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Topic: "Laser Isotope Separation"

AVLIS PROCESS FOR ISOTOPIC PURIFICATION OF PALLADIUM EXTRACTED FROM FISSION PRODUCTS

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Abstract

The atomic laser route AVLIS (Atomic Vapor Laser Isotopic Separation) was chosen for removing the ¹⁰⁷Pd from palladium extracted from the spent fuel because of the absence of convenient molecules for the ultracentrifugation process. Furthermore, an AVLIS-type process has the capacity to process large quantities of material. However, AVLIS applied to platinum metals implies specific difficulties that were not encountered on uranium, in particular due to a different electronic configuration. The work reported here presents the main scientific and technological difficulties encountered and the first characterizations paving the way to solutions, which still require industrial development.

Introduction

Radioactive platinumoids from the fission products of nuclear reactors are produced in quantities comparable to those produced by conventional mines, and are therefore gaining importance (e.g. ruthenium, palladium, etc.). The two main suppliers, worldwide, of natural palladium are struggling to meet the demand of around 200 t/year. The price of palladium (2023) is around 40 euros per gram (for comparison that of gold is 52 euros per gram). To envisage the use of certain platinumoids from irradiated fuel waste on the market, one or more radioactive isotopes must be removed, depending on the element considered. This is the case of palladium ($Z=46$), whose already very high demand continues to grow, for example for automotive catalysts (75%), alloys, capacitors, jewelry... A single isotope, ^{107}Pd , an artificial radionuclide beta emitter, with a half-life of 6.5 million years, has to be removed (15.5% of content in the palladium's fission product).

Japan, mainly for Reduction and Resource Recycle of High Level Radioactive Waste through Nuclear Transmutation has launched an Impact Program on the topic [1]. The main achievements are developing a method to recover only odd-nuclides of palladium isotopes by separation of even- and odd-nuclides, conducting a demonstration test of nuclear transmutation by irradiating the ^{107}Pd with a deuteron beam for the first time in the world, and completing a conceptual plant design of a large-capacity accelerator facility that carries out nuclear transmutation.

France has chosen, via the company Orano, to reprocess spent nuclear fuel from its power plants. Some elements are already recycled and recovered, such as uranium – partly (URE) – or plutonium for the production of MOX; the fission products are sorted and either vitrified and stored, or only stored. This waste is currently stored at La Hague. The cost, demand and scarcity of palladium fully justify its recycling as well as waste reduction efforts.

The EPONA project devoted to palladium purification is technically supported by the French CEA thanks to skills acquired on uranium, among other things, up to 2003 using the AVLIS technology. *In fine*, it should process the characteristic (quality, output quantities, etc.) material from the ORANO plant in La Hague. Returning the final product to civilian use requires a decontamination factor of around 20,000, although this is reduced in the nuclear industry. These decontamination factors are in negotiation with other countries, such as Japan. The ultimate goal of the EPONA project is to develop a new so-called unconventional palladium supply chain. The next step after this “Investment Plan for the Future” (PIA) – a governmental contribution to the project associated with ORANO GROUP, AMPLITUDE LASER GROUP (a pump laser provider) and CEA - would be to build up a scale 1 pilot workshop and then a production unit that could be implemented on the Tricastin site, which is the industrial site operated by Orano.

This article presents the difficulties to overcome for massive palladium purification via AVLIS technology, and some first results on the R&D. The main difficulties such as the weakness of isotope shift, non-selective two-photon photoionization, a first transition located in the ultraviolet spectrum and finally a high-efficiency pump laser for the dye lasers used should be solved. These different items constitute the paragraphs of this proceeding conference article after a short introduction on AVLIS.

AVLIS

AVLIS, in its basic version, uses the isotopic dependence of the energy of atomic electronic levels (and so of electronic transitions). The light emitted by lasers can be tuned to the frequencies of electronic transitions, causing the excitations followed by ionization of the chosen isotope. The ions are then separated by an electric field, and captured by dedicated collectors. This separation method is very selective (carrying out enrichment in a single step either in the case of uranium, or in the case of palladium). The basic physics is well-known [2].

