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Lasers and Optics

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Application of an orthogonally polarized laser scheme for selective photoionization of palladium isotopes

Clayton R. Locke[1] · **Tohru Kobayashi**[1] · **Takashi Nakajima**[2] · **Katsumi Midorikawa**[1]

Abstract We present a technique using two orthogonal linearly polarized lasers to improve practical implementation of the separation of odd- and even-mass-number palladium isotopes. Dye lasers are used for a three-step photoionization of vaporized palladium, where due to the transition selection rules only odd-mass-number isotopes are ionized and removed from the palladium beam via an electric field. Schemes presented in the literature use two counter-propagating circularly polarized beams, which are in practice difficult to implement perfectly. In contrast, two counter-propagating orthogonally polarized beams are technically less demanding to implement, yet the scheme retains the same high selectivity demonstrated in this work of >1200 (or 99.7 ± 0.3 %).

1 Introduction

High-level radioactive wastes produced from nuclear power plants contain yields of a few percent of platinum group metals such as palladium, rhodium, zirconium and plutonium; metals that are valuable in industry in quantities comparable to that available from natural reserves [1]. Considerable research has investigated the separation of these valuable metals from other nuclides [2–4] including recovery from tailings from previous decades of fission waste. However, these platinum group metals contained in radioactive waste are presently unable to be utilized due to the co-presence of long-lived radioactive isotopes. To date, techniques to selectively remove radioactive isotopes have not been established on a commercial scale.

Palladium is one of the platinum group metals and is of high value in industry, and as ore deposits are rare, motivation for recycling is high. Palladium is present in the yield from fission processes, containing the isotopes ^{104}Pd (16.9%), ^{105}Pd (29.3%), ^{106}Pd (21.3%), ^{107}Pd (17%), ^{108}Pd (11.7%) and ^{110}Pd (3.8%) [2]. The isotope ^{107}Pd is not naturally occurring and has a half-life of 6.5 million years, meaning simply storing for an extended period is not feasible (in contrast to rhodium, for example, which essentially becomes inactive after 50 years). There are three methodologies to recycle Pd with laser photoionization; firstly, resonance ionization mass spectrometry (RIMS) [5, 6]. Secondly, using very narrow line-width lasers precisely tuned to the transition for the isotope; this technique, however, is not considered viable as the isotope shifts for Pd [7] are much smaller than the Doppler-broadened absorption line-widths. Thirdly, a general technique proposed by Balling and Wright [8] using circularly polarized lasers for isotope selectivity, in which only odd-mass-number isotopes having nonzero nuclear spin (and thus having hyperfine structure) are able to be ionized due to selection rules. The feasibility and practicality of this third technique when applied to platinum group metals is reported by Chen [9], and may yield higher selectivity ratios than RIMS [10], although further development is required to fully assess any relative merits.

Presented here, as an extension to the third technique using circularly polarized lasers, is a means using two counter-propagating, orthogonally orientated, linearly polarized laser beams. This is a considerably simpler method, and we demonstrate complete selectivity of odd-mass-number

✉ Clayton R. Locke
  clayton.locke@riken.jp

1 RIKEN Center for Advanced Photonics, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

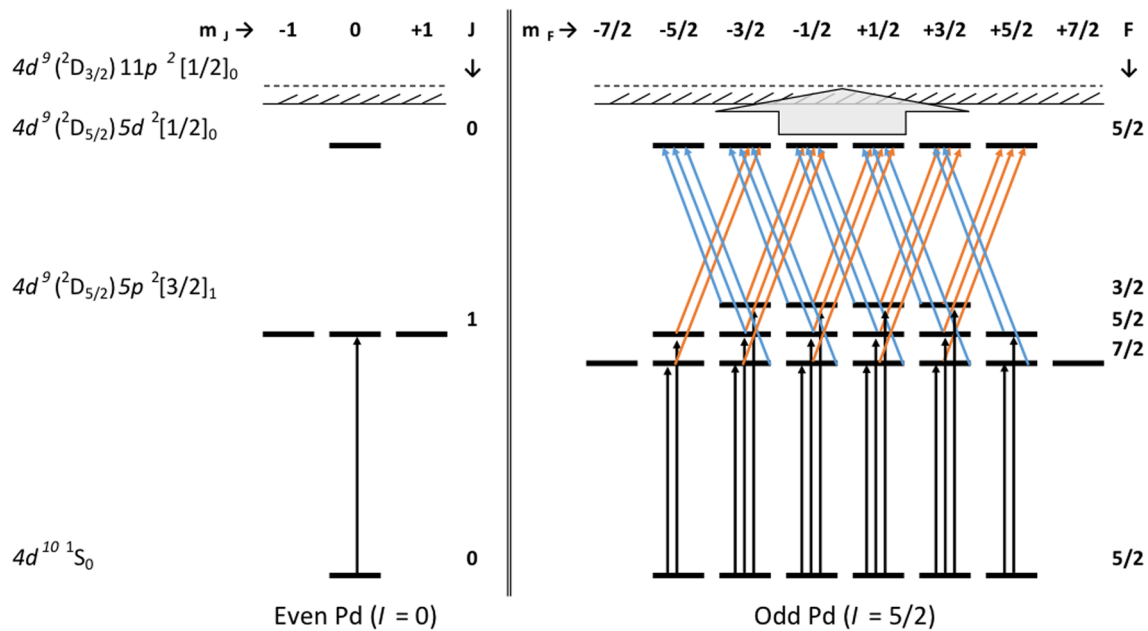2 Institute of Advanced Energy, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan

