



# Influence of the hyperfine structure on plutonium in resonant laser-SNMS

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## Abstract

Resonance ionization mass spectrometry is an ultra-sensitive and highly element selective tool for spectroscopy, ionization and detection of atoms and thus enables rare isotope determination. In combination with spatially resolved sputtering of neutrals by an initial ion beam, e.g. within a commercial secondary ion mass spectrometer, an isotope and isobar selective analysis technique with resolution on the micrometer scale for particles and surfaces is realized. Detection of minuscule amounts of specific actinides, e.g. of plutonium, in environmental and technical samples by this ultra-trace analysis technique requires detailed knowledge about the atomic physics of the element. Identification and characterization of the specific resonance ionization scheme applied within the particular geometry of the apparatus in use is needed. An analysis of the dependence of the specifications, specifically regarding the influence of the relative laser beam polarizations is presented here as an aspect, that could have a severe impact on isotope ratio precision and overall efficiency in the resulting ion signal.

**Keywords** Resonance ionization · SNMS · Plutonium · Trace analysis · Isotope ratio · Laser beam polarization

## 1 Introduction

The resonant laser secondary neutral mass spectrometry (rL-SNMS) system at the Institute of Radioecology and Radiation Protection (IRS) in Hannover, Germany was set up to analyze sample surfaces with highest elemental selectivity for their isotopical composition [1,

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2]. One targeted element is plutonium ( $Z = 94$ ), which was distributed into the environment by nuclear weapon explosions and still is released in small amounts by the reprocessing process of nuclear fuel and during accidents in nuclear facilities [3]. By determining relative plutonium isotope ratios in samples, their source, age and nuclear history can be evaluated [4, 5]. For this purpose, the accuracy and precision of the applied method in terms of relative isotope ratios and overall efficiency is very important. Tests and reliable characterization of the accuracy and precision of SNMS measurements on materials with known isotope ratios are therefore inevitable.

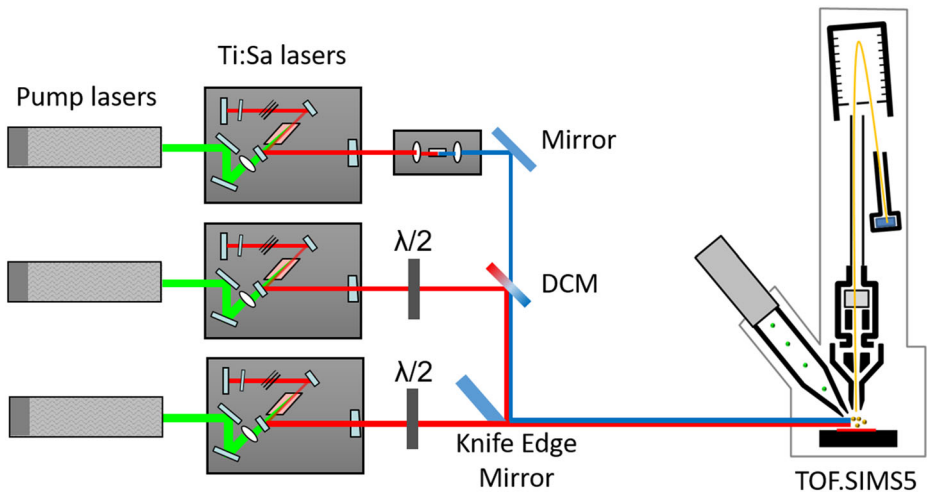
A material suiting those needs is mixed oxide (MOX) fuel, containing the uranium and plutonium isotopes  $^{235,236,238}\text{U}$  and  $^{238-242}\text{Pu}$  in known quantities. The material bears isobaric interferences of  $^{238}\text{U}$  for  $^{238}\text{Pu}$  and, after sufficient time for ingrowth of the beta decay product, also  $^{241}\text{Am}$  for  $^{241}\text{Pu}$ . However, these isobaric interferences can be suppressed by the resonance ionization process, as shown in [2], so that only plutonium signal remains. For these, the reproduction of isotope ratios without significant mass fractionation is a major concern of resonant laser SNMS. The technique requires the spatial overlap of up to three individual laser beams by polarizing and dichroic optics. The influence of relative laser beam polarizations could critically affect the sensitivity for different isotopes, particularly if large hyperfine structures are involved in the optical excitation and ionization process. This has been confirmed by a number of theoretical and experimental studies [6–8]. To specifically investigate the influence of the individual laser beam polarizations on isotope fractionation in laser SNMS on Pu, the studies described herein have been performed.

