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# Resonance Ionization Spectroscopy of Thorium

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**Abstract.** Here we describe experiments aimed at developing an element-selective ion source for thorium (Th). The technique applied is resonance ionization spectroscopy (RIS) with a thermal atom beam. Ionization schemes for isotopically nonselective ionization of Th as well as for isotopically selective ionization of $^{230}$Th are proposed. The RIS-scheme used is two-photon two-colour ionization with excitation in the ultraviolet spectral range between 244 nm and 267 nm or in the visible spectral range between 485 nm and 529 nm. Ionization of the excited atoms is performed either by ultraviolet photons or by visible photons, depending on the energy required for this process.

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Thorium (Th) is an important tracer in oceanography and environmental physics. The most important applications for the long-living isotopes $^{232}$Th (half-life $1.4 \times 10^{10}$ a) and $^{230}$Th (half-life 75400 a) are the dating of deep-sea cores [1], marine carbonates [2] and Mn-encrustations [3]. The concentrations of these isotopes can be determined by alpha-spectrometry [4] or, more precisely, by mass spectrometry [5]. However, the mass-spectrometric measurements of Th isotopes are restricted to selected samples with high $^{230}$Th/$^{232}$Th ratios, such as corals ($^{230}\text{Th}/^{232}\text{Th} \approx 10^{-1}$–$10^{-3}$), whereas most other natural sample materials show isotope ratios of about $10^{-6}$ and lower [5]. In particular, the measurements of such sample materials require abundance sensitivity for a mass spectrometer of at least $10^{-8}$.

The limits of these measurements are mainly determined by the thermal ionization sources used in these mass spectrometers. The ionization energy of Th is 6.08 eV [6]. If a Re-filament with a work function of 5.1 eV is used, the Langmuir-Saha equation gives an ionization probability of less than $3 \times 10^{-3}$ for Th. It was found that for samples with higher $^{232}$Th content the ionization probability even may be lower than $10^{-4}$ [7].

## 1 Resonant Photoionization Schemes for Thorium

To attain higher ionization probabilities, especially in the case of higher $^{232}$Th content, we ionize Th with the well-known RIS technique [8, 9]. The following ionization schemes are suited for Th.

1. Resonant absorption of an ultraviolet photon with more than 4 eV energy and subsequent ionization with a visible photon with more than 2 eV energy (Fig. 1A).
2. Resonant absorption of a visible photon with more than 2 eV energy and subsequent ionization with an ultraviolet photon with more than 4 eV energy (Fig. 1B)
3. Resonant absorption of an ultraviolet photon with more than 3 eV energy and subsequent ionization with a photon of the same wavelength (Fig. 1C).
4. The second ionization scheme presented above can be extended to a three-photon two-intermediate-level photoionization process. After two-resonant absorptions of visible photons with more than 2 eV energy, ionization is achieved by a third visible photon (Fig. 1D).

The third and fourth ionization schemes described above are not realized in this study. Here we focus our attention on the two-photon ionization schemes described in 1 and 2. However, with the two-photon ionization described in item 2 the basis is laid for three-photon-ionization.

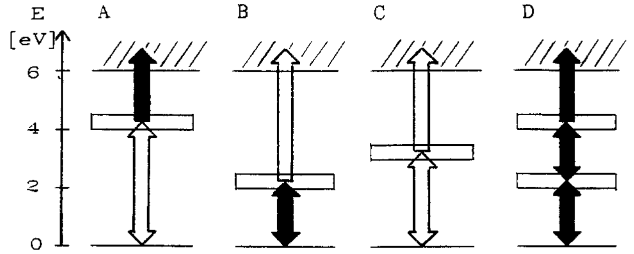

**Fig. 1.** Possible resonant ionization processes for Th: Transitions caused by visible photons are marked by *black arrows* and those caused by ultraviolet photons are marked by *white arrows*. Energy ranges with suitable transitions are marked by *rectangles*