Fig. 1 Selection scheme by two-step excitation of Pd using linearly polarized light with orthogonal polarization as viewed in the $|F, m_F\rangle$ representation. Selection rules for the first excitation ↑ (plane polarization) require $\Delta m_J = 0$ and $\Delta m_F = 0$. The second counter-propagating laser has polarization axis orthogonal to the first, and therefore, the selection rules are $\Delta m_J = \pm 1$ and $\Delta m_F = \pm 1$ (↑,↓). A third laser ionizes the atom via a Rydberg autoionizing state (hyperfine structure of this level is not relevant to the ionization scheme and for clarity is omitted from the figure)

isotopes from even-mass-number isotopes (within observation error), which is equally efficient as the selectivity obtained in this work using circularly polarized light.

2 Experiment

2.1 Principle of Pd isotope selective photoionization

Firstly, we briefly summarize the conventional scheme of selective ionization using lasers having circular polarization based on the selection rules for atomic absorption. For left circularly polarized (LCP) light, $\Delta m_J = +1$ for isotopes having zero nuclear spin ($I = 0$) and $\Delta m_F = +1$ for isotopes having non-zero nuclear spin ($I \neq 0$). Here, J is the total angular momentum of the electrons, and $F = I + J$ is the total angular momentum of the electrons and the nucleus. When the first excitation laser is LCP, the quantization axis is set, exciting electrons from the ground state ($^1S_0$) to the first intermediate state, populating the $m_J = +1$ sublevel of the first intermediate state ($^3P_1$). Excitation by a second LCP laser to the second intermediate state ($^3P_0$) is forbidden for even-mass-number isotopes ($I = 0$), but allowed for odd-mass-number isotopes ($I = 5/2$). Finally, a third excitation laser ionizes those isotopes having electrons in the second intermediate state.