## 2 Experimental setup

The resonant laser-SNMS system at IRS consists of three individually pumped titanium:sapphire (Ti:Sa) lasers for resonance ionization. They have a standard Z-shape resonator design of the “Johannes Gutenberg-University Mainz type” as described in [9]. The lasers are tunable from 690–1000 nm at a line width of 7 GHz and yield average output powers of well above 2.5 W at 10 kHz repetition rate and a temporal pulse length of about 35 ns. The wavelengths of the Ti:Sa lasers are controlled by a wavelength meter WS6-600 (HighFinesse). Each laser is pumped by a frequency doubled Nd:YAG laser (DM60-532 by Photonics Industries) at 10 kHz and 532 nm. The output of the first Ti:Sa laser is externally frequency doubled in single pass, the other two are operated in fundamental mode. The individual laser powers by far exceed the limit for saturation of optical resonance lines, which usually lie in the range of a few mW average power. Correspondingly, power attenuation by Glan-laser-polarizers is part of the beam transport. A subsequently installed wave plate defines the final beam polarizing axis.

The beams of the laser system are coupled into the laser-atom interaction region located within a modified commercial TOF.SIMS5 (IONTOF GMBH, Münster). This spectrometer is equipped with a Bi Nanoprobe, i.e. a 30 keV bismuth primary ion (PI) gun, for sputtering and a reflectron type time of flight (TOF) mass analyzer with a mass resolution well above 1000 for analysis of the secondary ion beam. The 30 keV ion beam from the PI source is scanned over the sample surface with a window size of up to  $0.5 \times 0.5 \text{ mm}^2$  to generate spatially resolved mass spectra. The PI beam can be focussed down to a spot size as low as 100 nm for optimum spatial resolution.

Pulses of the three lasers are temporally overlapped with 5 ns precision by using a master trigger in combination with a 4 channel delay generator (DG645 by SRS), triggering the



**Fig. 1** Experimental setup for resonant laser-SNMS of plutonium in solid samples. The beams of blue and red laser light are overlapped at a dichroic mirror (DCM), whereas the two red laser beams are overlapped by a knife edge mirror. The polarization axis of the first, blue laser beam was kept constant for all measurements. The polarization axes of the second and third laser beams were adjusted individually relative to the first laser beam by  $\lambda/2$  plates

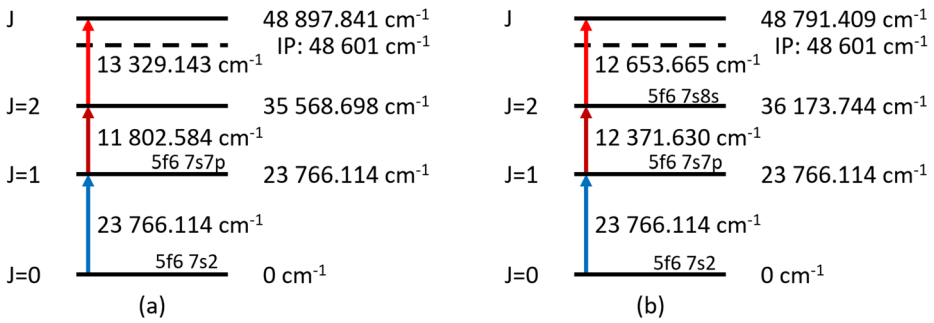
**Table 1** Reference isotope ratios of uranium and plutonium in the MOX-solution

