Gas cell studies of thorium using filament dispensers at IGISOL

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Abstract

Filament-based dispensers of thorium have been investigated at the IGISOL facility, Jyväskylä, for potential use as a thorium ion source for future collinear laser spectroscopy experiments. Several different filaments were manufactured in the Institute of Atomic and Subatomic Physics of TU Wien, with ^{232}Th and ^{229}Th prepared on tantalum substrates either by drying thorium nitrate solution or via molecular plating, while adding a layer of zirconium for oxide reduction. The filaments were characterized in a helium-filled gas cell by performing selective and efficient in-gas-cell resonance laser ionization and by analyzing the resulting ion beams by mass spectrometry. Additionally, the in-gas-cell laser ionization process of thorium was further characterized by wavelength scans, saturation measurements and by recording the temporal behavior of extracted ion pulses. Although an ion source was successfully created with mass-separated intensities over 10^6 ions/s, the required high filament temperature resulted in significant contributions from interfering impurities and deterioration of the filament structure.

Keywords: Ion source, Thorium, Resonance laser ionization, Gas cell

1. Introduction

High-resolution laser spectroscopy of atomic levels is a well-known method to probe fundamental properties of atomic nuclei. Measurements of isotope-dependent shifts in electronic transition frequencies and hyperfine structure of the optical resonance provides model-independent access to nuclear spins, magnetic dipole and electric quadrupole moments, as well as changes in nuclear size via mean-squared charge radii [1]. Additionally, and with pertinence to the current work, laser spectroscopy measures states rather than decays and thus the observation of resonance lines besides those expected from the nuclear ground state is proof of the existence of isomeric states. It is also noted, that the study of isomeric states by nuclear decay spectroscopy is limited if the states are too long-lived or too close in energy to the ground state to be cleanly separated with mass-purification techniques. At the IGISOL facility in the Accelerator Laboratory of the University of Jyväskylä [2], collinear laser spectroscopy [3, 4] of actinide elements is a currently ongoing program of research. By combining highly efficient laser resonance ionization in the IGISOL gas cell [5] with thermal desorption of long-lived actinide elements, an efficient ion source can be realized even with trace amounts of isotopes. There are many isotopes in the actinide region which have sufficiently long lifetimes to be produced for example in nuclear reactors, deposited onto filament dispensers and transported to a separate location with appropriate experimental facilities for detailed study. The deposited isotopes can then be

converted to an ion beam without the requirement of a primary beam from an accelerator. Recently, the first successful laser ion source at IGISOL for plutonium was realized in this manner [6] and subsequent high-resolution collinear laser spectroscopy of $^{239,240,242,244}\text{Pu}$ was performed, the heaviest element studied to date with this technique [7].

In recent years thorium has attracted considerable interest since ^{229}Th is known to possess an excited isomeric state with an exceptionally low energy of below 10 eV [8, 9], with the latest measurement resulting in a value of 8.28(17) eV [10]. This state was also very recently pumped optically for the first time using narrow band synchrotron radiation [11]. The isomer is foreseen to have a variety of possible applications, most notably to use the low-energy transition as the frequency reference in a highly precise nuclear-based clock [12, 13]. We do not intend to provide an extensive summary of the numerous theoretical and experimental efforts currently focused on this isomer, however we note the most recent highlights which include the detection of electrons emitted from the internal-conversion decay channel of the isomer in neutral thorium [14], the measurement of the half-life of the isomer in a closely-linked adaptation of this first experiment [15] and the successful laser spectroscopic investigation of the hyperfine structure of the doubly-charged ion, which led to the first direct determination of the magnetic dipole and electric quadrupole moment, as well as the nuclear charge radius [16].

At IGISOL, complementary efforts are underway to measure the hyperfine structure of the isomer and the ground state of ^{229}Th using collinear laser spectroscopy. Earlier efforts focused on a measurement of the ground-state hyperfine structure of neutral ^{229}Th with hyperfine coupling constants measured for the atomic ground state and three excited states [17]. Fol-

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lowing the measurement of the lifetime of the isomeric state in neutral form ($7 \pm 1 \mu\text{s}$) [15], our attention turned towards the study of singly-charged $^{229\text{m}}\text{Th}$ where open questions still remain. For example, it was noted that no signal indicating internal conversion of the isomeric state in $^{229\text{m}}\text{Th}^+$ was obtained, which may point to other decay channels such as collisional quenching, bound internal conversion or an electron bridge mechanism [18, 19]. The availability of on-line production of ^{229}Th at IGISOL, with possibly considerable feeding to the isomeric state through the fusion-evaporation reaction $^{232}\text{Th}(p, p3n)^{229}\text{Th}$, creates unique access to the isomer in the $1+$ charge state. On the other hand, a laser ion source for thorium using filament-based dispensers of ^{229}Th would afford access to a measurement of the hyperfine parameters for a ground state-only beam of $^{229}\text{Th}^+$ ions. Creation of such a laser ion source would therefore pave the way to a future measurement of both ground state and isomer using the on-line reaction.

Although filaments have been successfully used in gas cells as sources for monoatomic vapors of a variety of elements for the purpose of doing laser resonance ionization in connection with different gas cell-based experiments [20–23], the actinide region poses a special challenge for filament-based sources as the volatility of many actinide elements is relatively poor and the scarcity of some of the isotopes complicates the filament manufacturing. This is especially the case with ^{229}Th as the availability of high-purity ^{229}Th is limited. Thorium is also the least volatile of the actinide elements, therefore high filament temperatures are required, which can be detrimental to the high purity conditions necessary to successfully operate a gas cell.

This work concentrates on the developments towards a filament-based atomic vapor source for thorium and the phenomena and challenges faced while using such a source in combination with resonance laser ionization for the selective production of a singly-charged thorium ion beam. Several different filaments have been studied in a series of offline experiments, which led to the realization of a high yield $^{232}\text{Th}^+$ ion source. The article is organized as follows. In section 2 we describe the gas cell used in this work and the relevant aspects of the IGISOL facility. Section 3 presents the filament manufacturing process and analysis of the ^{229}Th activity. Laser resonance ionization of thorium is presented in section 4 while relevant gas cell processes and the gas-phase chemistry studies with analysis of mass spectra are detailed in section 5.