Two counter-propagating linearly polarized beams with orthogonal polarization have been applied to the selective resonant ionization of even- and odd-mass-number isotopes of Sn [11] and Yb [12–14]. Selective resonant ionization of ^{91}Zr from other Zr isotopes has also been investigated as a function of angle between the polarization axes of consecutive laser pulses [3]. The selectivity scheme for orthogonal polarization can be rationalized by considering that one of the linearly polarized beams can be decomposed into the superposition of right and left circularly polarized (RCP + LCP) beams with quantization axis parallel to the polarization direction of the first beam. Transitions involved in the first two steps of excitation obey the selection rules $\Delta m_J = 0$ and $\Delta m_J = \pm 1$ for even-mass-number isotopes and $\Delta m_F = 0$ and $\Delta m_F = \pm 1$ for odd-mass-number isotopes. Usually, the quantization axis is most conveniently defined with respect to the first beam, and hence, $\Delta m_J = 0$ and $\Delta m_F = 0$ can be applied to the first step, and $\Delta m_J = \pm 1$ and $\Delta m_F = \pm 1$ to the second step. However, the converse is equally valid, that is, $\Delta m_J = \pm 1$ and $\Delta m_F = \pm 1$ for the first step and $\Delta m_J = 0$ and $\Delta m_F = 0$ for the second step if the quantization axis is chosen with respect to the second beam. For the sake of simplicity, only the selection scheme based on the former choice of quantization axis is illustrated in Fig. 1. Irrespective of the choice of quantization axis, ionization is only allowed for isotopes with odd mass number.
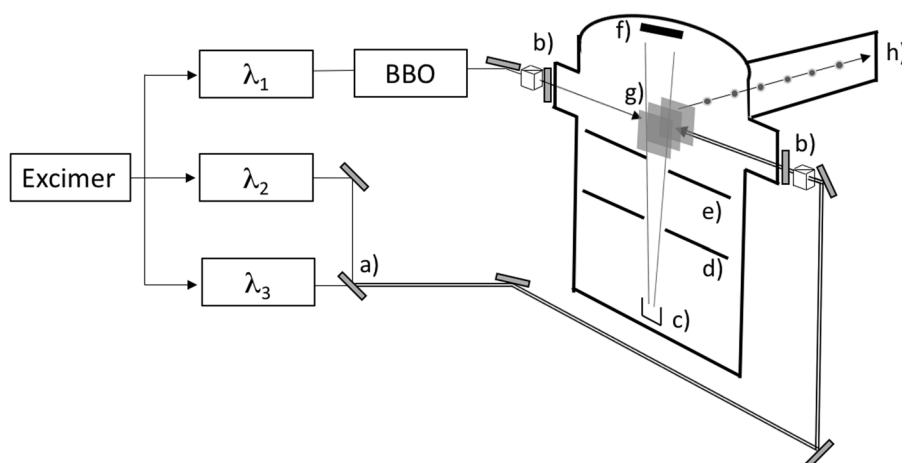
Fig. 2 Experimental setup showing common excimer pulse exciting three dye lasers used to produce the three-step ionization process. λ_2 and λ_3 are combined using a dichroic mirror (*a*) and directed through polarizing beam-splitter cubes (extinction ratio 1000:1) and wave plates (*b*) to arrive simultaneously with the counter-propagating pulse of λ_1 in the interaction region. Pd is vaporized in the crucible (*c*) by deflected electron beam bombardment and collimated by a 10-cm aperture in the (*d*) heat shield. A charged plate (*e*) deflects downwards any ions produced in the vaporization process. A thickness meter (*f*) is used to monitor the rate of atomic Pd. Charged plates in Wily-McLaren configuration (*g*) repel photoions produced in the interaction region toward a microchannel plate detector (*h*)

For completeness, we note that the selectivity scheme using orthogonally polarized lasers can be extended out of the 'plane' consideration and into a third dimension, as described in Chernomorets et al. [15], in which a three-dimensional excitation geometry is used to distinguish the angular momenta of autoionizing states of Pu.

In practice, the production of linearly polarized light with orthogonal polarization is significantly simpler than that of circular polarization, which is advantageous for the separation of even- and odd-mass-number isotopes of Pd. Specifically, a commercial broadband polarizing beam-splitter has a broadband high extinction ratio of greater than 1000:1 (or using a broadband alpha-BBO glan-laser polarizer, the extinction ratio is 100,000:1). Accordingly, orthogonally polarized beams with high purity are very easy to obtain. In contrast, the use of commercial quarter-wave plates which are not specifically designed for the wavelengths used in the two-step excitation scheme leads to the generation of elliptically polarized beams, which results in excitation of undesired even-mass-number isotopes and degradation in the selectivity. To obtain high selectivity, it is critical to employ custom-made quarter-wave plates for the particular wavelengths employed for the experiments.

2.2 Apparatus

In this study, an electron beam source (ULVAC EGK-3) is directed into a crucible of Pd and produces a Pd vapor that is then collimated by two 10-mm-diameter apertures, as shown in Fig. 2. The atomic density in the interaction region with the lasers is of order 10^{10} cm^{-3}. Any ions produced in the vaporization process are deflected by a charged plate before the interaction region.

Three dye lasers (Lambda Physik FL3002 $\times$ 2, Lumonics HD500) having pulse width of 20 ns and repetition rate of 10 Hz are pumped by a single excimer laser (Lambda Physik Compex 103) and have approximately equal path lengths to ensure synchroneity in arrival time in the interaction region with the Pd atoms. Note that all wavelengths reported here are in vacuum and are results of measurements using a frequency counter calibrated using an optogalvanic neon gas cell. The first dye laser at 552.6 nm is frequency doubled in a BBO crystal to produce the first excitation wavelength (λ_1) of 276.3 nm, exciting Pd atoms into the $4d^9(^2D_{5/2})5p$ $^2[3/2]_1$ state. The wavelength of λ_1 is optimally tuned by maximizing the fluorescence signal to the $4d^9(^2D_{5/2})5s$ $^2[5/2]_2$ state via emission of 351.8 nm light, detected by a photomultiplier tube (PMT). The second excitation wavelength (λ_2) of 521.1 nm is produced from the second dye laser and excites Pd atoms from $4d^9(^2D_{5/2})5p$ $^2[3/2]_1$ to $4d^9(^2D_{5/2})5d$ $^2[1/2]_0$. The wavelength of λ_2 is tuned by maximizing the decay emission to $4d^9(^2D_{3/2})5p$ $^2[3/2]_1$ at 666.4 nm.

