Source production for the neutrino mass experiment ECHo

Highly efficient ion implantation of ultrapure ¹⁶³Ho

Dissertation

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Abstract

The ECHo collaboration addresses the determination of the electron neutrino mass by recording the spectrum following electron capture of ¹⁶³Ho. Due to the tiny fraction of events (10^{-12} of counts) in the last 1 eV below the endpoint, where the major distortion of the spectrum by a non-vanishing neutrino mass is expected, the measurement is very sensitive to background events. The number of ¹⁶³Ho atoms, which is required for reasonable statistics in the decay spectrum is produced from enriched ¹⁶²Er by neutron capture and subsequent β -decay in the ILL high flux nuclear reactor. Unfortunately this also introduces significant contaminations of other radioisotopes, which have to be quantitatively removed by radio-chemical separation. The purity of the ECHo source material during the whole preparation process is monitored by a variety of analytical techniques, including γ -spectrometry, neutron activation analysis, inductively coupled plasma mass spectrometry, and resonance ionization mass spectrometry. The only radioactive contaminant remaining in the isolated Ho sample is the long-lived isomer ^{166m}Ho.

To reach sub-eV sensitivity, a large number of individual microcalorimeters of 180 µm × 180 µm size are required, into which ¹⁶³Ho must be fully embedded in chemically pure form. The application of resonance ionization at the RISIKO mass separator guarantees optimum elemental as well as the required high isotopic selectivity for purification of ¹⁶³Ho and suitable conditions for ion implantation directly into the ECHo Metallic Magnetic Calorimeters (MMCs). With a newly developed two-step resonance ionization scheme to an auto-ionization level at 48566.95(6) cm⁻¹, saturation in both optical transitions and a superior ionization and separation efficiency of $69(5)_{stat}(4)_{sys}$ % was reproducibly accomplished.

The ultimate ¹⁶³Ho activity per detector pixel is intrinsically limited to about 2 Bq because of resputtering effects. In-situ deposition of Au onto the implantation area of the absorbers using pulsed laser deposition, which is performed in parallel to the ion implantation process, allows to overcome this restriction and to achieve the required 10 Bq activity per detector pixel with an overall efficiency of 13(2) %, primarily limited by spatial overlap of ion beam and detector pixels. Additionally, it ensures homogeneous Au:Ho-layer formation with a ¹⁶³Ho concentration with respect to atom number in the order of 1%.

With the developed methods, a number of ECHo detectors have already been implanted which have yielded promising results including ¹⁶³Ho decay spectra in various measurements. Additionally, the majority of required specifications for the just started second project phase ECHo-100k are already met.

Contributions

This thesis is based on the five publications listed below. The author provided major contributions to the experiment, has performed the relevant simulations and data analysis. In addition, he is the main author of articles III and IV. His contribution to article I concerned the measurement and data analysis of the Dy and Ho isotope ratios via RIMS as described in Section 3.3 of the publication. In article II and V, the author has delivered a major contribution to the experiment and discussion.

Apart from the work presented here, the author has been involved in laser spectroscopic studies on Te at ORNL, USA and accelerator mass spectroscopic (AMS) measurements at HZDR, Germany. Additionally, he was contributing to laser and mass spectrometric measurements at the RISIKO and MABU facilities of the working group LARISSA at the Institute of Physics, JGU Mainz, Germany on many elements, e.g. Mn, Ra, and Lu.

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Chapter]

Introduction

The Royal Swedish Academy of Science has awarded Takaaki Kajita and Arthur B. McDonald in 2015 with the Nobel Prize in Physics. They have discovered neutrino oscillation and have thus showed that neutrinos are massive particles [1]. In the standard model (SM) of particle physics neutrinos are massless and therefore the unexpected observation of their oscillation is the first reference for physics beyond the SM.

In the recent years, extensive attempts on neutrino spectroscopy have been initiated but the majority of specific properties still remain unknown. Oscillation experiments can only hint to the squared mass differences

$$\Delta m_{ij}^2 = m_i^2 - m_j^2, \quad i, j \in \{1, 2, 3\}$$
(1.1)

of the mass eigenstates (ν_1 , ν_2 , ν_3), that are connected to the three neutrino generations (ν_e , ν_μ , ν_τ) by the Pontecorvo-Maki-Nakagawa-Sakata (PMNS) matrix [2]:

$$\begin{pmatrix} |\nu_e\rangle\\ |\nu_{\mu}\rangle\\ |\nu_{\tau}\rangle \end{pmatrix} = \begin{pmatrix} U_{e1} & U_{e2} & U_{e3}\\ U_{\mu1} & U_{\mu2} & U_{\mu3}\\ U_{\tau1} & U_{\tau2} & U_{\tau3} \end{pmatrix} \cdot \begin{pmatrix} |\nu_1\rangle\\ |\nu_2\rangle\\ |\nu_3\rangle \end{pmatrix}.$$
(1.2)

While we know that $\Delta m_{21}^2 \approx 7.4 \times 10^{-5} \text{ eV}^2 > 0$, the sign of the mass splitting $|\Delta m_{31}^2| \approx 2.5 \times 10^{-3} \text{ eV}^2$ is presently unknown [3, 4]. Therefore, two mass orderings are possible: $\Delta m_{31}^2 > 0$, the so called "normal" ordering (NO) or $\Delta m_{31}^2 < 0$, the "inverted" ordering (IO). At the moment, the global analysis of oscillation data favors the NO over the IO at more than 3σ [5].

To obtain the neutrino masses accurately and without model dependency, it is obligatory to perform direct mass measurements. For the electron anti-neutrino $\bar{\nu}_e$ and the electron neutrino ν_e this can be realized by analyzing the endpoint region of a β -spectrum or an electron capture (EC) spectrum, respectively. Since neutrinos

have no charge, they could be Majorana particles, i.e. their own antiparticles, but this remains to be proven. The mass determination by analyzing the β -spectrum is realized e.g. in the KATRIN [6] or Project 8 [7] experiment, while the EC spectrum analysis is the basis of the HOLMES [8] and the ECHo [9] project. The currently most accurate direct value of an upper limit for the anti-electron neutrino mass was determined to $m_{\nu} < 2.2$ eV from analyzing the tritium β -spectrum [10].

1.1 The ECHo experiment

The ECHo experiment explores the path of determining the electron-neutrino mass with the goal to access an energy range below 1 eV via a high precision, high statistics calorimetric measurement of the ¹⁶³Ho EC spectrum.

In electron capture, one proton in the nucleus absorbs an 1s electron from the K-shell or, in rare cases, an 2s electron from the L-shell of the atom. By emitting an electron neutrino, the proton transforms into a neutron:

$$p + e^- \to n + \nu_e. \tag{1.3}$$

The nuclear charge number *Z* becomes *Z* + 1, whereby the process competes with the β^+ -decay. However, this is only the case if the mass difference

$$\Delta M = M_A - M_T = \frac{Q}{c^2} > 2m_e,$$
 (1.4)

where M_A and M_T are the atomic masses of the mother and daughter nuclide, respectively, as otherwise the β^+ -decay is energetically forbidden. Q is the decay energy and $m_e \approx 9.1 \times 10^{-31}$ kg [11] is the electron mass. The radioisotope ¹⁶³Ho, which is used in the ECHo project, is particularly well suited for the analysis of the EC spectrum as it has the lowest decay energy of $Q_{EC} = 2.833(45)$ keV [12]. Thus, it is far below the limit for β^+ -decay of 1.022 MeV.

The mass of the neutrino dissipates energy during decay and thus causes the shape of the decay spectrum in the end region to change and especially the maximum achievable decay energy to be lower than that of the Q-value (mass difference between mother and daughter nuclide). Figure 1.1 shows a theoretical spectrum of the ¹⁶³Ho EC decay with and without neutrino mass.

For a high-resolution measurement of energy deposition below 3 keV, special detectors are required. As has been shown in [14], the prerequisites for such investigations are achieved by low-temperature microcalorimeters. For this purpose, the ECHo collaboration applies the most suitable properties of Metallic Magnetic Calorimeters (MMCs) [15]. For accurate measurements preventing any energy loss, it is important that the ¹⁶³Ho source is incorporated as an intrinsic part of the detector and is in this way completely enclosed by it. To protect against measurement errors, a compromise must be made between high counting rates for good



Figure 1.1.: Theoretical spectrum of the ¹⁶³Ho EC decay for a total number of 10¹⁴ events with and without neutrino mass. Only first order excitations are considered, for higher orders refer to [13]. Figure adapted from [9].

statistics and the reduction of unavoidable and non-resolvable pile-up events. This results in a maximum activity per detector of just 10 Bq, which corresponds to 10 events per second produced by a number of 2.08×10^{12} atoms ¹⁶³Ho. The high statistics which is desired in high resolution spectroscopy in low probability regions therefore requires the use of numerous detectors.

Ion beam implantation used for ¹⁶³Ho introduction into the MMCs is the favorite method because of the full incorporation of the source into the detector crystal structure under high-purity vacuum conditions. Additionally, it offers the ability to precisely monitor the ion current during the process, allowing in situ quantification of deposition amount. This work focuses on the sophisticated purification and efficient ion implantation of the ¹⁶³Ho source. The detection method and the analysis of the spectra are not discussed further here, for this I refer to other publications of the ECHo Collaboration [9, 13, 16, 17].

1.2 Resonance ionization mass separation

The synthetic radioisotope ¹⁶³Ho has a half-life of 4570(50) a [18]. Its production, chemical separation and full characterization is described in detail in Chapter 2. The sample resulting from this process primarily contains ¹⁶³Ho, stable ¹⁶⁵Ho, and the long-lived isomer ^{166m}Ho ($T_{1/2} = 1132(4)$ a) [19]. If ^{166m}Ho is present in the MMCs, its emitted radiation leads to unacceptable background in the spectrum of ¹⁶³Ho. The sample must therefore be mass-separated to ensure suppression of the content to an atom ratio of ^{166m}Ho/¹⁶³Ho < 5 × 10⁻⁹ within the detectors. In

order to reduce the required total sample quantity to a minimum, high efficiencies are required in all process steps.

The application of a resonance ionization laser ion source at a magnetic sector field mass separator has the advantages of exceptionally high overall efficiency including ionization as well as transmission. In addition, it has a high selectivity for the element of interest in the ionization process and the mass due to the magnetic separation. In this way the highest sample purity is ensured. The technique is therefore particularly well suited for the production of radioactive ion beams at isotope separation on-line (ISOL) facilities such as CERN-ISOLDE [20] or TRIUMF-ISAC [21], where both qualities are of great importance. Exotic nuclides are produced by projectile-induced nuclear reactions at a production target and are delivered to atomic and nuclear structure experiments. In addition, this method is used for the purification and implantation of single isotope samples for a number of applications as:

- 1. Off-line extraction of medical isotopes from accelerator targets as developed and applied in the CERN-MEDICIS project [22].
- Extraction of rare isotopes from accelerator beam dumps [23], e.g. highly pure ⁵³Mn for measurements of half-life and neutron capture cross-sections [24].
- Ion implantation of well-defined amounts of a given radionuclide as radioactive standard, e.g. ²²⁶Ra as source of ²²²Rn for detector calibration in the MetroRADON EU project [25].

1.2.1 Resonance ionization

Laser resonance ionization is a step-wise excitation process of atoms by precisely tuned laser light along strong optical dipole transitions. The final step has a significant probability for ionization, when the finally populated energy level is located above or near the ionization potential. The technique of resonance ionization spectroscopy (RIS) is a versatile tool to explore the atomic level structure because of the high ionization probability and intrinsic elemental selectivity [26].

The starting point of every resonant laser ionization is the atomic ground state or a thermally populated excited state. Optical dipole transitions are induced via radiation with energy of E = hv to transfer a valence electron from one energy level of the atomic shell to another. The electric dipole transitions are only allowed if the selection rules are preserved. In Table 1.1 the key rules are listed. The finally populated step is either an autoionizing state located above or a Rydberg state just below the ionization potential. In this way, high ionization probability and a fully resonant process is ensured (see Figure 1.2).

For autoionization, more than one electron is in an excited state. Either one is decaying into the ground state by photon emission or transfers its energy by

	selection rule	comment
Rigorous rules	$\Delta J = 0, \pm 1$ $\Delta M = 0$ $\Delta M = \pm 1$	$J = 0 \rightarrow J = 0$ forbidden linearly polarized light circularly polarized light or two linear polarized, perpendicular to each other
LS coupling	$\Delta l = \pm 1$ $\Delta L = \pm 1$	one-electron atom many-electron atom with $\Delta S = 0$
Intermediate coupling	$\Delta L = 0, \pm 1, \pm 2$	many-electron atom with $\Delta S = \pm 1$

Table 1.1.: Selection rules for electric dipole transitions [27].

Coulomb interaction to the other one. The total excitation energy E is than given by the sum of the excitation energies E_i of the individual electrons i which is well above the ionization potential. This leads to a distinct structure of the ionization continuum with well localized strong resonances.

Rydberg states with a large principal quantum number n also provide a high ionization probability because of the low residual binding energy. A small distortion from a collision or an electric field can easily ionize the Rydberg atom. This is the case e.g. inside the hot cavity or the extraction field of the laser ion source. The energy E_n of a Rydberg state with principal quantum number n with respect to the energy of the ionization potential E_{IP} is given by the Rydberg-Ritz formula:

$$E_n = E_{\rm IP} - R_{\rm red} \frac{1}{(n-\delta_n)^2}, \quad n \in \mathbb{N}.$$
(1.5)

Originally it was derived only for the single electron spectrum of the hydrogen atom [28]. The quantum defect δ_n is the correction for residual influences of the inner core of electrons [29]. The Rydberg constant is multiplied by the reduced mass $R_{\text{red}} = R_{\infty} \cdot m_{\text{nucleus}} / (m_{\text{nucleus}} - m_{\text{electron}})$ to account for the nuclear mass in a two-body representation.

Details on specific futures and properties of two- and three-step excitation schemes and their development for highly efficient ionization in the spectrum of Ho atoms for the ECHo project are described in Chapter 5 and Chapter 3, respectively.

1.2.2 Solid-state laser system

For reliable long-term operation of a laser ion source, an all solid state laser system is favorable because it provides a number of advantages like low maintenance



Figure 1.2.: Resonance ionization schemes with two or three steps. Optical transitions indicated by red and blue arrows are addressed by precisely tuned laser light. The two different final steps with high ionization probability are discussed in the text.

requirements and stability. Another important parameter is the broad, continuous tunability for initial level search and optical spectroscopy in either mid or high resolution. To ensure high ionization probability, a well adapted spectral bandwidth in the GHz range maintained with high stability as well as highly repetitive pulsed operation is essential. Because commercially available tunable lasers do not meet all requirements in parallel, the systems used here for resonance ionization are developed by the LARISSA group using Ti:sapphire crystals as active medium. They can be pumped with wavelengths between 420 nm to 600 nm, making commercially well distributed and supported frequency doubled Nd:YAG lasers with 532 nm an optimum choice as pumping source. The stimulated emission ranges from 650 nm to 1100 nm and the spectral operation range has to be selected and narrowed by frequency selective elements.

In this work, two different types of Mainz Ti:sapphire lasers were used. Both are pumped with 15 W to 18 W at 10 kHz repetition rate and have somewhat comparable parameters: a Z-shaped resonator provides a pulse length of about 50 ns, an average output power of 1 W to 4 W, and good beam quality with $M^2 < 1.3$. The standard version with birefringent filter and Fabry-Pérot etalon as frequency selective components is mostly used for highly efficient ionization using a previously developed ionization scheme [30]. The alternative grating-assisted version is equipped with a refraction grating for wide-range frequency selection and can be mode-hop-free tuned through almost the entire emission range of the Ti:sapphire crystal with a slightly lower linewidth as the standard one of about 2 MHz [31]. Therefore, it is specifically well suited for spectroscopic purposes and ionization scheme development.

The fundamental Ti:sapphire wavelength emission in the near-infrared region provides low photon energies between 1.1 eV to 1.9 eV. To reach the 6.0198 eV ionization potential of Ho [32], more than three excitation steps would be needed. With the pulsed laser radiation, higher photon energies can easily be reached by means of non-linear optical processes [33]. For second, third, and fourth harmonic generation (SHG/THG/FHG) as well as sum and difference frequency generation (SFG/DFG), optical active crystals with birefringent properties are used to fulfill the necessary phase matching condition. Applicable materials are e.g. β -barium borate (BBO) or bismuth borate (BiBO). SHG can be done outside the Ti:sapphire cavity with a single pass arrangement or in a dedicated enhancement cavity with multiple passes and higher output power in the second harmonic wavelength. To reach conversion efficiencies over 75% in a straightforward setup, it is favorable to place the conversion crystal directly inside the laser cavity intra-cavity second harmonic generation (ic-SHG) arrangement [34].

The accessible wavelengths for the Mainz Ti:sapphire laser system are shown in Figure 1.3. In Chapter 3 and Chapter 5 additional information of the laser systems in use is given.



Figure 1.3.: Wavelengths accessible with the Mainz Ti:sapphire laser system including frequency conversion methods. Adapted from [35].

1.2.3 RISIKO mass separator

The RISIKO¹ apparatus is a mass separation setup at the Institute of Physics, Johannes Gutenberg University Mainz assembled in 1990. It has initially been set up for laser-based ultra-trace analysis of environmental samples after the Chernobyl nuclear accident [36]. From the year 2000, the mass separator was mainly used for

¹German abbreviation for *Resonanzionisationsspektroskopie in kollinearer Geometrie*

resonant laser ion source development and laser spectroscopy. Figure 1.4 shows an overview of the latest RISIKO layout, which was specifically adapted to the requirements of the ECHo project within the thesis work described here.



Figure 1.4.: Sketch of the RISIKO mass separator setup. Adapted from [37].

The mass separator consists of four main parts:

- 1. The ion source comprises the sample reservoir and the ionization cavity. Both are resistively heated independently of each other. Within the ionization cavity, thermal ionization on the hot surfaces as well as (resonant) laser ionization may take place in parallel, depending on the operation conditions. All parts are in detail described in Chapter 4. The whole ion source unit is placed on a high voltage platform, typically operated at +30 kV. From there, the ions are accelerated to ground potential to undergo mass separation.
- 2. The ion optics involve the components of the extraction electrode, the Einzel lens, the orthogonal pair of electrostatic deflectors, and the quadrupole lens triplet directly ahead of the sector field separation magnet. After the magnet focus, the beam undergoes additional focusing and deflection as described in Chapter 5. In 40 mm distance to the ion source, the extraction electrode is accelerating the ions to about 10 keV. At the Einzel lens, the full kinetic energy of 30 keV is reached. The ion beam generated in this way has a large and constant spatial cross-section inside the magnet in order to ensure good mass resolution. To further optimize its entrance parameters into the magnet, the beam can be steered and shaped by the deflectors and the quadrupole lenses, respectively.
- 3. The tunable 60° sector field magnet separates different mass-to-charge ratios. At the separation slit, the desired species is transmitted while all other ones are blocked. Its slit width can be varied between 0 mm and 10 mm. For this work it is adjusted to a typical size of about 2 mm as a reasonable compromise between resolution and transmission.

4. Quantitative ion detection is realized by secondary electron multiplication (SEM) or by current measurement with a Faraday cup. The latter is used in this work because of the usually high ion currents in the nA range which would damage the SEV. For a reliable current readout, the Faraday cup is equipped with a ring electrode placed about 20 mm before it, which is set to -100 V in relation to the cup to suppress secondary electrons generated by the high-energy ion bombardment.

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1. Introduction

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Chapter 2

Publication I: Production, isolation and characterization of radiochemically pure ¹⁶³Ho samples for the ECHo project

This article was published in *Radiochimica Acta* volume 106, issue 7 (2018), pages 535-547. Since ¹⁶³Ho is not available in nature, it must be produced artificially. The most efficient production method for this purpose is neutron activation of stable ¹⁶²Er in a nuclear reactor. To avoid various contamination within the final ¹⁶³Ho sample a dedicated production, isolation, and purification strategy is necessary and was worked out as described in this publication. It includes multiple steps of chemical separation and involves a variety of sophisticated analysis techniques. The full characterization of the resulting ¹⁶³Ho sample for the ECHo project, as obtained from this strategy would be impossible without resonance ionization mass spectrometry. T. Kieck correspondingly delivered the dominant contributions of Section 2.3 and 2.4 as well as measured the data listed in Table 5 and 7. In addition, he was active coauthor of the corresponding text blocks.

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Production, isolation and characterization of radiochemically pure ¹⁶³Ho samples for the ECHo-project

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Abstract: Several experiments on the study of the electron neutrino mass are based on high-statistics measurements of the energy spectrum following electron capture of the radionuclide ¹⁶³Ho. They rely on the availability of large, radiochemically pure samples of ¹⁶³Ho. Here, we describe the production, separation, characterization, and sample production within the Electron Capture in Holmium-163 (ECHo) project. ¹⁶³Ho has been produced by thermal neutron activation of enriched, prepurified ¹⁶²Er targets in the high flux reactor of the Institut Laue-Langevin, Grenoble, France, in irradiations lasting up to 54 days. Irradiated targets were chemically processed by means of extraction chromatography, which allowed separating the formed Ho from the ¹⁶²Er target-material and from the main

byproducts ¹⁷⁰Tm and ¹⁷¹Tm, which are co-produced in GBq amounts. Decontamination factors of >500 for Er and of >10⁵ for Tm and yields of $3.6 \cdot 10^{16}$ and $1.2 \cdot 10^{18}$ atoms of ¹⁶³Ho were obtained, corresponding to a recovery yield of 95 % of Ho in the chemical separation. The Ho-fraction was characterized by means of γ-ray spectrometry, Inductively-Coupled-Plasma Mass Spectrometry (ICP-MS), Resonance Ionization Mass Spectrometry (RIMS) and Neutron Activation Analysis (NAA). In this process, the thermal neutron capture cross section of ¹⁶³Ho was measured to $\sigma_{_{Ho\cdot163 \text{ to } Ho\cdot164m}}\text{=}$ (23±3) b and $\sigma_{_{Ho\cdot163 \text{ to } Ho\cdot164g}}\text{=}$ (156±9) b for the formation of the two isomers of ¹⁶⁴Ho. Specific samples were produced for further purification by mass separation to isolate ¹⁶³Ho from the Ho-isotope mixture, as needed for obtaining the energy spectrum within ECHo. The partial efficiency for this second separation step is (32 ± 5) %.

Keywords: Neutrino mass determination, ¹⁶³Ho, neutron activation, lanthanide separation, extraction chromatography.

1 Introduction

The determination of the neutrino masses is one of the major challenges of contemporary particle physics. Different approaches are followed to push the boundaries of achievable sensitivity. Among them, experiments exploring the beta decay and electron capture processes of suitable nuclides promise to provide model-independent information on the electron (anti)-neutrino mass value. The electron capture in holmium-163 experiment, ECHo [1–3], is designed to investigate the electron neutrino mass in the sub-eV/c² range. This can be achieved by the analysis of the calorimetrically measured energy spectrum following the electron capture (EC) process of ¹⁶³Ho. This is an artificial radionuclide with a half-life T_{1/2} of (4570 ± 50) a [4]. It decays by EC with a very low Q-value to

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the ground-state of ¹⁶³Dy. Production of ¹⁶³Ho is achieved via different pathways. More specifically, these include reactor production by irradiating enriched ¹⁶²Er targets, or accelerator production using light-particle induced reactions on suitable targets. Different collaborations aiming to develop sensitive experiments based on ¹⁶³Ho have chosen different production pathways [5]. Besides the need for separating Ho from a wealth of neighboring elements, including the target material, a specific aspect of all these experiments is the separation of ¹⁶³Ho from long-lived ^{166m}Ho (T_{1/2}=1200 a [6], β^-/γ -emitter), the presence of which severely disturbs the electron neutrino mass determination. The different production pathways feature different intrinsic ¹⁶³Ho/^{166m}Ho ratios. According to the results obtained in [7], an accelerator-based production pathway appears more favorable in this respect. Reactor-based approaches, however, benefit from larger projectile fluxes and cross sections as well as the often better availability of reactor irradiation time. The ECHo collaboration has thus focused on this pathway so far, while evaluation of the accelerator pathway is continued in more detail [1, 8] in parallel. After production, highperformance chemical separation of the ¹⁶³Ho from the target material is required. Interesting processes have been already developed in the case of accelerator production using Dy targets [9]. Recent work on the separation of Ho from Er has been performed in the context of a re-measurement of the ^{166m}Ho half-life [10]. Separation of ^{166g}Ho from reactor-irradiated Dy targets is described in [11, 12].

Here, we present the production of milligram amounts of ¹⁶³Ho via neutron-irradiation of Er samples enriched in ¹⁶²Er in the high-flux reactor at the Institut Laue-Langevin (ILL), Grenoble, France, and the development of a highperformance chemical separation procedure for the produced ¹⁶³Ho from the massive Er targets as well as coproduced contaminants (most importantly GBq amounts of ^{170,171}Tm).

The energy spectrum following EC decay in ¹⁶³Ho will be measured by embedding the ¹⁶³Ho in metallic magnetic calorimeters (MMCs) [13], which exhibit optimum performance for the task at hand. The preparation of the required, isotopically pure samples by mass separation of the Ho samples and the implantation into the MMCs is described in [14]. Separate samples have been prepared for high-precision measurements of the Q_{EC} value of ¹⁶³Ho using Penning-Trap Mass Spectrometry (PTMS) [15] to provide a value independent of that evaluated from the energy spectrum, and the corresponding measurement of the Q_{EC} value was recently performed [16].

2 Experimental

2.1 Prepurification of erbium target material and neutron irradiation

Neutron activation of stable nuclides generally induces (n,γ) nuclear reactions, which lead to a more neutron-rich isotope of the same element. In many cases, this isotope is radioactive and undergoes β -decay to the isobaric nuclide of the next heavier element. Notable exceptions occur for neutron-deficient nuclides like ¹⁶²Er or ¹⁶⁴Er, whose (n,γ) products are still neutron-deficient and thus undergo β^+ / EC-decay to the isobaric nuclide of the adjacent lighter element, i.e. Ho in the case of Er.

Lower-Z (Z<68) nuclides are otherwise most dominantly produced only in rather unimportant sidereactions occurring with small probability, involving charged-particle emission following neutron-irradiation. In contrast, higher-Z nuclides are abundantly produced as byproducts during neutron irradiation. Overall, this results in the fact that most impurities lead to nuclides with higher Z, while the target isotope ¹⁶²Er yields the lower-Z product ¹⁶³Ho. In this context it is noteworthy to mention that commercially available Er samples typically contain trace amounts of impurities, including other lanthanides. Therefore, our strategy for the production of radiochemically pure Ho samples includes the removal of elements with Z below that of Er prior to irradiation, during which these would lead to the production of further undesired byproducts. At the same time, such a prepurification also minimizes the formation of ^{166m}Ho by reduction of the trace amounts of ¹⁶⁴Dy and ¹⁶⁵Ho present in the commercially available enriched ¹⁶²Er. Removal of above-target lanthanide impurities prior to irradiation is less critical as many above-target radionuclides will be produced from the Er target, and further because the elements above Ho will be removed anyway after irradiation along with the Er target element. In the same way, the elimination of impurities of strongly-activating elements as Sc, Co, Eu, Ta, and Ir, leading to neutron-capture products having rather long half-lives is additionally very important to minimize the dose rate of the irradiated sample.