	<sup>235</sup> U	<sup>238</sup> U	<sup>238</sup> Pu	<sup>239</sup> Pu	<sup>240</sup> Pu	<sup>241</sup> Pu	<sup>242</sup> Pu
absolute content	0.23 %	89.98 %	0.24 %	5.39 %	2.54 %	0.70 %	0.74 %
relative ratios U	0.25 %	99.75 %					
relative ratios Pu			2.52 %	56.14 %	26.42 %	7.25 %	7.67 %

individual pump lasers as described in [1]. The laser beams are transported into the vacuum chamber of the TOF-SIMS, where they are spatially overlapped just above the sample, which is mounted on a high-precision x, y, z positioning table. The overlap of the frequency doubled laser beam in the blue spectral region with the beam of the first fundamental laser operating in the red spectral range is performed by a dichroic mirror. In contrast to [1], the overlap with the second laser beam in the fundamental spectral region was achieved by a knife edge laser beam transport mirror instead of by polarization optics to retain the freedom of individually selecting a polarization angle for each laser beam (Fig. 1).

The sample for the TOF-SIMS was prepared from a solution of dissolved MOX-fuel in 0.1 M nitric acid containing uranium and plutonium in well-known ratios as given in Table 1. A droplet of 200 nL solution with concentrations of uranium of  $2.2 \cdot 10^{-7}$  g/g<sub>solution</sub> and  $2.3 \cdot 10^{-8}$  g/g<sub>solution</sub> plutonium, respectively, was placed on an aluminium target and evaporated to dryness. Afterwards, the residue was sputtered by the PI-gun until the laser ion signal achieved constancy.

Two excitation schemes were tested. For the first experiment, the lasers were tuned to plutonium resonances as reported in [10] for use on bulk material analytics. In addition, a second excitation scheme identified for spectroscopic investigations was applied [11, 12]. The transition wavenumbers for both schemes, which share the same first step, are given



**Fig. 2** Level energies for the two tested plutonium ionization schemes. If known, the total angular momentum quantum number  $J$  as well as the electron configuration is assigned to the corresponding state. **a** Scheme developed for ultra-trace analysis by resonance ionization mass spectrometry (RIMS) in a dedicated mass spectrometer for bulk material [10]. **b** Excitation scheme developed for spectroscopic investigations [11, 12]

**Table 2** Applied laser frequencies used for resonance excitation and the shift of the resonance lines of the isotopes  $^{239,242}\text{Pu}$  relative to them in  $\text{cm}^{-1}$

		shift of $^{239}\text{Pu}$	laser frequency	shift of $^{242}\text{Pu}$
scheme (a)	FES	0.194	23766.114	-0.170
	SES	-0.032	11802.584	0.146
	TES	0.027	13329.143	-0.063
scheme (b)	FES	0.194	23766.114	-0.170
	SES	-0.049	12371.630	0.053
	TES	-0.034	12653.665	0.053

in Fig. 2. Additionally, information on the total angular momentum quantum numbers as well as the electron configurations of corresponding states are outlined [13–16]. Applied laser frequencies and the shifts of the isotope lines of  $^{239,242}\text{Pu}$  relative to them are given in Table 2. Furthermore, laser powers were attenuated to exceed the saturation power of the corresponding excitation step by not more than a factor of 60 in the first transition, 10 for the second transition and three for the final one. The used average laser powers are displayed in Table 3.

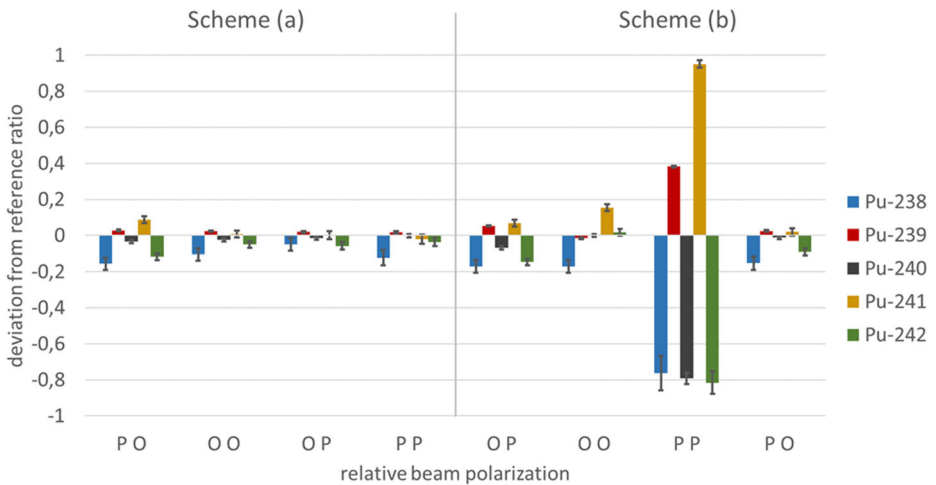
### 3 Polarization dependent plutonium signal