The third excitation wavelength (λ_3) at 730.9 nm is produced by the third dye laser which, rather than excitation into the continuum, enhances ionization efficiency via the Rydberg autoionizing state $4d^9(^2D_{3/2})11p$ $^2[1/2]_0$ [16]. The third laser is inserted co-linear to the second laser with a dichroic mirror >95 % reflective at wavelengths shorter than 633 nm and >95 % transmissive above 685 nm. The first laser is counter-propagating to the second and third lasers (Fig. 2). Of note are the 6 GHz bandwidths of the

lasers in our system, which are considerably wider than the isotope shifts of approximately 50 MHz for $4d^{10}$ $^1S_0 \rightarrow 4d^95p\ ^2[3/2]_1$ [7]. No change in the selectivity between odd- and even- mass isotopes was observed when the time delay between first- and second-step laser pulses was changed (delays of up to 4 ns, in increments of 0.1 ns).

We utilize custom-made quarter-wave plates (Castech Inc. WPCT-254-1/4-W276 and WPCT-254-1/4-W521) having manufacturing precision limited specifications of retardance of 89.774° at 276 nm for λ_1, and 89.25° at 521 nm for λ_2, both having a wavelength-dependent retardance of 0.25°/nm. Comparison is made between the circular polarization and orthogonal linear polarization schemes using the same optical pathways and excitation laser wavelengths: quarter-wave plates for λ_1 and λ_2 for the former scheme are simply interchanged with half-wave plates for the latter scheme.

Photoions are horizontally repelled by a set of three charged grids, and the relative amounts of Pd isotopes are detected using a microchannel plate (MCP), forming a time-of-flight mass spectrometer in a Wiley-McLaren configuration [17].

Mass separation of Pd photoions is done in a 1-m field-free flight tube before the MCP, with applied voltages on the three repeller plates of (4.0, 2.5, 0) kV, giving a flight time of photoions of approximately 16 μs. This provides a mass resolution ($m/\Delta m$) of 600, which is sufficient to distinguish the isotopes of Pd. Statistical fluctuations in the observed signal are averaged over several hundred laser shots on a 500-MHz storage oscilloscope.

3 Results and discussion

We have separated odd-mass-number isotopes of Pd from the Pd atomic vapor using the conventional circular polarization scheme and the proposed linear polarization scheme with orthogonal polarization. In these demonstrative experiments, we use natural samples in which the isotope ^{107}Pd is not present; however, as ^{105}Pd and ^{107}Pd have nuclear spin ($I = 5/2$), both isotopes are expected to behave identically in the separation process.

To compare with data reported in the literature, we present results in terms of the separation factor β commonly used to report results on fractional separation of a pair of similar elements, defined as the ratio of one element to the other in one fraction divided by the corresponding ratio in the other fraction, $\beta = \frac{A_1}{B_1} \cdot \frac{B_2}{A_2}$ [18]. This measure can thus be applied to quantify the efficacy of the even- and odd-mass-number isotopes before and after the separation process. In the results of Yamaguchi and Sasao implementing a three-step ionization process based on circular polarization [19, 20], the separation factor achieved is $\beta = 9.9$, or
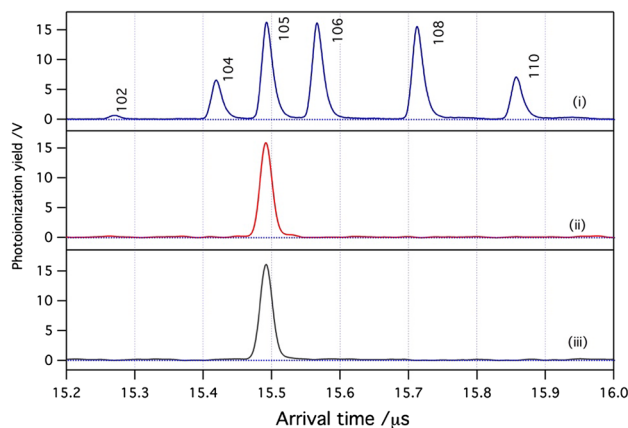