2. In-gas-cell filament source for thorium

The measurements presented in this work have been carried out with a dedicated gas cell developed for use with electrothermally-heated filaments that are fabricated in order to evaporate the element of interest in a neutral monoatomic state. In-gas-cell resonant laser ionization is performed on evaporated atoms to selectively (and efficiently) produce an ion beam which is extracted from the cell, guided through a differential pumping stage towards the high vacuum region of the mass separator and accelerated to a potential of typically 30 kV for mass separation, with a nominal mass resolving power of $M/\Delta M = 500$. Figure 1 presents a schematic overview of the

Figure 1: Schematic picture of the IGISOL mass separator showing the gas cell, acceleration region, separator magnet and detector station.

experimental setup. Mass-separated ions may be detected at the focal plane of the separator using either a Faraday cup or multichannel plate (MCP) detector. The gas cell has been characterized and described in earlier work [6] and therefore only a brief description is provided in the following.

A cross-sectional view of the gas cell and the immediate downstream ion optics consisting of the radiofrequency sextupole ion guide (SPIG) [24] are shown in Fig. 2. The gas cell volume of about 30 cm^3 is fed by purified helium gas via the transverse pipe located next to the sapphire window used for optical access. The helium gas pressure is maintained at $P_{\text{gc}} = 80 \text{ mbar}$ and measured after the regulating valve on the gas inlet line before the gas cell. The helium gas, along with filament-related atoms, laser ions and contaminants is extracted through a 1.2 mm diameter exit hole into a low pressure ($P_{\text{amb.}} = 10^{-2} \text{ mbar}$) vacuum chamber where the SPIG is used to capture the charged species while the neutral buffer gas is pumped away. An important parameter of the gas cell when studying the dynamic behavior of ion pulses, is the evacuation time of the gas cell volume, which is estimated to be $\sim 50 \text{ ms}$ at room temperature and gets shorter when the gas temperature increases. The evacuation time is, however, independent from

Figure 2: Cross-sectional view of the gas cell and the SPIG radiofrequency ion optics used to guide the ions towards the mass separator. The filament is connected between the copper high current feedthroughs. The first electrode after the gas cell, the front electrode, is highlighted with the typical potential applied. The wavy dotted lines portray ion trajectories in the SPIG.

the gas pressure, due to the pressure ratio between the ambient expansion chamber where the SPIG is located and the gas cell being much smaller than the critical pressure ratio for choked flow [25] ($P_{\text{amb.}}/P_{\text{gc.}} \ll 0.488$).

The filament is mounted between two high current feedthroughs located close to the exit hole of the gas cell and ~ 1 mm away the central extraction axis of the cell. This geometry results in an optimal spatial overlap between the lasers and filament atoms in order to probe the highest density of atomic vapor.

The purity of the carrier gas has been shown to be critical for the survival efficiency of ions during the extraction from the gas cell in an atomic form. Therefore, the IGISOL gas purification system [26] is used to purify the helium before it is fed to the gas cell. Purification of the gas to a sub parts-per-billion level of impurity is needed to prevent loss of the atoms to molecular form before the laser ionization process occurs or correspondingly, molecule formation of the laser ions following ionization. The ions of actinide elements in particular can be strongly reactive towards oxidizing reactants of which O_2 and H_2O are the most abundant impurities in the helium gas. Ions of thorium compared to other actinide elements exhibit large reaction rate coefficients, emphasizing the importance of cleanliness of the gas in this work [27].

3. Operational principle and description of the filament dispensers

The prerequisite for resonant laser ionization of neutral atoms is to have the element of interest in monoatomic form. Evaporation of various actinide elements in atomic form has been successfully demonstrated using so-called *actinide sandwiches*, in which an actinide is electrolytically deposited on a substrate and then covered by a layer of reducing agent, as demonstrated by Eichler *et al.* [28]. In that work, the authors showed that the most promising method for actinide elements was using a tantalum substrate with a titanium layer covering the deposition. This resulted in stable sources of atoms delivering a nearly constant flux for long periods of time.

Element volatility plays an important role in the evaporation process with less volatile elements requiring higher temperatures for evaporation. Of all the actinide elements, thorium is the least volatile requiring temperatures of over 2000°C in order to be efficiently desorbed. As tantalum has a high melting point of about 3000°C [29], it was similarly selected as a substrate material. In our approach the deposition of thorium was done by two different methods. First, a thorium nitrate solution was directly applied by pipetting it on to the substrate as droplets that were allowed to dry between consecutive drops. The second method used molecular plating [30] of thorium material on to the substrate.

3.1. Structure, manufacturing and preparation of the filaments

In the work presented here, several different thorium filaments were sequentially tested while iteratively improving the

Figure 3: Photographs of the thorium deposition spots that were subsequently cut into filaments investigated in this work. The three spots prepared using the drip-dry process are numbered 1, 2, and 4, of which filament spot 1 contains only ^{232}Th . On the filaments 1 and 4, the dot of deposited ^{232}Th is only just visible while on filament spot 2 the deposit for ^{229}Th can be clearly seen due to considerable build-up of material. Filament spot 3 is prepared using molecular plating. A 1 cm bar is given for scale and red dashed lines depict the final size of the filaments.

filament structure and manufacturing process. The actual thorium deposition and the production of the substrate-thorium-reducing layer sandwiches was performed at the Institute of Atomic and Subatomic Physics (ATI) of TU Wien. All of the filaments presented have the same basic structure: thorium deposition on a substrate with a reducing layer on top of the deposition. The substrate in all filaments is a tantalum foil on top of which a micron layer of Ti or Zr has been added depending on which is used as the reducing layer. First investigations involved a series of drip-dry filaments in which the direct application of thorium in solution was done with a repeated drip-dry method resulting in a hydrated thorium nitrate ($\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$) deposition. After drying, a $1\text{-}\mu\text{m}$ reducing layer of either titanium or zirconium was added by sputtering. The layer thickness was accurately controlled with a quartz balance down to nm resolution. The second type of filament investigated was one in which the thorium was deposited electrochemically on the substrate by molecular plating. Lastly, an improved version of the drip-dry method was tested. Figure 3 shows the different depositions prior to cutting of the substrate into the dimensions required for the gas cell.