Figure 1 shows the main steps involved in the production and chemical isolation procedure for ¹⁶³Ho. An initial amount of 46 mg Er in the chemical form of {¹⁶²Er}Er₂O₃ (Oak Ridge National Laboratory, Tennessee, USA) with the Er isotope distribution of (20.4 ± 0.1) % ¹⁶²Er, (3.91 ± 0.05) % ¹⁶⁴Er, (33.5 ± 0.1) % ¹⁶⁶Er, (17.6 ± 0.1) % ¹⁶⁷Er, (17.3 ± 0.1) % ¹⁶⁸Er, and (7.29 ± 0.1) % ¹⁷⁰Er was dissolved in concentrated nitric acid (65 %, Suprapur, VWR, Darmstadt, Germany).



Figure 1: Block diagram showing the production and isolation strategy of ¹⁶³Ho.

After evaporation to dryness the residue was redissolved in MilliQ-water (18.2 M Ω · cm, Millipore water purification system, Milli-Q-Biocel, Millipore AG, Zug, Switzerland) and loaded onto a 9 mm diameter · 300 mm length cation exchange column (GE Healthcare Europe GmbH, Glattbrugg, Switzerland), filled with a strongly acidic, macroporous cation exchange resin in its NH,+-form. Elution was performed with 0.1 M α -hydroxy isobutyric acid (α -HIBA, Sigma Aldrich, Steinheim, Germany) solution, adjusted with concentrated ammonia (25%, Suprapur, VWR, Darmstadt, Germany) to pH=5 prior to use. The eluate was collected in 10 mL fractions. Relevant fractions for Er, which were identified in a prior test separation of neutron-activated Er (natural isotopic composition) via the 308-keV γ line of ¹⁷¹Er (analyzed by γ -ray spectrometry using a high purity germanium detector EURISYS Mesures, EGC 06-185-R operated with Interwinner 5.0 software, Baechli instruments, Affoltern am Albis, Switzerland), as well as the unpurified starting material were analyzed by inductively-coupled plasma optical emission spectroscopy (ICP-OES) for Sc, Co, Eu, Gd, Tb, Dy, Ho, Ta, and Ir. Their presence would result in relatively long-lived radioactive byproducts produced with high yields in neutron irradiations. The purified Er fractions were acidified with concentrated nitric acid (65 %, Suprapur) and loaded onto a cation exchange column (5 mm diameter · 180 mm length, H+-form). The column was rinsed with MilliQ-water and

1 M nitric acid. Afterwards the Er was stripped with 4 M nitric acid. The obtained Er solution was evaporated to dryness and redissolved in MilliQ-water. Two irradiation targets of 6.7 mg and 30 mg Er were prepared by evaporation of aliquots of this solution in quartz ampoules (suprasil, Heraeus, Kleinostheim, Germany), which were subsequently sealed for irradiation.

The quartz ampoules were irradiated in the high flux reactor of Institut Laue-Langevin (Grenoble, France) at (unperturbed) thermal neutron fluxes of $\approx 1.4 \cdot 10^{15}$ cm⁻² · s⁻¹ (6.7 mg target) for 3.9 days and $\approx 1.3 \cdot 10^{15}$ cm⁻² · s⁻¹ (30 mg target) for 53.7 days.

2.2 Isolation of holmium from the irradiated erbium targets

2.2.1 Production of tracers ¹⁶⁶Ho and ¹⁷¹Er

Tracers of ¹⁶⁶Ho (without ^{166m}Ho) and ¹⁷¹Er were produced by neutron activation of 10 mg ^{nat}Dy und 1 mg ^{nat}Er at the spallation neutron source SINQ of Paul Scherrer Institut (Villigen, Switzerland) (cf. Figure 1). No carrier added (n.c.a.) ¹⁶⁶Ho was isolated from the irradiated ^{nat}Dy target in a two step separation procedure: the target was dissolved in 0.1 M nitric acid and afterwards loaded onto an extraction chromatographic column (10 mm diameter, ca. 250 mm length), filled with LN resin (Triskem, Bruz, France). The elution of the column was performed with 1 M nitric acid applying a flow rate of 0.5 mL/min and the eluate was collected in 10 mL fractions, which were analyzed by γ -ray spectrometry for their ¹⁶⁶Dy and ¹⁶⁶Ho content. Dy containing fractions were unified, evaporated to dryness and redissolved in 0.1 M nitric acid. The process was repeated in the same way for the isolation of ¹⁶⁶Ho formed in the decay of ¹⁶⁶Dy.

The Er-tracer obtained from the activated ^{nat}Er was dissolved in 0.1 M nitric acid after its production.

2.2.2 Chemical isolation of Ho

The irradiated ¹⁶²Er targets were processed following a 4-months cooling period after irradiation. The quartz ampoules containing the neutron irradiated ¹⁶²Er were crushed and their content was dissolved in 0.1 M nitric acid. The tracers of n.c.a. ¹⁶⁶Ho and ¹⁷¹Er were added (cf. Figure 1) to enable the monitoring of the distribution of Ho and Er in the later separation process by γ -ray spectrometry. The mixture was loaded onto the same chromatographic column, which has been used for the previously described Ho-tracer isolation. The elution of the column and the collection of the fractions was done in an analogous way as the separation of the ^{nat}Dy target, but applying 2 M instead of 1 M nitric acid. The fractions were analyzed by γ -ray spectrometry (using the above mentioned detector) for their ¹⁶⁶Ho, ¹⁷¹Er, and ¹⁷⁰Tm activities.

Exclusively the Ho containing fractions isolated from the same target were unified and evaporated to dryness. The residue after evaporation was surveyed for radioactive impurities by γ -ray spectrometry using the germanium detector system specified in Section 2.1, and afterwards dissolved in 1 mL (Ho isolated from 6.7 mg Er-target) or 5 mL (Ho from 30 mg Er-target) MilliQ-water. Small aliquots of these samples were employed for the Penningtrap mass measurements of ¹⁶³Ho as reported in [15, 16].

The Er fractions were unified separately and are available as starting material for a new neutron irradiation at ILL for ¹⁶³Ho production (cf. Figure 1).

2.3 Characterization of the isolated holmium samples

To perform a more detailed analysis of the obtained Ho samples, including the determination of the stable isotopes content (especially Ho and Dy), further analytical techniques have been applied.

For Inductively-Coupled-Plasma Mass Spectrometry (ICP-MS) analysis aliquots of 100 μ L solution of Ho

isolated from the 6.7 mg Er-target or 5 μ L solution of Ho isolated from the 30 mg Er-target were added to 900 μ L and 995 μ L MilliQ-water, respectively. These samples were further diluted by 4 % nitric acid by factors of 1000 and 8196, respectively. Ir was added as internal standard to 100 ppb concentration in the solutions. The measurement was performed using an ICP-MS 7500ce (Agilent Technologies, Santa Clara, USA). The absolute concentrations of ¹⁶⁵Ho (calibration curve done with stable Ho) as well as the isobar ratios from 157 u to 174 u and 193 u (Ir standard) were determined. Additionally, a sample of the 4 % nitric acid used for dilution was analyzed in the same way as background measurement. The results were corrected by subtraction of this background.

Resonant Ionization Mass Spectrometry (RIMS) was applied for analysis of the isotope ratios of Dy in both samples. The RISIKO mass separator at the Institut für Physik, Johannes Gutenberg-Universität Mainz [14, 17] was employed. Aliquots also of 10 µL were evaporated to dryness on Zr foil pieces (Alfa Aesar, Karlsruhe, Germany, $5 \text{ mm} \cdot 5 \text{ mm}$ large, 0.025 mm thickness). Some metallic Y (more than 10 times the amount of the sample) was sputtered from a massive Y foil (Goodfellow, Bad Nauheim, Germany, 25 mm · 25 mm large, 0.125 mm thickness, 99 % purity with respect to the content of the remaining rare earth elements) over the evaporated sample aliquots on the Zr foils by use of pulsed laser deposition in an external vacuum chamber. After finishing the sputtering procedure the samples sputtered with Y were immediately transferred into the RISIKO ion source after venting the vacuum chamber with argon in order to minimize the contact of the Y metal with the ambient air. The tantalum ion source of the RISIKO facility was resistively heated by a current of about 170 A to a temperature in the range of 1300–1600 K. Ionization specific to the single element Dy was accomplished by the use of a dedicated resonant three stage laser excitation scheme based on laser radiation of 404.71 nm, 802.72 nm, and 837.66 nm wavelength [18]. Obtained ions were extracted from the ion source by applying a high voltage of 30 kV, followed by mass separation in a homogenous electromagnetic 60° sector field of 0.43 T. The detection of the ions is achieved by a Faraday cup where secondary electrons are suppressed by a repeller electrode and measurement of the resulting current by a picoamperemeter (Keithley 617, Tektronix UK Ltd., Berkshire, UK). Mass spectra were recorded by varying the field strength of the magnet in the range corresponding to collect ions of masses from 159 u to 167 u in the focal plane. After normalization to the temporal evolution of the total ion beam intensity, the Dy isotopic composition was determined this way. Additionally a background measurement of a blank Zr foil sputtered with an equal amount of Y without any sample had been performed in order to check the potential introduction of Dy-isotopes from these materials. As given in Section 3.3, no stable Dy-ion beam resulted.

Neutron activation analysis (NAA) was applied to determine the absolute content of ¹⁶⁴Dy. For this, aliquots also of 10 µL of the solutions described at the end of Section 2.2 were evaporated to dryness in small polyethylene (PE)capsules and then irradiated in the carousel irradiation position of the TRIGA Mainz research reactor at a thermal neutron flux of about $7 \cdot 10^{11} \text{ cm}^{-2} \cdot \text{s}^{-1}$ for 60 min. Simultaneously, two 3.2 mg and 4.0 mg pieces of Al-Au wire (Ortec GmbH, Munich, Germany) containing 0.1124 % Au were irradiated in separate PE-capsules placed at the bottom and top of the two stacked sample capsules for neutron flux determination. Subsequently, the aliquots of both solutions and the Al-Au wire pieces were measured repeatedly by γ -ray spectrometry using a high purity germanium detector (Canberra GX7020, relative efficiency ≥70 %) in the range of 15 min to 3 days after the end of irradiation.

2.4 Magnetic isotope separation for isolation of ¹⁶³Ho from chemically purified Ho fractions

The ¹⁶³Ho samples obtained after the chemical separation described in Section 2.2 contain minor amounts of ^{166m}Ho as the sole radioactive contaminant of concern for ECHo. For its removal, magnetic isotope separation is applied, which is suitable to suppress this contaminant sufficiently well. Therefore, samples obtained after the procedure described in Section 2.2 were used as source for subsequent laser resonance ionization and magnetic isotope separation [19]. Besides the primary purpose of removal of ^{166m}Ho, this step also enabled a reduction of the ¹⁶⁵Ho content (important to avoid significant changes in heat capacity of the MMCs). As one of the main applications of radiochemically pure ¹⁶³Ho for ECHo involves the preparation of samples fully embedded in the MMCs, the mass separation step simultaneously enabled the direct implantation of the ¹⁶³Ho ions into the ECHo MMCs [14]. The RISIKO and the General Purpose Separator (GPS) at CERN-ISOLDE [20] were tested and applied for this process of separation and implantation. Samples of the mixture of ¹⁶³Ho, ¹⁶⁵Ho and ^{166m}Ho were prepared on Ti foil pieces (Alfa Aesar, Karlsruhe, Germany, 5 mm · 5 mm large, 0.0127 mm thickness for mass separation at RISIKO; Goodfellow, Bad Nauheim, Germany, 10 mm · 10 mm large, 0.0125 mm thickness for use at ISOLDE) in the procedure as follows: A hemispherically-shaped depression was pressed into the

center of the foils and it was afterwards filled with 1–20 μ L of solution, which is described at the end of Section 2.2, followed by evaporation at 80 °C. Accordingly, samples with a ¹⁶³Ho content in the order of 10¹⁴ to 10¹⁶ atoms were inserted into ovens connected to the ion sources of the mass separators. Additionally, ^{nat}Ho samples containing a known amount of ¹⁶⁵Ho (either 10¹⁴ or 10¹⁵ atoms) were prepared for measurements of the ionization- and transmission-efficiency of RISIKO for Ho [14].

For separation using the GPS, the ¹⁶³Ho was ionized by the ISOLDE RILIS [21] using an ionization scheme specifically investigated for this experiment. A three-step RILIS ionization scheme of $(\lambda_1, \lambda_2, \lambda_3) = [406 \text{ nm}, 623 \text{ nm}, 532 \text{ nm}$ (not resonant)] [22] was applied, resulting in an enhancement factor of 55 compared to surface ionization alone. Details of the optimization and adaptation of the RISIKO mass separator regarding the laser ionization process, the ion source lay-out and a final post-focalization stage will be given elsewhere.

3 Results and discussion

3.1 Prepurification of the erbium target and irradiation

According to the results of the ICP-OES analysis, the initial 46 mg of 162 Er-enriched Er contained 0.83 µg of Eu, 82 µg of Dy, and less than 11 µg of Ho, whereas contents of all other elements analyzed for were below the limit of quantification. Chemical purification of this portion of enriched 162 Er material by cation exchange chromatography resulted in the 10 mL fractions given in Table 1. Fractions 6 to 13 were

 Table 1: Results of ICP-OES measurement of relevant fractions of

 ¹⁶²Er-enriched Er after chemical separation.

Fraction no.	Elution-time	Dy (µg)	Ho (µg)	Er (µg)
6	50-60 min	_	_	2105
7	60-70 min	-	-	3794
8	70-80 min	-	-	7252
9	80-90 min	-	-	8793
10	90-100 min	-	2	9777
11	100-110 min	3	2	10,422
12	110-120 min	92	-	1397
13	120–130 min	-	-	2
Q. L.ª	-	0.5	2	0.5

Fractions 6–11 were used for the neutron-irradiation at ILL Grenoble. ^aQ. L., Quantification limit. Values below the quantification limits were obtained for Sc (0.5 μ g), Co (10 μ g), Eu (0.2 μ g), Gd (2 μ g), Tb (2 μ g), Ta (2 μ g), Ir (3 μ g).

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analyzed for all the chemical elements mentioned in the footnote of Table 1; fractions 6 to 11 were used for the erbium targets. The separation provided thus a total yield of 92 %.

About 97 % of the Dy contained in the Er as obtained from the supplier were removed by the purification procedure. Concerning the Ho content, no strict quantitative statements are possible as the content is close to the quantification limit; furthermore, the distribution follows that of Er, which might reflect some interference of the at least 4000-fold higher Er concentration.

During irradiation of the Er with thermal neutrons ¹⁶³Er, decaying by EC with a half-life of 75 min to ¹⁶³Ho, is formed by neutron capture of ¹⁶²Er. The number of ¹⁶³Ho atoms $N_{_{163}_{160}}$ produced within an irradiation of the duration $t_{_{1}}$ can be calculated using eq. 1.

since they are based on the "unperturbed" neutron flux. Self-attenuation by the sample and its encapsulation will reduce the effective ("perturbed") flux. Initially the self-attenuation in the target is dominated by the ¹⁶⁷Er content that is, however, reduced over time through burnup.

These results show that the amount of stable Ho formed during the irradiation due to neutron capture on ¹⁶⁴Er exceeds the amount of Ho, which may have been present after chemical separation due to incomplete Ho removal.

3.2 Isolation of holmium from the irradiated targets

After the cooling period of four months, the activity of the irradiated Er-targets was dominated by up to GBq

$$N_{_{163}_{Ho}} = N_{_{162}_{Er_{0}}} \cdot \sigma_{_{162}_{Er}} \cdot \phi \cdot \lambda_{_{163}_{Er}} \cdot \frac{\left[\left(\lambda_{_{163}_{Er}} + \sigma_{_{163}_{Er}} \cdot \phi - \left(\sigma_{_{162}_{Er}} \cdot \phi + \sigma_{_{163}_{Ho}} \cdot \phi \right) \right) \cdot e^{-\sigma_{_{162}_{Er}} \cdot \phi t_{I}} + \left(\lambda_{_{163}_{Ho}} + \sigma_{_{163}_{Ho}} + \sigma_{_{163}_{Er}} \cdot \phi \right) \cdot e^{-\left(\lambda_{_{163}_{Er}} + \sigma_{_{163}_{Er}} \cdot \phi \right) \cdot t_{I}} \right]}{\left[\left(\lambda_{_{163}_{Er}} + \sigma_{_{163}_{Ho}} \cdot \phi - \sigma_{_{162}_{Er}} \cdot \phi \right) \cdot \left(\lambda_{_{163}_{Er}} + \sigma_{_{163}_{Ho}} + \sigma_{_{163}_{Ho}} \cdot \phi - \sigma_{_{162}_{Er}} \cdot \phi \right) \right]} \right]$$

$$(1)$$

where $N_{_{162}E_{T_0}}$ is the number of ^{162}Er atoms at the start of the irradiation, ϕ the thermal neutron flux, λ_i the decay constant of isotope i, σ_i the thermal neutron capture cross section of isotope i, and t_i the duration of the neutron irradiation.

There are no reliable data available for the neutron capture cross sections of ¹⁶³Er and ¹⁶³Ho. Thus, values of 0 barn were used for initial estimates of the ¹⁶³Ho content after irradiation. This approach corresponds to neglecting the double-neutron capture to ¹⁶⁴Er as well as the product burn-up of ¹⁶³Ho. In an analogous way, the production of ¹⁶⁵Ho from the neutron capture on ¹⁶⁴Er, the latter being present with an isotopic abundance of (3.91 ± 0.05) % in the Er targets, can be estimated with results as given in Table 2. Note that these values tend to be overestimated

Table 2: Calculated ¹⁶³Ho and ¹⁶⁵Ho content (atom numbers) afterirradiation.

Nuclide	6.7 mg Er target (atoms)	30 mg Er target (atoms)
¹⁶³ Ho (from ¹⁶² Er)	4.4 · 10 ¹⁶	2.5 · 10 ¹⁸
¹⁶⁵ Ho (from ¹⁶⁴ Er)	5.7 · 1015	2.8 · 10 ¹⁷
¹⁶⁵ Ho (initially present) ^a	6.9 · 1015	3.1 · 1016
	(1.9 µg)	(8.5 μg)

^aAssuming no loss of Ho in chemical prepurification, cf. Section 3.1.

amounts of the relatively long-lived side-products 170 Tm (T_{1/2}=128.6 days) and 171 Tm (T_{1/2}=1.92 a), which were produced from 167 Er [(17.6 ± 0.1) % isotopic abundance in the target], 168 Er [(17.3 ± 0.1) %] and 170 Er [(7.29 ± 0.05) %]. Initial γ -ray spectrometric analysis of the irradiated ampoules prior to further processing resulted in values of 3.6 MBq 170 Tm and 35.5 MBq 171 Tm for the 6.7 mg target and 3.3 GBq 170 Tm and 2.5 GBq 171 Tm for the 30 mg target at the end of bombardment (EOB). These unwanted Tm byproducts as well as the excess of remaining Er needed to be separated from the produced Ho.

Short-lived, γ -emitting radioisotopes of Ho and Er were added to enable the monitoring of the Ho and Er distribution by γ -ray spectrometry during chemical separation. Suitable tracers are ¹⁶⁶Ho (T_{1/2}=26.80 h) and ¹⁷¹Er (T_{1/2}=7.52 h), since they have suitable γ lines and are short-lived enough for their complete decay after the separation, before the further use of Ho [for Electromagnetic Mass (EM) separation and implantation] and Er (for a new neutron irradiation cycle). ¹⁶⁶Ho was used in n.c.a. quality to avoid introduction of additional ¹⁶⁵Ho and ^{166m}Ho, as would happen with neutron activated ¹⁶⁵Ho tracer. As shown in Figure 1, the ¹⁶⁶Ho had been prepared from a neutron irradiated ^{nat}Dy target in two separation steps and added to the solution of the irradiated targets prior to the Ho isolation (cf. Figure 1). About 250 kBq of ¹⁶⁶Ho and

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Figure 2: Elution profile of the 30 mg Er-target separation, performed by extraction chromatography at room temperature applying a flow rate of ~0.5 mL/min of eluate.

The separation was monitored by tracing ¹⁶⁶Ho, ¹⁷¹Er, and ¹⁷⁰Tm with γ -ray spectrometry. No Er above detection limit was found in the last Ho-containing fraction, and no Ho above detection limit in the first Er-containing fraction.

400 kBq ¹⁷¹Er were added to each of the irradiated targets before the chemical separation.

Figure 2 shows the elution profile of the column chromatographic separation of the 30 mg Er-target, which evidences successful separation of the three adjacent lanthanides Ho, Er and Tm. The desired Ho was obtained within 30 mL of the eluate (from 50 mL to 80 mL elution volume). A Ho recovery vield of 95.4 % was achieved for the 30 mg Er-target. The last Ho fraction was directly followed by the first Er fraction. No Er-activity was detected in the Ho fraction and no Ho-activity in the Er-fractions. A more detailed analysis (see Section 3.3) quantified the remaining amount of Er (from all stable Er isotopes) in the Ho fraction after its isolation from the irradiated target to about one eighth of the produced $^{\rm 163}{\rm Ho},$ whereas $^{\rm 169,170,171}{\rm Tm}$ were present in amounts lower than our detection limit. The decontamination factors achieved in the separation were experimentally determined to 560 ± 70 for Er and $>2.3 \cdot 10^5$ for Tm (based on the evaluation of ¹⁷⁰Tm). Isolation of Ho from the 6.7 mg Er-target was performed in the same way, and a recovery of 99.4 % was achieved. In contrast to the separation of the 30 mg Er-target, no remaining Er was found, not even via a more detailed analysis (see Section 3.3) of the Ho sample.

3.3 Characterization of the isolated holmium samples

The ¹⁶³Ho does not emit any γ radiation, in contrast to the relevant irradiation byproducts, which have easily detectable γ lines of sufficient intensity. Analysis via γ -ray spectrometry is therefore an excellent method for obtaining information about the presence of such γ -ray emitting byproducts in the produced ¹⁶³Ho. In the ideal case of ¹⁶³Ho being the sole radionuclide in the sample, a completely



Figure 3: Spectrum from γ -ray spectrometry (real counting time 603 s) of the residue from the evaporation of the unified Ho-containing fractions which were obtained by processing of the 30 mg Er target.

flat γ -ray spectrum without any peaks above background would result. The obtained γ -ray spectrum of Ho isolated from the 30 mg Er target is shown in Figure 3.

All lines prominently visible in the spectrum originate from ^{166m}Ho, which passed the chemical separation procedure along with ¹⁶³Ho. Quantitative analysis revealed activities of (16.0 ± 1.3) Bq ^{166m}Ho (Ho from the 6.7 mg target) and (7.0 ± 0.4) kBq ^{166m}Ho (Ho from the 30 mg target). No evidence for the presence of ¹⁷⁰Tm was found; from the absence of counts above background at the energy of 84 keV (i.e., the position of the main peak of ¹⁷⁰Tm), an activity of ¹⁷⁰Tm of <7 kBq follows.

The contents of species in the mass range of 157–174 u (i.e. including ¹⁶³Ho) were quantified with ICP-MS. The content of Ho was calibrated for stable ¹⁶⁵Ho. The content of ¹⁶⁵Ho in the whole Ho preparations was determined to $(4.53\pm0.07)\cdot10^{15}$ atoms (Ho from 6.7 mg target) and $(6.29\pm0.78)\cdot10^{17}$ atoms (Ho from 30 mg target).

In a next step, the isobar ratios were determined. The results given as percentage in Table 3.

All nuclides, which are stable or have sufficiently long half-lives to still be present in the Ho preparations at the time of the ICP-MS measurement (performed ~980 days after the chemical separation), are therefore given in the second column of Table 3. The observed isobar ratios show that in the mass region 157–174 u (lanthanides from Gd to Lu) the mass 163 u is clearly the major constituent in both samples. Since this method cannot resolve the very

Table 3:	Results of the ICP-MS measurements of the examined
isobars,	given as percentages of the samples.

Mass (u)	Nuclide(s)	Ho fraction of the 6.7 mg target (%)	Ho fraction of the 30 mg target (%)
157	¹⁵⁷ Gd	_a	0.05±0.39
158	¹⁵⁸ Gd, ¹⁵⁸ Dy	_a	_a
159	¹⁵⁹ Tb	_a	_a
160	¹⁶⁰ Gd, ¹⁶⁰ Dy	0.01 ± 0.04	0.11 ± 0.33
161	¹⁶¹ Dy	0.03 ± 0.05	a
162	¹⁶² Dy, ¹⁶² Er	0.11 ± 0.06	2.17 ± 0.86
163	¹⁶³ Dy, ¹⁶³ Ho	88.62 ± 0.50	57.45±2.53
164	¹⁶⁴ Dy, ¹⁶⁴ Er	0.07 ± 0.06	1.06 ± 0.68
165	¹⁶⁵ Ho	11.10 ± 0.46	$29.17\pm\!0.91$
166	^{166m} Ho, ¹⁶⁶ Er	0.02 ± 0.04	3.72 ± 0.56
167	¹⁶⁷ Er	_a	0.31 ± 0.33
168	¹⁶⁸ Er, ¹⁶⁸ Yb	0.01 ± 0.03	4.89 ± 0.97
169	¹⁶⁹ Tm	0.01 ± 0.02	_a
170	¹⁷⁰ Er, ¹⁷⁰ Tm, ¹⁷⁰ Yb	_a	0.83 ± 0.59
171	¹⁷¹ Tm, ¹⁷¹ Yb	_a	0.16 ± 0.20
172	¹⁷² Yb	_a	0.06 ± 0.29
173	¹⁷³ Yb	0.01 ± 0.02	0.02 ± 0.29
174	¹⁷⁴ Yb, ¹⁷⁴ Hf	0.01 ± 0.03	_a

^aValue below or equal to background.

minor mass difference between isobars, only information about the sum of all isobars of a certain mass number, but no information on the contribution of isobars from different elements is obtained.

The Ho-fraction isolated from the 6.7 mg Er target contains almost exclusively species of mass 163 u (about 89 %) and mass 165 u (about 11 %). The latter mass is entirely ascribed to ¹⁶⁵Ho, as this is the only stable or long-lived mass 165 u isobar. The signals from the neighboring masses 162 u and 164 u accounting for less than 0.2 % of the total mass might originate from Dy impurities or might be due to a neighbor-mass effect of the huge mass 163 u signal. An origin due to ¹⁶²Er and ¹⁶⁴Er from the target, which might have remained in the Ho after the chemical isolation, is ruled out, since ¹⁶⁶Er and ¹⁶⁸Er were more abundant in the Er target used, but are not present. The results of all other examined masses are below the range of uncertainty or equal to or below the background measurement.

In the Ho sample isolated from the 30 mg target, the most abundant isobars are again at mass 163 u (¹⁶³Dy and ¹⁶³Ho) with about 57 %, followed by the one at 165 u with nearly 30 %, which is ¹⁶⁵Ho. Additionally, the masses 162 u, 164 u, 166 u, 168 u, and 170 u contribute between about 0.8 % and 5 % for each isobar (cf. Table 3). These are attributed to the stable Er-isotopes from the irradiation target, which have remained in the Ho fraction. To confirm this, the isotopic composition of the Er obtained from the post-irradiation chemical separation was determined in separate ICP-MS measurements. The results agree well with those of the isotopic composition of Er in the Ho fraction, cf. Table 4.

