ionizer. As

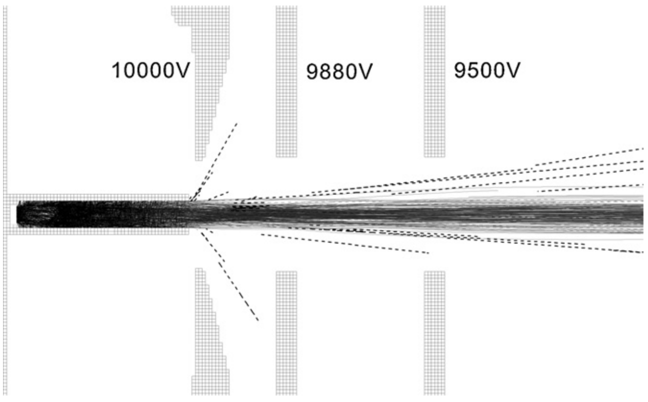

Fig. 4. The horizontal cross-section of the TIC ion source, the trajectories of atoms (dashed lines), ions and the nearby electrodes in the simulation.

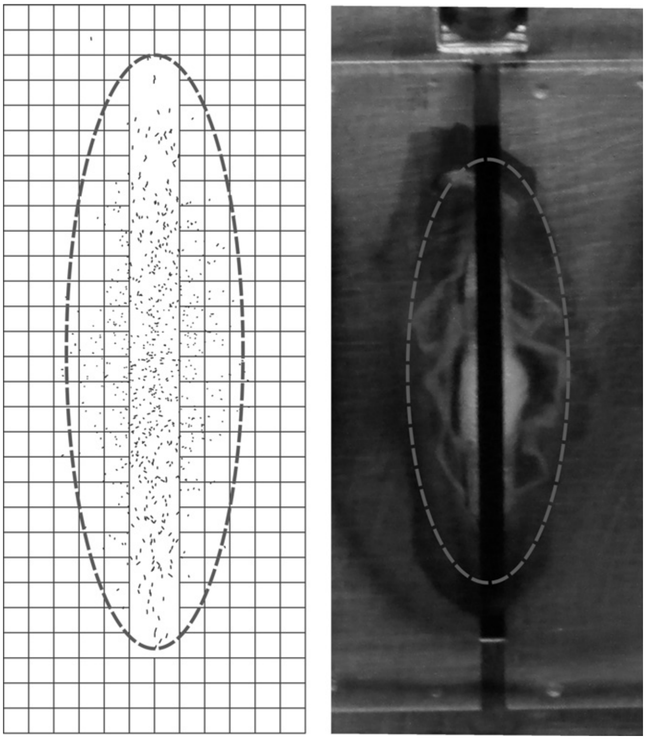

Fig. 5. The ion beam cross-section in front of the source slit in the simulation (left) and the source slit after several experiments (right). Ellipses delineate the edges of the ion beams.

we mentioned in Section 2.2, a ‘hot point’ in the ionizer reduces the working life of the ion source considerably. In real life, maintaining strictly even temperature is impractical. Although a well designed ion source used with the ohmic heating method can last for several tests, the lack of durability is obvious in comparison with the method of electron bombardment [21].

3.2. Total efficiency and ionization efficiency

Total efficiencies for several elements, including U and Pu, are listed in Table 2. The estimated ionization efficiencies of the new TIC ion source are also listed, with the transmission efficiency evaluated in our experiments.

The efficiencies measured for a particular element varied because the data were collected during instrument improvement period. Other factors might have contributed to the differences in the ionization or transmission efficiencies, such as the difference in the structure and location of the ion source, low accuracy of ion optics parameter changes in manual operations and differences between the SIMION model and the actual system.

The ionization efficiencies are comparable to the results reported in the literature [19–23]. It means that the multiplication at high temperatures takes effect in the ohmic heated tube. It is worth noting that the independent control of ionization and evaporation reduces the possible loss of sample before the ionizer reaches the necessary high temperature. It is similar to the adsorption of carbon in other TIC ion sources [20–26].

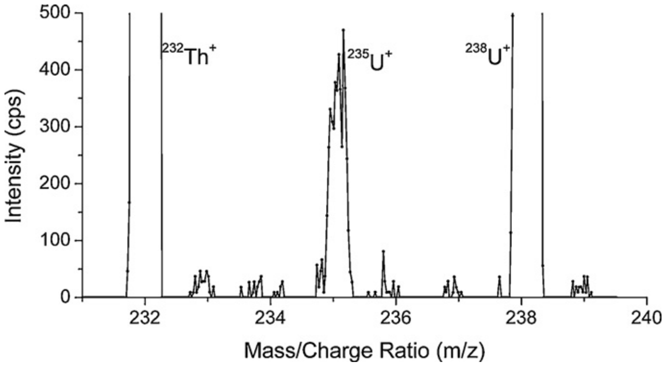

Fig. 6. An abridged blank spectrum (m/z from 232 to 239) of a new TIC ion source scanned at channel A (with ion counting efficiency ~80%) of the mass spectrometer before the end of baking. The intensity for ^{232}Th$^+$ is ~1.1×10^5 cps and the intensity of ^{238}U$^+$ around 4.3×10^4 cps.