As a proof-of-concept for a thorium laser ion source, the very first filaments contained only ^{232}Th , prepared by drying a single $1\text{ }\mu\text{l}$ droplet of dissolved $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ on the substrate over night at 60°C . The initial samples containing approximately 10^{15} atoms were covered by a $1\text{ }\mu\text{m}$ thick sputtered titanium layer. The titanium however did not result in the expected evaporation of monoatomic thorium atoms, rather strong mass-separated titanium beams were observed before achieving the temperature required for thorium release. In effect, the reducing layer was evaporated before thorium began to diffuse through in sufficient quantities and even though atomic thorium was released and detected in response to the laser ionization, the ion yield and the longevity of the titanium-covered filaments were poor.

Zirconium, which is a chemical homolog of titanium, has better temperature stability and it has been reported to have low adsorption enthalpy for actinide elements, but high adsorption enthalpy for oxygen [31]. Therefore, a $1\text{ }\mu\text{m}$ layer of zirconium was chosen to replace titanium as the reducing agent on the

improved version of the proof-of-concept ^{232}Th filament. The deposition spot of this filament is shown as spot 1 in Fig. 3. These filaments had good tolerance for high temperatures and successful evaporation of atomic thorium was achieved.

After successful operation of the proof-of-concept filaments, the results of which are discussed in the following sections, tests were performed on filaments containing ^{229}Th along with a similar amount of ^{232}Th , again covered with a zirconium layer by sputtering. A solution from 3.8 kBq of ^{229}Th was made by dissolving in 5 ml 0.1 M HNO_3 and was distributed among four spots. Unfortunately, in the first version of the ^{229}Th drip-dry filaments (filament spot 2, Fig. 3) the physical size of the spot was much larger than for the ^{232}Th -deposited spots. This was caused by the thorium nitrate solution being so dilute that it had to be sequentially accumulated and dried on to the tantalum substrate up to 30 to 40 times, leading to significant material build-up.

Filament 3 was manufactured by a molecular-plating technique in a dedicated plating cell. To create the plating solution, 4.2 μg of ^{232}Th and 5 kBq ^{229}Th were dissolved in 5 μL 0.06 M HNO_3 which was diluted with 8 ml isopropanol. The plating was performed for 30 minutes with a current of 0.8 mA on a cathode of circular shape 2 mm in diameter that was facing a Pt wire anode at a distance of 1-2 mm. Then the plated spot was dried under argon flux at 100 °C for 30 minutes and 1 μm Zr sputtered on top.

Finally, filament 4 in Fig. 3 was again manufactured by drying a solution containing ^{229}Th on a Zr-coated tantalum foil. This time the solution was obtained by dissolving 8 MBq of ^{229}Th as dried nitrate salt in 8 ml of H_2O . This resulted in a sufficiently high concentration such that only one 1 μL drop was required.

The filament manufacturing with molecular plating (filament spot 3) and the second version of the drip-dry filaments (filament spot 4), both containing ^{229}Th , had a much lower material build-up. Challenges remained however as the molecular-plating process had a very low efficiency of transferring activity to the Ta substrate, and the second version of the ^{229}Th drip-dry filaments had mechanical stability problems.

Before the preparation of the gas cell, the filaments were cut out from the tantalum foil forming 1-3 mm wide and 10-mm long strips depending on the spot size, with the thorium nitrate spot positioned in the middle. After mounting across the feedthroughs, the gas cell was placed under vacuum in the IGISOL target chamber. In order to minimize the outgassing of impurities into the gas during the experiment, the gas lines and body of the gas cell were baked under a flow of purified helium using resistive heating elements for at least 12 hours prior to the measurement if possible. During this time, the filaments were heated to a low temperature (< 900 °C) in order to bake out additional impurities which were seen to be continually released at higher temperatures.

3.2. Decomposition and reduction of the thorium nitrate

Of the filaments manufactured with the drip-dry method, the dried thorium nitrate hydrate, $\text{Th}(\text{NO}_3)_4 \cdot 5 \text{H}_2\text{O}$, is expected to

decompose into ThO_2 in a series of evaporation processes when the temperature increases from 330 °C to 630 °C [32, 33]. On the electroplated filament, thorium is also assumed to be in an oxide form.

At the operational temperature near 2000 °C, the reduction of thorium oxide to thorium occurs with the aid of zirconium [28], and atomic thorium starts to evaporate out of the filament. The temperature can be then increased further to get a larger release rate of atoms. In order to reach the operational temperature, a heating current between 15 A to 30 A was applied depending on the width of the filament, resulting in ~ 1 V across the filament feedthroughs and about 15 W to 30 W of heating power. The constantly flowing helium gas provides considerable dissipation of this heat which is seen as a strong dependence of the filament temperature on the gas pressure. The upper limit to the temperature is restricted by the evaporation of the tantalum substrate.

3.3. Gamma spectroscopic analysis

In the filaments containing ^{229}Th , the attained yield in the deposition process was verified using gamma-ray spectroscopy by measuring the filaments in a low-background high purity germanium (HPGe) detector station. For the first iteration of the drip-dry filaments (filament 2, Fig. 3), an activity of approximately 160 Bq per spot, or about 15% of the amount expected to be present in the sample, was determined from the strongest gamma-ray transitions. The gamma spectrum, which was measured for approximately 1 week in the energy region from 3 keV to 422 keV, is shown in Fig. 4 with the strongest and most distinct gamma lines identified using tabulated values in literature [34–37]. All of the identified lines belong to ^{229}Th or its daughters down to ^{209}Tl . The isotopes of ^{217}At , ^{213}Po and ^{209}Pb are missing in the spectrum as they do not have any intense gamma lines. The X rays from the tantalum substrate are visible, originating from decay particle-induced X-ray emission.