## 2 Experimental Set-Up

### 2.1 The Laser System

We use a pulsed tunable dye laser (Lamda Physik, FL2000), providing 10 ns pulses with 25 mJ energy. With the dye coumarin-307 the wavelength range from 485 nm up to 529 nm is accessible. The bandwidth of the laser is approximately 0.8 $\mathrm{cm}^{-1}$ and can be reduced with an intracavity etalon down to 0.08 $\mathrm{cm}^{-1}$. For the experiments described here the laser is operated without intracavity etalon. The dye laser is pumped by a XeCl-excimer laser (Lambda Physik, EMG201MSC), working at 308 nm with pulse energies up to 400 mJ and 28 ns pulse duration. The maximal repetition rate of the system is 80 Hz. Via excitation of the Th atoms in the visible spectral range ionization is achieved by overlapping a part of the excimer laser beam to the dye laser beam. For excitation in the ultraviolet range, tunable ultraviolet laser light is produced by frequency-doubling in a BBO crystal (Castech, China). The pulse energy of the ultraviolet laser light is about 1 mJ, the bandwidth approximately 0.6 $\mathrm{cm}^{-1}$ (with etalon 0.06 $\mathrm{cm}^{-1}$). The excited atoms are ionized by the fundamental wavelength of the dye laser. The dye laser is calibrated against spectral reference lines of xenon (Xe) which are also observed by RIS (Xe has three two-photon resonance in the spectral range investigated here [10]). The spectrum of Th is well known and shows a high line density [11]. Exact calibration of the dye laser is therefore carried out by line identification of the measured Th RIS lines.

### 2.2 The Ionization Chamber

To be accessible to RIS, solid-state bodies like Th have to be transferred to the gas phase. To measure long times without the need to open the vaccum system, we constructed an oven to evaporate Th in the mg range from a tungsten boat (Balzers, BD482 000-T). Boat temperatures during analysis are 1400–1500° C using continuous heating with an electric current of 65 A.

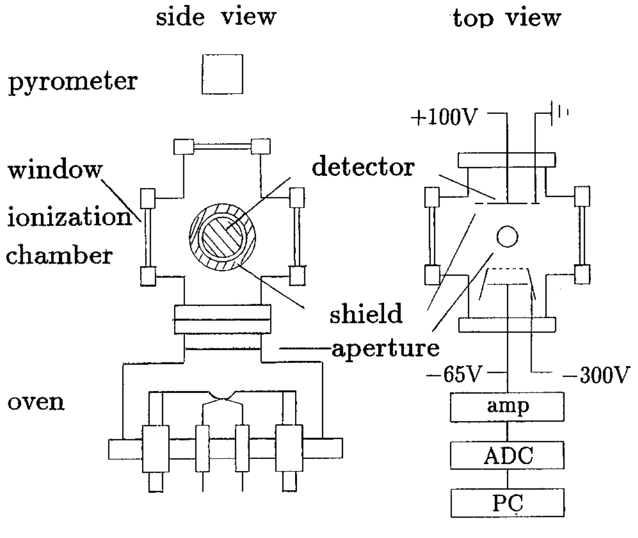

**Fig. 2.** The ionization chamber with oven and ion detector

**Table 1.** Operating conditions of the detector

| $U_{\text{anode}}$ | $U_{\text{ring}}$ | $U_{\text{cathode}}$ | $U_{\text{shield}}$ |
|---|---|---|---|
| +100 V | 0 V | −65 V | −300 V |

$U_{\text{anode}}$: Anode voltage, $U_{\text{ring}}$: Voltage applied to the ring around the anode, $U_{\text{cathode}}$: Cathode voltage, $U_{\text{shield}}$: Voltage applied to the shield of the cathode

A part of the evaporated atoms enters the ionization chamber through an aperture (Fig. 2). Optical access is provided by three quartz windows. One of these windows is positioned opposite the oven, making it possible to measure the temperature with an optical pyrometer. The other two windows are viewports for the laser beams. Additionally, it is possible to measure the temperature in the middle of the boat with a W-Re thermo couple.

The view from the top in Fig. 2 shows the ion detector. The anode of the detector is constructed as a circular plate. A 4 mm thick ring lies concentrically around this plate.

The cathode is also constructed as a circular plate, situated in the inner part of a funnel-shaped shield. The ions reach this plate after passing through a grid in the middle of the shield. The shield and the outer ring of the anode suppress the detection of photo electrons and ions generated at the windows. The resonantly generated ions are detected by the two inner plates.