¹⁶⁷Er is missing, because it has been extensively burned up during the long irradiation duration due to its high thermal neutron capture cross section of ca. 650 barn [23]. The relative content at 164 u with respect to the other masses due to Er isotopes is higher in the Ho fraction than in the separate analysis of the Er fraction. This is due to the presence of some ¹⁶⁴Dy, which was formed in the neutron

 Table 4: Results of the ICP-MS measurements of the isobars that contain a stable Er-isotope.

Mass (u)	Nuclide(s)	Ho fraction of the 30 mg target (%)	Er fraction of the 30 mg target (%)
162	¹⁶² Dy, ¹⁶² Er	17.1	17
164	¹⁶⁴ Dy, ¹⁶⁴ Er	8.4	4
166	^{166m} Ho, ¹⁶⁶ Er	29.4	31
167	¹⁶⁷ Er	-	2
168	¹⁶⁸ Er, ¹⁶⁸ Yb	38.6	39
170	¹⁷⁰ Er, ¹⁷⁰ Tm, ¹⁷⁰ Yb	6.5	7

The values are normalized to the sum of all these isobars equaling 100 %.

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capture of the product nuclide ¹⁶³Ho, as was confirmed in the later stages of the analysis (cf. Table 7). For all other analyzed masses, the findings do not exceed the levels of the background measurement or are lower than the range of uncertainty of the measurements.

Combination of the quantitative results for ¹⁶⁵Ho and the isobaric ratios given in Table 3 lead to the absolute atom numbers of the contribution on mass 163 u (¹⁶³Dy and ¹⁶³Ho). These were determined to $(3.62\pm0.16)\cdot10^{16}$ atoms on mass 163 u (Ho fraction from the 6.7 mg target) and $(1.24\pm0.17)\cdot10^{18}$ atoms of mass 163 u (Ho fraction from the 30 mg target).

The ICP-MS technique does not allow to differentiate between the desired product nuclide ¹⁶³Ho and impurities of ¹⁶³Dy. To this end, RIMS was additionally applied, which combines elemental-specific ionization induced by resonant multi-step laser excitation with magnetic mass separation. It is thus an excellent method to obtain precise isotope ratios of a given chemical element. For these measurements, which were carried out at the RISIKO mass separator, avoiding (or at least minimizing) surface ionization on hot parts of the ion source, was key, as this kind of ionization is not element specific among the rare earth metals. This condition was ensured by keeping the ion source temperature low enough to prevent significant contributions from surface ionization, but high enough to facilitate thermal decomposition of the lanthanide nitrate (hydrate) to the lanthanide oxide, followed by reduction of the lanthanide oxide to the metal, and finally sublimation of at least parts of the solid lanthanide metal under the high vacuum conditions. This yielded a stable ion beam formed almost exclusively by resonant laser ionization. A sputtered Y layer served as an agent for the reduction of the lanthanide oxide at the comparatively low temperatures. Information on the contribution from surface ionization was obtained by monitoring the 165 u mass signal. As there is no stable Dy-isotope on this isobar, but sufficient amounts of ¹⁶⁵Ho (see Table 3) for unspecific surface ionization in both samples, the appearance (and magnitude) of a 165 u signal in the mass scan would be precisely indicating any

Table 5: Isotopic distribution (in %) of the Dy content in the Hosamples obtained via RIMS.

Dy-isotope	Natural abundance	Ho fraction of the 6.7 mg target (%)	Ho fraction of the 30 mg target (%)
¹⁶⁰ Dy	2.329	1.6±0.1	0.5±0.2
¹⁶¹ Dy	18.889	13.5 ± 0.6	4.2 ± 0.8
¹⁶² Dy	25.475	29.9 ± 0.5	8.0 ± 0.8
¹⁶³ Dy	24.896	29.9 ± 0.3	14.1 ± 0.6
¹⁶⁴ Dy	28.260	$25.1\!\pm\!0.9$	73.5±2.2

contribution from surface ionization. However, this was found to be of negligible influence on the results of the Dy isotopic distribution in both Ho samples.

These numbers show different distributions of the stable Dy isotopes in both analyzed aliquots, which also significantly differ from the abundances in natural Dy (cf. Table 5). While perhaps surprising at first glance, this can be understood by considering the different history of these Dy-isotopes.

First, some Dy of unknown isotopic distribution remained in the Er targets after the prepurification (see Section 3.1) and might have ended up in the Ho fraction. Since the material underwent isotopic enrichment (aimed at ¹⁶²Er), the isotopic composition also of the Dy impurities might differ from the natural abundance. Secondly, during the irradiation the isotopic ratios were changed as isotopes having a comparatively high neutron capture cross section like 164Dy (2650 b) and 161Dy (600 b) were burned up to a larger extent than others with lower cross sections. The content of the latter ones might rather have increased due to formation through neutron capture of the neighboring lighter isotope. At all steps of handling described above there always was the possibility of having introduced some impurities of Dy of natural isotopic composition. If this had happened before irradiation the isotopic distribution was changed, otherwise not. For verification of the absence of any input of Dy through the materials applied for the RIMS measurement (i.e. the Zr foil and the sputtered metallic Y) background measurements with blanks of these materials were performed. Obtaining stable beams of Dy-ions with enough intensity for measurement was impossible from these samples. Therefore, the Zr foil and the sputtered Y layer can be excluded as further significant source of Dy in the RIMS measurement. Additionally, ¹⁶³Dy was continuously produced from the decay of ¹⁶³Ho (about 0.04 % of the initially obtained ¹⁶³Ho were thus converted into ¹⁶³Dy during the 980 days period) and ¹⁶⁴Dy had been formed during the irradiation from the product burn up of ¹⁶³Ho through neutron capture to ¹⁶⁴Ho ($T_{1/2}$ =29 min, 40 % β^- decay, 60 % EC decay) and the following EC decay.

Based on these facts, the isotope content of Dy in the Ho fraction isolated from the 6.7 mg Er target can be supposed to be mainly due to an impurity, which was already present in the Er target. The initial Dy isotopic distribution underwent some changes during irradiation. Addition of ¹⁶³Dy and ¹⁶⁴Dy occurred through the above described processes of the decay and burn up of product nuclide ¹⁶³Ho. In contrast to this, Dy in the Ho fraction isolated from the 30 mg Er target was predominantly consisting of the isotope ¹⁶⁴Dy and only to a much lower extent of ¹⁶³Dy, whereas the other Dy isotopes were only present in minor shares. Therefore, Dy was mostly originating from burn up of ¹⁶³Ho and at much lower level from decay of already produced ¹⁶³Ho. Impurities of Dy in the target or introduced during the processing procedure played only a marginal role as Dy sources in this sample.

Thanks to the RIMS results, the Dy isotope ratios were now known, though not yet their absolute amounts. This, however, is needed for the 163 u isobar differentiation between ¹⁶³Ho and ¹⁶³Dy. To get information on the absolute atom numbers of all examined Dy isotopes, it was sufficient to determine this for one Dy isotope. The values of the other isotopes can be calculated from the obtained isotope ratios. Neutron activation analysis (NAA) offers the possibility to easily specify the absolute atom number of ¹⁶⁴Dy. This nuclide undergoes thermal neutron capture with high cross section to ¹⁶⁵Dy (T_{1/2}=2.33 h), which can then be measured by γ -ray spectrometry. Additionally it gives also results for other potentially existent elements if they are accessible by this analytical method.

For correct quantification of the particular isotopes knowledge of the thermal neutron flux during the activation is indispensable. Therefore standard samples of known amounts of gold were co-irradiated and afterwards analyzed by γ -ray spectrometry. Neutron flux values of $(8.48\pm0.17)\cdot10^{11}$ cm⁻² · s⁻¹ at the bottom and $(8.59\pm0.15)\cdot10^{11}$ cm⁻² · s⁻¹ at the top of the stacked samples were evaluated. The thermal neutron flux which the samples were exposed to is assumed to be the average, as the samples were located between the irradiation positions of the gold standards, i.e. $(8.54\pm0.11)\cdot10^{11}$ cm⁻² · s⁻¹. This value has been used for further evaluation of the NAA results.

The γ -ray spectra of irradiated aliquots of the Ho samples showed the activation products ²⁴Na, ¹⁶⁵Dy, ¹⁶⁶Ho, ¹⁶⁷Ho, and ¹⁷¹Er (besides ^{166m}Ho, which was present already in the original samples). From these, the contents of stable (or long lived) impurities of ²³Na, ¹⁶⁴Dy, ¹⁶⁵Ho, ^{166m}Ho, and ¹⁷⁰Er as given in Table 6 were evaluated.

The results show a rather large amount of stable sodium to be present in the samples. This is probably a contamination from the glass container, in which the solution has

 Table 6: Number of atoms of detected nuclides in the whole samples as resulted from the NAA.

Nuclide	Ho fraction of the 6.7 mg target (atoms)	Ho fraction of the 30 mg target (atoms)		
²³ Na	(1.1±0.1)·10 ¹⁸	$(3.5\pm0.2)\cdot10^{18}$		
¹⁶⁴ Dy	$(2.5\pm0.2)\cdot10^{13}$	$(6.3\pm0.3)\cdot10^{15}$		
¹⁶⁵ Ho	(5.3±0.2) · 10 ¹⁵	$(7.7\pm0.3)\cdot10^{17}$		
^{166m} Ho	$(1.4\pm0.3)\cdot10^{12}$	$(3.5\pm0.2)\cdot10^{14}$		
¹⁷⁰ Er	-	$(1.5\pm0.3)\cdot10^{16}$		

been stored since its production. It will, however, be quantitatively eliminated in the subsequent mass separation step and is hence of no concern. The content of ¹⁶⁴Dy is more than a factor of 100 smaller than the ¹⁶⁵Ho content or the sum of the 163 u isobar. The 165Ho contents determined via NAA are about 15 % (Ho from 6.7 mg Er target) and about 25 % (Ho from 30 mg Er target) higher than those determined via ICP-MS. This could be due to an epithermal neutron component present in the neutron spectrum used in the NAA leading to more efficient activation of ¹⁶⁵Ho compared to that of ¹⁹⁷Au, due to differences in epithermal to thermal activation cross section ratios for the two reactions. The neutron capture cross section value of ¹⁶⁵Ho and ¹⁹⁷Au used for the calculations are for a purely thermal neutron spectrum. Due to the high thermal neutron capture cross section of ^{166m}Ho of 3100 barn and therefore the high sensitivity of NAA, the long-lived radionuclide ^{166m}Ho, contained in comparatively small amounts, was also found via the detection of ¹⁶⁷Ho in both of the aliquots. The contents of ^{166m}Ho as determined

via NAA are in good agreement with those obtained via γ -ray spectrometry (see above at the beginning of this section). Remains of the Er target due to incomplete separation which are visible via the activation of ¹⁷⁰Er in NAA, were only located in the Ho fraction from the 30 mg target, whereas no evidence of Er was measured in Ho from the 6.7 mg Er target. Further, no hints for the presence of stable or long-lived Tm isotopes in either sample were seen.

In addition to the mentioned nuclides ²⁴Na, ¹⁶⁵Dy, ¹⁶⁶Ho, ¹⁶⁷Ho, and ¹⁷¹Er, activities of (46.8±6.3) kBq ^{164m}Ho ($T_{1/2}$ =37 min) and (390±15) kBq ^{164g}Ho ($T_{1/2}$ =29 min) were formed during the neutron activation in the aliquot of Ho from the 6.7 mg Er target as well as (17.0±2.4) kBq ^{164m}Ho and (138.3±5.2) kBq ^{164g}Ho in the aliquot of Ho from the 30 mg Er target. The production of both isomers of ¹⁶⁴Ho can be described by eq. (2)–(4):

$$A_{_{164m}_{Ho}} = N_{_{163}_{Ho}} \cdot \sigma_{_{163}_{Ho} \rightarrow ^{164m}_{Ho}} \cdot \phi \cdot \left(1 - e^{-\lambda_{_{164m}_{Ho}} \cdot t_{_{I}}}\right)$$
(2)

 $A_{164g_{Ho}}$ (direct activation) =

$$N_{_{163}_{Ho}} \cdot \sigma_{_{163}_{Ho} \rightarrow ^{164g}_{Ho}} \cdot \phi \cdot \left(1 - e^{-\lambda_{_{164g}_{Ho}} \cdot t_{_{1}}}\right)$$
(3)

$$A_{164g_{H_0}}$$
 (indirect activation) = $N_{163_{H_0}} \cdot \sigma_{163_{H_0}}^{164m_{H_0}}$

$$\phi \cdot \left(1 + \frac{\lambda_{_{164m}_{Ho}} \cdot e^{-\lambda_{_{164m}_{Ho}} \cdot t_{_{I}}} - \lambda_{_{164m}_{Ho}} \cdot e^{-\lambda_{_{164m}_{Ho}} \cdot t_{_{I}}}}{\lambda_{_{164m}_{Ho}} - \lambda_{_{164m}_{Ho}}} \right)$$
(4)

where $N_{_{163}Ho}$ is the number of ^{163}Ho atoms, ϕ the thermal neutron flux, λ_i the decay constant of isotope i, and t_i the duration of the neutron activation. ° $_{_{163}Ho\rightarrow}{}_{164m}_{Ho}$ is the

thermal neutron capture cross section of $^{163}\mathrm{Ho}$ to $^{164m}\mathrm{Ho},$ and $^{\circ}$ $_{^{163}\mathrm{Ho}\rightarrow}{}^{164g}\mathrm{Ho}$ the thermal neutron capture cross section of $^{163}\mathrm{Ho}$ to $^{164g}\mathrm{Ho}.$

Equation (2) gives the activity of ^{164m}Ho at the end of bombardment (EOB), which has been formed by neutron capture of ¹⁶³Ho with thermal neutron capture cross section ° $_{_{^{163}\text{Ho}}\rightarrow^{^{164m}\text{Ho}}}$. Analogous to this, eq. (3) leads to the activity of ^{164g}Ho at EOB, which has been directly produced from ¹⁶³Ho with the thermal neutron capture cross section $^{\circ}$ $_{^{_{163}}\text{Ho}\rightarrow^{^{164g}}\text{Ho}}$. In eq. (4) $^{^{164g}}\text{Ho}$ has been formed as the metastable state isomer ^{164m}Ho (with thermal neutron capture cross section $\,\,^{\circ}\,_{_{^{163}\mathrm{Ho}\rightarrow}{}^{^{164m}}\mathrm{Ho}}$), but already decayed to $^{^{164g}}\mathrm{Ho}$ during the neutron activation. The total activity of ^{164g}Ho at EOB is thus the sum of eq. (3) and (4). Equations (2)-(4)do neither consider the target burn-up of ¹⁶³Ho during the neutron irradiation, which is insignificant (less than 1 % deviation up to ° $_{_{163}_{HO}\rightarrow^{164m}_{HO}}$ + ° $_{_{163}_{HO}\rightarrow^{164e}_{HO}}$ = ° $_{_{163}_{HO}}$ > 3·10⁶ b under the applied irradiation conditions), nor the negligible decay of ¹⁶³Ho in the time frame of activation, cooling, and measurement due to the comparatively very long halflife. Also, neutron capture of ^{164m+g}Ho, which is insignificant under these conditions, is neglected.

Since thermal neutron capture cross sections of ¹⁶³Ho to both states in ¹⁶⁴Ho, ° $_{^{163}\text{Ho}\rightarrow}^{^{164}\text{Ho}}$ and ° $_{^{163}\text{Ho}\rightarrow}^{^{164}\text{Ho}}$ are unknown, but the activities of ¹⁶⁴mHo and ¹⁶⁴gHo were experimentally determined in our experiments, it is possible to obtain the values for ° $_{^{163}\text{Ho}\rightarrow}^{^{164}\text{Ho}}$. Inserting of the data and solving these equations lead to ° $_{^{163}\text{Ho}\rightarrow}^{^{164}\text{Ho}} = (22.6 \pm 3.2)$ b and ° $_{^{163}\text{Ho}\rightarrow}^{^{164}\text{Ho}} = (155.0 \pm 10.0)$ b for ¹⁶³Ho from the 6.7 mg Er target as well as ° $_{^{163}\text{Ho}\rightarrow}^{^{164}\text{Ho}} = (24.2 \pm 4.8)$ b and ° $_{^{163}\text{Ho}\rightarrow}^{^{164}\text{Ho}} = (160.1 \pm 24.6)$ b for ¹⁶³Ho from the 30 mg Er target. From these values the thermal neutron capture cross section of ¹⁶³Ho was evaluated to ° $_{^{163}\text{Ho}\rightarrow}^{^{164}\text{Ho}} = (23 \pm 3)$ b and ° $_{^{163}\text{Ho}\rightarrow}^{^{164}\text{Ho}} = (156 \pm 9)$ b for the formation of the two isomers of ¹⁶⁴Ho.

Applying the values of ° $_{^{163}\text{Ho}\rightarrow^{164\text{m}}\text{Ho}}$ = 23 b and ° $_{^{163}\text{Ho}\rightarrow^{164\text{m}}\text{Ho}}$ = 156 b as cross sections for the product burn-up in eq. (1), the irradiation yield for ^{163}Ho that was estimated in Section 3.1 (cf. Table 2) reduces from $4.4 \cdot 10^{16}$ atoms ^{163}Ho to $4.2 \cdot 10^{16}$ atoms ^{163}Ho for the 6.7 mg Er-target and from $2.4 \cdot 10^{18}$ atoms ^{163}Ho to $1.4 \cdot 10^{18}$ atoms ^{163}Ho for the 30 mg Er target. These data are closer to the experimentally obtained yields of $(3.64 \pm 0.16) \cdot 10^{16}$ atoms ^{163}Ho (6.7 mg Er target) and $(1.30 \pm 0.18) \cdot 10^{18}$ atoms ^{163}Ho (30 mg Er target). The residual discrepancies are easily accounted for by the difference of perturbed and unperturbed neutron flux.

Combining the data obtained from the different analytical methods allows for a comprehensive characterization of both Ho-samples. These final results are given in Table 7.

 Table 7: Number of atoms in the total Ho samples obtained from the combination of the results from all analytical techniques.

Nuclide	(atoms)	Share ^a (%)	Analytical technique(s)
	Ho fraction of the		
²³ Na	$(1.1\pm0.1)\cdot10^{18}$	-	NAA
¹⁶⁰ Dy	$(1.6 \pm 0.2) \cdot 10^{12}$	0.004	RIMS, NAA
¹⁶¹ Dy	$(1.3\pm0.2)\cdot10^{13}$	0.032	RIMS, NAA
¹⁶² Dy	(3.0±0.3) · 10 ¹³	0.074	RIMS, NAA
¹⁶³ Dy	(3.0±0.3) · 10 ¹³	0.074	RIMS, NAA
¹⁶⁴ Dy	$(2.5\pm0.2)\cdot10^{13}$	0.062	NAA
¹⁶³ Ho	$(3.6 \pm 0.2) \cdot 10^{16}$	89.000	ICP-MS, RIMS, NAA
¹⁶⁵ Ho	$(4.5 \pm 0.1) \cdot 10^{15}$	11.000	ICP-MS
^{166m} Ho	$(8.7\pm0.7)\cdot10^{11}$	0.002	γ -ray spectrometry
	Ho fraction of the	30 mg target	
²³ Na	$(3.5\pm0.2)\cdot10^{18}$	-	NAA
¹⁶⁰ Dy	(4.3±1.8)·1013	0.002	RIMS, NAA
¹⁶¹ Dy	$(3.6\pm0.8)\cdot10^{14}$	0.018	RIMS, NAA
¹⁶² Dy	$(6.9 \pm 0.8) \cdot 10^{14}$	0.034	RIMS, NAA
¹⁶³ Dy	$(1.2\pm0.1)\cdot10^{15}$	0.059	RIMS, NAA
¹⁶⁴ Dy	(6.3±0.3) · 10 ¹⁵	0.310	NAA
¹⁶³ Ho	$(1.2\pm0.2)\cdot10^{18}$	59.000	ICP-MS, RIMS, NAA
¹⁶⁵ Ho	$(6.3 \pm 0.8) \cdot 10^{17}$	31.000	ICP-MS
^{166m} Ho	$(3.8\pm0.3)\cdot10^{14}$	0.019	γ-ray spectrometry
¹⁶² Er	$(3.4\pm0.7)\cdot10^{16}$	1.700	NAA, ICP-MS
¹⁶⁴ Er	$(8.7 \pm 1.7) \cdot 10^{15}$	0.430	NAA, ICP-MS
¹⁶⁶ Er	$(6.2 \pm 1.2) \cdot 10^{16}$	3.000	NAA, ICP-MS
¹⁶⁷ Er	$(4.2\pm0.8)\cdot10^{15}$	0.210	NAA, ICP-MS
¹⁶⁸ Er	$(7.5 \pm 1.5) \cdot 10^{16}$	3.700	NAA, ICP-MS
¹⁷⁰ Er	$(1.5\pm0.3)\cdot10^{16}$	0.740	NAA

^aNormalized to the total content in the mass region around A=163, i.e. without considering ²³Na, which is easily quantitatively removed in the mass separation step.

The desired product nuclide ¹⁶³Ho is the main component in both samples, with the exception of large amounts of stable sodium. The isobaric Dy-isotope ¹⁶³Dy contributes a share of only (0.08 ± 0.01) % (Ho from the 6.7 mg Er target) and (0.10 ± 0.02) % (Ho from the 30 mg Er target) to the 163 u isobar and is thus insignificant in both samples.

3.4 Magnetic isotope separation for isolation of ¹⁶³Ho from chemically purified Ho fractions

As follows from Table 7, the atom ratios of ^{166m}Ho:¹⁶³Ho varies for individual samples, and reaches a value of $<4 \cdot 10^{-4}$ in the sample with the higher concentration. To comply with the requirements of maximum concentrations of $5 \cdot 10^{-8}$ in the current phase and $5 \cdot 10^{-9}$ in the next phase of the ECHo project (cf. Section 8.4 in [1]), further suppression by an additional factor of at least $3 \cdot 10^{-5}$ is thus necessary. This was achieved by applying magnetic isotope separation at RISIKO and at the GPS/CERN-ISOLDE. Using the prepared samples of stable Ho, the ionization- and transmission-efficiency of the resonant laser ionization at the RISIKO mass separator has been determined to be (32 ± 5) % for Ho [14]. First implantations of ¹⁶³Ho into ECHo MMC detectors have been performed at RISIKO [1].

By utilizing a sample of $1.2 \cdot 10^{14}$ atoms ¹⁶³Ho a separation run was performed at the GPS of ISOLDE, which resulted in implantation of about $4 \cdot 10^{10}$ atoms ¹⁶³Ho into each of the 32 MMC pixels of one detector chip. It has been used for test measurements, obtained results are published in [3].

4 Conclusion

The strategy for the production of radiochemically pure ¹⁶³Ho samples has been described. This involves target prepurification, neutron irradiation, as well as post irradiation target processing. Samples of >1018 atoms of 163Ho have been isolated, sufficient for the current stages of the ECHo project. By performing a similar production sequence, but starting with moderately larger samples of more highly enriched ¹⁶²Er, samples on the order of 10¹⁹ atoms can be obtained, as needed for the next phase of the ECHo project. The Ho samples obtained by chemical separation were characterized by various analytical methods, i.e. ICP-MS, RIMS, and NAA, which verified the suitability of the final samples for their use within the current and future stages of the ECHo-project. The only radioactive impurity that was identified in the chemically isolated Ho samples was ^{166m}Ho, present at levels of $<4 \cdot 10^{-4}$ with respect to ¹⁶³Ho (cf. Table 7). For its further suppression, magnetic mass separation is applied, providing an additional separation factor on the order of 10⁻⁵, leading to samples of the purity as required for the ECHo project [1, 14]. This last separation step also serves for the ion-implantation of ¹⁶³Ho into the ECHo MMCs used for the neutrino mass determination within the ECHo-project.

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Chapter 3

Publication II: Resonance ionization of holmium for ion implantation in microcalorimeters

The LARISSA¹ group is investigating resonance ionization for radioactive ion beam production as well as for spectroscopic and analytic purposes for more than three decades. The specialization in high-efficiency isotope separation and ion implantation is a new field requested on the basis of the known expertise and triggered by the ECHo project requirements for the quantity and purity of the ¹⁶³Ho EC source. Publication II describes the application of resonance ionization mass separation as an exceptional element selective and efficient method for ion implantation, perfectly matching the needs for production of a high purity ¹⁶³Ho EC source for ECHo. T. Kieck contributed to all measurements described in this publication and co-authored the manuscript.

This article was published in *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* volume 376 (2016), pages 388-392. It gives an overview of the state of resonant laser ionization of Ho at the beginning of the Mainz contribution to the ECHo project.

¹German abbreviation for LAser Resonanz Ionisation für Spektroskopie in Selektiven Anwendungen

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Resonance ionization of holmium for ion implantation in microcalorimeters



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ABSTRACT

The determination of the electron neutrino mass by calorimetric measurement of the ¹⁶³Ho electron capture spectrum requires ultra-pure samples. Several collaborations, like ECHo or HOLMES, intend to employ microcalorimeters into which ¹⁶³Ho is implanted as an ion beam. This makes a selective and additionally very efficient ion source for holmium mandatory. For this purpose, laser resonance ionization of stable holmium ¹⁶⁵Ho was studied, using a three step excitation scheme driven by pulsed Ti:sapphire lasers. Five measurements with sample sizes of 10¹⁴ and 10¹⁵ atoms were performed for the efficiency investigation. In average, an excellent ionization efficiency of 32(5)% could be shown, demonstrating the suitability for ion beam implantation.

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1. Introduction

Resonance ionization is an efficient and exceptionally selective ionization method. It is thus especially well suited for the production of radioactive ion beams, where both qualities are of major relevance. In several on-line facilities, for example at CERN-ISOLDE [1] or TRIUMF-ISAC [2], resonance ionization laser ion sources are used in conjunction with accelerator based production of exotic nuclides and are regularly requested by experimentalists. In addition, radioactive beams of long-lived isotopes can also be produced in off-line facilities from an external sample. An isotope of increasing interest is ¹⁶³Ho which decays with a half-life of 4570a through electron capture. Its very low decay energy of 2833(30)_{stat}(15)_{sys} eV [3] makes it the prime candidate for calorimetric measurements of the electron neutrino rest mass [4]. Several collaborations investigating this decay have been started, including ECHo [5] and HOLMES [6]. To facilitate the desired high precision and low background measurements, highly pure ¹⁶³Ho is to be implanted into the calorimeters. Direct production in an

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http://dx.doi.org/10.1016/j.nimb.2015.12.012 0168-583X/© 2015 Elsevier B.V. All rights reserved. on-line facility would introduce too many contaminants in the implanting ion beam. Therefore, a more intricate pathway has to be taken. In the case of ECHo, ¹⁶³Ho is produced in the high-flux nuclear reactor at ILL, Grenoble [7] by irradiating ¹⁶²Er. Following neutron capture to ¹⁶³Er, it decays with a half-life of 75 min by electron capture to ¹⁶³Ho. After irradiation, co-produced contaminants and the erbium target material are chemically separated. From this sample, a holmium ion beam is extracted by resonance ionization, mass separated to isolate ¹⁶³Ho and subsequently implanted into the microcalorimeters. High efficiencies in all process steps are needed to keep the required total sample amount reasonably low. Ion beam implantation offers the ability to precisely monitor the ion current during the process, allowing accurate quantification of isotope deposition. The combination with a resonance ionization laser ion source not only has the advantage of a high ionization efficiency but in addition further purifies the sample by exclusively ionizing the element of interest.