The yield from the second iteration of the drip-dry filament (filament 4, Fig. 3) was measured to be 760 Bq showing a significant improvement compared to the first drip-dry filament. Finally, the electroplated filament yield was 190 Bq. In general, while the gamma peak intensities varied between the different filaments, all the gamma spectra showed the same composition and did not show any identifiable contaminant demonstrating the radiochemical purity of the deposited ^{229}Th .

4. Laser resonance ionization of thorium

Resonance laser photo-ionization has been a very successful method to produce isobarically pure ion beams from neutral atom sources in both hot cavities as well as buffer gas stopping cells [38, 39]. At IGISOL, the FURIOS laser facility provides tunable pulsed laser radiation for the purpose of doing laser resonance ionization, spectroscopy as well as optical manipulation [40]. Laser resonance ionization can be performed even in small volume gas cells with fast extraction times. By carefully selecting an appropriate ionization scheme, high ionization efficiencies can be achieved in short laser exposure times and with

Figure 6: The experimental setup for laser resonance ionization of thorium from a filament dispenser. In addition to laser ionization in the gas cell, a separate reference cell was used to study the ionization under vacuum. This latter setup was only used with stable ^{232}Th . DM = dichroic mirror, SHG = second harmonic generation, FM = folding mirror. See text for further details.

duced by three broadband titanium-sapphire (Ti:sa) lasers operated at a repetition rate of 10 kHz with ~ 40 ns pulse duration. In order to generate the UV light of the first step, two approaches were implemented. Intra-cavity second harmonic generation (SHG) was used for high output power [46] and a single-pass external SHG station was preferred when wavelength scanning was required. The first step Ti:sa laser was pumped separately with its own Neodymium YAG (Nd:YAG) laser, which gave independent control over the timing of the first step laser pulses. The second and third step lasers were pumped by a second Nd:YAG laser and the temporal overlap was adjusted by fine tuning the pump laser power to each resonator. Figure 6 shows a simplified schematic of the laser setup.

4.1. Frequency scanning

It is essential to study the mass-separated ion beam at the correct mass-to-charge (A/q) ratio of thorium by scanning the frequency of the lasers across the expected resonant frequency for each of the three excitation steps. Detection of the corresponding signal can be used to confirm whether the mass-separated ions are resonantly-produced thorium ions, the selectivity (in other words the fraction of laser-ionized thorium to non-resonant ions) as well as the contribution of the total thorium signal from each individual laser step. Simply verifying a laser response in the mass-separated ion signal by (un)-blocking the laser light is not necessarily sufficient confirmation for laser ionization of thorium as the beam usually contains ions that have not originated from thorium atoms, rather from contaminant molecules which nevertheless respond to the lasers. This

is because of the tendency of contaminant molecules to be ionized by UV laser light in a non-resonant manner due to the low ionization potential of molecules.

Resonance frequency scans for thorium were performed for Scheme 1 in two environments, the gas cell and a vacuum reference cell [47]. The latter was used to obtain a reference scans free from effects arising from the gaseous environment of the gas cell. The ion count rate from the gas cell was measured by recording the mass-separated ($A/q = 232$) ion beam with the MCP detector. The vacuum reference cell contains a resistively-heated tantalum tube that acts as an oven. A small sample (~ 0.5 mg) of ^{232}Th foil was cut, wrapped in zirconium foil and inserted into the oven. Following heating, an atomic thorium vapor is formed, a fraction of which passes through a small aperture above the oven and is intersected in a perpendicular geometry by cross-propagating laser beams. The resonantly ionized thorium ions are deflected to an electron multiplier tube (EMT) detector using electric fields. Due to the laser-atomic beam overlap geometry, a nearly Doppler-free method of spectroscopy can be performed and compared to the environment of the gas cell. We note that the reference cell has no mass-selectivity and due to the inefficiency of this method of spectroscopy, no filament dispensers were used.

Figure 7 illustrates the frequency scans (Scheme 1) for each of the three excitation steps in both the gas cell and vacuum reference cell. The spectra taken in the vacuum reference cell are normalized to the maximum count rate of the gas cell for comparison. In all steps, the resonance peak obtained in the vacuum reference cell is located at the expected wavelength corresponding to the atomic states in the laser ionization scheme, and there

Figure 7: The ion count rate as a function of laser wavelength for mass-separated ions at $A/q = 232$ from the actinide gas cell for each of the three laser resonance excitation steps (triangle symbols). The solid lines with data as crossed symbols present the same wavelength scans done in a vacuum reference cell without mass separation.

is little or no background detected on either side of the peaks. The resonance peak width is a convolution of the bandwidth of the laser light (in the fundamental this is typically ~ 5 GHz) and a power broadening effect.

The spectra measured in the gas cell also show resonant peaks. However, a significant background is visible in all three laser scans. In the case of the second and third step, the background is mainly due to the first step UV laser light non-resonantly ionizing thorium. This can happen by populating the first excited state and then either ionizing directly across the ionization potential, or by collisional de-excitation to a lower excited state from which another resonant transition is available

with a frequency similar to the first step transition and within the bandwidth of the laser. See reference [48] for further details. There is also a constant background count rate that most likely originates from impurities on the same nominal mass as ^{232}Th or possibly from surface-ionized thorium.

In the case of the first excitation step the background can only be due to impurities or thorium leaving the hot filament as an ion. The worse signal-to-background ratio in the first step wavelength scan is mainly due to the higher temperature being applied to the filament as the measurement was made towards the end of the filament life. The linewidth of the resonance of the first step is significantly larger in the gas cell. This is attributed to strong power broadening as the reference scan was obtained in a separate experiment (and at a lower laser power). Finally, it is notable that a small frequency shift of the final step frequency scan is seen between the gas cell and the vacuum reference cell. This is likely to be due to the well-known pressure shift of transitions to both AI and Rydberg states in helium (or argon) gas. We did not probe this effect further as a variation in the pressure resulted in a strong dependence on the temperature and thus release rate of thorium atoms.