Scheme (a) of Fig. 2 was already used for first tests regarding plutonium RIMS at the rL-SNMS system [2]. The isotope ratios obtained in the analysis of the introduced MOX sample as a function of the different possible relative polarization directions of the laser beams reveal strengths and weaknesses of this scheme in the specific setup.

The laser beams were tuned with  $\lambda/2$  plates and tested on a polarizing beam splitter cube to achieve parallel or orthogonal orientation relative to the first laser beam, which was kept constant for all experiments. Additionally, the average laser powers were kept constant for all experiments as well as the spatial position above the sample. Therefore, the only altered parameters were the relative beam polarizations of the second and third laser beams.

**Table 3** Applied average laser powers in mW for the transitions and their corresponding saturation powers. The \* indicates a non-saturable transition

	FES	applied power	SES	applied power	TES	applied
scheme (a)	0.58(5)	32.6(5)	22(37)	132(1)	-*	314(3)
scheme (b)	0.58(5)	32.9(1)	14.87(48)	161(1)	62.74(23)	255(5)



**Fig. 3** Measured plutonium isotope ratios normalized to the values determined by ICP-MS given in Table 1 for the isotopes <sup>238–242</sup>Pu. The ratios for each isotope are plotted for the two schemes with all combinations of relative beam polarizations. The polarization is measured with regard to the polarization axis of the first laser beam. Parallel polarization relative to the first laser beam is indicated by P, orthogonal polarization by O. The highest deviation is caused by a mixture of fine and hyperfine structure influences

In the following, the orientations of polarization axes of the second and third laser beams are abbreviated by doublets (O P), where an O represents an orthogonal and P a parallel polarization of the second and third laser beam relative to the first, respectively.

The difference of the resulting values for isotopic signatures by rL-SNMS relative to reference ratios with single standard deviations are displayed for the individual isotopes <sup>238–242</sup>Pu in Fig. 3, separately for scheme (a) and (b) according to the equation

$$X = \frac{\text{relative fraction of isotope } x \text{ by SNMS}}{\text{relative fraction of isotope } x \text{ by ICP-MS}} - 1 \tag{1}$$

In absence of any mass fractionation effects values for each isotope and relative polarization would be 0 within the uncertainty. However, for all variations of relative beam polarizations of both schemes the signals of even numbered isotopes are significantly lower in rL-SNMS with respect to the reference values. In case of <sup>238,242</sup>Pu this effect ranges between 10 and 20 %. It is most likely caused not just by polarization influences but by insufficient spectral broadness of the Ti:Sa lasers, which leads to a reduced ionization rate for the lightest and heaviest isotope. In contrast to this, the similar trend of the central isotope <sup>240</sup>Pu cannot be explained by the spectral shape of the excitation lasers.

The “underestimation” of even numbered isotopes, i.e. <sup>240</sup>Pu, and “overestimation” of odd numbered isotopes, i.e. <sup>239,241</sup>Pu, is ascribed to differences in the absorption profile of

the laser light. The presence of a nuclear spin leads to hyperfine splitting of levels, which distributes the transition strength over an enlarged spectral range for odd numbered isotopes compared to even ones [7, 8]. This effect yields isotope specific variations in photon absorption probability, leading to deviations in obtained isotope signatures. Variations in between different relative polarizations for single isotopes can be explained to a certain extent due to small spatial shifts introduced by polarization changes and the long beam path of about ten meters from the laser into the vacuum chamber. As the light is focussed down to at least 300  $\mu\text{m}$  diameter within the vacuum chamber, even minor changes can affect the overlap between sputter cloud and laser beam foci. Additionally, the three applied laser beams can walk over time individually, as a position stabilization is currently not available.