Resonance ionization of holmium has been successfully demonstrated at the Ion Source Test Facility 2 (ISTF2) at the Oak Ridge National Laboratory (ORNL) [8]: Liu and coworkers achieved an outstanding ionization efficiency of 40 %, surpassing specifications reported for all other elements in resonant laser ion sources. We report confirmation studies using stable ¹⁶⁵Ho at the RISIKO mass
separator at the University of Mainz, where the ion beam implantation for the ECHo experiment is foreseen.

2. Experiment

The measurements were performed at the RISIKO mass separator (see Fig. 1) equipped with the pulsed titanium–sapphire laser system developed at the University of Mainz [9]. A known number of ¹⁶⁵Ho atoms was inserted into the sample reservoir. After evacuation of the system, the sample was evaporated, ionized by resonant laser radiation, mass separated and finally collected in a Faraday cup for ion beam current quantification. The ionization efficiency was calculated as the ratio of the number of detected ions to the initial sample size. Future implantations of ¹⁶³Ho will be performed in the same way, with the microcalorimeters positioned inside the Faraday cup, so that incoming ions will be implanted to a depth of a few nm in the absorber of the microcalorimeter.

2.1. Samples

The samples were prepared from commercially available Holmium(III) nitrate-pentahydrate $(Ho(NO_3)_3 \cdot 5H_2O)$ with a purity of 99.9 %. This was transferred to aqueous solutions with mass concentrations of either $2.74(16)\cdot10^{-2}$ g/l or $2.74(16)\cdot10^{-3}$ g/l. 10 μl of these solutions, containing $1.00(6) \cdot 10^{15}$ (or $1.00(6) \cdot 10^{14}$, respectively) atoms of holmium were deposited on 99.8 %-purity titanium substrates of $6 \times 6 \text{ mm}^2$ size and 12.5 μ m thickness and evaporated to dryness. The chemical form of the residuum was likely $Ho(NO_3)_3 \cdot 3H_2O$. To exclude systematic errors or losses in the process, the samples were quantified by neutron activation in the research reactor TRIGA Mainz [10]. The nominal sample sizes could be confirmed within an uncertainty of 4 %. After placement in the sample reservoir, the remaining water is released by heating of the reservoir and the compound decomposes in several steps until at temperatures above 560 °C conversion into the form of the oxide Ho_2O_3 is completed [11]. It is partially reduced to elemental oxide in the equilibrium state of the redox reaction $2Ho_2O_3 + 3Ti = 4Ho + 3TiO_2$. At temperatures above the melting point of holmium under the applied high vacuum conditions, elemental Ho begins to evaporate leading to a shift of the equilibrium to the right side. Hence, the higher evaporation rate of Ho with increasing temperature is followed in response by higher reduction rate of Ho₂O₃ and thus providing a continuous supply of Ho for the ionization.

2.2. Ion source

The measurements were performed with a split, hot cavity-type laser ion source consisting of a main hot cavity and a separated sample reservoir. The reservoir is a tantalum capillary of 200 mm



Fig. 1. Schematic overview of the experimental setup, showing the main components of the RISIKO mass separator and the connected Ti:sapphire laser system. For ion beam implantation, the microcalorimeters are mounted inside the Faraday cup.

length and 1.1 mm inner diameter. It can be resistively heated to a temperature of 2000 °C at a maximum current of 100 A. For a measurement, the current is slowly ramped from 0 A to 100 A to sequentially drive the dehydration and reduction process and once the melting point of Ho of 1460 °C is exceeded - to control the rate of released holmium atoms. The hot cavity serves as the atom-laser interaction volume. It is also made of tantalum with a length of 30 mm and an inner diameter of 2.2 mm. It is resistively heated by an electrical current of 270 A, to reach a maximum temperature of 2000 °C, which is kept constant during the measurement. The operating temperature is chosen to be high enough to prevent condensation of the holmium vapor, but at the same time as low as possible to minimize surface ionization of the atoms by contact with the hot surface. Ideally, the temperature should be equal over the complete volume, but in reality, the occurrence of temperature gradients is inevitable. Using computational fluid dynamics, a simulation model to reproduce the temperature distribution was created. It is based on the geometry and material properties of the individual parts. After calibration to pyrometrically measured temperatures, the coldest part of the ion source could be identified as the mounting point between the hot cavity and the sample reservoir. When operated at maximum temperatures of 2000 °C, the temperature at this point is around 1400 °C.

2.3. Titanium-sapphire laser system

Laser ionization was achieved using the resonant three step excitation scheme with pulsed titanium-sapphire lasers shown in Fig. 2. The design of the Ti:sapphire lasers is developed by the LARISSA group at the institute of Physics of the University of Mainz. Its most recent iteration is presented by Rothe et al. in [12]. The lasers were pumped by a single commercial Nd:YAG laser operating at a repetition rate of 10 kHz. It delivered 15.5 W of frequency doubled light of 532 nm wavelength to each of the lasers. Tuned to the desired wavelengths, output powers of 2.8-3.2 W were achieved. The laser driving the ground state transition was frequency doubled with a BBO crystal placed in the resonator. In this configuration, the output power was 300 mW at the second harmonic frequency. Temporal synchronization of the 50 ns long pulses was achieved by adjusting the position of the pump beam focus in the Ti:sapphire crystal. The wavelengths were tuned by a birefringent filter and a solid etalon with 300 GHz free spectral range. The latter was stabilized with a piezo stepper motor adjusting the tilt angle. With the feedback from a HighFinesse WS6/600



Fig. 2. Excerpt of the atomic level structure of holmium, showing the excitation scheme used in the measurements. Level energies and configurations are taken from [13], the ionization potential from [14].

wavemeter a wavelength variation of less than 2 GHz was achieved. All three beams were overlapped and focused collinearly into the hot cavity through a viewport in the separator magnet.

2.4. Mass separator

For the RISIKO mass separator, a 30 kV acceleration voltage is used. Ions are accelerated from this high voltage potential towards ground through an intermediate-potential extraction electrode as depicted in Fig. 1. The ion beam is collimated by an einzel lens and sent through a double focusing 60° sector field magnet for mass separation. Assuming a kinetic energy of 30 keV and a charge state of 1^+ , 165 Ho ions are separated from ions with mass m = 164 u or m = 166 u by 4 mm in the focal plane. An adjustable slit, set to a width of 1 mm, transmits more than 90 % of the beam while blocking neighboring ions and retaining a mass resolution of $m/\Delta m \ge 400$. The ion beam is then collected in a Faraday cup behind the focal plane with the beam current read out by a sensitive electrometer.

3. Results

3.1. Excitation scheme

The chosen excitation scheme (Fig. 2) was developed by Gottwald et al. [15] using the identical laser system and the mass separator at ISTF2, ORNL. It is based on transitions known previously from literature from the ground state up to the second excited state. The final step populates a strong auto-ionizing resonance. To evaluate the excitation scheme beforehand, the spectral profiles and saturation behavior of all three transitions were recorded by correspondingly tuning the exciting laser and varying the laser power with an adjustable attenuator, respectively. The results of these measurements are shown in Fig. 3. The laser line shapes were fitted using a Gaussian function



Fig. 3. Resonances and saturation curves of transitions one, two and three, stacked from bottom to top. Results from the fitted curves are listed in Table 1. For more details, see text.

$$I(v) = C_1 \exp\left(-\frac{(v - v_{\text{center}})^2}{2\sigma^2}\right) + C_2.$$
(1)

The power dependence of the ion current was fitted using

$$I(P_{\rm in}) = C_1 \frac{1}{1 + P_{\rm sat}/P_{\rm in}} + C_2 P_{\rm in} + C_3,$$
⁽²⁾

including a linear term to account for non-resonant photoionization as well as signal background. In cases of spectral profiles recorded at laser powers above the saturation level P_{sat} , a combination of Eqs. (1) and (2) was used to describe a power broadened Gaussian distribution:

$$I(v) = C_1 \frac{1}{1 + S^{-1} \exp\left(-\frac{(v - v_{center})^2}{2\sigma^2}\right)} + C_2,$$
(3)

with *S* representing the level of saturation. The numerical results of the fitting are presented in Table 1.

The first transition exhibits a strongly broadened spectral shape at a laser power of 267 mW, and is still significantly broadened at 4.2 mW. Only below a power level of 1 mW, the spectral shape is an undisturbed Gaussian profile with a width of FWHM = 6.0(1)GHz. This is partly caused by Doppler broadening of the transition at the source temperature of 2000 °C, which amounts to 2 GHz, and in most parts by the laser linewidth. The Ti:sapphire lasers have a linewidth of typically 4 GHz, here additionally broadened by a factor of $\sqrt{2}$ to 5.5 GHz in the second harmonic generation. The dependence of the ion current *I* on the laser power P_{in} similarly shows an early onset of saturation and is well described by Eq. (2) with a saturation power level $P_{\text{sat}} = 1.0(1)$ mW. The non-vanishing second, linear term indicates the one-color, two-photon ionization, i.e., a resonant excitation to the intermediate state and a non-resonant absorption of a second photon into the ionization continuum.

The transition to the second excited state has a width of FWHM = 31.2(6) GHz. Power broadening is not as strong in the first transition, in this case the available laser power equals about 2.5 times the saturation power of $P_{\text{sat}} = 1070(140)$ mW. The large linewidth cannot solely be caused by the laser linewidth (4 GHz) and the Doppler Broadening (1 GHz), thus is most likely caused by a wide hyperfine structure in the excited state. The ionization step has a comparable width of FWHM = 25.2(6) GHz. The transition could not be saturated with the available 2600 mW laser power. Accordingly, the line profile is well described by a Gaussian without having to take power broadening into account.

The excitation scheme therefore is well suited for use in a resonant ionization laser ion source, with the large linewidths of the transitions ensuring an efficient excitation, even in the case of small drifts in the laser wavelengths. The single drawback is the non-saturated ionization transition which could be improved in the future by enhancement of the exciting laser power.

3.2. Ionization efficiency

For a reliable determination of the ionization efficiency, five measurements were carried out, three of these with a sample size of 10^{15} atoms and two with 10^{14} atoms of 165 Ho. Fig. 4 shows the course of measurement #2 with 10^{15} atoms. The black curve in the center panel is the ion current measured in the Faraday cup. At regular intervals, the lasers were blocked, interrupting resonance ionization, then allowing to determine the ion current of surface ionization and signal background. This level was used to calibrate a background curve, plotted in gray, allowing to extract the ion current from resonance ionization.

Results of the analysis of spectral profiles and saturation curves of the three transitions used. The given linewidth are measured at maximum output powers P_my.

-						
Transition	$ \nu_{exp} $ (cm ⁻¹)	v_{lit} [13] (cm ⁻¹)	P _{sat} (mW)	P _{max} (mW)	$FWHM$ (cm^{-1})	FWHM (GHz)
1	24660.822(4) _{stat} (20) _{sys}	24660.80(5)	1.0(1)	267	1.06(2)	31.8(6)
2	12212.934(6) _{stat} (20) _{sys}	12212.96(5)	1070(140)	2600	1.04(2)	31.2(6)
3	11935.052(7) _{stat} (20) _{sys}	-	-	2600	0.84(2)	25.2(6)



Table 1

Fig. 4. Resistive heating current and measured ion current over the course of a measurement with a sample of 10¹⁵ atoms. The gray curve represents the background from surface ionization. The trend of the ion current is divided in four phases as indicated by the roman numerals. The lowermost panel shows the accumulated ionization efficiency calculated from the integrated ion current. For more details, see text.

The overall trend is representative for all measurements, dividing the cycle into four phases. The first phase is the process of heating up, during which only a low ion current is produced. Starting at a heating current of 50 A, the ion current increases strongly in the second phase. The third phase is the main part of the measurement, here the ion current is kept between 10 nA and 100 nA by increasing the heating current in small steps. Above this current, space charge effects would reduce the transmission through the beamline. When the sample is emptying, the evaporation rate decreases and in the last phase, when the heating current is at its maximum, the ion current decreases and settles to a level around 1 nA. As shown in the middle panel in Fig. 4, the majority of the ions are detected in the third phase. Even though the last phase extends in time beyond the range shown in Fig. 4, its contribution to the total detected charge is significantly less than 10 %. Variations in the general trend between individual measurements are limited to the duration and the maximum ion current of phase three, as well as the ion current in phase four. Fig. 5 shows the deduced ionization efficiencies for all five measurements, giving an average value of 32(5)%. In comparison, the signal and ionization efficiency from surface ionization is 20-50 times lower. During measurement #2 a titanium foil was placed in the Faraday cup, allowing to implant and collect the ions. This allowed to quantify the total ion charge additionally by neutron activation analysis in the same way the samples were quantified beforehand. The result of 37(2)% is in agreement with the directly measured value of 34(2)%, thus excluding systematic errors in the measurement beyond the given uncertainty.



Fig. 5. Overview of the ionization efficiencies in the different measurements. The average efficiency is 32(5) %, as indicated by the shaded area.

It should be emphasized that for all samples the beginning of the main ion production phase appeared at a heating current of 50–55 A. According to simulation results, this current corresponds to a temperature at the sample position between 1400 °C and 1480 °C. This value matches the melting point of holmium of 1460 °C, indicating the start of the evaporation driven reduction of Ho₂O₃ to Ho. But, even at maximum heating currents, the joint between sample reservoir and hot cavity does not reach temperatures above 1400 °C. Here, holmium atoms can condensate with a long retention time leading to the extended last phase of the measurements. Possible ways to significantly increase the temperature at this position are currently being investigated.

4. Conclusion

For the future application of ion beam implantation of ¹⁶³Ho, the ionization efficiency of holmium in a resonant laser ion source has been measured. With several samples of either 10¹⁴ or 10¹⁵ atoms of stable ¹⁶⁵Ho a reproducable, average ionization efficiency of 32(5)% was achieved. In comparison to the value of 40% from Liu [8], this is similar, albeit slightly lower, which could be attributed to the difference in the source geometry, especially the length of the laser ionization region. In addition, the laser power of the third laser was not sufficient to saturate the final, ionizing transition towards the auto-ionizing level at 48809.2 cm⁻¹. With modifications of the ion source to alleviate the temperature differences and optimizations in respect to the final optical transition, an increase in the ionization efficiency is expected, possibly matching the value from [8]. Already without these improvements, the ionization efficiency is most suitable for use in the ion beam implantation as part of the ECHo project.

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Publication III: Optimization of a laser ion source for ¹⁶³Ho isotope separation

This article has passed the refereeing procedure by *Review of Scientific Instruments*. It provides detailed information on simulations and measurements to optimize the laser ion source for the ECHo project. The initial ion source concept and design is based on the hot cavity thermal surface ionization, as used for on-line RIB production at ISOLDE/CERN and at other facilities. T. Kieck has optimized its efficiency and performance for the laser resonance ionization of Ho. Finite element thermal electricity calculations and chemical equilibrium simulations were used to optimize both the temperature profile within the ion source and the chemical reduction of the initial Ho compound. This led to a significant improvement in beam purity and ionization efficiency. It was the first of two major development steps of the resonant laser ionization of Ho at the RISIKO mass separator. All aspects described in this Publication III were initiated and performed by T. Kieck, who also provided the manuscript.

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Optimization of a laser ion source for ¹⁶³Ho isotope separation

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ABSTRACT

To measure the mass of the electron neutrino, the "Electron Capture in Holmium-163" (ECHo) collaboration aims at calorimetrically measuring the spectrum following electron capture in ¹⁶³Ho. The success of the ECHo experiment depends critically on the radiochemical purity of the ¹⁶³Ho sample, which is ion-implanted into the calorimeters. For this, a 30 kV high transmission magnetic mass separator equipped with a resonance ionization laser ion source is used. To meet the ECHo requirements, the ion source unit was optimized with respect to its thermal characteristics and material composition by means of the finite element method thermal-electric calculations and chemical equilibrium simulation using the Gibbs energy minimization method. The new setup provides an improved selectivity of laser ionization vs interfering surface ionization of 2700(500) and an overall efficiency of 41(5)% for the ion-implantation process.

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I. INTRODUCTION

A resonance ionization laser ion source (RILIS) provides an element-selective and remarkably efficient way to produce ions of almost any element. Such sources are widely used at isotope separator online (ISOL) facilities for the efficient production of isotopically and isobarically pure ion beams of rare isotopes.^{1–3} It has been shown that multistep laser excitation is particularly useful for selective and efficient isotope separation in the rare earth elements.⁴ Therefore, this process is also well suited for ion production to separate and ion-implant the rare unstable isotope ¹⁶³Ho⁵ used in the ECHo (Electron Capture in ¹⁶³Ho) project.⁶ This aims at measuring the electron neutrino mass by recording the spectrum following electron capture of ¹⁶³Ho using metallic magnetic calorimeters (MMCs).⁷ The synthetic radioisotope ¹⁶³Ho has a half-life of 4570(50)a.⁸ For ECHo, it is produced artificially by intense neutron irradiation of enriched ¹⁶²Er samples in the Institute Laue-Langevin (ILL) high flux nuclear reactor. The ¹⁶³Ho is then chemically separated from the target material and unwanted byproducts.⁹ The obtained sample mainly consists of the Ho isotopes 163, 165, and 166 m. While 165 Ho is stable, the isomer 166m Ho is a long-lived $[T_{1/2} = 1132(4)a]$ radioisotope.¹⁰ If present in the MMCs, its emitted radiation will lead to undesired background in the spectrum of ¹⁶³Ho. Therefore, the sample is mass separated at the RISIKO isotope separator at Johannes Gutenberg University Mainz to ensure a single-isotope ion implantation into the Au-absorber arrays of the ECHo MMCs. The RISIKO facility in its application for the ECHo source implantation is described in Ref. 5 including all details on the laser system and the all-resonant three-step laser excitation and ionization process, which makes use of strong optical resonance lines of the Ho atom. A sketch of the major components of the mass separator is provided in Fig. 1.

For future phases of the ECHo experiment large amounts of 163 Ho of up to 1×10^{17} atoms are intended to deliver suitable statistics in the decay spectrum.⁶ Correspondingly, for the ion implantation high ion currents in the order of 1 μ A and beyond for long term operation over months will be needed. Because of the limited availability of 163 Ho, an excellent efficiency of the ion source as well as the overall implantation process is required. For this purpose, the RISIKO mass separator is equipped with an advanced RILIS, allowing for dedicated and well controlled insertion, evaporation, atomization, and final ionization of a multitude of elements



including Ho under appropriate conditions. The sample material is usually available only in limited quantities. Therefore, high mobility and negligible losses inside the ion source unit during evaporation and transfer from the sample reservoir to the location of ionization is essential. In addition, highest reliability, mechanical stability during long term operation, and reusability of the major ion source components are indispensable. All these features depend on the physical, thermal, and chemical properties of the sample material, the carrier foil (which is introduced in most cases to assist complete chemical reduction of the sample), and the mechanical ion source components that were studied and optimized in this work. Different surface ion sources for online applications were already analyzed and optimized with similar methods¹¹⁻¹⁴ but results from these sources are not directly transferable to the RISIKO RILIS. At online facilities, the sample of interest is typically generated by proton-induced reactions inside a thick target of several hundred grams of porous material (such as UCx). The temperature profile of the target and ion source assembly is therefore different to that of the reservoir/cavity arrangement of the RISIKO setup. Substantial molecule formation in online sources is caused by the target material and cannot be suppressed by adding reducing agents as in case of the off-line RILIS at RISIKO.

In general, multistep resonant laser ionization is entirely element selective but influenced by a number of disturbances and unwanted side effects. Ionization on the hot surfaces¹⁵ that are necessary to produce and sustain single-atom metal vapors contribute to ion-formation alongside resonance ionization. The influence of this effect depends on the purity of the initial sample and on the carrier foil material. In addition, upon heating the sample, evaporation may partially occur in the form of molecular species. They may either ionize on hot surfaces as molecules, or decompose, thus releasing atomic or ionic species. Only the neutral atoms are accessible for the selective resonance ionization. At present, different techniques to overcome this problem of unwanted contaminations in the ion beam have been developed. These include decoupling the ionization volume from the atomizer (e.g., in the LIST or IG-LIS approach^{13,16}) or using dedicated low-work function materials for lining the inside of the ion source.¹⁷ The main arguments against using these techniques in case of the ECHo ion implantation are high sample losses of typically around 90% and low ion beam currents due to temperature limitations with rapid degradation of the ion source material in use.

II. THERMAL-ELECTRIC SIMULATION

A. Model and implementation

The conventional RISIKO laser ion source (denoted here as version 1 and sketched in Fig. 2) which was the starting point for the current work, consists of two main parts that are resistively heated independently by electric direct currents. Part 1, the sample reservoir (a1) serves to produce, transport, and confine the sample vapor and is jointly connected to part 2, the hot cavity (a2), wherein the atoms are ionized. The sample is placed in the upper part of the reservoir, a 165 mm long tantalum capillary with 1 mm inner diameter, closed in the upper third. In the adjacent hot cavity (a2), a 35 mm tantalum



FIG. 2. Cross section through the RISIKO laser ion source version 1. The parts are described in the text. Points of pyrometric measurements for Sec. IV A are indicated as p1 and p2.

tube with 2.5 mm inner diameter, the lasers are focused to resonantly excite and ionize the atoms. Generated ions are guided by the electric field of the heating currents toward the exit hole to access the electrostatic extraction field of the mass separator. Heating currents (maximum 150 A and 400 A for reservoir and hot cavity, respectively) are applied via an air-cooled clamp to the end of the reservoir and from a water-cooled rod through a multilayer tantalum spring (b1) to the hot cavity. Both are grounded through the electrode (b2), which is mounted on a water-cooled plate. The tantalum mounting part (c1) is attached to the spring using a washer (c2) and nut (c3), both made of graphite, to prevent hot surface welding. Heat radiation of the hot cavity is shielded radially by a tantalum tube (d1) surrounded by a multilayer foil and an additional tantalum sheet (d2) toward the extraction gap.

The ion source is drawn as a 3D computer aided design (CAD) model in detail. Before computing the temperature distribution a preprocessing step was performed: the model was stripped of irrelevant components and shapes to lower the geometric complexity and save computer run-time. Especially, round shapes not significantly affecting the power dissipation or heat transfer were transformed to preferably parallel-edged shapes leading to lower node densities in meshing the finite elements. Figure 3 shows the ion source version 1 before and after preprocessing.

The finite element method (FEM) calculations are carried out by Autodesk® CFD (version 2019 Build 20180307) with temperature-dependent material properties.¹⁸⁻²² Three thermodynamical effects are considered to obtain reliable results.²³



FIG. 3. 3D CAD model of the RISIKO laser ion source version 1 before (a) and after (b) preprocessing.

1. The heating power *P* which is produced by a constant current *I*, assuming a resistivity *R* depending on the temperature *T* as

$$P(T) = R(T) \cdot I^2$$

2. The transfer of heat *q* by thermal conduction is given by

 $\dot{q} = -\lambda(T)\nabla T,$

where λ is the temperature-dependent thermal conductivity.

3. The heat radiation acting as heat transport

$$\dot{q} = \varepsilon(T)\sigma T^4$$

with temperature-dependent hemispherical emissivity ε and the Stefan-Boltzmann constant σ .

Numerical approximations of the differential equations used in the simulation need to be analyzed for convergence in node distance $\Delta x = |x_A - x_B|$ of the mesh and iteration steps n.²⁴ For the first calculation step, a rough standard mesh is created and the solver runs in steady-state mode at highest heating currents until convergence is reached. In three subsequent steps, areas of high temperature gradients are localized and the mesh in these regions is refined to enhance accuracy. The resulting adaptive mesh, as shown exemplarily for the hot cavity in Fig. 4 with about 500 000 elements is used for the subsequent calculations, in which the heating currents are varied.

B. Simulation results

The result of the initial design version 1 shows a significant temperature drop in the connection region between sample reservoir



FIG. 4. Adaptive mesh of the hot cavity (a2) with higher node density in the regions of high temperature gradient because of contact to cooler adjacent parts.

and hot cavity, where significant heat losses occur through the tantalum spring and adjacent parts. The overall temperature distribution along the source unit is shown in Fig. 5 by the black curve. This leads either to a condensation point for the sample vapor at this position or to a high surface ion background and mechanical instability while overheating the whole setup to raise the coldest spot above the sample melting point. One aspect of primary importance for optimum source performance was thus to modify the design in such a way that the coldest temperature in this region could be kept above the melting point of Ho of 1472 °C.²⁵

The region near the ion source exit hole is only of minor relevance for possible condensation effects. Already generated ions are confined by a negative thermal plasma potential and guided to the extraction gap.²⁶ Neutral atoms in the wall region are lost anyway because they are most likely no longer crossing the laser interaction region before exiting the hot cavity. The refined version 2 of the RILIS evidently includes three improvements at the central current support between the reservoir and hot cavity (c1) to significantly reduce heat-loss through thermal radiation.

- 1. The spring (b1) is cut off at the top to the smallest possible geometry conserving current and mechanical stability.
- 2. Because of the very high emissivity of graphite ($\varepsilon \approx 0.85^{20}$), the material of nut (c3) is changed to molybdenum.
- 3. The graphite washer (c2) is also replaced by one made of molybdenum.

The resulting temperature curve for version 2 is rather similar to before but now every point of the atom path from reservoir to hot cavity has a temperature above the melting point of Ho as indicated in Fig. 5 by the red line.

In the next optimization step toward version 3, special attention was given to the mechanical stability of the reservoir (a1) to prevent any possible sample-material losses or measurement disruptions by distortion or rupture of ion source components. A copper supporting ring was constructed that uses the existing infrastructure of two water cooled copper rods for a stable positioning and optimum cooling of the rear end of the reservoir as shown in Fig. 6.







FIG. 6. Computer-rendered drawing of the ion source version 3 with a 1/4 cutout to see the inner structure.

The sample reservoir was shortened to half its original length and now consists of a 90° bent capillary, held securely on the copper supporting ring. This design allows for a reliable connection of the reservoir to the hot cavity also at high temperatures, where Ta is getting soft. It also significantly reduces the heat generation at the ion source, while fully conserving the thermal profile of version 2 along the atom path. The related heat stress of the various materials inside the vacuum chamber is thus minimized.

III. CHEMICAL EQUILIBRIUM SIMULATION

As second step, the high-temperature chemistry of the different interacting materials inside the ion source unit was studied. The chemical composition of the sample material is of high relevance for the achievable RILIS efficiency. Dissolved metals, such as those used to make accurately dosed samples for laser ion sources, are often diluted into nitric acid (e.g., AAS standards). Therein the metals are present as oxides (e.g., Ho₂O₃). Before insertion into the ion source, the sample is typically dried on a $3 \times 3 \text{ mm}^2$ piece of $12.5 \,\mu\text{m}$ thick carrier foil, which is co-introduced to serve as reducing agent. The foil is folded a few times to fit into the sample reservoir. The overall mass separator ion current emitted from the ion source is composed of the total of all ionized species. To minimize this ion load, and therefore preserve efficiency and beam quality, the reducing agent should have a low vapor pressure at the ion source operation temperature and a high ionization potential.

For minimizing the Gibbs energy of the chemical reaction system between sample and reducing agent,²⁷ the Equilibrium Composition Module of Outotec HSC Chemistry (version 9.4.1 Build 09.01.2018) is used. The results are interpreted considering that this type of chemical simulation does not take into account reaction kinetics. Obtained results indicate that binary compounds of lanthanide with nitrogen are energetically favorable. Experimentally, they were never observed and seem to be strongly inhibited. Thus, these compounds were excluded from the simulation.