4.2. Saturation of the laser signal

The level of saturation of each resonant excitation step of Scheme 1 was measured in the gas cell. In Fig. 8 the ion count rates are shown as a function of the laser intensity, which was determined from measured laser powers and transportation losses, as well as from the laser beam spot sizes at the entrance to the gas cell. The laser powers were adjusted for each individual step by using a combination of the rotation of a half-waveplate combined with a polarizing beam splitter cube and a series of neutral density filters. The errors on the measurement data points are statistical only.

All of the excitation steps in the gas cell exhibit the typical saturation behavior in which the signal A as a function of the intensity I is described by,

$$A(I) = A_{\max} \frac{I/I_{\text{sat}}}{1 + I/I_{\text{sat}}}, \quad (1)$$

where the parameters I_{sat} and $A_{\max}$ are the saturation intensity and the signal amplitude when the transition efficiency approaches unity. In other words, $A_{\max}$ is the maximum attainable signal if the laser intensity of a particular transition was increased towards infinity. Fits of such saturation curves to the data are shown as solid lines and the resulting saturation intensity is indicated for each step. In all transitions, the measured data is closely reproduced by the saturation equation, however, there is a much larger scattering in the data points than the statistical error of the ion count rate. This is due to fluctuations in the output power of the Nd:YAG laser pumping the Ti:sapphire laser used for the first excitation step. Even though the Ti:sapphire laser power does not necessarily fluctuate so strongly with small variations of the pump power, the effect is primarily observed in a temporal jitter in the timing of the first step laser pulses with respect to the second and third step, and

Figure 8: Saturation curves of the three excitation steps used in Scheme 1 measured in the gas cell. All curves show a deviation from a linear behavior towards saturation.

hence is reflected in a non-statistical variation of the ion count rate.

Although saturation is usually accepted as an indication of high efficiency of laser ionization, here we cannot state that the ionization efficiency would be approaching high values even though saturation is seen in the gas cell ionization. This is because even if all three laser steps would be fully saturated, the ionization from the autoionizing state can be in competition with other loss channels from the lower levels of the ionization scheme which populate long-lived “dark” states from which the atoms are no longer accessible. These de-excitation transitions can be radiative but also collisional in nature in the high pressure environment of a gas cell. In fact, these collisions are thought to be observed in our work, because the ionization of thorium via the UV-UV (non-resonant) scheme in the gas cell is much more efficient compared to the similar process in vacuum [48].

By slowly increasing the filament temperature, the maximum intensity of photo-ions using the ^{232}Th filament (filament 1) at $A/q=232$ was $\sim 10^7$ ions/s, a yield which was dominated by $^{232}\text{Th}^+$ ions. At such high intensities, observed using a Faraday cup, the longevity of the filament reduced to approximately 30 mins. However, for collinear laser spectroscopy experiments a yield of typically 10^4 ions/s is more than sufficient, and thus it is expected that a filament could last for a period of several days.

5. In-gas-cell processes and gas phase chemistry

The required high temperature of the filament for efficient evaporation of thorium atoms has the disadvantage that a considerable amount of contaminants is also evaporated from the filament. This has been observed to be a more critical problem if the filament is not heated slowly and initially baked at a low temperature. The evaporating contaminants result in intense ion beams due to direct surface ionization (given a sufficiently low ionization potential) or non-resonant ionization by the UV laser

light. The contaminant ions may undergo further chemical reactions or form adducts with impurities in termolecular reactions with the helium atoms inside the gas cell or downstream in the adiabatically expanding supersonic gas jet. As will be presented in this work, the mass-separated ion beam contains a large variety of molecular species, unfortunately resulting in overwhelmingly large peaks at the mass of interest.

To investigate the ionization of thorium and possible losses of ions through molecule formation reactions with the evaporated contaminants during evacuation from the gas cell, the dynamic behavior of the $^{232}\text{Th}^+$ ions was investigated by mechanically chopping the laser light. To further study the chemistry occurring inside the gas cell, a series of mass spectra were recorded at the focal plane of the IGISOL separator at different stages of the filament heating.

5.1. Estimation of ion loss mechanisms from temporal profiles

When the laser light to the gas cell is blocked by a fast shutter (Fig. 6), the resonant ionization of the thorium atoms stops immediately. The detected rate of the ionized species gradually reduces over a timescale reflecting the evacuation time of the gas cell assuming the gas flow is laminar and no ions are lost or transformed to molecules during transport towards the exit hole. By measuring the rise and fall times of an ion pulse intensity profile when the laser light is periodically chopped, it is possible to extract information on the ion loss mechanisms [20]. Fast molecule formation, for example, will be imprinted onto the time profile as a shorter rise and fall time compared to the expected evacuation time of the gas cell, as only the atomic ions created very close to the nozzle will survive extraction. A non-laminar flow can be expected to appear as a longer signal fall time, if, for example, the ions are trapped in the gas cell due to the presence of a vortex in the gas flow.

Figure 9 illustrates the time profiles of the thorium ions at $A/q = 232$ and its corresponding oxide $A/q = 248$, obtained using filament1 (Fig. 3). In all such measurements it is the first step laser which is pulsed. The profiles are measured

Figure 9: Dynamic behavior of the Th^+ and ThO^+ ion signal when the UV laser radiation is mechanically chopped. Growth and decay times are determined by fitting the rising (+) and falling (-) edges with an exponential decay function.

by connecting, the signal from the MCP after the mass separator to a Stanford Research Systems SR430 multi-channel scaler (MCS), which recorded the time difference between a trigger signal and an ion detection for each ion individually. The MCS was triggered by a timing signal from a Spincore Technologies PulseBlaster PB24-100-32k precision timing card, which was also used to create a TTL signal for the fast mechanical shutter located at the focal point of the telescope as indicated in Fig. 6. The shutter is built from the actuator of a readout head of an old magnetic hard drive allowing blocking of the laser with a timing accuracy below $100 \mu\text{s}$ [20, 47]. The overall timing cycle was 2.5 s of which a period of 1.4 s was used with the UV laser radiation entering the gas cell. Several hundreds of time profiles were recorded consecutively to obtain sufficient statistics for subsequent fitting and to ensure repeatability of the time profile.