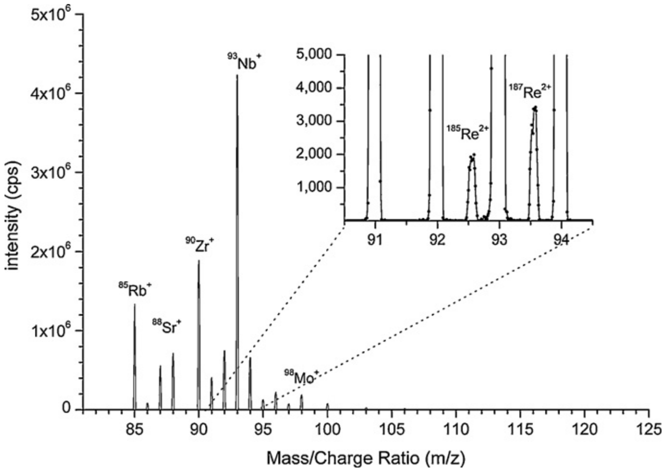

Fig. 7. Mass spectrum of m/z from 82 to 125 and the detailed part for masses from 90.5 to 94.5 with the intensity of ^{187}Re$^+$ ion current of 1.2×10^8 cps.

3.3. The background

Because our TIC ion source is still at the stage of development, a strict cleaning and purification procedure has not been established yet. Fig. 6 shows a part of blank spectrum (m/z from 232 to 239) scanned before the end of preheating. The signals at $m/z = 233$, 234, 236, 237, 239 (about 20–50 cps) might come from the metallic oxides or a combination of atoms. The Th and U peaks come mainly from the rhenium impurities and laboratory environment.

A large range of mass spectra was scanned during the test with multi-elements standard (140-130-321/325) loaded. Fig. 7 shows the m/z range from 82 to 125 with the intensity of ^{187}Re$^+$ ~1.2×10^8 cps. The two peaks at $m/z = 92.5$ and 93.5 are ^{185}Re^{2+} and ^{187}Re^{2+}. The ratio of Re^{2+}/Re$^+$ is around 10^{-5}, several orders

Table 2
Total efficiencies for some elements obtained with the newly designed TIC ion source.

Element/sample size	Method of sample loading	Total efficiency (%)	Ionization efficiency (%)
Eu/10ng	On filament and put into cavity	5–10	30–40
Pu/0.1–30 pg	On filament and put into cavity	4–9	20–60
Er/10 pg	On filament and put into cavity	2–4	20–40
U/50–12 ng	On filament and put into cavity	0.5–2	3–7

Note: the total efficiency = (ions detected)/(atoms loaded); the ionization efficiency = (total efficiency)/(transmission efficiency evaluated during each test); the transmission efficiencies vary in the range of 10–30% in different tests.

lower than the ratio of W^{2+}/W^{+} obtained with the method of electron bombardment [20]. These results are difficult to explain – a temperature of more than 8000 K is needed to get a Re^{2+}/Re^{+} in the range of 10^{-5} in a rhenium tube when the process is evaluated by Saha-Langmuir equation for surface ionization.

A time consuming step of ion source 'baking' is needed if the ion source is to be reused. Even though the residual count rate can be restored and subtracted from the results for the subsequent tests, it is better to load the same sample type at a higher concentration or to change the target element to avoid a possible memory effect.

3.4. The effect of ohmic heating

In comparison with the electron bombardment method, the ohmic heating method is more prone to a drift voltage along the ionizer, which might change the delicate equilibrium of the atoms and ions in the ionizer and affect ionization efficiency.

To observe the effect of the drift field along the ionizer, a current direction test was carried out. First, we optimized the parameters of ion optics with the heating current in normal direction and recorded $^{187}Re^{+}$ intensity. Next, the parameters of ion optics were optimized with reversed connections at the same current and $^{187}Re^{+}$ intensity recorded, and, finally, we switched the connections again and assured that the $^{187}Re^{+}$ intensity returned to the original range. The ratio ($^{187}Re^{+}$ intensity with normal direction/$^{187}Re^{+}$ intensity with reversed direction) was about 2.6 at the temperature of around 1650 °C and about 13 at 1950 °C. These results demonstrate that the drift field can improve or reduce the extraction of ions at high temperatures.

4. Conclusions

We developed a new ohmic-heated TIC ion source, coupled to a magnetic sector mass spectrometer, for trace element analysis. Our implementation of the system, employing independent control of ionization and evaporation, achieved high total efficiencies (4–9% for Pu, 0.5–2% for U).

Using the method of ohmic heating, a simple blank spectrum was obtained. In a simple test, we proved that the drift field can improve the extraction of ions in the ionizer. However, the lifetime of the ion source is reduced in the comparison with the method of electron bombardment.

We expect to introduce further improvements in the lifetime and transmission of the system and conduct more evaluation studies in isotope ratio measurements for mixed trace element samples.

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