The standard carrier foil material for the RISIKO laser ion sources, i.e., Ti, shows disadvantages in the temperature regime needed for high ion currents starting at around $1500 \,^{\circ}C^{5}$ by HoO



agents, obtained with Outotec HSC Chemistry.

gas formation as shown in Fig. 7. A part of the molecules will be lost because they are not ionized or separated in the magnet. Another portion will be cracked and ionized at hot surfaces. Because of the chemical similarity, the same would happen for any lanthanide contained in the sample, leading to a nonselective beam contamination. This effect can be avoided by using Zr, which has the additional advantage of a higher melting point. The addition of a small amount of Y in the same order of magnitude as the Ho sample material (about 10¹⁵ atoms), applied, e.g., by pulsed laser deposition after sample dehydration, lowers the reduction point to room temperature according to our simulations. This leads to a more uniform and slightly slower rise of the ion current during ion source heating because the Ho gas formation is no longer depending on reduction kinetics but only on the Ho vapor pressure. At the moment, there is not enough data on this to experimentally confirm the simulations.

IV. EXPERIMENTAL RESULTS

The different adaptations from the simulation results were extensively tested before implementation for routine use in the different implantation phases of the ECHo project and for other experiments at the RISIKO mass separator. For this purpose, additional measuring capabilities regarding relevant parameters and their systematics were introduced.

A. Temperature measurement

A two color pyrometer (Heitronics KT 81R) is used for a contactless temperature measurement under full operation conditions. While measuring at two infrared wavelengths, the results are widely independent of the vacuum window properties and any kind of pollution because of source material vaporization and condensation. The material-dependent emissivity ratio was precisely calibrated by measuring temperatures of a Ta wire up to the melting point with an 10 °C statistic and 22 °C systematical error.



FIG. 8. Comparison of ion source version 2 temperature measurement and simulation result at the sample reservoir and the hot cavity heat shield. The hot cavity is heated with 325 W.

The measurement was performed at two characteristic positions of the ion source version 2: heat shield (p1) and sample position in the reservoir (p2) as indicated in Fig. 2, combined with heating-power measurements of reservoir (a1) and hot cavity (a2) inside the vacuum chamber. The comparison of measurement and simulation at the reservoir is given in Fig. 8, showing a very good absolute temperature agreement within uncertainties. To compare the relative effects of heat radiation and conduction, a measurement of the heat shield is given too, which also agree with results from the simulation.

B. Ionization efficiency

To evaluate the effect of temperature profile optimization and homogenization, overall efficiencies as described in Ref. 5 with the different ion source versions 1-3 were measured and compared in Fig. 9. The 32(5)% mean value of the earlier measurements with version 1 is increased to 41(5)% of version 2 and 3. This is in good agreement with a 40% value, as obtained independently by Liu with a



FIG. 9. Overview of the ionization efficiency measurements. The average efficiencies of 32(5)% and 41(5)% with standard deviation are indicated by the shaded area.

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slightly different ion source type.²⁸ This new value seems to be independent from condensation effects in the ion source and to reflect the ionization rate achievable with the particular ionization scheme at the available laser power. This makes further ionization scheme development and comparison possible. The newly chosen reducing agent of Zr or even Zr + Y does not show any influence to the overall efficiency within the experimental accuracy. Therefore, one can conclude that there is no significant loss of Ho in the form of HoO⁺ or neutral HoO/Ho gas. Additionally, at the ion current level between 1 nA and 100 nA, where the measurements are performed, the Ti⁺ load of the ion beam does not influence the efficiency.

C. Mass spectrometry

Surface ionization gives the possibility to compare the chemical simulation results with the experimental situation. Depending on the ionization potential almost every species in the hot cavity is ionized to a certain extent. Figure 10 compares the measured mass spectra for resonance ionization of Ho with residual surface ionization for the two reducing agents Ti and Zr. The mass spectrum with Ti shows peaks of Ho, HoO, HoO₂, and Ti, also with its oxide. Due to the low melting point of Ti, the number of all Ti ions is almost in the same order of magnitude as that of Ho ions. This might affect the mass spectrum with Zr as a reducing agent shows a negligible amount of ions beside Ho. The absence of HoO confirms the excellent reduction capability of Zr as predicted by the simulation.

D. Laser selectivity

A further way to analyze the chemical composition inside the ion source is to measure the surface-ion current while blocking the laser beams and to compare it to the laser ion signal. These measurements are shown in Fig. 11. Ti as reducing agent leads to a rather



FIG. 10. Relevant parts of the mass spectrum by resonance ionization of Ho with residual surface ionization, measured at reservoir temperatures of about and 1550 °C.



FIG. 11. Overview of the laser-to-surface ionization selectivity measurements. The average ratios of 60(50) and 2700(500) with standard deviation are indicated by the shaded area.

low laser-to-surface ion ratio of 60(50) (see Fig. 11). This background signal is most significant at high ion current as produced at temperatures of about 1500 °C. Zr as reducing agent significantly lowers the surface ion signal and leads to a laser ionization selectivity of 2700(500) in the ratio of laser to surface ions, almost 50 times surpassing the earlier value. This difference can be assigned to two diverse effects. First is the decomposition and direct ionization of HoO gas on the hot surfaces. The second is a difference in ionization probability of Ho on the hot sample carrier foil. It is calculated by the Saha-Langmuir equation, showing that the probability on Ti only exceeds the value on Zr by a factor of two. Therefore, it should only make a small contribution and the majority should come from the first effect. Because of the chemical similarity, for both effects the results can be transferred to the neighboring lanthanides. Thus, Zr as reducing agent significantly lowers the unselective ionization of these lanthanides present in the sample.

V. CONCLUSION

Extensive thermal and chemical simulations have been performed to improve the off-line RILIS used at the RISIKO mass separator of Johannes Gutenberg University Mainz for the present and upgrading it for the future phases of the ECHo experiment. Temperature and mass spectrometric measurements confirm the simulation predictions and the usefulness of the corresponding experimental improvements. The final ion source design has shown reliable operation over many measurements and an efficiency in Ho ionization of 41(5)%, in good agreement with the value 40% of Liu obtained at the ISTF2 facility of ORNL in a rather similar approach.²⁸ The newly chosen reducing agent Zr increases the laser-to-surface ionization selectivity by almost two orders of magnitude. It thus prevents contamination from isobaric ¹⁶³Dy surface ions in the ¹⁶³Ho implantation for ECHo. Zr also enables to operate the ion source at high temperatures as needed for the envisaged ion currents in the 1 μ A range without adding significant ion load to the limited beam current of the mass separator.

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Chapter 5

Publication IV: Highly efficient isotope separation and ion implantation of ¹⁶³Ho for the ECHo project

This article was submitted to *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment* and is currently undergoing the reviewing process of the journal. It describes the further important step of optimization towards higher efficiency within the resonance ionization laser ion source of the RISIKO mass separator. For this purpose, a simplified and optimized two-step excitation scheme was identified and characterized, which leads to an efficiency gain of about the factor 1.5. In addition, the complete separation and implantation process required to fabricate the fully closed ¹⁶³Ho source was analyzed. The maximally permitted ion current was derived, which allows to achieve a high geometric efficiency within the implantation into the arrays of small-scale single MMC detector pixels. The document status confirms that the majority of the second phase specifications of ECHo (100k) are met.

All studies were carried out by T. Kieck and compiled by him in this manuscript. Additional material on the implantation of the ECHo detectors can be found in Chapter 8 and in Appendix A.1.3.

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Highly efficient isotope separation and ion implantation of ¹⁶³Ho for the ECHo project



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ABSTRACT

The effective electron neutrino mass measurement in the framework of the ECHo experiment requires radiochemically pure ¹⁶³Ho, which is ion implanted into detector absorbers. To meet the project specifications in efficiency and purity, the entire process chain of ionization, isotope separation, and implantation of ¹⁶³Ho was optimized. A new two-step resonant laser ionization scheme was established at the 30 kV magnetic mass separator RISIKO. For ionization and separation, an average efficiency of $69(5)_{\text{stat}}(4)_{\text{sys}}$ % was achieved using intra-cavity frequency doubled Ti:sapphire lasers. The implantation of undesired ^{166m}Ho, which is present in trace amounts in the initial ¹⁶³Ho sample is suppressed by about five orders of magnitude by the mass separation. A dedicated implantation stage with focusing and scanning capability enhances the geometric implantation efficiency into the ECHo detectors to 20(2) %.

1. Introduction

The ECHo [1] (Electron Capture in ¹⁶³Ho) project is aimed at measuring the effective electron neutrino mass by analyzing the spectrum following electron capture in ¹⁶³Ho implanted in large arrays of Metallic Magnetic Calorimeters (MMCs) [2,3]. There are several other projects using direct kinematic methods to perform model-independent measurements on the neutrino mass. These can be divided into two groups according to the element and decay to be measured: the ³H β -spectrum measurements are performed by the projects KATRIN [4], Project8 [5] and PTOLEMY [6]; besides ECHo, the EC-spectrum of ¹⁶³Ho is also measured by HOLMES [7] and NuMECS [8]. In the ECHo project, the synthetic radioisotope ¹⁶³Ho with a half-life of 4570(50) a [9] is produced by intense neutron irradiation of an enriched ¹⁶²Er target in the Institute Laue-Langevin (ILL) high flux nuclear reactor [10]. The Ho fractions are then chemically separated from the target material and any other interfering elements [11]. The Ho samples obtained after chemical separation contain ¹⁶³Ho, ¹⁶⁵Ho (stable) and ^{166m}Ho (radioactive). The latter is a long-lived nuclear isomer ($T_{1/2}$ = 1132(4) a [12]). If present in the MMCs, the emitted radiation leads to undesired background in the spectrum. Therefore, it has to be separated before incorporation of the sample into the detector absorbers. The most suitable method is the mass separation of an ionized Ho beam with subsequent ion implantation, which is used by both HOLMES and ECHo.

For the ECHo project a resonance ionization laser ion source (RILIS) is applied at the RISIKO isotope separator [13] at Johannes Gutenberg University Mainz. Compared to other ionization methods, e.g. thermal or by particle impact, RILIS offers elementary selectivity in the production of high-quality ion beams of almost all elements. This property is not of the highest relevance for ECHo, since the contamination by non-Ho elements in the sample could already be greatly reduced by chemical purification but the very high efficiency of the ionization process makes it the best choice for the project.

For the presently running ECHo 100k phase of the experiment for a neutrino mass measurement in the sub-eV range, large amounts of 163 Ho of more than 1×10^{16} atoms enclosed in more than 10^4 detectors (10 Bq per detector) are required to deliver adequate statistics in the decay spectrum in a reasonable time frame [1]. Due to the limited availability of 163 Ho and to keep the required implantation time of the ECHo arrays low, excellent efficiency of the ion source and implantation process as well as transfer through the separator is required. For this purpose, the RILIS of the RISIKO mass separator is specifically optimized for Ho gas formation and ionization with minimum losses [14] but further improvements are needed. The project

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also requires the ^{166m}Ho: ¹⁶³Ho ratio to be $\leq 5 \times 10^{-9}$ to delimit the background level to a value $< 10^{-5}$ counts/eV/det/day [1].

Fig. 1 shows the major components of the RISIKO mass separator. It consists of four main parts:

- The ion source comprises the sample reservoir and the ionization cavity. Both are resistively heated independently of each other. Within the ionization cavity, the resonant laser ionization takes place. All parts are in detail described in our previous publication [14]. The development of a new laser ionization scheme with higher ionization efficiency is presented in Section 2. The whole ion source unit is placed on a high voltage platform, typically operated at +30 kV. From there, the ions are accelerated to ground potential for mass separation.
- 2. The ion optics involve the components of the extraction electrode, the Einzel lens, the orthogonal pair of electrostatic deflectors, and the quadrupole lens triplet directly ahead of the sector field separation magnet. In 40 mm distance to the ion source, the extraction electrode is accelerating the ions to about 10 keV. At the Einzel lens, the full kinetic energy of 30 keV is reached. The ion beam generated in this way has a large and constant spatial cross-section inside the magnet in order to ensure good mass resolution.
- 3. The tunable 60° sector field magnet separates different mass-tocharge ratios. To optimize the beam entrance parameters into the magnet, it can be steered and shaped by the quadrupole lens. At the separation slit, the desired species is transmitted while all other ones are blocked. The magnetic mass separation is characterized in Section 3.
- 4. After the magnet focus, the beam undergoes additional focusing in an Einzel lens and deflection. Quantitative ion detection is realized by current measurement with a Faraday cup, where also the MMC implantation takes place. This is described in Section 4.

Similar combinations of a RILIS with a mass separator are commonly used worldwide at isotope separation on-line (ISOL) facilities for the efficient production and delivery of isotopically and isobarically pure ion beams of rare isotopes. These are typically produced by high-energy proton bombardment in a nuclear reaction target situated immediately at the ion source [15–17].

2. Resonance ionization of Ho

In general, multi-step resonant laser ionization is a highly elementselective process leading to reduction of components of unwanted elements in the ion beam. The ultimate limitation of selectivity is given by thermal ionization processes occurring on the hot surfaces [18] that are necessary to produce and sustain single-atom vapor. Correspondingly, the influence of surface-ionization has to be characterized individually for each elemental composition in the ion source.

2.1. Sample material and atomization

All systematic measurements on stable ¹⁶⁵Ho were performed using commercially available atomic absorption standard (AAS) nitric acid solution with a Ho concentration of 1 g/L (99.9% purity). The solution was diluted by a factor of ten with distilled water (2% random volume accuracy). Individual drops (3 μ L volume, 2% random volume accuracy) were dripped onto 3 mm × 3 mm × 25 μ m Zr foil (99.2% purity), which served as reducing agent, and were evaporated to dryness. Each drop contained 1.10(4) × 10¹⁵ Ho atoms. The Zr foil was than folded a few times in one direction and inserted into a Ta tube with 1.1 mm inner diameter and 2 mm outer diameter. The ion source region was kept at vacuum (about 10⁻⁷ mbar) and at temperatures of about 560 °C. Under these conditions, the initial compound Ho(NO₃)₃ · 5H₂O of the AAS solution is fully decomposed leading to Ho₂O₃ [19]. At about 800 °C reduction by the Zr foil sets in and elemental Ho sublimates.

This diffuses to the ionization cavity where interaction with the laser radiation takes place [14].

All simulations and measurements performed with 165 Ho are representative for the case of 163 Ho, since the samples are in the same chemical form and purity [11].

2.2. Titanium-sapphire laser system

For resonant two-step excitation, two lasers of the Mainz titaniumsapphire laser system were used in conventional Z-shaped resonator geometry [20]. The lasers operate in pulse mode at 10 kHz repetition rate and can be tuned from 680 nm to 960 nm, thus almost completely covering the Ti:sapphire amplification range. Each of the lasers was pumped with 15 W to 18 W of 532 nm light from a commercial 60 W frequency-doubled Nd:YAG laser. An average output power of 3 W in the required range of fundamental wavelength was measured.

To overcome the low power of external single-pass second harmonic generation with values below 300 mW for Ho [21], the technique of intra-cavity frequency doubling [22] was used. The efficient conversion leads to about 500 mW output power of the second-step laser far away from the gain-maximum wavelength of the Ti:sapphire crystal. The second advantage of intra-cavity multi-pass second harmonic generation is a resulting high-quality beam profile without astigmatism, thus increasing the relative photon flux in the ionization volume.

The laser beams were focused into the ionization cavity and overlapped there. By adjustment of the pump focus position within the Ti:sapphire crystal the 50 ns long output pulses were temporally synchronized and optimized for highest ion production rate, rather than for maximum laser power.

2.3. Excitation scheme development

In previous works on highly efficient laser ionization of Ho [14, 21,23,24], a fully resonant three-step scheme was used, developed by Gottwald et al. and shown in Fig. 2. As was pointed out by Schneider et al. [21] in detail, the third step does not exhibit saturation even for the maximum accessible laser power. With the resulting reduced excitation probability, an ionization efficiency of about 40% was reached [14,21,24]. Accordingly, the main goal for the ECHo project was the identification of an ionization scheme, for which full optical saturation and thus maximum possible ionization efficiency can be realized.

If g_i is the degeneracy of the *i*th ionization scheme level, the partial level population of the final state f, as described in [25], is given by

$$n_f = \frac{g_f}{\sum_i g_i}.$$
 (1)

Consequently, the ionization probability and efficiency for a two-step scheme is expected to be higher than for a three-step scheme if the intermediate transition is fully saturated and the second step leads to a sufficiently strong auto ionizing transition.

The enhanced output power in the second harmonic range and the higher spatial beam quality of the intra-cavity frequency-doubled titanium-sapphire laser system served to obtain full saturation in both transitions of a newly developed resonant two-step ionization scheme for Ho (Fig. 2). In the present work, both steps were characterized by studying the spectral profile and the laser-power dependence by recording the ion current. The measured data are shown in Fig. 3 and the fitting results are summarized in Table 1.

The first step was identical to that used in the three-step scheme. The spectral profile of the first transition was measured at full laser power. The data were fitted with a power-broadened Gaussian function with the level of saturation *S*, the central wavenumber v_c , and the variance σ^2 :

$$I(v) = C_1 \frac{1}{1 + S^{-1} \exp(-\frac{(v - v_c)^2}{2\sigma^2})} + C_2.$$
 (2)

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Fig. 1. Overview of the RISIKO mass separator. The ion source development is described in Section 2, the magnetic mass separation in Section 3, and the implantation into the metallic magnetic calorimeters (MMCs) in Section 4.



Fig. 2. Comparison of the previously used three-step (left path) and the newly developed two-step (right path) excitation scheme for Ho with the same first excitation step showing the corresponding atomic levels. The configurations and energies are taken from [21,26,27] and this work.



Fig. 3. Spectral profile and saturation curve of the auto-ionizing transition. Results are discussed in the text.

The second step was found by spectroscopic investigation of Ho and leads to a strong auto-ionizing state located just $1 \, \mathrm{cm}^{-1}$ above the

Table 1

Numerical results of the line and saturation measurements of the two scheme transitions, shown in Fig. 3. $P_{\rm sat}$ is the saturation power of the transition and $C_{\rm photo}$ the factor of the non-resonant photo-ionization.

Transition	(cm^{-1})	(cm^{-1})	P _{sat} (mW)	C _{photo}
1	24660.80(5)	24660.8(4)	3.3(3)	$7(2)\times 10^{-4}$
2	-	23906.16(3)	240(80)	$0(3) \times 10^{-4}$

ionization potential (IP) of $48565.910(3) \text{ cm}^{-1}$ [27]. The data are fitted with the theoretical model for the natural line shape of an auto-ionizing state from Fano [28]:

$$I(\epsilon) = \frac{(C+\epsilon)^2}{1+\epsilon^2}, \quad \epsilon(\nu) = \frac{\nu - \nu_c}{\Gamma/2}.$$
(3)

The spectral shape of the first transition is strongly powerbroadened with FWHM = $1.11(5) \, \text{cm}^{-1} = 33(2) \, \text{GHz}$ width. This is much broader than the sum of about 2 GHz Doppler broadening and 6 GHz second-harmonic laser linewidth. The Fano profile of the second transition shows a width of FWHM = $1.12(3) \, \text{cm}^{-1} = 34(1) \, \text{GHz}$.

The saturation is measured by gradually reducing the laser power with a variable attenuator. The data are shown in Fig. 3. Both transitions were fitted to a laser-power dependent ion current model with constant background mainly caused by surface ionization (C_{bg}), a power-dependent linear term for non-resonant photo-ionization with the slope C_{photo} , and the saturation term for resonance ionization converging to the limit C_{sat} :

$$I(P) = C_{\text{sat}} \frac{1}{1 + P_{\text{sat}}/P} + C_{\text{photo}}P + C_{\text{bg}}.$$
(4)

In Table 1, the negligible coefficient $C_{\rm photo}$ confirms that the resonant photo-ionization is dominant over the non-resonant one. For the first transition, the power level P_{sat}, at which half of the maximum ion current is reached, is about three times higher than in the measurements of Schneider et al. [21]. This can be caused either by a broader spatial profile or by a worse overlap of the atom cloud and the laser in the ionization region at the same laser power. Nevertheless, the first step is addressed with a laser power well above saturation and this completely compensates for a potentially worse overlap. A saturation behavior is clearly observed in each step, including the ionization step, which was not the case in the previously used three-step scheme. With Eq. (4), the ultimate ionization rate in the second step for the maximum achievable laser power of $P_{\text{max}} = 500 \,\text{mW}$ can be calculated to $I(P_{\text{max}})/I(\infty) =$ 70%. In addition, the saturated broad excitation profiles provide the advantage that both transitions tolerate small drifts in laser wavelength without measurable reduction in efficiency.

2.4. Ionization efficiency

The characterization of the new two-step excitation scheme for Ho was done via a measurement of the ionization efficiency. For this



Fig. 4. Time sequence of the fourth efficiency measurement from the current work, shown in Fig. 5. Upper panel: sample temperature. Lower panel: ion current and cumulative efficiency. The vertical line indicates the time, where the melting point of Ho [29] was reached.

purpose, a well-defined number of Ho atoms (cf. Section 2.1) is fed into the ion source. These samples are then ionized and guided through the mass separator. The ion current is measured in a Faraday cup directly after the separator slit. With a ring electrode before the cup operated at -100 V, most of the secondary electrons from ion bombardment of the collecting electrode are repelled, thus ensuring a reliable ion current measurement. In Fig. 4 an example of such a measurement is shown. The temperature at which the sample was kept is indicated. The solid curve in the lower graph is obtained from the time integral of the current measured by the Faraday cup. An efficiency of 100% corresponds to the charge of the total number of atoms in one sample (Section 2.1), singly ionized and collected by the Faraday cup.

The ionization cavity is gradually heated to constant operation condition with temperatures from 1500 °C to 2100 °C, measured at the coldest and hottest region inside the ion source, respectively. The sample reservoir is then heated to a value of about 1400 °C. At this temperature, the ion current is high enough for laser and ion optics optimization. When the melting point of Ho of 1470 °C [29] is exceeded, the ion current rapidly increases. For implantation of real Ho samples into the MMCs, the ion current will be stabilized between 50 nA and 200 nA by adaptively increasing the reservoir heating current and consequently controlling the sample temperature. The same regime was applied in the present measurements. After a period of $45\,\mathrm{min},$ over 95%of the final efficiency is reached and an ion current drop by more than one order of magnitude is observed. The temperature was not increased any further at this time as this no longer has any significant influence on the ion current. With the sample approaching full exhaustion, a final release of even the last few percent of the initial amount takes several hours.

Before each efficiency measurement a blank Zr foil was placed in the ion source and heated up to verify the absence of any contamination with stable Ho or any other interference on mass 165 u present in the foil or the source, e.g., from memory effects of a previous run. Five efficiency measurements $x_{1...5}$ were performed and show results in very close agreement. Fig. 5 compares the data with previous measurements on Ho performed with three-step resonance ionization [14,21,24], which resulted in significantly lower mean efficiencies. The measurement errors Δx_i for values x_i are dominated by the inaccuracy of the sample preparation, as described in Section 2.1, i.e. by the uncertainty of the number of Ho atoms introduced. The mean efficiency

$$\bar{x} = \frac{\sum_{i} w_{i} x_{i}}{\sum_{i} w_{i}}$$
(5)

of 69% is obtained by instrumentally weighting $(w_i = 1/\Delta x_i^2)$ the five values $x_{i=1,...5}$. We define the statistical error of the mean efficiency as



Fig. 5. Efficiency measurements on Ho with two-step ionization scheme compared to previous measurements with three-step scheme. The mean value of the two-step scheme is $69(5)_{stat}(4)_{sys}$ %, as indicated by the horizontal lines.

the fluctuation between individual measurements that is well described by the mean absolute deviation

$$\Delta \bar{x} = \frac{\sum_{i} w_{i} |x_{i} - \bar{x}|}{\sum_{i} w_{i}}.$$
(6)

Earlier measurements additionally indicated a systematic error occurring during the current recording of the 30 keV ion beam in a Faraday cup because of secondary-electron and possible secondary-ion ejection from the collection electrode by sputtering. This leads to either an overor underestimation of the ion current, respectively. We assess this systematic error with 5% of the measured efficiency. The new data confirm the expectations described in Section 2.3 about enhanced efficiency of a two-step ionization scheme over the previously employed three-step scheme. An increase of almost a factor of two was obtained.

2.5. Element selectivity

The elemental selectivity is another advantage of resonant laser ionization compared to processes using high temperatures or electron/ion bombardment for ionization. During identification of suitable ionization schemes, the excitation steps must be monitored to ensure that no isobars of the isotope of interest are ionized. If this condition is met, non-laser ionized isobars and isotopes in the mass-selected ion beam will mainly be caused by three effects:

• Thermal ionization of isobaric atoms and molecules (including Ho) on the hot surfaces needed for the production of single atom vapor.

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Fig. 6. Laser to background ion ratio measurements on Ho compared to previous measurements. The mean value is 1200(900), as indicated by the horizontal lines.

- Electron impact ionization of atoms or molecules induced by electron emission in the high electric field of the extraction gap. The ionization of species in the gap leads to a lower kinetic energy. Ions with a higher mass therefore contribute to the beam because of the same deflection radius in the magnet as the desired mass.
- Insufficient mass separation.

While the mass separation of Ho isotopes is strongly influenced by the laser ionization as discussed in more detail in Section 3, a discrimination of the three interfering effects and the ionized species is not possible. Correspondingly, the sum of the ion beam species produced by these effects will be termed as background signal and is measured by repeatedly blocking the laser beams for about 10 s. This is responsible for the sharp drops in signal intensity every 2 min, visible in Fig. 4. The ratio of laser to background signal for the five efficiency measurements is calculated by dividing the accumulated ion charge by an integrated curve of the interpolated ion current extracted from these points. The results are given in Fig. 6 in comparison to previous measurements. The mean value of 1200 for signal to background is calculated using statistical weights $w_i = 1/x_i$. It is about a factor of 2 lower than the value measured with the three-step scheme. With Eq. (6) a high mean absolute deviation of 900 is calculated due to the substantial scatter of the data points. Additionally, it indicates a trend to higher values. As the data points in Fig. 6 are plotted in chronological order of their measurement, this could hint at the influence of the optimization of spatial and temporal overlap of the lasers applied along the measurements. The average of the last two data points is 2400(400), which is identical within the experimental uncertainties with the three-step-scheme measurements taken in 2018 [14].

3. Ho isotope separation

The elementally pure ion beam from the resonance ionization process is mass separated in a 60° double-focusing sector field magnet with a FWHM mass resolution of $m/\Delta m \ge 400$. An astigmatism of the ion beam caused by manufacturing tolerances of the magnet is adjusted by a quadrupole lens operated at 20 V difference between horizontal and vertical electrodes. At the magnet focal plane, the desired mass number is separated from its neighbors by a vertical slit of about 2 mm width, reducing the transmission by less than 5%. While the mass resolution primarily describes the central Gaussian part of the mass peak down to half of its maximum, the quantity is not suitable to calculate isotope separation factors with mass difference of 3 u or more. For recording an entire peak in the mass spectrum, the ion current of stable ¹⁶⁵Ho is measured in a Faraday cup by an electrometer with high dynamic range (about 10 fA noise level), installed directly behind the separation slit and recorded while slowly scanning the magnetic field. Every data point represents a spatial integral of the ion beam current over the slit width. A convolution of the mass peak and a top-hat function of the slit transmittance results (cf. Fig. 7). The tailing towards lower



Fig. 7. Mass scan performed with 1 nA of $^{165}{\rm Ho}$. The separation factor of $^{166m}{\rm Ho}$ in the $^{163}{\rm Ho}$ implantation can be observed in the signal level at $-3\,u.$

mass numbers is caused by resonant laser ionization of atoms present between ion source and extractor (cf. Fig. 1) [30]. The ionization of species in this gap leads to a lower kinetic energy. Ions with a higher mass therefore contribute to the beam because of the same deflection radius in the magnet as fast ions of the desired mass.