We note that the spectra in Fig. 9 are dominated by the atomic $^{232}\text{Th}^+$ ions indicating the high purity of the gas cell conditions. This is in clear contrast with time profiles obtained using plutonium-based filament dispensers [6] in which a source of impurities was suspected from a “dead” volume in the filament holder. In order to characterize the time profiles, rising and falling exponential decay curves were fitted to the data. The corresponding time parameter, τ , is tabulated in Table 1. The falling edge of the profile describes the system evolving from a steady state of laser ionization and thus is a more natural parameter to use in the determination of an effective volume for laser ionization. The characteristic time τ for Th^+ ions presented in Table 1, 54.8 ms, can be converted to an effective volume $V_{\text{eff}} = C\tau$ using the exit hole conductance for helium gas, $C = 0.026 \sqrt{T} d_t^2$ [l/s], in which T is the gas temperature at the nozzle in K and d_t is the exit hole throat diameter in mm. This simplified equation can be derived from the conductance

τ parameter	Rising	Falling
Th^+	$65.8 \pm 1.0 \text{ ms}$	$54.8 \pm 0.6 \text{ ms}$
ThO^+	$93 \pm 8 \text{ ms}$	$81 \pm 8 \text{ ms}$

Table 1: The parameter τ of the rising and falling edges of Th^+ and ThO^+ time profiles extracted from the exponential fits of the data presented in Fig. 9.

of choked flow through an orifice [25, 48].

Although the electric power applied to the filament is known in this case ($\sim 15\text{W}$), the helium temperature at the nozzle is difficult to estimate as there is also active cooling of the gas cell. The heat power can therefore be dissipated by means other than adsorption to the helium gas. Assuming 30-70% of the power input is left as heated helium gas, a temperature of between 400 K and 600 K can be estimated. This translates to effective volumes of about 40 cm^3 to 50 cm^3 . This is larger than the physical volume of the gas cell ($\approx 30 \text{ cm}^3$), and therefore it can be concluded that there are no significant loss mechanisms to the atomic ions during evacuation. The larger volume, however, indicates that a turbulent region of flow exists inside the gas cell, trapping the atomic ions before extraction, which is not surprising due to the presence of the filament feedthroughs.

The reason for the longer τ parameters for the ThO^+ molecule compared with the atomic Th^+ ion is due to the formation process of the oxide. This proceeds initially from laser ionization of Th atoms followed by oxidation with a characteristic time constant $\tau_{\text{mol}} = 1/([M]k_2)$, defined by the impurity concentration $[M]$ and the bimolecular reaction rate k_2 . Reaction efficiencies (k_2/k_{ADO}) of 1.12 and 0.57 have been reported by Schwartz et al. [49] for the oxidation of Th^+ by O_2 and H_2O respectively, while Santos et al. [27] have reported respective efficiencies of 0.86 and 0.20. The k_{ADO} parameter is a reaction rate according to the average dipole orientation theory [50], which can be used to convert the reaction efficiencies to absolute reaction rate coefficients. In this case the reaction efficiencies result in $k_2(\text{O}_2) = 5 \cdot 10^{-10}$ to $6 \cdot 10^{-10} \text{ cm}^3/\text{s}$ and $k_2(\text{H}_2\text{O}) = 3 \cdot 10^{-10}$ to $1 \cdot 10^{-9} \text{ cm}^3/\text{s}$ using the k_{ADO} values calculated with Equation (7.14) and listed parameters from Ref. [51] assuming room temperature.

The obtained time parameters for ThO^+ are a convolution of the gas cell evacuation time with the molecule formation time. In this case, if one converted the molecular time constant τ into an effective volume, it would result in a larger volume than the effective volume calculated for Th^+ . This simply indicates that molecule formation is not a dominant loss mechanism in this measurement.

5.2. Mass spectra from a ^{232}Th filament (Filament 1)

Figure 10 shows mass spectra recorded in the mass region A/q from 230 to 290, with (solid red and blue lines) and without (solid black line) the UV laser radiation entering the gas cell while ^{232}Th filament dispenser 1 (Fig. 3) was heated at a temperature of $\sim 2000 \text{ }^\circ\text{C}$. A clear enhancement of the ion signal is seen at $A/q = 232$ indicating a successful laser ionization of ^{232}Th atoms. At 16 mass units above atomic thorium a mass peak is observed which corresponds to ThO^+ . Although the

Figure 10: Mass spectra recorded at the focal plane of the IGISOL separator while using a ^{232}Th filament dispenser (Filament 1). The red solid line shows the effect of the resonant laser ionization enhancing the yield of thorium and its corresponding oxide in comparison to the mass spectrum obtained with the UV laser radiation blocked (black solid line). A mass spectrum with laser ionization and without molecular suppression is shown as a blue solid line. U is the suppression voltage.

molecule is not expected to be ionized directly by the lasers, there is a noticeable response to the laser radiation, which reflects formation of ThO^+ following laser ionization of neutral thorium atoms. Impurities seen at even higher masses, for example above $A/q=270$, usually do not respond to the laser radiation although occasionally an increase was seen indicating non-resonant ionization of molecules.

Even without the UV laser radiation of the first resonant step, mass peaks corresponding to $A/q=232$ and $A/q=248$ can be identified, implying that either some impurity is present at those mass values or, more likely, that the thorium and its oxide in the filament are being ionized through a non-resonant process. This has the effect of reducing the selectivity provided by laser resonance ionization. The only conceivable process to account for this would be surface ionization at the hot filament.