Fig. 3 Isotopes of Pd: (1) measured natural isotope abundances of ^{102}Pd: 0.9 %, ^{104}Pd: 10.2 %, ^{105}Pd: 26.3 %, ^{106}Pd: 25.5 %, ^{108}Pd: 25.5 %, ^{110}Pd: 11.6 %; (2) selective ionization using circular polarization having relative amounts ^{even}Pd: 0.3 %, ^{odd}Pd: 99.7 %; (3) selective ionization using linearly polarized light with orthogonal polarization having relative amounts ^{even}Pd: 0.3 %, ^{odd}Pd: 99.7 %
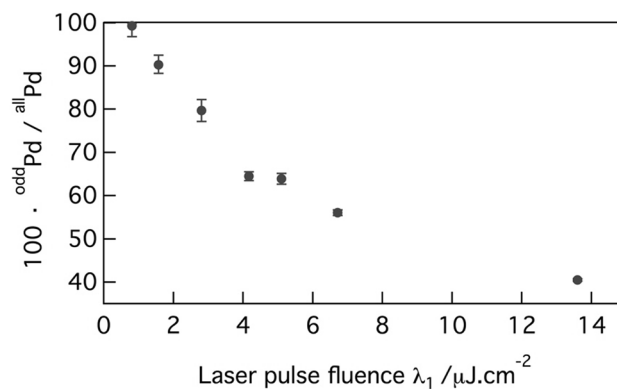

Fig. 4 Degradation in even-odd mass isotope separation due to two-photon, single-wavelength ionization with increasing pulse fluence (pulse duration 20 ns) for laser λ_1

equivalently, an increase in odd isotopes relative to all isotopes (^{odd}Pd/^{all}Pd) of 23–74 %. As will be discussed later, we suspect that the relatively poor performance in separation is due to λ_1 having excessive fluence.

The results obtained in the work presented here are shown in Fig. 3 where (1) is the observed natural abundance observed using two-photon excitation of 276.3 nm light, which is in agreement to that reported in the literature [21], (2) selectivity of 99.7 ± 0.3 % or equivalently $\beta \approx 1220$ achieved using the circular polarization scheme, and (3) identical performance in selectivity and yield (within experimental error) using linearly polarized light with orthogonal polarization.

In this work, it is found that the separation factor β is very much dependent on the fluence of λ_1. To obtain high

selectivity of even- and odd-mass-number isotopes (for both schemes), the fluence of laser λ_1 must be sufficiently low such that the single-color (λ_1) two-photon ionization yield is negligible. The relative percentage of odd-mass-number isotopes of Pd as a function of laser fluence of λ_1 is shown in Fig. 4, where complete separation is achieved at comparatively low fluence <0.8 μJ/cm^2. Investigation into the photoionization yield as a function of λ_1 only (ie., no λ_2 or λ_3) reveals that this decrease in selectivity is entirely due to single-color ionization. This condition has to-date been overlooked in the literature yet is of critical importance in practical application of Pd isotope separation projects.

In contrast, the restriction on the fluence of λ_2 is considerably lower as the transition from the first excited state $4d^9(^2D_{5/2})5p\ ^2[3/2]_1$ to the second excited state $4d^9(^2D_{5/2})5d\ ^2[1/2]_0$ is forbidden for even-mass-number isotopes, and therefore, selectivity will degrade only when the fluence of λ_2 is greater than the threshold at which selection rules break down. We found the separation ratio is unchanged even at the maximum available fluence with our laser system of 1300 μJ/cm^2.

Given the requirement of retaining high selectivity, the necessarily low fluence of λ_1 is in conflict with the need for high yield in Pd recycling projects. The beam area can be increased (although this is limited by the diameter of the Pd vapor column), but available power of λ_2 and λ_3 becomes a limiting factor if the beam areas of these lasers are correspondingly increased. A multi-pass configuration in which the interaction volume of Pd and lasers can be extended significantly by multiple reflections of the lasers (extending incrementally in the direction of the Pd atoms) is an effective method of increasing yield with the available laser power.

4 Conclusion

Separation of even- and odd-mass-number isotopes of Pd using orthogonally polarized lasers has been demonstrated and yields identical performance of 99.7 % selectivity compared to a scheme using lasers with circular polarization. The orthogonally polarized scheme has the advantages of being simpler to implement and also lends itself favorably to a multi-pass configuration.