Expectedly, ^{166m}Ho is the dominant contamination in the ion beam before the separator magnet. Even if the mass peak in Fig. 7 was measured with ¹⁶⁵Ho, all laser-ionized Ho isotopes have almost the same peak shape with different intensities. If the peak maximum at relative mass 0u is from 166m Ho, the magnet is tuned to -3u for the ¹⁶³Ho implantation. The relative current level at this position gives the respective level of ^{166m}Ho isotopic contamination in the implant. From -2u to still lower masses, the signal fluctuates at the electrometer noise level of about 10 fA. The mean value of the data points between -2u to -5u is used for calculation of the minimum expected isotope suppression in this range. In this way RISIKO is shown to reduce the ^{166m}Ho and other contaminants with mass 166 u and higher in the $^{163}\mathrm{Ho}$ implant to ${\leq}1.4(6)\,{\times}\,10^{-5}$ of the amount before the magnet. The suppression factor of 165 Ho, shown at -2u, i.e. in the lower-mass tailing of the peak, is $1.0(5) \times 10^{-4}$. The suppression of lower masses is significantly better because there is no mass tailing to higher masses. The separation factor for a relative mass-difference of +1 u and $\ge +2 u$ is $3(1) \times 10^{-5}$ and $\leq 8(5) \times 10^{-6}$, respectively.

4. Direct ion implantation

4.1. Implantation setup

The ECHo $10 \text{ mm} \times 5 \text{ mm}$ detector chips are composed of an array of 64 MMCs with Au absorbers on top, $180 \,\mu\text{m} \times 180 \,\mu\text{m} \times 4 \,\mu\text{m}$ each [1] and glued on a glass substrate for handling. Prior to ¹⁶³Ho ion implantation, the array must be prepared to protect the substrate as well as the sensitive superconducting circuits from being degraded by the impinging ¹⁶³Ho ions and by possible electric charging up. For that purpose they are covered with a few µm thick photoresist layer. In the center of every absorber, an implantation area of $160 \,\mu\text{m} \times 160 \,\mu\text{m}$ is left uncovered. The top surface of the chip including the absorbers and the glass support is then covered with a 100 nm gold layer by sputtering. For implantation, the chip is conductively fixed inside a Faraday cup to measure the ion current (cf. Fig. 8). To exclusively implant into the preselected area of absorbers on the chip, a $8 \text{ mm} \times 3 \text{ mm}$ copper aperture is placed in the flight path of the ions about 9 mm in front of the implantation spot, as shown in Fig. 8. The rear surface of this aperture is isolated from the grounded outer parts and kept in electric contact to the Faraday cup interior in a way ensuring that most secondary electrons and ions cannot escape and falsify the ion current measurement.

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Fig. 8. Setup for selective ion implantation into the calorimeter absorbers.

The aperture is mounted in a rotatable XY positioner with micrometer adjustment to align it relative to the MMC array (cf. Fig. 8). For accurate positioning before installation into the mass separator, a 1 mW laser beam is introduced in perpendicular geometry onto the implantation area of the detector chip. Subsequently, the aperture is installed and positioned precisely relative to the laser beam. This procedure allows a position accuracy in the order of 200 μ m.

4.2. Geometric implantation efficiency

Behind the beam waist, which must be set into the separation slit of the magnet (cf. Fig. 1), the ion beam is diverging. In the implantation region, the beam diameter would thus be about 5 mm (FWHM). In this way only 9% of the ¹⁶³Ho ions would be implanted into the absorber array, while the majority would be incorporated into the surrounding gold layer and the aperture. To enhance the low implantation efficiency, a dedicated Einzel lens together with an electrostatic XY deflector was installed between separation slit and implantation region. Operated at values around 14 kV, this arrangement leads to a secondary focal plane at the implantation position on the chip. In addition, the properly focused ion beam is scanned approximately 1000 times per chip with a rectangular pattern over the surface of the detector chip to cover all 64 absorbers.

To characterize the performance of this arrangement and a possible broadening of the ion beam by space charge effects in the focal plane, the beam was measured by imaging it at the implantation position at different ion currents from 0.001 nA to 325 nA. The ion beam density profile was analyzed using a chevron stack of two micro channel plates with an adjacent phosphorous screen (Proxivision OS 25 Z-V). The spatial resolution of the detector is about $100 \,\mu\text{m} \times 100 \,\mu\text{m}$ [31]. Images were recorded by a digital camera (Ximea MQ013MG-E2) with an intensity resolution of 10 bit. In Fig. 9 the intensity profiles are shown as a function of the planned implantation current in the order of 100 nA.

With increasing ion current, the two-dimensional intensity distribution starts to deviate from a circular profile as low-intensity wings start to appear. These regions do not substantially change the implantation efficiency into the MMCs because of the $10 \text{ mm} \times 5 \text{ mm}$ detector chip area can compensate some beam deformations. However, the horizontal wing extends towards lower x-positions, where ions of lower magnetic rigidity, hence lower mass, are present. This asymmetry is the same as already described in Section 3 with the mass-peak tailing to lower masses and shows a current dependence in shape. This is most critical in case of 166m Ho ions, where this low energy wing could extend into the beam of 163 Ho and be co-implanted. In the sample, the amount of 166m Ho is about four orders of magnitude lower than the one of

Table 2

Calculated composition change of the two analyzed ECHo¹⁶³Ho samples through resonance ionization (RI) and mass separation (MS). *Source:* The initial composition is taken from [11].

Ì	Sample from	Nuclide	Initial	Ionized	Implanted M		Method	
6.7 mg		¹⁶⁰ Dy	$4(1) \times 10^{-5}$	$2(1) \times 10^{-8}$	$\leq 2(1) \times 10^{-13}$	RI	+	MS
		¹⁶¹ Dy	$3(1) \times 10^{-4}$	$1.3(3) \times 10^{-7}$	$\leq 1.2(8) \times 10^{-12}$	RI	+	MS
		¹⁶² Dy	$7(1) \times 10^{-4}$	$3(1) \times 10^{-7}$	$1.0(4) \times 10^{-11}$	RI	+	MS
	(7 Entrance	¹⁶³ Dy	$7(1) \times 10^{-4}$	$3(1) \times 10^{-7}$	$4(1) \times 10^{-7}$	RI		
	6./mg Er target	¹⁶⁴ Dy	$6(1) \times 10^{-4}$	$3(1) \times 10^{-7}$	$4(2) \times 10^{-11}$	RI	+	MS
		¹⁶³ Ho	0.887(6)	0.889(6)	0.9999978(8)			
		¹⁶⁵ Ho	0.111(6)	0.111(6)	$\leq 2(1) \times 10^{-6}$			MS
		^{166m} Ho	$2.1(2)\times 10^{-5}$	$2.1(2)\times 10^{-5}$	$\leq 3(1) \times 10^{-10}$			MS
30 mg Er tarş		¹⁶⁰ Dy	$2(1) \times 10^{-5}$	$2(1) \times 10^{-8}$	$\leq 2(1) \times 10^{-13}$	RI	+	MS
		¹⁶¹ Dy	$2(1) \times 10^{-4}$	$8(2) \times 10^{-8}$	$\leq 1.0(7) \times 10^{-12}$	RI	+	MS
		¹⁶² Dy	$3(1) \times 10^{-4}$	$2(1) \times 10^{-7}$	$7(3) \times 10^{-12}$	RI	+	MS
		¹⁶³ Dy	$6(1) \times 10^{-4}$	$3(1) \times 10^{-7}$	$4(1) \times 10^{-7}$	RI		
		¹⁶⁴ Dy	$3(1) \times 10^{-3}$	$1.4(3) \times 10^{-6}$	$2(1) \times 10^{-10}$	RI	+	MS
		¹⁶³ Ho	0.59(5)	0.66(5)	0.999992(4)			
	20 m - En tonnot	¹⁶⁵ Ho	0.31(4)	0.34(5)	${\leq}7(4){\times}10^{-6}$			MS
	50 mg Er target	^{166m} Ho	$1.9(2) \times 10^{-4}$	$2.1(3) \times 10^{-4}$	$\leq 4(2) \times 10^{-9}$			MS
		¹⁶² Er	$1.7(4) \times 10^{-2}$	$8(2) \times 10^{-6}$	$4(2) \times 10^{-10}$	RI	+	MS
		¹⁶⁴ Er	$4(1) \times 10^{-3}$	$2(1) \times 10^{-6}$	$3(2) \times 10^{-10}$	RI	+	MS
		¹⁶⁶ Er	$3(1) \times 10^{-2}$	$1.4(4) \times 10^{-5}$	$\leq 3(2) \times 10^{-10}$	RI	+	MS
		¹⁶⁷ Er	$2.1(4)\times10^{-3}$	$1.0(3) \times 10^{-7}$	$\leq 2(1) \times 10^{-11}$	RI	+	MS
		¹⁶⁸ Er	$4(1) \times 10^{-2}$	$2(1) \times 10^{-5}$	$\leq 4(2) \times 10^{-10}$	RI	+	MS
		¹⁷⁰ Er	$7(2) \times 10^{-3}$	$3(1) \times 10^{-6}$	$\leq 7(4) \times 10^{-11}$	RI	+	MS

¹⁶³Ho [11]. Hence, the ion beam current of ^{166m}Ho will be well below 1 nA, in which case no appreciable wing extending into the ¹⁶³Ho region is expected. The vertical extent of the ion beam profile is also a reproducible effect, which could be caused by small manufacturing defects of the magnet pole pieces. It does not affect the beam purity but lowers the implantation efficiency at high ion currents. The beam shape and dimensions remain roughly the same within the range of 3 nA to 210 nA, assuring identical characteristics for ion implantation. In this range, the mean implantation efficiency is 20(2)% obtained from a simulation of a 64-pixel detector chip implantation. At 325 nA, the dimension increases, as the system limitation is reached.

5. Conclusion

The RISIKO mass separator at the Johannes Gutenberg University Mainz has been upgraded and optimized for ion implantation of ¹⁶³Ho into the MMC detector array of the ECHo experiment for neutrino mass determination. Special emphasis was placed on achieving the highest efficiency and beam purity. The enhanced output power of the intracavity doubled Ti:sapphire lasers allowed obtaining high saturation in both transitions of the newly-developed two-step resonance ionization scheme. A high efficiency of $69(5)_{stat}(4)_{sys}\%$ has been reproduced in a series of five measurements using samples with $1.10(2) \times 10^{15}$ atoms of stable Ho. To our knowledge this is presently the highest overall efficiency obtained with a laser ion source, and is in the same range as data for Pd measured at Mainz and ORNL [32]. The ion source can be accurately controlled to deliver a stable output current in the order of 100 nA, by which a sample of 10^{15} atoms is depleted within a few hours.

The combination of resonance ionization and high-transmission magnetic sector field mass separation will increase the purity of the implanted ¹⁶³Ho source to at least 99.9992(4)%. Using starting materials with a ^{166m}Ho: ¹⁶³Ho ratio of $2.4(3) \times 10^{-5}$ and $3.2(6) \times 10^{-4}$ [11], this will lead to a ^{166m}Ho content in the MMCs below $3(1) \times 10^{-10}$ and $4(2) \times 10^{-9}$, respectively, with respect to the number of ¹⁶³Ho atoms. The project requirement of a value below 5×10^{-9} [1] is thus met. This, however, should be verified in independent studies using Accelerator Mass Spectrometry (AMS) or comparable techniques capable of determining extreme isotope ratios. In Table 2 the abundance of all relevant isotopes is calculated for every separation step.



Fig. 9. MCP images of the focused ion beam at different ion currents with the same position scaling. The color profile is normalized to the maximum intensity within each of the seven shown profiles. Color version online.

With the newly developed ECHo implantation setup, an ion beam up to 210 nA can be handled and accurately implanted. A geometric efficiency of 20(2)% has been extracted for the typical arrangement of the ECHo detector array. With the current sample amount of $1.2(2) \times 10^{18}$ atoms of ¹⁶³Ho after the chemical separation [11], this would deliver $1.7(4) \times 10^{17}$ atoms in the detectors by applying ionization, separation and geometric implantation efficiency, which corresponds to an activity of about 800(200) kBq. This is more than the 100 kBq requested for the presently running project phase of ECHo 100k [1]. With ion currents of 210 nA, the implantation of an ECHo chip with 10 Bq in each of the 64 absorbers takes about 10 min.

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Chapter 6

Publication V: Atom beam emersion from hot cavity laser ion sources

This article has successfully passed the refereeing procedure and is accepted by *Nuclear Instruments and Methods in Physics Research Section B: Proceedings* for publication in 2019. It analyzes residual loss and contamination channels occurring in the laser ion source. With respect to the ECHo project and the publications presented here so far, Section 3.1 is of great interest and gives the prospect of a further reduction of the ^{166m}Ho contamination in the ¹⁶³Ho implantation by considering the temporal structure of the ion bunches. The measurements were performed by R. Heinke in close collaboration with T. Kieck on stable ¹⁶⁵Ho, who also contributed text passages to the manuscript.

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Atom beam emersion from hot cavity laser ion sources

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ARTICLE INFO	A B S T R A C T
Keywords: Atom effusion Laser ion source Resonance laser ionization ISOLDE Ion source development Mass separation	Ion sources exploiting laser resonance ionization offer efficient and element-selective radioactive ion beam production at the leading isotope separation on-line facilities worldwide. Most commonly, laser resonance ionization takes place inside a resistively heated atomizer tube directly coupled to the production target, where the element of interest is evaporated and provided as atomic vapor. While naturally the majority of atoms is ionized inside this hot cavity, a fraction of the neutrals effuses towards the high voltage beam extraction system of the subsequent mass separator. We report on several systematic investigations on this phenomenon regarding its significance and implications on the operation of resonance ionization laser ion sources. Experiments suggest a less sharply directed atom cone than expected from theoretical model, up to a lateral opening angle of 45°. Inside the tubular volume defined by the laser beam diameter around the central axis behind the source exit, more than 90% of potentially ionizable atoms are found within the first 2 cm. Geometrical constraints for the construction of devices based on

by fast electrostatic beam deflection to overcome these problems are presented.

1. Introduction

Stepwise resonant laser excitation and subsequent ionization of atoms is a well-established method for highly efficient and inherently element-selective production of ion beams of both, radioactive and stable isotopes. Such resonance ionization laser ion source (RILIS) systems are used worldwide for a number of applications:

- They either selectively provide exotic nuclei from an irradiated production target for atomic and nuclear structure experiments [1] at isotope separation on-line (ISOL) facilities such as CERN-ISOLDE [2].
- They are in use for purification and implantation of isotopically clean samples for further applications [3,4].
- Finally, direct in-source laser spectroscopy has evolved to be a very sensitive and useful technique for atomic and nuclear studies on exotic nuclides [5].

Besides the laser installation, the corpus of a RILIS system involves a

hot cavity environment. Within this device, potential molecular bonds are broken up, the atoms are presented in the vapor phase and interaction with the laser radiation takes place. Most commonly, the system employs a simple tubular cavity, resistively heated to temperatures of 2000 °C and above, taken over from the design of standard surface ionization sources [6]. While radial confinement of the vapor is ensured by the cavity walls, the thermal movement of the atoms leads to effusion of neutral particles through the orifice on the ion beam extraction side; the mean residence time of atoms in an ISOLDE-type cavity of 34 mm length and an inner diameter of 3 mm can be estimated to 100 µs [7], with typically a few hundred wall interactions [8]. In the operation mode of surface ionization, ionization efficiencies close to 100% can be achieved for species with a low ionization potential in a cavity made from material with a suitably high work function, and the effusing atom fraction is negligible. For operation as a RILIS system, even though in some exceptional cases ionization efficiencies above 50% are reported (e.g. palladium [9]), a considerable portion of neutral particles will exit the cavity and potentially be available for laser ionization just in front of it. On the one hand, this opens up the way for decoupling the hot

ionization in the effusing atom beam directly downstream of the hot cavity are derived, and causes for crossmass beam contamination are identified. Counter measures using laser repetition rate synchronized beam gating

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cavity environment with potential surface ionization of contamination from a clean laser-atom interaction volume immediately downstream. This is realized in ISOLDE's LIST [10–12] or TRIUMF's IG-LIS [13] ion sources (later on referred to as "LIST-type" sources) and involves a construction shielding against the strong electrical extraction field of typically some kV/mm, e.g. by a radio-frequency quadrupole structure. On the other hand, ions that are just created in this region outside the hot cavity will experience a prominently lower accelerating potential. They will be transmitted on the trajectories of lighter masses through a separating magnet and become contaminants themselves. Exploiting the specific location of these contaminants in the ion bunch time structure, an ion beam purification by fast deflection can be applied.

For these phenomena and related applications, a detailed understanding of the profile and range of the atom's emersion is necessary: They contribute to the determination of geometrical constraints for further developments of LIST-type ion sources, regarding highest efficiency and potential crossed laser-atom beam modifications [14].

2. Atom effusion investigations

2.1. Theoretical description of atom beam emersion

Model descriptions for molecule emersion from both simple orifices and elongated tubular connections between two reservoir volumes based on kinetic gas theory have been developed and experimentally verified as early as in the first half of the last century. Of special interest are the works in the low pressure regime, meaning a mean free path length considerably higher than the geometric dimensions of the ion source. Here, the process is governed by individual trajectory evolution of the particles within the outer boundaries and not by mutual influence. Typical measured pressures in the target unit vessel are below the 10^{-5} mbar regime, corresponding to meters of free path, thus the assumption even holds if the partial pressure inside the source is significantly higher. Closely following the pioneering work of [15–18], the models for a) emersion from an orifice (essentially a cosine distribution) and b) emersion through a channel with the dimensions of the atomizer as given in Section 2.2 are presented in Fig. 1.

The fundamental difference of both models is clearly evident: The tube produces a very directed, sharp atom beam, while the emersion from an orifice has an extremely wider distribution. E.g., 90% (50%) of the intensity in forward direction is already reached at a lateral angle of 0.6° (3.1°) for the tube, but 25.8° (60°) for the orifice. The following investigations' results will be compared to these two models, but also stand for themselves as actual operation experience.

Experimental information on the opening angle of the effusing atom cone can, complementary to the work presented here, also be deduced from laser spectroscopic absorption in the atom beam. Such investigations were carried out in preparation for simulation studies for the earliest LIST concept for comparable source geometries (length $l_{cav} = 20$ mm, inner diameter $d_{cav} = 3$ mm) and yielded a convolution of a ~15%-abundant cone with ± 4° opening angle and respectively a ~85%-abundant one exhibiting ± 20° [19]. These results already imply that sole description by the model of emersion from a tube-like source might be insufficient.

2.2. The RISIKO mass separator

Measurements to examine the behavior of effusing atoms from a hot cavity laser ion source were carried out at the RISIKO¹ off-line mass separator at the Institute of Physics at Mainz University [20]. Its front end is based upon the ISOLDE 2 design and is compatible to the current ISOLDE target and ion source unit layout [2]. For the test and

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Fig. 1. Depiction of the atom beam shape (relative atom flow per solid angle element $d\Omega$) as a function of lateral angle predicted by models for a simple orifice [15] and a tubular channel [18] with the dimensions of the atomizer as described in Section 2.2. Figure (a) follows the presentation in [18], while (b) gives the correlation in a direct way.

characterization measurements presented here, samples of atoms are enclosed in a reduction agent foil and placed either directly in the hot cavity (length $l_{cav} = 35$ mm, inner diameter $d_{cav} = 2.2$ mm) itself or an independently heatable reservoir capillary ($l_{\rm res} = 45 \text{ mm}$, $d_{\rm res} = 1 \text{ mm}$) equivalent to the ISOLDE mass markers, both made of tantalum. A 10 kHz repetition rate Ti:sapphire laser system [21] pumped by the 532 nm light of commercial Nd:YAG SSDP lasers provides two to three beams of precisely tuned laser light for resonance ionization with spot size matched to the source dimensions ($\approx 1 \text{ mm}$ diameter FWHM), also defining a channel of potential laser ionization in front of the hot cavity around the central axis. The ions are extracted from a 30 kV starting potential in a two-stage acceleration system by an extraction electrode on typically 20 kV at a distance of 40 mm and subsequently to ground potential. The beam is shaped by ion optical components and mass separated in a 60° sector field magnet of up to $0.6\,T$ and a bending radius of 0.7 m, enabling a mass resolution of $\frac{M}{\Delta M} \approx 1000$. Downstream of a vertical slit diaphragm in the magnet's focal plane, the ion current can be monitored by either a Faraday cup or a secondary electron multiplier (SEM), which features time-resolved single ion counting. A schematic overview of RISIKO is given in Fig. 2. Besides ion source development for ISOLDE, the separator is in use for various resonance ionization mass spectroscopy related applications such as ionization scheme development [9,22], ion implantation [4] or atomic and nuclear structure investigations.

2.3. Investigation by mass separator transmission behavior

Information about the spatial distribution of atoms downstream of a standard RILIS configuration can be obtained by investigating the kinetic energy of ions created by the anti-collinear laser beams at a distance z outside the hot cavity in the acceleration field. A different starting potential U(z) of (singly charged) ions of the same mass then translates into a different momentum

$$\frac{p}{q} = \frac{mv}{q} = \frac{m}{q}\sqrt{\frac{2qU(z)}{m}} = \sqrt{\frac{2mU(z)}{q}}$$
(1)

and therefore transmission on different trajectories through the analyzing magnet. Particularly, ions of mass *m* with lower starting potential $U_{\text{start}}(z)$ compared to the source's full nominal potential U_{nom} will be transmitted as if they had lower apparent masses m_{app} according to

$$m_{\rm app}(z) = \frac{U_{\rm start}(z)}{U_{\rm nom}} m.$$
⁽²⁾

To unambiguously distinguish these beam constituents and to quantify their significance, the bunch structure of the ion beam imprinted by the pulsed laser ionization process is used. Fig. 3 shows an exemplary record of the time structure of resonantly ionized ^{174}Yb at the detector after the magnet, accumulated over several laser shots.

The main features are well-understood [23] and reproduced by ion

 $^{^1\,{\}rm German}$ acronym Resonanz Ionisations
Spektroskopie In KOllinearer Geometrie.

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Fig. 2. Schematic sketch of the RISIKO off-line mass separator at Mainz University. Samples of atoms enclosed in a reduction agent are provided either in the hot atomization cavity or an independently heatable reservoir capillary. 10 kHz repetition rate pulsed laser radiation tuned to resonantly ionize the element of interest is converged into the source. Ions are extracted from the 30 kV source region by an extraction electrode typically set to 20 kV. The ion beam is shaped and guided to magnetic mass separation and detected by either a Faraday cup or a secondary electron multiplier.



Fig. 3. Time structure of an ion bunch of laser-ionized ^{174}Yb from a standard RILIS source after transmission through the mass separator on nominal mass 174 u, acquired over several laser pulses. The interval marked in gray shows a very narrow feature within the pre-bunch of immediately extracted ions from the source: These spikes represent heavier ions which are created in the extraction field and which are transmitted on the trajectory of lower nominal mass through the magnet.

trajectory simulations [24,25]: A short, time-focused pre-bunch stemming from the exit region of the source, where the penetrating extraction field accelerates the ions immediately after creation is followed by a broader, more intense main peak (typically containing far more than 90% of the overall yield) of ions from inside the source which are guided by the voltage drop of the heating current along the cavity. Additionally, a DC-type non-laser pulse related ion current underneath originates from different mechanisms as surface ionization inside the hot cavity. These known characteristics will not be dealt with here, as of special interest for this work are additional, very narrow spikes briefly after the pre-bunch.

An extensive investigation over a broader mass range in this prebunch time window allows for tracking these species on the energy scale. For this investigation, a two-step resonance laser ionization scheme for ytterbium ($\lambda_1 = 267.3 \text{ nm}$, $\lambda_2 = 736.7 \text{ nm}$) [11], exploiting an auto-ionizing state above the first ionization potential, was used in a tantalum hot cavity heated to about 1850 °C. Besides driving the resonant transitions in ytterbium, especially the UV laser is also capable of non-selectively photo-ionizing various molecules present in the hot vapor. Fig. 4 depicts the flight time versus nominal mass and features three main structural components: Most prominent in intensity are straight vertical lines. These are ions created by non-laser pulse related mechanisms as e.g. surface ionization inside the hot cavity. These structures are therefore without visible energy spread and dispersion on the mass scale. A specific diagonal structure leading from lighter to heavier masses and earlier to later arrival times represents ions created in the vicinity of the extraction field but inside the ionizer on the full starting potential, which are immediately accelerated. They correspond

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Fig. 4. Laser pulse correlated ion flight time structure in the domain between pre- and main bunch recorded over a broad mass regime. Diagonal traces towards lighter masses and later arrival times indicate ions created at respectively lower starting potentials, which are therefore transmitted on lower nominal masses. For comparison, simulation results for these diagonal structures from a complete electrostatic model of the separator are included (solid black lines, indicated with respective mass number). See text for details.

to the pre-bunch in Fig. 3 and their trend is explained by the \sqrt{m} -dependence of the acceleration's total duration. The second narrow peak mentioned above is formed by the traces starting at this structure's border and stretching towards lighter nominal masses and later arrival times. These are the particles ionized outside the cavity in the extraction gap: With increasing distance, their transmission smoothly alters as in Eq. (1) to lower momentum, associated with lower terminal velocity and thus later arrival time at the detector.

A complete electrostatic computer model of the separator, including the two-stage extraction system as well as the beam shaping ion optics downstream, was generated using SIMION 8.1 [26]. The structures mentioned above could be reproduced as indicated by the solid black lines in Fig. 4. At the same time, a translation of starting energy into the position *z* of ion creation in the extraction field becomes possible from the software's calculated potential in the extraction gap on the central axis. For the most abundant mass m = 197, non-resonantly photo-ionized TaO molecules, the evolution of relative ion signal intensity is depicted in Fig. 5 in relation to the distance of the respective position inside the tubular ionization volume defined by the laser diameter around the central axis from the hot cavity exit.

A rapid decline is clearly visible. Assuming a solely cone-like effusion of atoms from this point, a reciprocally quadratic distribution of atom density I(z) along the central axis is expected, which is directly proportional to the respective measured ionization rate.

$$I(z) = I_0 \frac{a}{(z - z_0)^2}$$
(3)

with an offset of z_0 for the cone's top in respect to the cavity exit is used. Besides the combination of scaling factor *a* and the total effusing atom current I_0 , a characteristic parameter of $z_0 = -1.6 \pm 0.1$ mm is obtained.

The significance of this effect in respect to contaminating beams of lower masses with ions of heavier species as well as applicable countermeasures are discussed in Section 3.1.

2.4. Direct spatial screening of the atom beam

A more direct approach for the measurement of the atom density evolution on the central axis was done using the Perpendicularly



Fig. 5. Signal rate evolution of ions with mass 197 as a function of distance from the hot cavity exit, extracted from the data of Fig. 4. The inset shows the starting potential as determined from an electrostatic model of the system which is used for translation into spatial starting positions. The upper part of the inset depicts the difference of starting potential at a lateral position 0.5 mm away from the central axis, where ions will also be created by the Gaussian laser beam. The relative change is below 10^{-4} and therefore negligible. A reciprocally quadratic function corresponding to a homogeneous cone-like effusion is used to describe the rapid decline (fitted with a solid red line).