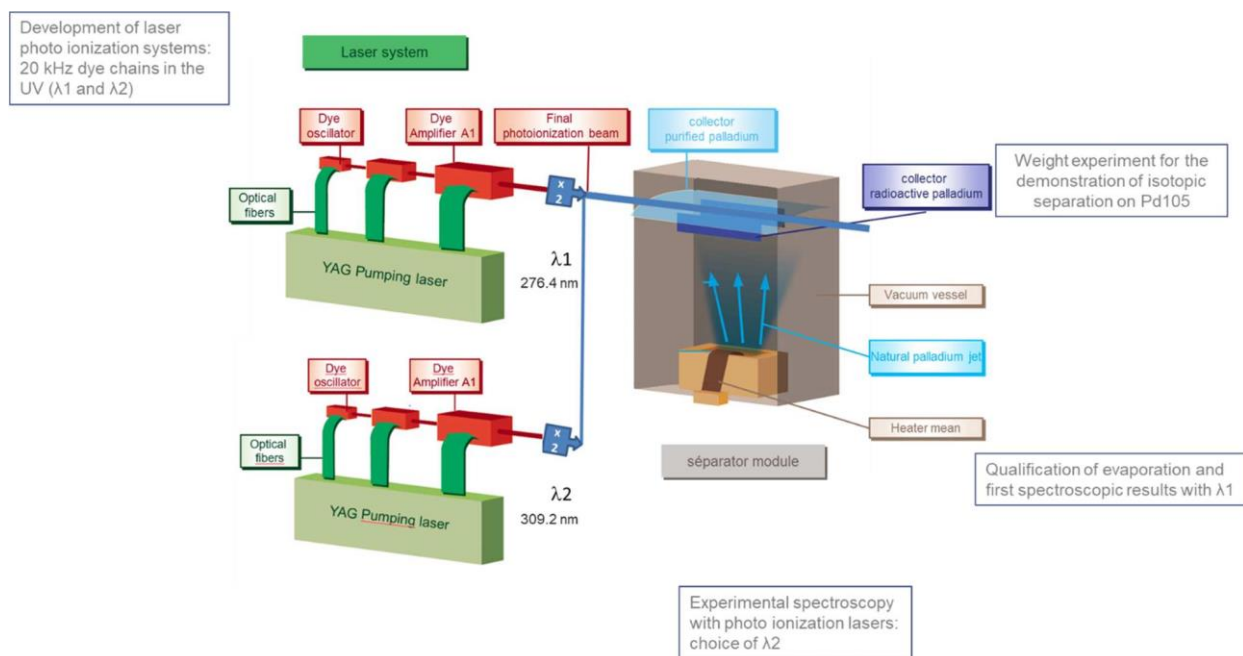


Figure 1: AVLIS Configuration for palladium. Second-harmonic generation for the two dye chains superimposed.

At the end of the last century, France was to have autonomous and competitive means of enriching uranium in a context of strong international competition. Indeed, 40 years ago CEA decided to develop the AVLIS process (Isotope Separation by Laser on the Atomic Vapor of Uranium), a process based on laser photo-ionization of uranium atomic vapor. This decision gave rise to a major research and development program, carried out jointly by CEA and the industrial company COGEMA until 2003, after a successful

final demonstration at that date, on a scale 1 full system. An amount of 203 kg of enriched uranium at 2,5% -limited by investments- from around one ton of natural Uranium was produced in little more than one hundred hours [3].

Palladium isotope spectral shift

The first difficulty encountered by all the teams having envisioned applying AVLIS to palladium is the weakness of the isotope spectral shifts for the three possible first dipolar transitions in the photoionization ladder [4]. Any significant atomic vapor production generates Doppler effects incompatible with a high spectral selectivity. In the following spectrum (ure 2), even with a high laser resolution (3 MHz), spectral lines are not separated, except two hyperfine transitions for the $^{105}\text{Pd}^{3/2,7/2}$.