The Saha-Langmuir equation may be used to estimate the fraction of atoms evaporating as ions [52]. By combining the work functions of tantalum ($\phi^e = 4.25$ eV [53]) and zirconium ($\phi^e = 4.05$ eV [54]) as well as the ionization potentials of Th (6.3067 eV [55]) and ThO (6.1 eV [56]) results, however, in only small fractions produced ($n_{+1}/n_0 < 10^{-4}$). As the ratio of photo-ion to non-resonant ions at $A/q = 232$ is approximately 10, having such a low n_{+1}/n_0 fraction would indicate quite a low total laser ionization efficiency. The exact work function, however, is difficult to estimate. The effective work function for ion emission ϕ^+ is usually higher than for the electronic emission ϕ^e especially for polycrystalline surfaces, and the work function can be significantly increased due to adsorption of electronegative elements such as oxygen which is known

to be present as an impurity [57]. There is therefore a possibility that the work function is over 1 eV higher than the values stated above leading to significant surface ionization of Th and ThO ($n_{+1}/n_0 = 10^{-2}$). A more quantitative estimation is difficult to provide because the sample conditions are not known accurately.

When the measured yield of mass-separated impurities became significant around the thorium mass region, an accelerating potential immediately after the gas cell was introduced and was used to suppress the transmission of impurities. This was realized by applying a larger negative voltage on the front electrode of the SPIG, which captures and guides the ion beam from the gas cell towards the 30 keV acceleration stage of the IGISOL separator. The typical operating voltage of this first electrode is a few volts below zero (used in the mass scan with laser ionization shown by the solid blue line of Fig. 10). By providing additional kinetic energy to the ions in the supersonic jet region, often complete suppression of the molecular ion signal was observed without a pronounced decrease in the atomic ion signal. In connection to Fig. 10, an applied voltage of -85 V was used for the mass scans represented by the red and black solid lines. The background count rates seen with this voltage are clearly lower and an additional intense mass peak visible at $A/q=231$, postulated to arise from TaO_3H_2^+ , has been suppressed. We note that intense beams of Ta^+ , TaO^+ and TaO_2^+ were seen concurrently along with frequent water adduct formation and that TaO_3H_2^+ and related compounds have been observed experimentally [59]. The impurities seen at $A/q=271$ and 287, attributed to TaZr^+ and TaZrO^+ according to the mass

Figure 11: A mass spectrum using a drip-dry ^{229}Th filament dispenser (Filament 2). Considerable amounts of zirconium and its oxide are being produced and ionized at the filament, and heavier clusters can also be seen. Each identified molecule is shown with its calculated isotopic pattern [58] highlighting a good concordance.

values and isotopic patterns, do not exhibit any evidence of suppression.

The suppression of molecules can be attributed to collision induced dissociation (CID) as this mechanism has been reported in connection with gas cells in similar configurations [60–63]. Computational simulations suggest that molecules may be suppressed also through other means. These simulations suggest that the higher the collision cross section of molecules due to their larger physical size compared to atoms, leads to their suppression due to a larger number of collisions and kinetic energy loss within the helium gas jet environment. A more detailed picture of this mechanism is provided in [48].

5.3. Results from ^{229}Th drip-dry filament dispensers (filaments 2 and 4)

The set of filament dispensers containing ^{229}Th were also investigated in the gas cell in same configuration as described for the ^{232}Th filaments. As indicated in Fig. 3, the drip-dry method for the application of ^{229}Th onto the tantalum substrate resulted in a considerable build-up of material over a larger surface area for the second filament type compared with the ^{232}Th dispensers. As a result, the contaminant concentration was notably higher in these filaments, and a large yield of zirconium and its oxide compounds was seen evaporating and being surface-ionized at the filament. In addition to being used for reduction, zirconium was also used in the original ^{229}Th solution, which we expect to be the most likely source of the zirconium-related impurities observed. Figure 11 indicates two mass regions of interest recorded at a filament temperature close to 2000 °C. In the lower mass region, ion beams of Zr^+ and its oxide ZrO^+ are observed, while in the higher mass region three other zirconium

oxide compounds Zr_2O^+ , Zr_2O_2^+ and Zr_2O_3^+ are highlighted. These compounds form the majority of the impurity signal detected from these filaments. For each compound the natural isotopic pattern for zirconium was calculated [58] and plotted as normalized curves overlaid with the experimental mass spectra, precisely matching the mass peaks and thus validating the compound identification.

This illustrates the problem that can arise if elements having a large number of stable isotopes are used in filament-based dispensers in combination with a significant number of impurities transferred in the preparation of the source. Although the mass peaks of the zirconium isotopes (used as the required reducing agent) and corresponding oxides are not at the same nominal mass as $^{229}\text{Th}^+$ and $^{232}\text{Th}^+$, the combination of dimerization and additional molecule formation leads to wide isotopic patterns, which in this case overlapped with the expected thorium mass peaks. Even with the additional acceleration voltage used to suppress the transmission of molecules the background was too high to see any signal of either $^{229}\text{Th}^+$ or $^{232}\text{Th}^+$. Additionally, the large concentration of nitrate and water transferred due to the repeated drip-dry process appears to have oxidized the reducing zirconium layer, evident from the amount of detected zirconium oxide. This might have reduced or hindered the oxygen absorption by the zirconium layer resulting in the thorium being released only in oxide form, which would not be affected by the laser ionization process.

The last version of the drip-dry filaments (filament 4 in Fig. 3) resulted in considerable improvement of the deposition process resulting in a visibly reduced amount of material deposition. However, the problem with these filaments was their mechanical instability. During the cutting of the filaments, flaking

Figure 12: Mass spectra obtained with thorium filament dispensers manufactured with molecular plating (Filament 3) containing ^{232}Th and ^{229}Th . The spectra were obtained without lasers (yellow), with laser tuned to wavelengths (blue) and with lasers but the second step detuned (red).

of the top layer, most likely the zirconium layer, was observed so that majority of the ^{229}Th was lost. Still, using this particular filament type, we were able to confirm that the ionization scheme 2 using the 845.87 nm and 765.54 nm transitions (see section 4) performs comparatively well to ionization scheme 1. Testing of these filaments, regardless of the structural weakness, was possible with ^{232}Th as the concentration was 10 to 100 times higher than ^{229}Th . This scheme also reproduced the strong ionization occurring with the first step UV laser light alone, providing about 50% of the ion intensity obtained using the additional two resonant steps.