Fig. 6. (a) Schematic overview of the measurement setup using the PI-LIST ion source. The first step laser of a three-step ionization scheme on holmium is applied perpendicularly, while the second two are used in standard collinear geometry. By moving a slit diaphragm in the widened perpendicular beam outside the vacuum vessel, the atom density on the intersection of all lasers on the central axis is probed. See text for details. (b) Evolution of ion signal rate in the screened region as a function of distance from the hot cavity exit. After a steep increase behind the repelling electrode structure, a reciprocally quadratic behavior is observed, fitted with a solid red line).

Illuminated PI-LIST, a modified version of the LIST ion source featuring lateral laser access into the quadrupole structure directly downstream of the hot cavity exit [14]. Charged particles created inside the cavity are blocked by two electrostatic electrodes, so that only neutral vapor can enter and solely be ionized by laser radiation. For this investigation, three-step resonance scheme ($\lambda_1 = 405.5 \text{ nm}$, $\lambda_2 = 818.8 \text{ nm}$, а $\lambda_3 = 837.8$ nm) was applied on holmium [4]. While the second and third step lasers were set up in standard configuration irradiated anti-parallel to the ion beam into the source, the first step was introduced perpendicularly and largely expanded to cover a significantly wider elongation than the 30 mm diameter side entrance window in the vacuum vessel. From the laser beam's central part, this window could then be covered with uniform power distribution, as confirmed by laser power measurements. By using a movable 1 mm slit diaphragm before this window, a distinct, well-defined ionization point at the intersection of all lasers (bounded radially by the collinear beams' diameter and by the lateral beam's width in direction towards the extraction system) inside the quadrupole structure can be selected (Fig. 6a). Through stepwise translation of the diaphragm, ionization rates can be probed axially along the structure. As neither laser beam intensity nor size changes,

and assuming a constant ion transport efficiency towards the extraction system, the signal rate directly represents the available atom density in the intersection. Fig. 6b shows the evolution, recorded for -20 V on the first and +20 V on the second repelling electrode.

Immediately behind the two repelling electrodes of 1 mm thickness with a distance of 1 mm between them and towards the cavity exit, a steep increase of ion signal is visible. This feature was shown in SIMION trajectory simulations to be due to the electrode geometry, which creates an electric potential ridge slightly behind the physical electrode position. Further downstream, again a rapid decline of signal rate is observed. Applying the same fitting procedure as in chapter 2.3 using Eq. (3) for this region, and taking an uncertainty of 0.5 mm for mechanic positioning into account, a parameter of $z_0 = -1 \pm 1$ mm is derived. The remaining signal rate in the regions outside these areas is ascribed to scattered light from the edges of the entrance window.

The derived numerical values for both methods are consistent and the results can be compared to the predictions from Section 2.1 in a semi-qualitative way. The resolution of both methods is limited by the radial width of the collinear lasers. Assuming an effective beam diameter of 1 mm, at a distance of 5 (10, 20) mm, a lateral angle of \pm 5.7 (2.9, 1.4)° is covered. To be consistent with the observed reciprocally quadratic behavior, effusion density should be nearly constant in this regime. Fig. 1 suggests this for wide effusion following the cosine law, but the sharply directed beam of effusion from a tube would cause a less pronounced decline in ionization rate when covering less solid angle around the central axis, as relative density decreases significantly for these lateral angle values. Therefore, sole description as such a directed atom cone seems to be insufficient, an a higher effective opening angle can be assumed.

2.5. Angular dependent material deposition

An investigation of atom emergence characteristics off the central axis can be done by analyzing deposition of material stemming from the hot cavity on the surrounding structures. As one specific LIST unit has been used at Mainz University for several measurement campaigns on long-lived radioactive isotopes of numerous elements (holmium, actinium, promethium and protactinium), deposition of sample material inside this structure can be screened by spatially resolved radioactive decay detection. Therefore, the LIST unit was dismantled and parts were investigated in a simple setup: A commercial hand-held contamination monitor (Berthold LB 122) was placed behind a 3 mm wide slit diaphragm made from aluminum plates. The parts under investigation were then moved past this opening on a guiding sled. The four quadrupole rods are of highest interest, as they cover a significant area besides the central axis and were, unlike other parts, neither cleaned nor exchanged throughout the whole operation period of the source.

A CAD cut view of the LIST setup is given in Fig. 7, together with the measurement results for simultaneous screening of all rods on α and β radiation intensity. The obtained activity is background-corrected and normalized to solid angle coverage of the investigated part seen from a point 1.5 mm inside the cavity, as suggested from the investigations in chapter 2.3. It is clearly visible that deposition is uniform on the majority of the back part, while decreasing towards the hot cavity. The onset of this decrease coincides with the direct line of sight to the cavity orifice, as it is also suggested by visible coloring of the metal from heat radiation. Therefore the hypothesis of at least a fraction of the expanding cone of atoms from the cavity exhibiting a significant lateral opening angle is supported. A lower limit of roughly 45° for the overall opening angle can be deduced, while higher values are geometrically blocked by the LIST electrodes. A comparison of the results from the experimentally accessible angle regime of only roughly 9°-20° to the calculations in Section 2.1 does not allow a differentiation, as the relative intensity is predicted to be roughly constant and within the scattering of the obtained data points for both models (see Fig. 1).



Fig. 7. (a) CAD view of the LIST with sketched emersion cone of atoms from the hot cavity, constrained by the repeller electrodes. (b) Spatial radiation screening of the LIST's four quadrupole rods after operation for long-lived radioisotopes over several months. The data is normalized to solid angle coverage. A photograph of one rod is shown for comparison to the heat radiation induced coloring, which also indicates direct line of sight to the hot cavity. The lateral angle is calculated in respect to a point 1.5 mm inside the hot cavity, as indicated from chapter 2.3.

3. Implications for laser ion sources

3.1. Cross mass contamination suppression via ion beam gating

The extensive study presented in chapter 2.3 reveals a potentially harmful inherent characteristic of standard RILIS hot cavity sources for ion beam production. Species laser-ionized in the extraction gap (either resonantly ionized heavier isotopes of the element of interest or non-resonantly photo-ionized different species) pass the separation magnet on trajectories of lower nominal masses and appear as quasi-isobaric contamination afterwards. Although this admixture may only contribute a small fraction of the initial beam intensity, it can be crucial if the contaminating isotopes are produced at a much higher rate, or if highly pure beams are required.

The effect is visible as a tailing of the ion signal in the mass spectrum towards lower masses. Fig. 8 depicts this behavior. It was recorded at the RISIKO mass separator for resonantly ionized holmium isotopes, with stable ^{165}Ho being the most abundant. Fortunately, the time structure of the ion bunch imprinted by the pulsed laser system also opens up a way to counteract this effect: As shown in Fig. 3, the transmission of heavier species is limited to a very short time interval within the whole structure. Inhibiting transmission of the ion beam for



Fig. 8. Mass scans in holmium region for different configurations. Ions produced in standard laser configuration exhibit an asymmetric tailing towards lower nominal masses, caused by ionization outside the hot cavity in the extraction field. This effect can completely be suppressed at cost of negligible reduction of transmission of the species of interest by applying laser synchronized ion beam gating. Thus the peak shape of a surface ion source where ionization solely takes place inside is resembled. Scans with and without lasers were taken on different occasions and do not reflect actual signal ratios.

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this brief period therefore completely eliminates these interferences while only slightly affecting the main constituent which appears in the significantly longer main peak. For this purpose, a fast high voltage pulser (CGC Instruments, AMX500-3) was connected to electrostatic deflection plates in the beam line 1 m after the extraction system (see Fig. 2). A voltage of 300 V was applied for 1 µs, in synchronization and with an appropriate delay to the 10 kHz trigger signal of the laser system. This is sufficient to completely deflect the beam from the detector at additional 4 m distance for the critical time duration. The resulting mass scan clearly shows complete disappearance of the asymmetry in tailing and a more pronounced significance of the ion signal of ¹⁶³Ho, also present in the sample. The resulting peak shape is identical to the one from surface ionization. As the time window of deflection lies within the bunch of ions of interest, this method nevertheless inherently introduces a slight loss in the overall efficiency. The actual quantity of this depends on the time behavior of the particles, i.e. mass, chosen acceleration voltage and position of the deflector in the beam line. Although the contaminating species are extracted directly, they have a lower terminal velocity then the ones from the source itself. Therefore, at some point they merge into the broad main time structure and thus higher losses are caused when deflection is applied. For this investigation, the significance of this heavy mass contamination can be quantified to be in the order of 10⁻⁴ or less compared to the initial ion beam intensity on its nominal mass. While the gain in contamination suppression can be quantified to be at least one order of magnitude for differences of two masses or more in this regime, a change in shape on the base of the peak is still apparent. This broad symmetric tailing is ascribed to elastic and inelastic scattering processes in the ion beam throughout the whole separator system [27,28], is unavoidable and will not be discussed here. Comparison to the peak shape of an ion beam produced by sole surface ionization and thus only within the hot cavity confirms that it is not a laser-related effect.

3.2. Geometric constraints for LIST-type ion sources

Besides the "standard" RILIS sources which rely on ionization inside the hot cavity, high purity sources which comprise spatial separation of the hot atomization volume from a clean laser-atom interaction region by electrostatic repelling electrodes are in use [10,13]. As already seen in the integration process of these devices, spacing between the oven exit and the active ionization volume outside is extremely critical. The reciprocally quadratic behavior demands distances as small as possible to be included in the design goal for electrode layout and isolator design. At the same time, perpendicular laser irradiation for Doppler-reduced spectral resolution using a non-widened laser beam reflected inside the vacuum vessel [14] is reasonable with acceptable geometric losses in efficiency. On the other hand, the overall length of the RFQ unit shielding the extraction field is a more variable parameter and can be adapted to other concepts, e.g. matching its length to that of the cavity for a time-of-flight based source for very sharp ion bunches [29,30]. For these considerations, naturally also the diameter of the structure's exit aperture has to be taken into account in respect to penetration of the adjacent acceleration field.

Special attention must also be paid to the solid angle coverage of parts in the unit, namely vicinity and thickness of the RFQ rods, on which material is deposited within line of sight to the hot cavity. This is a possible cause for contamination arising within the structure [11].

4. Conclusion

Investigations on the atom emersion from a hot cavity type ion source as used at various facilities worldwide were conducted with several techniques. Direct screening using resonant laser ionization in the effusing atom cloud and examination of lateral material deposition reveal a wide, cone-like character with an apparently higher opening angle (up to 45°) then predicted from sole effusion from a capillary with

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the hot cavity's dimensions, supporting findings by laser absorption spectroscopy [19]. More work is needed to resolve these discrepancies, possibly connected to temperature gradients and desorption behavior of the source. The atom density within a tubular channel defined by the collinear laser diameter around the central axis can mathematically be described as reciprocally quadratically declining from an origin at roughly 1.5 mm inside the cavity. Integration yields more than 90% of all atoms inside this laser channel to be found within its first 2 cm behind the source exit. The results are consistently confirmed by extensive investigations on the transmission behavior of ions generated directly in the extraction field downstream of the hot cavity, where a full description of behavior in the nominal mass and time structure regime was developed. An implicated application of this work, a fast laser pulse synchronized ion beam deflection method to clean the beam from contaminations which arise by ionization in the extraction field, is presented. Furthermore, geometrical constraints for "LIST-type" laser ion sources which rely on ionization outside the hot cavity are derived, demanding minimal spacing to the atomizer cavity exit. Additionally, more freedom in designing the overall length of the quadrupole structures is given, while special attention must be paid to low solid angle coverage of structural parts for possible contamination deposition [10].

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Chapter 7

Pulsed laser deposition for sputter damage curing

This chapter describes developments in the field of Pulsed Laser Deposition (PLD), which are dedicated to resurfacing after ion-induced sputtering to reduce losses during the 30 keV ion implantation process.

While the penetration of α -particles in condensed matter has been studied for more than 100 years and is quantitatively well understood [1], not all fundamental interactions in bombardment of solids with heavier ions are fully described in literature yet. Therefore, the consequences of this process are not conclusively predictable. The colliding ion causes a number of different effects on the solid materials. In the energy region below 5 keV, condensation and backscattering of the ion is predominant [2]. Ions with higher energy are implanted into the target while atoms of the bulk material can be excited, displaced or entirely removed. The de-excitation process causes emission of photons and electrons. Sputtering is the process by which atoms, molecules, and clusters are ablated through ion bombardment. The sputter yield strongly depends on the energy and mass of the impinging ion in a nonlinear complex manner. In general, the yield maximum occurs between 100 keV and 1 MeV when Au is bombarded with heavy ions like Ho [3]. Also the ion implantation of Ho into the ECHo detectors, performed with 30 keV kinetic energy, is strongly affected by sputtering. The effect of surface modification by the impinging particles can cause extensive material removal, as used e.g. in the method of focused ion beam (FIB) micro machining [4]. In the case of ion implantation it is undesired.

7.1 Characterization of sputter damage

For characterization of the surface sputtering, implantation studies with stable Ho were performed. Three calorimeter pixels were implanted with 10, 100 and

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1000 times the amount of atoms as for a 10 Bq 163 Ho dose, corresponding to an atom fluence of about 8 Å^{-2} , 80 Å^{-2} and 800 Å^{-2} . Figure 7.1 shows images of the pixels taken by light microscopy with a magnification factor of about 200. With increasing fluence, the surface roughness drastically increases, which is visible by the dark color shade. After irradiation, the calorimeter pixels were cleaned in an ultrasonic bath. During this process, the one with the highest implantation dose was destroyed due to a loss of structural integrity.



Atom fluence: 8 Å^{-2}

Atom fluence: 80 Å^{-2}

Atom fluence: 800 Å^{-2}

Figure 7.1.: Microscope images of ECHo calorimeter pixels ($180 \,\mu m \times 180 \,\mu m$ each) after ion irradiation with different fluence. The implanted amount correspond to 10, 100 and 1000 times the number of atoms as for a 10 Bq ¹⁶³Ho dose.

7.1.1 Simulation of ion-solid collisions

In order to obtain information about the Ho implantation process, Monte Carlo simulations of the ion-solid collisions were performed with the software routines SRIM [5, 6] and TRIDYN¹ [7]. In both codes Ho projectiles with a kinetic energy of 30 keV are impinging onto an Au area of $160 \,\mu\text{m} \times 160 \,\mu\text{m}$, which is equal to a single implantation area of an ECHo calorimeter pixel, under the same conditions. The main difference between the codes is the use of Krypton–Carbon interaction potentials [8] in TRIDYN instead of the Ziegler-Biersack-Littmark (ZBL) universal interaction potentials [6] in SRIM. This leads to a deviation in the calculated sputter yields. In TRIDYN, about 12 atoms of the Au surface are sputtered and leave the bulk material with every impinging Ho ion. The SRIM calculations predict a much higher sputter yield of 24 atoms per ion [5]. Unfortunately, there are no experimental values for this projectile-target combination in the literature for comparison. In addition, the yield depends by up to a factor of two on the Au surface roughness [9].

¹TRIDYN2017 version Nov-2018

The 30 keV Ho projectiles have only a short mean implantation depth of about 7 nm. Correspondingly, during sputtering of the covering Au layer, already Ho is increasingly removed as well. At some point an equilibrium state between implantation of additional ions and ablation of Ho from already doped detector material is reached and the deposited Ho content is no longer increasing with further implantation. Hence, the Ho density in the Au layer saturates, as shown in Figure 7.2. Because of the different calculation of the sputtering yield, the saturation activity for ¹⁶³Ho implantation, as extracted from the TRIDYN code is much higher than the one which was calculated with SRIM.



Figure 7.2.: Area integrated density of Ho atoms in the Au detector. The saturation activity is 4.4 Bq for TRIDYN and 1.8 Bq for SRIM.

As already mentioned, no experimental value for the Au sputter yield due to the impact of Ho ions is known for any energy. Therefore, the maximum Ho saturation level in the detectors can currently only be estimated from the simulations with limited precision and should be measured independently, e.g. by long-term readout of the ECHo detectors. Since the predicted range of achievable activity is below the required value of 10 Bq per detector pixel, an addition of new Au layers during implantation seems necessary.

7.1.2 Cone formation by ion irradiation

Like any surface, the ECHo detectors have an initial roughness from the manufacturing process. The sputtering which occurs during ion implantation amplifies these surface defects because the yield depends on the angle of incidence and has a global maximum. In the case of Au as target, the angle of maximum yield Φ_{max} is between 60° and 80° [10]. On the projectile side, the sputter yield is mainly dependent on mass and kinetic energy. Due to a lack of experimental data for Ho ions as projectiles, an element with comparable mass was chosen as reference. Figure 7.3 shows the angle-dependent sputter yield for Xe on Au. After a certain duration of ion beam irradiation, cone-like structures with a lateral surface at an angle of Φ_{max} are formed on the target [11].



Figure 7.3.: Angle-dependent sputter yield for $Xe \rightarrow Au$. The data is taken from [10] and fitted by an empirical function [12].

This so-called ion-induced cone formation, which is regularly observed on metal targets [13], causes the different color shading of the samples which was described in Section 7.1. For a more detailed view of the cones, Figure 7.4 shows a Scanning Electron Microscope (SEM) image of the sample implanted with 1000 times the amount of atoms as applied for a 10 Bq 163 Ho dose.



Figure 7.4.: SEM picture of a calorimeter pixel after ion irradiation with high fluence. The implantation amount correspond to 1000 times the number of atoms as applied for a 10 Bq ¹⁶³Ho dose. Magnification: 3000x.

7.2 Pulsed laser deposition (PLD)

Au deposition in parallel to ion implantation requires a fast and reliable controlling of the process. Therefore, the techniques of Chemical Vapor Deposition (CVD) and thermal deposition are not suitable. Also the well-established magnetron sputtering is not applicable because it requires an Ar atmosphere inside the vacuum chamber that would hamper the Ho ions to reach the detector to be implanted.

The method of pulsed laser deposition does not imply such disadvantages. A high-energy laser pulse is used to produce thin films by condensing the ablated material from an arbitrary target on any substrate. With sufficient pulse energy, the major part of the ablated material is ionized and a dense, homogeneous plasma is formed. The primary parameter for the fast spread of the method is the sto-ichiometric transfer of material from the target to a thin film, as used e.g. to build layers of high-temperature superconducting composite materials [14]. For the ECHo project the following process advantages are important:

- high purity of the deposited layer,
- relatively high deposition rate with narrow angular distribution,
- real time thickness control by single-pulse controlling, and
- the possibility for parallel ion implantation.

7.2.1 Basic interactions

The interaction between laser beam and target material, which causes a plasmaplume to build up, is not yet fully understood. For an accurate description, several processes must be taken into account [15]. These interactions can be divided into primary effects occurring immediately during laser material interaction at the laser incident point and secondary effects following the preceding ones with a certain temporal delay. The primary effects as described here, are not including contributions from collisions, which are not of relevance for photons due to their vanishing rest mass of $m_{\gamma} = 0 \text{ eV}/\text{c}^2$.

Thermal sputtering happens, when the process temperature exceeds the sublimation temperature of the target material. Especially under vacuum conditions, this limit is easily reached for many target materials. For a significant contribution to the laser deposition by vaporization, the temperature has to be well above the melting or boiling points [15]. Wave-like structures can be observed on the target surface when this effect contributes [16] which can thus be used for characterization.

Electric sputtering comprises different forms of excitation and ionization of the surface material including plasmons. The rapid energy deposition in the target leads to a prompt transition of the solid material to a packed and repulsive gas, whose particles are ejected with high energies into all directions [17]. During this Coulomb explosion, the projectiles are excited and/or ionized and form an expanding plasma plume afterwards. The plume can be easily observed due to excessive de-excitation processes in the energy range of visible light (cf. Figure 7.16).

Macroscopic sputtering includes exfoliation and hydrodynamic sputtering. The first process is not discussed here because it mainly occurs for high-melting materials. Hydrodynamic stands for drop formation and subsequent separation from the surface. For this phenomenon the laser pulse has to melt the material quantitatively. The quasi-instantaneous expansion of the liquid causes formation and acceleration of a significant amount of droplets. Furthermore, impurities and defects on the surface increase the number of generated droplets [15]. By ablation with short-wavelength laser light the amount and size of the droplets can be reduced [18]. This is a reason to make use of a UV laser in the ECHo experiment.

The secondary effects are even more complex and of some relevance, while their consequences have not been studied in this work. As a consequence they are not further described here, but we refer to the book of Chrisey et al. [19] for this. Exceptionally, collisions of the ablated species among themselves shall be mentioned, because they lead to a strong forward peaking of the plume. This angular distribution becomes even narrower with increasing laser spot size [20] which enhances the deposition rate on small surface areas such as the ECHo detector arrays.

7.2.2 Characterization of Au layer formation

For characterization measurements of the Au layer formation a test setup was used, which is schematically shown in Figure 7.5. The Nd:YAG-laser (Quantel Brilliant)
has a repetition rate of f = 10 Hz and a pulse duration of about $\tau = 5$ ns. In order to reach different wavelengths, a frequency doubling unit is used to change the fundamental wavelength from $\lambda_0 = 1064$ nm to $\lambda_{2\omega} = 532$ nm. The combination of fundamental and second harmonic beam in a further nonlinear crystal leads to $\lambda_{3\omega} = 355$ nm. Tilting of the 3ω crystal angle is used to change the output pulse energy. The chosen number of laser pulses is PC controlled. Simultaneous spinning of the target and linearly scanning of the beam with a motorized mirror leads to a homogeneous ablation of the whole target surface.



Figure 7.5.: Setup for PLD characterization: The laser beam is generated by a Nd:YAG-Laser with frequency doubling (2ω) and tripling (3ω). The beam position is adjustable by two mirrors and is focused onto the target via a slide-able lens.

The laser pulse energy is determined by measuring the mean laser beam power with a Gentec PSV-3103 power detector that covers a wide spectral range from 300 nm to 1200 nm for high energy pulses. The maximum power measured after two mirrors and the lens is about 400 mW and corresponds to an energy per pulse of 40 mJ. The lens is mounted on a rail for translation along the beam path and allows for variation of the laser spot size on the Au target. Depending on the irradiated area, the fluence in the center of the Gaussian beam, is in the order of 1 J cm^{-2} .

The Au layer thickness was determined by deposition on Si substrates and measurement via nulling ellipsometry [21]. For the numerical analysis of the measured ellipsometry parameters, a stacked model of Si, SiO₂, Au, and air was used, where only the Au thickness was a free parameter. Two different Si substrates were used, one with a natural oxide layer of about 1 nm [22] thickness and one with an artificially grown oxide slice of 100 nm. Additionally, the Au layer quality was

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examined by SEM.

In order to check the reproducibility of the experiment and measurement method, in the first step only the pulse number was varied. In two series measurements were performed with a fixed fluence, for which in the first one Au was deposited on Si wafer and in the second one on SiO_2 wafer. The result is shown in Figure 7.6.



Figure 7.6.: Linear correlation $m \cdot x$ between the number of laser pulses and the layer thickness, with m = 6.7(1) pm. The samples were deposited on substrates with different SiO₂ layer thickness.

Linearity is confirmed over the entire range of the measured samples. Deviations of the values from the linear function and the larger error bars in the thinnest and thickest layers are ascribed to the resolution of the ellipsometer: With small values, the Au layer is too transparent to be detected, and at the other extreme, the layer can no longer transmit sufficient laser light for detection. The error bars are composed by two different error values that have been taken into account: The first part is the fit model error from the ellipsometric thickness calculation, which is larger for the thicker oxide layer between Si wafer and Au layer. The second part assumes, that the actual maximum value on the single sample was not accurately met, while 9 area points were measured. Therefore, the average half of the height difference between the maximum and all surrounding points is added to the error.

Areal distribution and opening angle

An important aspect in characterizing the coating of the ECHo detectors is the spatial Au distribution that accumulates on the sample to assess the effects of misalignment. After the laser beam hits the target surface, the angular distribution of the out-bursting plasma material can be well described by the cosine power distribution

$$f(\theta) = \frac{C}{h^2} cos^{p+3}(\theta), \tag{7.1}$$

where *C* is a constant that takes into account various parameters, e.g. geometry and temperature. *h* is the distance from the target to the surface to be coated and *p* the exponent [20]. A geometrical conversion from the angle θ to relative distances *x* on the substrate surface leads to the expression

$$f(x) = a \cdot \cos^n \left(\arctan\left(\frac{x}{h}\right) + b \right).$$
 (7.2)

The exponent *n* is equal to p + 3 because of the geometry [20] and *b* is a spacial offset of the thickness maximum.

The wafer for collecting the Au plasma has an area of about $50 \text{ mm} \times 50 \text{ mm}$. In order to catch all the ablated material within the measurement range of the ellipsometer (about 1 nm to 30 nm), the substrate is placed in a distance of 38(1) mm to the Au target. A measurement was performed on each node of a grid with 2 mm edge length. Figure 7.7 shows a contour plot of the resulting distribution. The layer thickness almost equally decreases from the maximum to each side. Therefore, it seemed sufficient to analyze the distribution only one dimensionally.

Figure 7.8 shows a maximum crosscut through the horizontal axis. The relative distances x = 2 mm between the measurement points and the constant distance h = 38.0(5) mm between the substrate and the target were transformed into an angular distribution.

The thickness profile expectantly has a cosine power distribution as described by Equation 7.2. The consistence of the data points with the fitting curve and the value of $\chi^2_{red} = 0.992$ being very close to 1, confirm the theoretical expectation into this measurement. The fitting function has three free parameters: $b = 5.69(5)^\circ$ is the angular displacement of the maximum to the zero position of the measuring arrangement. Furthermore, the coefficient a = 34.1(3) nm is the maximum layer thickness and n = 27.2(3) is the power of the cosine distribution. The measured value is converted to p = n - 3 = 24.2(3) as described above. Compared to the literature value of p = 6.3 [23], the distribution is narrower than expected. The reason for this discrepancy could be non-coinciding other parameters of the experiments, e.g. the size of the laser spot area or the incident angle of the laser. But the results are comparable to measurements on other materials like Re or W, where the exponents are p = 18.7 and p = 26 [24], respectively.



Figure 7.7.: Contour plot of the Au distribution produced by PLD. The contour lines next to each other have a difference in layer thickness of 1 nm; the gray dots mark the positions where ellipsometrical measurements have been performed.

The strong forward direction of the plasma, as it is known for PLD, has been confirmed and even exceeded in our application case. This makes the method very suitable for the coating of ECHo detector chips, as only a small area of about $8 \text{ mm} \times 3 \text{ mm}$ has to be plated with Au. Thus a high plasma fluence on the detector pixels is achieved with moderate laser power without the need to laterally move the plasma plume.

Droplet generation

In addition to all the positive properties of PLD, there is one major disadvantage: the formation of droplets, which are deposited on the grown layer. In order to investigate this effect in our special case, the target and substrate surface structure were imaged using SEM. Due to the well conducting Au layer, the mechanism of formation, the size and the amount of droplets can be investigated directly, without further preparation.