Table 1 lists the voltages applied to the detector. They have been determined experimentally to allow maximal suppression of background while at the same time allowing detection of the ions in the plateau of the detector. The photons in our experiment have energies up to 5.0 eV (corresponding to wavelengths greater than 245 nm). To provide suppression of photo electrons being generated directly at the detector, the detector is nickelplated (work function 5.1 eV).

Data processing is done by a PC-controlled CAMAC system. Detected signals are digitalized by a peak sensitive ADC (Le Croy, 2259B) triggered by the delayed pulse of the excimer laser. Ion signal, pulse energy and laser bandwidth are measured simultaneously, measuring the bandwidth by observation of interferences behind an etalon while scanning the laser.

## 3 Measured Resonant Ionization Spectra of Thorium

The ion signal recorded as a function of the wavelength in the spectral range investigated is presented in Figs. 3 and 4. Maximal intensities measured correspond to about $3 \times 10^4$ ions per laser pulse. With a repetition rate of about 80 Hz this results in an ion current of about $2.4 \times 10^6$ ions per second.

Tables 2 and 3 show the relevant levels for the ionization schemes described. The data are ectracted from [11, 12]. A comparison of the measured spectra with the levels listed in the tables shows that ions can be generated via all know levels with $J = 1, 2$ or 3. In addition to these lines, a variety of others were found, the majority of them with lower intensity. To understand their origin it is important to recognize that due to evaporation a fraction of the Th

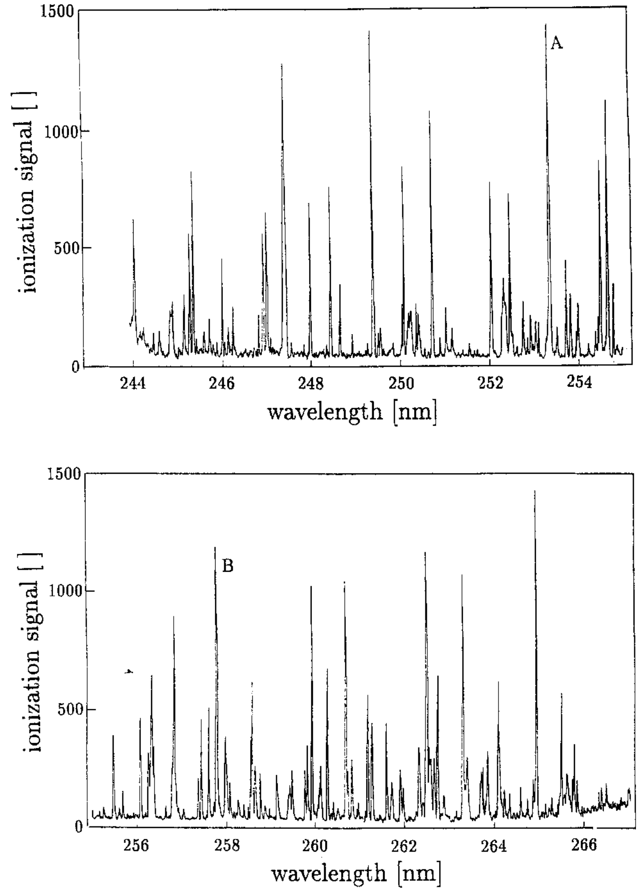

**Fig. 3.** The ion signal of Th in the ultraviolet spectral ranger investigated. The ion signal is given in arbitrary units

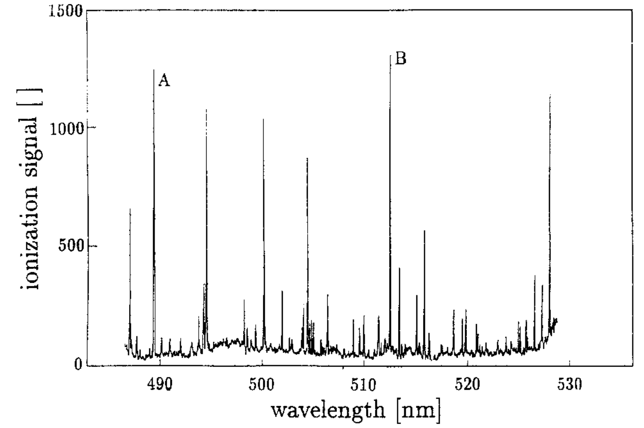

**Fig. 4.** The ion signal of Th in the visible spectral range investigated. The ion signal is given in arbitrary units

**Table 2.** Levels for two-photon ionization of Th with excitation in the ultraviolet spectral range. The data are extracted from [12]