5.4. Results from molecular-plated dispensers (filament 3)

The performance of the filament dispenser (filament 3 in Fig. 3) manufactured with molecular plating was investigated in a similar manner as the drip-dry dispensers using laser ionization scheme 1. Figure 12 presents three mass spectra: one obtained without the lasers, a second with the lasers tuned into resonance in all three excitation steps, and a third with the second step laser λ_2 detuned off resonance by ~ 0.1 nm.

Notably, compared to the drip-dry ^{229}Th filaments, the thorium ion signal was obtained with much less evaporation of impurities, while the stability and sensitivity was greatly improved. Also, there are no noticeable compounds containing tantalum and zirconium, indicating a lower temperature required for thorium to be evaporated in sufficient quantities to be observed. The impurities evident in the spectrum were observed to decrease over time, indicating insufficient conditioning of the filament beforehand.

When λ_2 is tuned onto the resonance there is an increase of about 50% in the ^{232}Th signal confirming that the observed ion signal at $A/q = 232$ is indeed thorium. The signal obtained

with a detuned λ_2 represents the ionization of thorium by the first step laser alone.

The largest peak at $A/q = 248$ and the smaller peak at $A/q = 245$ are attributed to $^{232}\text{ThO}^+$ and $^{229}\text{ThO}^+$ respectively, not only from the peak position but also from the fact that their behavior was similar to that of ^{232}Th when the filament temperature was changed. Also the ratio of $^{229}\text{ThO}^+$ to $^{232}\text{ThO}^+$ (1:15) is reasonably similar to the ratio of ^{229}ThO to ^{232}ThO in the solution (1:7) used for molecular plating.

The $^{232}\text{ThO}^+$ signal only drops by about 10% when λ_2 is detuned indicating that the majority of the thorium oxide ions are formed by UV light ionizing neutral ^{232}ThO rather than formation via oxidation of the $^{232}\text{Th}^+$ ions. The ratio of atomic thorium ions to thorium oxide ions is significantly smaller compared to the previous mass spectra in Fig. 10. The reason for this is unknown however it could be related to variations in the reduction capability of the zirconium layer. There was also abundant $^{232}\text{ThO}(\text{OH})^+$ (not shown in Fig. 12) indicating a strong presence of water in the system which might be due to residual water being evaporated from the filament or the gas cell as the system was not thoroughly baked beforehand.

^{229}Th is believed to be present as a small peak in the mass spectra, about a factor of 10 smaller than ^{232}Th . The ^{229}Th peak does not react to the detuning of λ_2 because the wavelengths used for λ_2 and λ_3 should be corrected for isotope shifts which, in scheme 1 of Fig. 5, are not known. The first step has only a small isotope shift of about 50 cm^{-1} (0.008 nm) [45] and is therefore well within the laser linewidth. Laser ionization of ^{229}Th has therefore proceeded via λ_1 alone.

6. Conclusions and outlook

We have successfully developed a thorium ion source by combining laser resonance ionization and evaporation of atomic thorium from filament dispensers fabricated at the Institute of Atomic and Subatomic Physics (ATI) of TU Wien. Some of the filaments resulted in reasonably pure mass-separated thorium ion beams exceeding 10^6 ions/s, which is easily sufficient for a collinear laser spectroscopy measurement. The largest challenge was in the manufacturing of a filament dispenser with good cleanliness and with sufficient reduction capability for thorium to be evaporated as an atomic species while maintaining a good structural integrity. Impurities not only resulted in thorium being released in an undesired oxide form, but it also caused interfering ion beams due to the rich gas phase chemistry. These problems were exacerbated by the high filament temperature required for efficient evaporation of thorium.

Table 2 summarizes the performance of the different filaments in this work. The molecular-plated filament showed the most promising results while the drip-dry filaments varied depending on the purity and integrity of the deposited material and reducing layer. These two characteristics are critical for controlled and efficient evaporation of thorium. It should be ensured that no substantial shedding of the deposited material or reducing layer occurs when the deposition spot on the filament is subjected to physical forces such as bending due to heat expansion or during filament cutting. Also, the substrate

Filament	Solution	Droplet application	Isotopes	^{229}Th -Activity	Performances
1. Drip-dry	9.5 mg $^{232}\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ to 10 ml	$1 \times 1\mu\text{L}$	^{232}Th	-	Intense and stable yields.
2. Drip-dry	3.8 kBq in 5 mL 0.1M HNO_3 dried and redissolved to 40 μL 0.01M HNO_3	$30\text{-}40 \times 1\mu\text{L}$	$^{229,232}\text{Th}$	160 Bq	Problem of Zr-impurities
3. Mol. plating	5 kBq in 5 μm 0.06M HNO_3 which mixed to 8 ml isopropanol	(plating)	$^{229,232}\text{Th}$	190 Bq	Good stability, poor deposition efficiency.
4. Drip-dry	8 MBq in 8 mL H_2O	$1 \times 1\mu\text{L}$	$^{229,232}\text{Th}$	760 Bq	Poor mechanical stability, flaky.

Table 2: Summary table of the filaments used in this work. All filaments listed in the table have Ta backing with 1 μm Zr coating as substrate and 1 μm Zr layer on top for reduction. Activities refer to ^{229}Th activities.

and reduction layer material should be chosen to withstand the temperature required for the evaporation of thorium while the adsorption enthalpies favor efficient desorption [28]. Although the present work was solely focused on thorium, all of these attained insights are also applicable to other filament sources in which actinides or other refractory elements are deposited between a substrate and reducing layers.

This work demonstrated the importance of understanding the complexities when performing resonance excitation on actinides with lasers in gaseous environments. The high atomic level density in actinides can lead to unexpected phenomena, notably the difference in the ionization scheme behavior between the vacuum and gaseous environments. Effects including collisional quenching phenomena will be explored in future work. Such studies are also of interest for resonance ionization spectroscopy of the heavier actinides, including nobelium [23], and superheavy elements that can only be produced on-line with very low cross sections and with sparsely known atomic structure.

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