There is a quasi-instantaneous expansion of the molten target, which causes the droplet to form and accelerate. As described in Section 7.2.1, droplet formation is enhanced by impurities and defects in the target surface. A high purity Au target (99.99%) is used to reduce the probability of droplet formation. Before use, the target surface is polished and cleaned to minimize defects. However,



Figure 7.8.: Angular dependency of the material deposited by PLD, tolerance band of 99%. The measured values behave like the theoretically expected cosine power distribution. The fit parameters are given in the text.

after a few laser pulses, the remaining irregularities on the surface is enhanced with effects similar to those described for ion bombardment in Section 7.1.2. SEM image 7.9 shows the transition zone between the laser irradiated area and the blank target material. The target modification due to laser irradiation starts at residual scratches and other defects that are not removed by polishing.

Figure 7.10 shows two different magnifications of the Au target, with the measurement scale in the lower right corner. The ripples, called laser-induced periodic surface structures (LIPSS), that occur in the low-fluence laser-material interaction region of $0.1 \,\mathrm{J}\,\mathrm{cm}^{-2}$ to $1 \,\mathrm{J}\,\mathrm{cm}^{-2}$ [11] can be seen; at a higher magnification factor, the SEM image shows a single wave of the same sample more accurately. There are small structures in which the Au droplets are frozen before they leave the surface. No completely formed cones are visible, which is ascribed to the value of laser fluence well below the formation threshold as well as by the low ablation amount before imaging.

Since the quantity of droplets is linearly correlated with the number of laser pulses, it can be extrapolated from the sample shown in Figure 7.11 with an Au layer thickness of 15(2) nm to the 120 nm required for the ECHo project. Most drops are smaller than the Au detector layer thickness of 4 µm, which is added after the implantation process by different deposition method. It should therefore have no influence on the detector performance.



Figure 7.9.: SEM image of the transition zone between non-irradiated and irradiated PLD target. The laser-induced surface modification is most significant at defects like scratches, clearly visible by the striped structure from top left to bottom right. Magnification: 480x.



Wave-like structures. Magnification: 270x.

Droplet formation. Magnification: 1150x.

Figure 7.10.: SEM images of the Au target after long-time laser irradiation with different structures, as mentioned in the text. The right image is a magnification of the center of the left image.



Figure 7.11.: SEM image of a 15(2) nm Au layer produced by PLD. The red framed area corresponds to the 160 μ m \times 160 μ m implantation area of a single ECHo detector. Magnification: 700x.

7.3 Final implantation and deposition setup

The final arrangement for a parallel ion implantation of ¹⁶³Ho and pulsed laser deposition of Au is shown in Figure 7.12. The 355 nm laser beam is generated by a frequency-tripled Nd:YAG laser (Quantel Q-smart 850) with a maximum output energy of 230 mJ per pulse at a repetition rate of 10 Hz. The angle of the target is variable to accurately adjust the center of the plasma plume onto the calorimeter. The laser setup is shown in Figure 7.5 complemented with the addition of a polarizing beamsplitter cube and a waveplate for laser power adjustment. In order to prevent deep cone formation on the Au target, the laser beam can be scanned linearly over the entire target by the motorized last mirror. Thus, the irradiation comes alternately from two opposing directions and destroys the cones during formation. The construction details can be found in the bachelor thesis of L. Schmitz [25].



Figure 7.12.: 3D CAD drawing of the setup developed for parallel PLD and ion implantation. The high-energy UV laser pulse is generating an Au plasma from the target which is deposited while ¹⁶³Ho ions are implanted into the ECHo calorimeter chip.

7.3.1 Ablation rate

The material transfer rate in the PLD process can be either measured on the substrate as deposited layer thickness or as ablation depth of target material. The ablation rate (depth or volume per pules or time) depends on several properties of laser beam and target material. While in most cases the laser and the ablationtarget material cannot be easily exchanged, the remaining free parameter is the laser fluence Φ . It should therefore be preferred to the deposition rate, as otherwise the size of the irradiated surface and the laser power distribution would represent further influencing factors.

The energy deposited by the laser has to be high enough for PLD, because a significant amount of material is only ablated above a certain threshold Φ_{th} . This minimum required laser fluence is mainly determined by the melting point of the material. The theoretical model described here has been developed by Arnold et al. [26] and can be divided into three regimes:

 $\Phi \leq \Phi_{\text{th}}$ For fluences Φ , which are smaller than or approximately in the order of the previously discussed threshold fluence Φ_{th} , the following ablation rate results:

$$\Delta h \approx C_1 \exp\left(-\frac{C_2}{\Phi}\right),$$
(7.3)

where C_1 and C_2 are material and laser dependent constants. This relation is called Arrhenius law.

 $\Phi > \Phi_{\text{th}}$ At moderate fluences Φ , the ablation rate can be represented by a linear approximation. This is due to the not self-evident thermal behavior of the material parameters. It yields the dependence:

$$\Delta h \approx B(\Phi - \Phi_{\rm th}),\tag{7.4}$$

where *B* is a quantity composed of different material constants.

 $\Phi \gg \Phi_{\text{th}}$ For fluences Φ , which are much larger than the threshold fluence Φ_{th} , the shielding of the laser by the generated vapor/plasma must be considered. For this, an absorption coefficient α_p is defined for the plasma. If the Beer-Lambert law is applied, a logarithmic dependence for the ablation rate is resulting:

$$\Delta h = \frac{1}{\alpha_p} \ln(1 + \alpha_p B(\Phi - \Phi_{\rm th})), \qquad (7.5)$$

with the same parameters *B* and Φ_{th} as before.

In Figure 7.13 the three models for the three regimes are compared. It can be seen that in the low fluence range the linear curve does not reflect the smooth increase in ablation rate. On the other hand, the linear approximation significantly overestimates the rate of ablation at high fluence. In the moderate range from 0.6 to 1, the Arrhenius law and the logarithmic saturation are very well approximated by a linear curve.

Since we can only determine the deposited layer thickness, we must establish a connection to the ablation rate. The number of laser pulses can be well controlled



Figure 7.13.: Theoretical model of the normalized laser ablation rate [26]. The Arrhenius tail describes the rate for fluences $\Phi \leq \Phi_{\text{th}}$ followed by the linear approximation for $\Phi > \Phi_{\text{th}}$. At high fluences, the screening causes logarithmic saturation.

via the computer interface of the laser and the deposition rate can be calculated without errors. By preservation of the irradiated surface, there is a direct correlation between ablation and deposition rate. In order to change the laser fluence without influencing the beam shape, the power of the laser was gradually reduced by means of the above-mentioned combination of polarizing beamsplitter cube and waveplate. The beam diameter on the Au target is measured by observing burning spots on thermal paper. We estimate that power levels down to about $0.1 \,\mathrm{J}\,\mathrm{cm}^{-2}$ which leads to the measured $2\sigma = 1.7(2) \,\mathrm{mm}$ of the Gaussian beam. Due to that beam distribution, it can be assumed that its center has the greatest influence on the generation of the plasma plume and thus the fluence is given by the peak value of the distribution.

As can be seen in Figure 7.14, the deposition rates are almost identical and unequal to zero at fluences below $1.5 \,\mathrm{J}\,\mathrm{cm}^{-2}$, which is not a realistic behavior. It can therefore be assumed that the ellipsometer for layer thicknesses below 2 nm, which corresponds to a deposition rate of $10 \,\mathrm{pm}\,\mathrm{s}^{-1}$, does not provide exact results and the error is strongly underestimated by the ellipsometer fit routine (c.f. Table A.2). For this reason the error is not included in the graph because it has no influence to the fit routine.

Because the data obviously show an Arrhenius-like increase, they are fitted to Equation 7.3, weighted with the deposition rate error bars. Then the linear parts of its best fit and the edges of the 1σ confidence band are approximated with Equation 7.4 to obtain a value with error estimation. The threshold fluence Φ_{th} is thus determined to $1.8 \,\text{J}\,\text{cm}^{-2} - 2.3 \,\text{J}\,\text{cm}^{-2}$. The value range is extended to $1.5 \,\text{J}\,\text{cm}^{-2} - 2.8 \,\text{J}\,\text{cm}^{-2}$ taking into account the systematic error in the measurement



Figure 7.14.: Measurement of the fluence-dependant deposition rate in the final PLD setup. The linear approximations are extracted from the straight part of the Arrhenius function and the edges of its confidence band.

of the beam diameter.

7.3.2 Ho concentration profile

At moderate operation conditions of the laser, 120 mJ pulses are hitting the 1 inch diameter, 0.125 inch thick Au target, corresponding to a maximum fluence of $2.6(8) \text{ J cm}^{-2}$ in the center of the beam. Under this condition, the deposition rate of the Au layer is $73(8) \text{ pm s}^{-1}$, generating the required thickness of 120 nm [5] in 27(3) min. This is almost equal to the mean implantation time of 30 min for one array of 64 calorimeters. Assuming the most probable linear approximation of the deposition rate, the achievable pulse energy of 230 mJ produces about 300 pm layer thickness per second. The required deposition time is thus reduced to about 7 min and allows further improvement of the ion implantation process with the same PLD setup. These assumptions do not include the shielding effect described in Equation 7.5 as its strength cannot be estimated from the available data points.

With PLD of Au layers in parallel to the ion implantation, the Ho losses can be minimized. In order to give an estimation on the depth profile and the residual loss channels, the dynamical process has been simulated with TRIDYN. The implantation of $10.6 \text{ Bq} = 2.21 \times 10^{12} \, {}^{163}$ Ho atoms with PLD of 120 nm Au leads to a finally implanted activity of 10 Bq because of residual losses described below. On the 160 µm × 160 µm implantation area on a single calorimeter this is equal to a total atom fluence of 71.6 Å⁻² with 1.2% Ho and 98.8% Au. The Ho ions impinge

the surface at an angle of 90° with 30 keV, while the angle of incidence of the Au PLD plasma is 66.5° due to the target placed next to the ion beam (cf. Figure 7.5). The energy distribution of the plasma is taken from [27] (laser incidence angle: 55° ; fluence: 1 J cm^{-2} ; mean energy: 6 eV). The resulting depth profile in Figure 7.15 shows a homogeneous Ho distribution of 1.3% atom concentration in the first 110 nm of the 5 µm thick calorimeter.



Figure 7.15.: Simulated depth profile of implanted Ho with Au co-deposition in the first 175 nm of the 5 µm thick calorimeter. The TRIDYN parameters are described in the text.

Table 7.1 summarizes the loss channels for Ho and Au. Significant amounts of Au are lost by sputtering due to the Ho-ions impinging with high kinetic energy. But the deposited Au amount is sufficient to almost completely suppress the resputtering of earlier implanted Ho. The remaining Ho losses are due to surface scattering, which cannot be avoided in this projectile-target combination.

Table 7.1.: TRIDYN simulation of atom loss channels from combined Ho implantation with Au co-deposition.

incident	scattered (%)	sputtered (%)	final
10.6 Bq	3.5	0.6	10 Bq
120 nm	0.0	15.5	101.4 nm

7.3.3 Time evolution of the plasma plume

The excitation of atoms and ions during pulsed laser deposition as described in Section 7.2.1 results in a plasma plume which is clearly visible even at the low repetition rate of 10 Hz. The lifetime of the plume is only a few microseconds, which means that many photons are emitted within this short time. This allows to take time-resolved images of the plasma with a conventional CMOS camera (Ximea xiQ MQ013MG-E2). The images were obtained at the minimum exposure time of 15.625 µs. The trigger time was coupled to the Q-switch of the laser by means of a delay generator with a resolution of 100 ps. The image was shifted forward in time until the impact of the laser radiation on the target is just visible, which was defined as $t_0 = 0$ µs. The approx. 5 ns long laser pulse is thus occurring towards the end of the exposure interval. A series of images were then taken at intervals of 100 ns to analyze the formation of the plasma plume. The gain of the camera was adjusted so that the plume is always well visible. A collection of these images is shown in Figure 7.16. Due to the long exposure time and the short plasma lifetime, each image is an integration over a 15.625 µs interval.



Figure 7.16.: Images of the time evolution of the PLD plasma plum. $t_0 = 0 \,\mu s$ is the time of laser impact on the target. Every image is normalized to its maximum intensity.

In the last image of the time evolution in Figure 7.16, the distance of the maximum intensity of the plasma plume to the target can be estimated to 7.5 mm. The time from the plasma generation in the second image is about 1.6 µs what leads to a velocity of $v \approx 4700 \text{ m s}^{-1}$. This value is in good agreement to a velocity as calculated from the peak of the energy distribution of $E_{\text{peak}} \approx 5 \text{ eV}$ for Au ($m_{\text{Au}} \approx 197 \text{ u}$) measured by Bennett et al. [27] with a laser incidence angle of 55° and a fluence

7. Pulsed laser deposition for sputter damage curing

of $1 \text{ J} \text{ cm}^{-2}$ to

$$v_{\rm peak} = \sqrt{\frac{2E_{\rm peak}}{m_{\rm Au}}} \approx 5000 \,{\rm m \, s^{-1}}.$$
 (7.6)

For a distance of about 50 mm from the target to the substrate in the final implantation and deposition setup (cf. Figure 7.12) the plasma plume will exist for about 50 µs. The 10 Hz repetition rate of PLD is very low compared to the rate of 10 kHz for ¹⁶³Ho resonant laser ionization. Since the duty cycle of an ion bunch is 100 µs, only every thousandth can be influenced by the Au plasma. The expected losses of ¹⁶³Ho ions due to the parallel laser deposition of Au are therefore negligible and the Faraday cup readout can be gated in such a way that the ¹⁶³Ho ion current measurement is absolutely not influenced by the incoming PLD ions.

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Chapter 8

First implantation results

In the context of this thesis, a number of detectors of various designs were implanted at the RISIKO mass separator using the methods described in the previous chapters. The samples applied cover the isotopes ¹⁶³Ho, ¹⁶⁵Ho and ^{166m}Ho to provide different detectors for the following tasks:

- 1. Measurements of the thermodynamical properties of Ho doped Au
- 2. Test for background determination in the obtained decay spectrum
- 3. ¹⁶³Ho implantation tests into the detector arrays
- 4. High statistics measurement of the ¹⁶³Ho decay spectrum
- 5. Tests of different absorber materials
- 6. Studies of influence of solid state effects in the spectrum
- 7. Verification of the simulated sputter yield
- 8. Test of parallel processing of ion implantation of ¹⁶³Ho and pulsed laser deposition of Au

The implantations were carried out from the beginning of the year 2016 and during each individual stage of development, to verify the effectiveness of these and to exclude possible negative impacts on the measurement. Most detector chips have already been read out for those different testing purposes for a certain measurement time, whereby the suitability of the ion implantation could be verified. In addition to the isotope of interest ¹⁶³Ho, the stable ¹⁶⁵Ho was also used at the beginning of the ECHo project to test the fundamental influence of the embedded Ho on the thermodynamic properties of the detectors. Meanwhile, it could be shown that Ho concentrations of about 1 % as obtained by the current implantation procedure (cf. Section 7.3.2) have no negative influence to the detector performance and are well suited for the ECHo project [1]. Test implantations of ¹⁶³Ho in possible host materials (Au, Ag, Al) have shown that Ag and Au share similar positive features while solid state effects are negligible and are most suitable for the project [2]. So far about 10⁶ events have been recorded for the high statistics EC spectrum

8. First implantation results

of ¹⁶³Ho and the results will be published soon. The implantation parameters and measurement tasks are compiled in Table 8.1. Additional material on the preparation of the ECHo detectors for implantation can be found in Appendix A.1.3.

Year	Absorber	Implanted	Implanted	Dose per	Task
	material	pixels	isotope	pixel	
2016	Au	2x4	¹⁶⁵ Ho	$10^{11}/10^{12}$ atoms	1)
2016	Au	1	^{166m} Ho	0.29 Bq	2)
2017	Au	8	¹⁶³ Ho	0.5 Bq	3)
2017	Au	64	¹⁶³ Ho	0.7 Bq	3) 4)
2017	Au	64	¹⁶³ Ho	1 Bq	1) 3) 4)
2017	Au	64	¹⁶³ Ho	1 Bq	1) 3) 4)
2017	Ag	64	¹⁶³ Ho	2 Bq	3) 4) 5) 6)
2017	Al	64	¹⁶³ Ho	2 Bq	3) 4) 5) 6)
2018	Au	32	¹⁶³ Ho	10 Bq	3) 4) 7)
2018	Au	32	¹⁶³ Ho	10 Bq + 120 nm Au	3) 4) 8)

Table 8.1.: Compilation of the different samples implanted at the RISIKO mass separator. The tasks are described in the text.

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Chapter 9

Conclusion and Outlook

The ECHo experiment requires to embed an activity of about $10 \text{ Bq} (\approx 2.2 \times 10^{12} \text{ atoms})$ of ¹⁶³Ho in numerous individual calorimeter pixels of $180 \,\mu\text{m} \times 180 \,\mu\text{m}$ size. In the first phase of the project (ECHo-1k) a total activity of 1 kBq is foreseen within about 100 detector pixels to achieve a statistical sensitivity for the neutrino mass just below 2 eV. In the recently started second phase (ECHo-100k) this is increased to a total activity of 100 kBq within 10^4 detector pixels. A major prerequisite for the scalability of the experiment is the purity of the ¹⁶³Ho sources in order to keep background interferences from radioactive contaminants to a minimum. This work describes the fabrication of the ultrapure electron capture source within the first phase of the ECHo experiment. All steps necessary to fully control the implantation of the ¹⁶³Ho sample into the ECHo micro-calorimetric detectors were developed, experimentally realized at the RISIKO resonance ionization mass separator of the Johannes Gutenberg University Mainz, Germany, and analyzed in detail. This includes:

- full characterization of the ¹⁶³Ho sample,
- suppression of intolerable contamination, and
- generation of high efficiency in all process steps.

The production of the artificial radionuclide ¹⁶³Ho is performed in three main steps: chemical pre-purification of the initial target material ¹⁶²Er, neutron activation and radiochemical target processing after irradiation. Currently, samples of the order of 10^{19} atoms are in production, as required for the ECHo-100k project phase. More than 10^{18} atoms of the sample have already been chemically separated and were fully characterized by various analytical methods, including ICP-MS, RIMS, and NAA. Results confirm the suitability for the ECHo project. The only radioactive contaminant identified in the isolated Ho sample is ^{166m}Ho with an amount below 4×10^{-4} with respect to ¹⁶³Ho.

In order to characterize the starting point of the ¹⁶³Ho ion beam implantation, the ionization efficiency of Ho was studied in a resonant laser ion source at the RISIKO mass separator. Considering the scaling of ECHo to a large experiment, the overall process efficiency must be as high as possible to prevent the need of further large scale ¹⁶³Ho production. The fully resonant three-step ionization scheme developed by Gottwald [1] achieved an average ionization efficiency of 32(5) %. Compared to the value of 40% of Liu [2] this is slightly lower, which was probably due to a different geometry of the ion source. Furthermore, the laser power of the third laser was not sufficient to saturate the final ionizing transition to an auto-ionization level at 48809.2(1) cm⁻¹. In the first iteration to optimize the resonant laser ionization, a new, more reliable ion source layout was developed. With the same ionization scheme a higher efficiency in the Ho ionization of 41(5) % was measured confirming the value reached by Liu. In the second upgrade, a newly developed two-step resonance ionization scheme to an auto-ionization level at 48566.95(6) cm⁻¹ was used. An intra-cavity doubled Ti:sapphire laser with increased output power achieved saturation in both transitions. With this, a superior efficiency of $69(5)_{\text{stat}}(4)_{\text{sys}}$ % was reproducibly accomplished.

In the scope of optimizing the atomization process in the ion source, the performance of several reduction agents was simulated and tested experimentally. The results indicate that Zr should be used to increase the selectivity expressed in the laser-to-surface ion ratio by almost two orders of magnitude compared to Ti. It thus prevents contamination of the ECHo detectors by isobaric ¹⁶³Dy surface ions in the ¹⁶³Ho implantation. Zr also allows the ion source to operate at high temperatures, as required for the intended μ A ion currents for large scale implantation, without adding a significant load of unwanted ions to the limited beam current of the mass separator. In this latest setup, the output current can be precisely controlled to a stable value of up to 300 nA. This is sufficient for the next 3 years of the ECHo-100k phase, but further development must be invested in the optimization of ion optics for achievement of still higher currents.

The combination of resonance ionization and high-transmission magnetic sector field mass separation increases the purity of the implanted ¹⁶³Ho source to at least 99.9992(4)%. Using the above mentioned starting materials, this will result in a ^{166m}Ho contamination with respect to ¹⁶³Ho in the calorimeters below 4×10^{-9} . The abundance of this interfering isotope in the implant meets the requirements of a value below 5×10^{-9} for the ECHo project [3]. However, this should be verified in independent studies, e.g. by using Accelerator Mass Spectrometry (AMS) or comparable techniques capable of determining extreme isotope ratios. Investigations on the atom emergence from the hot cavity type ion source as used in the RISIKO mass separator shows the possibility for fast laser-pulse synchronized ion beam deflection to further clean the beam from contaminations which arise by laser ionization in the extraction gap, as well as by reducing the continuous component of surface ionized species. This would further suppress the amount of

^{166m}Ho to a value below 4×10^{-10} with respect to ¹⁶³Ho.

With the newly developed implantation setup, an ion beam up to about 200 nA can be handled and accurately implanted into the ECHo-1k and ECHo-100k detector arrays without decreasing the geometric implantation efficiency of 20(2) %. However, the ultimate ¹⁶³Ho activity per detector is intrinsically limited to about 2Bq because of resputtering effects. With pulsed laser deposition (PLD) of Au layers in parallel to the ion implantation process, this limitation can be overcome. The required layer of 120 nm for the 10 Bq implantation [4] is generated in about 10 min and allows further improvement regarding the required time for the implantation. The Au co-deposition almost completely suppresses the resputtering of Ho. The remaining Ho losses of about 4% in the implantation process are due to backscattering from the detector surface.

In conclusion, this thesis describes the successful development and characterization of all necessary steps and techniques to obtain a high-purity ¹⁶³Ho EC source and to embed it highly efficiently into the ECHo detectors by a combination of laser resonance ionization, mass separation, and subsequent ion implantation. A number of these detectors were implanted with the help of the methods described, which have yielded promising results in a variety of different measurements. It has been shown that ion implantation with parallel laser deposition makes it possible to achieve the required activity of 10 Bq per detector with a total efficiency of 13(2) % including statistical and systematic errors. This already meets the majority of requirements of the just started second project phase ECHo-100k.

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Appendix

A.1 RISIKO mass separator

A.1.1 Operation parameters

The RISIKO mass separator has been in operation for many years and the working parameters have been continuously optimized during this time. These settings differ for each element and are also strongly dependent on the source geometry. In the process of this work, optimized operating parameters for the efficient mass separation and ion implantation were generated for Ho in the ion source version 3 (cf. Chapter 4), which are summarized in Table A.1.

Table A.1.: Operation parameters of the RISIKO mass separator used for most of the measurements presented in this work. They are optimized for Ho mass separation and ion implantation with the ion source version 3.

Parameter	Value
Atomizer heating current	280 A
Acceleration voltage	30 000 V
Extraction voltage	$10000\mathrm{V}$
Einzel lens potential	9650 V
Deflector voltages (horizontal / vertical)	0V/15V
Quadrupole lens voltages (horizontal / vertical)	0V/20V
Separator slit width	2 mm
Pre-focussing lens potential	$14200\mathrm{V}$

A.1.2 Thermal simulation results

The correlation of chemical composition of the sample and its temperature described in Chapter 4 is not only important to understand reducing process of Ho as needed for the ECHo project, it influences any mass separation and spectroscopic measurement for which a laser ion source is used. Due to the placement of the sample within the cylindrical reservoir, the temperature of the sample is almost the same as the outside temperature of the tantalum tube. The available two-color pyrometer (Heitronics KT 81R) enables the measurement of the reservoir temperature in the range from 1200 °C to 2500 °C. The lower regime, which is important to predict the starting point of reduction for many elements and therefor to well control the vapor generation, cannot be reached directly. However, the finite element method (FEM) thermal-electric calculations in Chapter 4 make it possible to reliably predict temperature values even for low heating. Figure A.1 shows the calculated sample temperature dependent on the heating power/current of the sample reservoir. In addition, the hot cavity adds heat to the reservoir so that the sample temperature also depends on its heating power and distance from it. The solid lines show the temperature at different power losses through the hot cavity for a sample placed exactly at one third of the capillary length, measured from atop. A maximum deviation of 1 cm is shown as a red colored area for the case of 325 W hot-cavity heating power.



A.1.3 Chip preparation for implantation

After production, the ECHo detector chips are glued to $3 \text{ cm} \times 3 \text{ cm}$ glass substrates and coated with an Au protective layer. As described in Chapter 5 and shown in Figure A.2a, these chips are first attached to a Faraday cup with conductive copper adhesive tape for implantation. A weak laser beam is then shined vertically onto the detector pixels to be implanted and moved over the implantation surface with the aid of an adjustable mirror. The aperture is than placed over the chip and adjusted with the millimeter screws so that the laser beam passes through (cf. Figure A.2b). The previously mentioned mirror is adjusted in the way noted and ensures that the laser beam is located over the entire surface inside the aperture opening.



(a) ECHo-1k chip glued on a supporting glass substrate, covered with Au, and bonded to the Faraday cup with conductive copper tape.



(b) The full implantation setup with a green laser spot for adjustment on the aperture.

Figure A.2.: Preparation steps for implantation of ECHo-1k chips. Procedure described in the text.

A.2 Pulsed laser deposition

A.2.1 Results of the ellipsometry measurements

The PLD of the Au layers in this thesis was characterized in large parts by the measurement of the layer thicknesses by means of ellipsometry. Table A.2 summarizes the data. The calculation of the fluence is described in section 7.3.1. The given uncertainties of the thickness measurement values originate from the numerical fit routine of the ellipsometer. Further error sources are added and discussed during the respective evaluation.

		Table A	.2.: Compilation c	of the PLD characteriz	cation measurements	
Figure	Laser power	Pulses	Beam diameter	Fluence in beam	Target-to-substrate	Measured layer
reference	(mW)		(mm)	maximum (J cm $^{-2}$)	distance (mm)	thickness (nm)
		10				0 ± 1
		100				0 ± 1
		1000				6 ± 1
		1500				10 ± 1
		2000				13 ± 2
7.6	400 ± 5	2500	0.6 ± 0.2	30^{+20}_{-10}	29 ± 1	17 ± 1
		3000				21 ± 1
		3500				26 ± 5
		4000				31 ± 5
		4500				34 ± 7
		5000				33 ± 3
7.7 and 7.8	400 ± 5	2000	2.6 ± 0.3	$6.5^{+2.5}_{-1.5}$	38 ± 1	variable
7.11	1200 ± 10	2000	3.4 ± 0.4	$2.6^{+0.8}_{-0.5}$	160 ± 5	15 ± 2
	270 ± 10			$0.60\substack{+0.20\\-0.15}$		0.8 ± 0.1
	300 ± 10			$0.65\substack{+0.20\\-0.15}$		0.8 ± 0.1
	340 ± 10			$0.75\substack{+0.25\\-0.20}$		0.9 ± 0.1
7.14	420 ± 10	2000	3.4 ± 0.4	$0.9^{+0.3}_{-0.2}$	160 ± 5	1.1 ± 0.1
	580 ± 10			$1.3^{+0.4}_{-0.3}$		1.4 ± 0.8
	900 ± 10			$2.0\substack{+0.6\\-0.4}$		5 ± 1
	1200 ± 10			$2.6^{+0.8}_{-0.5}$		15 ± 2

A.2. Pulsed laser deposition

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