In contrast to the other seven cases, the strong differences for the relative polarization combination (P P) of the scheme (b) cannot be assigned to hyperfine interactions and spatial movement of the laser beams alone. A general suppression of the signal can be understood as a consequence of a possibly forbidden transition. The total angular momentum quantum number is known for the ground state ( $J=0$ ), first ( $J=1$ ) and second excited state ( $J=2$ ) [13]. With respect to selection rules, a transition between states with  $\Delta J=0$  and  $\Delta m=0$  can only be driven by linear and a transition with  $\Delta J=0$  and  $\Delta m=\pm 1$  by circular polarized light. Additionally, different linear polarized laser beams combine depending on the relative polarizations of the applied laser beams. In the case of parallel relative polarization, the effective polarization of the combined beams adds up to linear polarized light. Opposed to this, orthogonal orientation of linear polarized laser beams adds up to elliptical or circular polarization depending in relative phase. Hence, linear and orthogonally polarized laser beams can drive different transitions according to the initial and final state. In case of ( $\Delta J=0$ ,  $\Delta m=1$ ) only orthogonally linear polarized laser beams can excite all isotopes equally and drive the transition, whereas parallel polarized beams cannot.

In contrast, the hyperfine structure of odd numbered isotopes opens up the possibility to drive formerly forbidden transitions resulting in the fact, that the even numbered isotopes are suppressed, whereas the odd numbered isotopes are ionized much more efficiently. Therefore, the strong difference between ionization of odd and even numbered isotopes in case of (P P)-polarization of scheme (b) leads to the conclusion, that the total angular momentum quantum number of the third state can be assigned  $J=2$ .

## 4 Summary and outlook

In the course of tests performed, a general influence of the relative laser beam polarization on the isotope signal of plutonium has been demonstrated. For both tested schemes, the relative deviation from reference values is in the range of less than 5 %, with slight underestimation of even-numbered isotopes and overestimation of odd-numbered ones due to the “odd-even” effect generated by the underlying hyperfine structure. From this point of view, both schemes are almost equally suitable for resonant laser SNMS measurements, if one selects the relative polarisation accordingly.

The saturation of optical transitions for all isotopes has to be fulfilled, so that an underestimation of the isotopes at the edges of the laser excitation profile can be ruled out. In the case of the schemes investigated in this work, it was shown that the minor isotopes were slightly underestimated. Since the isotopes  $^{238,242}\text{Pu}$  are equally suppressed by 10 to 20 % relative to the reference, it can be further concluded that isobaric interferences from  $^{238}\text{U}$  and  $^{241}\text{Am}$  have only minimal contributions to the corresponding mass signals and can be neglected for the presented evaluation.

However, there is a very strong influence of relative beam polarization on the resulting isotope signal in case of the combination (P P) of scheme (b), which cannot be explained by interaction of the nuclear spin with the electron shell alone. Here, a combination of a forbidden dipole transition for linearly polarized light ( $\Delta J = 0$ ,  $\Delta m = 1$ ) with the hyperfine splitting of odd-numbered isotope lines gives the explanation for suppression of the even-numbered isotopes.

From this assumption and based on the known quantum numbers of the ground state and the first two excited states of plutonium ( $J=0 \rightarrow J=1 \rightarrow J=2$ ) [13], in combination with the selection rules, the total angular momentum quantum number of the autoionizing resonance of scheme (b) at  $48\,791.409\text{ cm}^{-1}$  can be determined to be  $J=2$ . For the first scheme (a) a total angular momentum quantum number cannot be assigned, since the  $J$  of the second excited state is unknown.

Since laser beams of the resonant laser SNMS system at the IRS in Hannover are overlapped on a daily basis by polarizing optics due to easier handling, only combinations of (P O) and (O P) relative to the first laser are usable. Hence, the case (P P) discussed above does not play a role in routine measurements, but shows that a general examination of the influence of relative beam polarizations can be of crucial importance for individual schemes. If, furthermore, relative isotope ratios are to be determined with high precision ( $< 0.1\%$  uncertainty) by resonant laser SNMS, measurements of suitable reference materials are indispensable to account for the odd-even effect.

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