| $k$ [cm$^{-1}$] | $\lambda$ [nm] | $J$ [$\hbar$] | $I_S$ [mK] |
|---|---|---|---|
| 37635.96 | 265.698 | 3 | −674.3 |
| 37737.00 | 264.987 | 2 | −215.2 |
| 37954.96 | 263.465 | 3 | −661.1 |
| 37970.27 | 263.359 | 2 | −350.2 |
| 38053.04 | 262.786 | 3 | −195.2 |
| 38089.00 | 262.538 | 2 | −531.7 |
| 38216.95 | 261.659 | 3 | −465.7 |
| 38278.88 | 261.235 | 1 | −508.4 |
| 38355.34 | 260.715 | 2 | −403.6 |
| 38416.23 | 260.301 | 3 | −449.6 |
| 38669.77 | 258.595 | 2 | −677.9 |
| 38675.35 | 258.557 | 3 | −752.1 |
| 38788.84 | 257.801 | 3 | −646.9 |
| 38814.24 | 257.632 | 2 | −769.5 |
| 38840.55 | 257.458 | 1 | −506.4 |
| 38998.97 | 256.412 | 3 | −584.7 |
| 39264.69 | 254.677 | 3 | −482.5 |
| 39411.91 | 253.725 | 1 | −380.6 |
| 39468.68 | 253.360 | 3 | −242.5 |
| 39611.52 | 252.447 | 3 | −696.9 |
| 39985.72 | 250.084 | 3 | −660.7 |
| 40096.23 | 249.395 | 2 | −465.5 |
| 40254.97 | 248.412 | 3 | −518.9 |
| 40980.70 | 244.012 | 3 | −326.4 |

$k$ [cm$^{-1}$]: Wave number, $\lambda$ [nm]: Wavelength, $J$ [$\hbar$]: Total angular momentum, $I_S$ [mK]: Isotope shift (1 mK = 0.001 cm$^{-1}$, $I_S = [k(^{232}\text{Th}) - k(^{230}\text{Th})] \times 1000$)

**Table 3.** Levels for two-photon ionization of Th with excitation in the visible spectral range. The data are extracted from [11, 12]

| $k$ [cm$^{-1}$] | $\lambda$ [nm] | $J$ [$\hbar$] | $I_S$ [mK] |
|---|---|---|---|
| 18614.33 | 537.0710 | 1 | −475.4 |
| 18930.29 | 528.1069 | 3 | −445.7 |
| 19039.15 | 525.0873 | 2 | −153.0 |
| 19503.14 | 512.5902 | 3 | −363.6 |
| 19516.98 | 512.3541 | 2 | −418.6 |
| 19817.18 | 504.4720 | 1 | −397.4 |
| 20214.92 | 494.5459 | 3 | −440.2 |
| 20423.49 | 489.4955 | 1 | −239.0 |
| 20522.71 | 487.1290 | 2 | −448.9 |

$k$ [cm$^{-1}$]: Wave number, $\lambda$ [nm]: Wavelength, $J$ [$\hbar$]: Total angular momentum, $I_S$ [mK]: Isotope shift (1 mK = 0.001 cm$^{-1}$, $I_S = [k(^{232}\text{Th}) - k(^{230}\text{Th})] \times 1000$)

atoms is excited to low-lying metastable states. There are no lower states to which they can relax by emission taking the selection rules into consideration. If the laser provides the wavelength necessary to achieve excitation of an atom from a metastable state to a higher level, RIS occurs too. These lines can also be identified with known transitions from [11, 12].