References

1. K. Naito, T. Matsui, Y. Tanaka, Recovery of noble metals from insoluble residue of spent fuel. J. Nucl. Sci. Technol. **23**, 540–549 (1986). doi:10.1080/18811248.1986.9735017
2. R. Bush, Recovery of platinum group metals from high level radioactive waste. Platin. Metals Rev. **35**, 202–208 (1991)
3. L. Green, G. Mcrae, P. Rochefort, Selective resonant ionization of zirconium isotopes using intermediate-state alignment. Phys. Rev. A **47**, 4946 (1993). doi:10.1103/PhysRevA.47.4946
4. H. Niki, Two-color ionization spectroscopy and laser isotope separation of zirconium for efficient transmutation of long-lived fission products. J. Korean Phys. Soc. **56**, 190–194 (2010)
5. L.P. Smith, W. Parkins, A. Forrester, On the separation of isotopes in quantity by electromagnetic means. Phys. Rev. **72**, 989 (1947). doi:10.1103/PhysRev.72.989
6. M. Payne, L. Deng, N. Thonnard, Applications of resonance ionization mass spectrometry. Rev. Sci. Instrum. **65**, 2433–2459 (1994). doi:10.1063/1.1144702
7. E. Van Duijn, S. Witte, R. Zinkstok, W. Hogervorst, Hyperfine structure and isotope shift measurements on 4d10 1s0 → 4d9 5p $J = 1$ transitions in Pd I using deep-Uv Cw laser spectroscopy. Eur. Phys. J. D **19**, 25–29 (2002). doi:10.1140/epjd/e20020051
8. L.C. Balling, J.J. Wright, Use of angular-momentum selection rules for laser isotope separation. Appl. Phys. Lett. **29**, 411 (1976). doi:10.1063/1.89100
9. H.L. Chen, Laser cleanup of Pt group metals. UCID-18837 (1980). doi:10.2172/6748034
10. A.N. Tkachev, S.I. Yakovlenko, On laser rare-isotope separation. Quantum Electron. **33**, 581 (2003). doi:10.1070/QE2003v033n07ABEH002465
11. W. Fairbank Jr., M. Spaar, J. Parks, J. Hutchinson, Anomalous odd-to even-mass isotope ratios in resonance ionization with broad-band lasers. Phys. Rev. A **40**, 2195 (1989). doi:10.1103/PhysRevA.40.2195
12. C. Haynam, B. Comaskey, E. Worden, and J. Paisner, *Measurement of Atomic Oscillator Strengths in Ytterbium by Observation of Coherent Rabi Oscillations of Excited-State Populations* (Lawrence Livermore National Lab., CA, USA, 1987). http://www.iaea.org/inis/collection/NCLCollectionStore/_Public/19/014/19014761.pdf
13. G. Bekov, A. Zherikhin, V. Letokhov, V. Mishin, and V. Fedoseev, Difference in the yields of even and odd Yb isotopes in multistep photoionization by polarized laser beams. JETP Lett. **33** (1981)
14. V. Fedoseev, A. Yusupov, Effect of polarization of laser emission on the multistage photoionization yield of ytterbium isotopes. Opt. Spectrosc. **57**, 552–554 (1984)
15. M. Chernomorets, M. Dubov, G. Klishevich, Determination of the Pu autoionizing level angular momenta by a multistep excitation with linearly polarized laser light. Opt. Commun. **171**, 253–261 (1999). doi:10.1016/S0030-4018(99)00558-1
16. N. Karamatskos, M. Müller, M. Schmidt, P. Zimmermann, Rydberg series in the photoionization spectrum of Pd I. Phys. Lett. A **102**, 409–411 (1984). doi:10.1016/0375-9601(84)91066-1
17. W. Wiley, I.H. Mclaren, Time of flight mass spectrometer with improved resolution. Rev. Sci. Instrum. **26**, 1150–1157 (1955). doi:10.1063/1.1715212
18. B. Weaver, Separation factor. Anal. Chem. **26**, 474–475 (1954). doi:10.1021/ac60087a013
19. H. Yamaguchi, N. Sasao, in *Proceedings of the International Symposium on Advanced Nuclear Energy Research* (1989)
20. H. Yamaguchi (1995) [cited March 2016]. http://jolissrch-inter.tokai-sc.jaea.go.jp/pdfdata/PNC-TN8410-95-077.pdf
21. M. Berglund, M.E. Wieser, Isotopic compositions of the elements 2009 (Iupac Technical Report). Pure Appl. Chem. **83**, 397–410 (2011)