The intensities of the lines measured depend on the grade of saturation of excitation and photo-ionization, respectively, on the population of the state resonantly ionized and on the number of atoms in the interaction zone between evaporated atoms and laser beam. Because the laser beam has been focused we expect the whole process to be saturated. Furthermore, temperature and, so, evaporation rates have been constant during analysis. Therefore, measured intensities should mainly reflect the population of the state resonantly ionized.

## 4 Conclusion

When applying the RIS ion source to a mass spectrometer it has to be taken into account that isotope shifts up to −700 mK occur between spectral lines of $^{230}$Th and $^{232}$Th

[12]. These isotope shifts are on the order of the bandwidth of the laser. It is therefore possible that, upon ionization, one isotope will be enriched. Depending on weather one wants isotopically selective ionization or not, ionization has to be achieved via levels with high or low isotope shift and the laser has to be run with narrow or broad bandwidth, respectively. Finally, the influence of isotope shift has to be determined in mass-spectrometric measurements of standards.

On account of isotope shifts known from [12] and the observed line intensities in this experiment, we propose lines for isotopically selective and isotopically nonselective ionization of Th. These lines are marked in Figs. 3 and 4 with "$A$" for isotopically nonselective ionization ($\lambda = 253.56$ nm and $\lambda = 489.50$ nm) and with "$B$" for isotopically selective ionization of $^{230}$Th ($\lambda = 257.80$ nm and $\lambda = 512.60$ nm). Depending on the bandwidth $\Delta k_{\mathrm{L}}$ of the laser used for excitation and on the isotope shift $I_{\mathrm{S}}$, it is possible to calculate the enrichment $A$ of two-photon ionization [9]:

$$A = \left(\frac{2I_{\mathrm{S}}}{\Delta k_{\mathrm{L}}}\right)^2 . \tag{1}$$

For three-photon ionization selectivity can be increased substantially according to

$$A = A_1 A_2 , \tag{2}$$

with $A_1$ and $A_2$ being the enrichment of first and second excitation, respectively.

A quantitative consideration of the levels one can excite from the ground state (Tables 2, 3) with (1) shows that only with narrow-bandwidth excitation with the help of an intracavity etalon in the resonator of the laser and with isotope shifts greater than 500 mK is significant enrichment of $^{230}$Th upon ionization possible. For example level $k = 38788.84\,\mathrm{cm}^{-1}$ ($I_{\mathrm{S}} = -646.9$ mK) and a bandwidth $\Delta k_{\mathrm{L}} = 0.06\,\mathrm{cm}^{-1}$ in the ultraviolet spectral range provide an enrichment greater than 400.

For three-photon ionization, for example by subsequent excitation of the levels $k_1 = 19503\,\mathrm{cm}^{-1}$ with $I_{\mathrm{S}} = -363.6$ mK and $k_2 = 37893\,\mathrm{cm}^{-1}$ with $I_{\mathrm{S}} = 735.7$ mK, (2) yields an enrichment factor of 10000 if the laser bandwidth is $\Delta k_{\mathrm{L}} = 0.08\,\mathrm{cm}^{-1}$. However, the precondition is the use of three lasers: two for the excitations and the third for ionization. The lasers used for excitation should provide only moderate photon fluxes to avoid saturation broadening. Thus the full selectivity of excitation is achieved. To saturate ionization the third laser should provide sufficiently high photon fluxes.

In the case of isotopically nonselective ionization, excitation can be saturated to broaden the linewidth and thus to suppress isotope selectivitiy. Hence, for isotope shifts between $-200$ mK and $-300$ mK and a laser bandwidth of $0.8\,\mathrm{cm}^{-1}$, the enrichment is expected to be negligible. Recently published investigations of the influence of isotope shift in resonance ionization mass spectra of Ti and Os confirm this hypothesis [13]. Because pulsed laser systems provide higher photon fluxes than continuous-wave lasers do, they are better suited to suppress isotope effects by saturation broadening. For example in contrast to the investigations of Ti and Os with pulsed lasers cited above, investigations of resonance ionization mass spectra of Th with continuous-wave lasers show undesirable isotope biases in $^{230}$Th/$^{232}$Th ratios [14].

Further investigations of the transitions proposed, in particular investigation of saturation behaviour and determination of the cross sections of the different steps, are in progress and will be published elsewhere in the future.

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