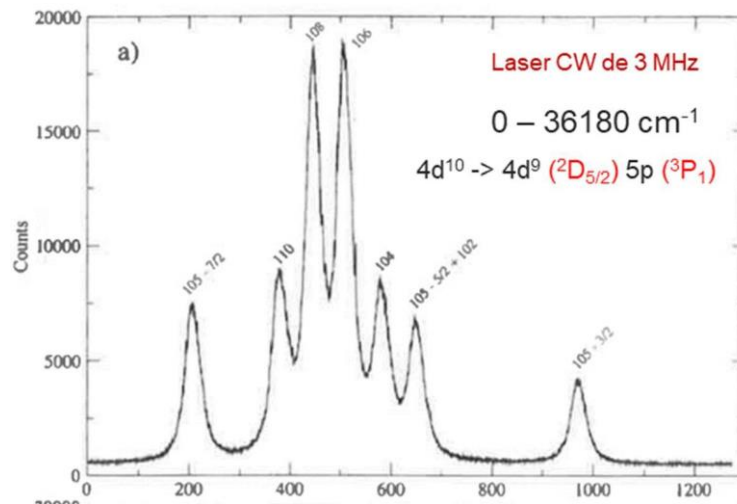


Figure 2 : High resolution spectrum of natural palladium in UV. Even and odd isotopes partly resolved (x axis in MHz) from van Duijn et al. [5]

An alternative technique, based on the use of dipolar transition selection rules, proposed by [6] enables in some cases odd and even isotopes to be separated with a judicious choice of laser polarizations. The technique was used several times, in particular with gadolinium[6,7, 8].

Fortunately, palladium from spent fuel has only two odd isotopes ^{105}Pd and the radioactive ^{107}Pd . The isotope ratio is given in the next table, and we see that 28.3% +15.5% are removable with the AVLIS technique [8].

Table 1 : Isotope ratios in natural and fission products

A=	102	104	105	106	107	108	110
Natural	1,02%	11,14%	22,33%	27,33%	0	26,46%	11,72%
Fission products	-----	17,3%	28,3%	25%	15,5%	10,3%	3,6%

Figure 3 shows how selective photoionization is obtained. For electric dipole transition the good quantum number for the interaction with two linearly polarized lasers is $F=J + I$, J is the electronic level quantum number and “ I ” the nuclear spin quantum number. The latter is zero for palladium even isotopes, $5/2$ otherwise. For an even isotope and a properly aligned linearly polarized laser, $J = 1 mJ=0$ to $J = 1 mJ=0$ is a forbidden electric dipole transition. Hence, the autoionizing state chosen as final state of the second step for the odd isotopes should have $J=1$ and of course have an efficient cross section. Our first result on odd/even isotope separation of natural palladium will be discussed in the next paragraph.

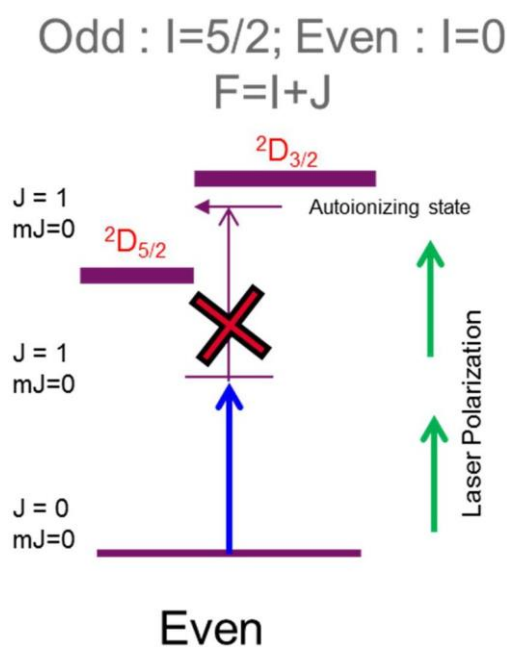


Figure 3 : Even and odd isotope separation using quantum rules. Photoionization allowed for odd isotopes (two ionization thresholds core dependant in red)

One-color resonant two-photon ionization ($\lambda_1 + \lambda_1$)

One-color resonant two-photon ionization (1C-R2PI) is a parasitic phenomenon, which occurs when twice the energy of the first step photon overcomes the ionization energy of the atom considered, allowing the excited state of the first step to be photoionized by the same laser light. This process competes with the photoionization induced by the second laser, which leads to the selective photoionization desired. The non-selective absorption of the first or the second laser also gives ions but isotopically non-selective.

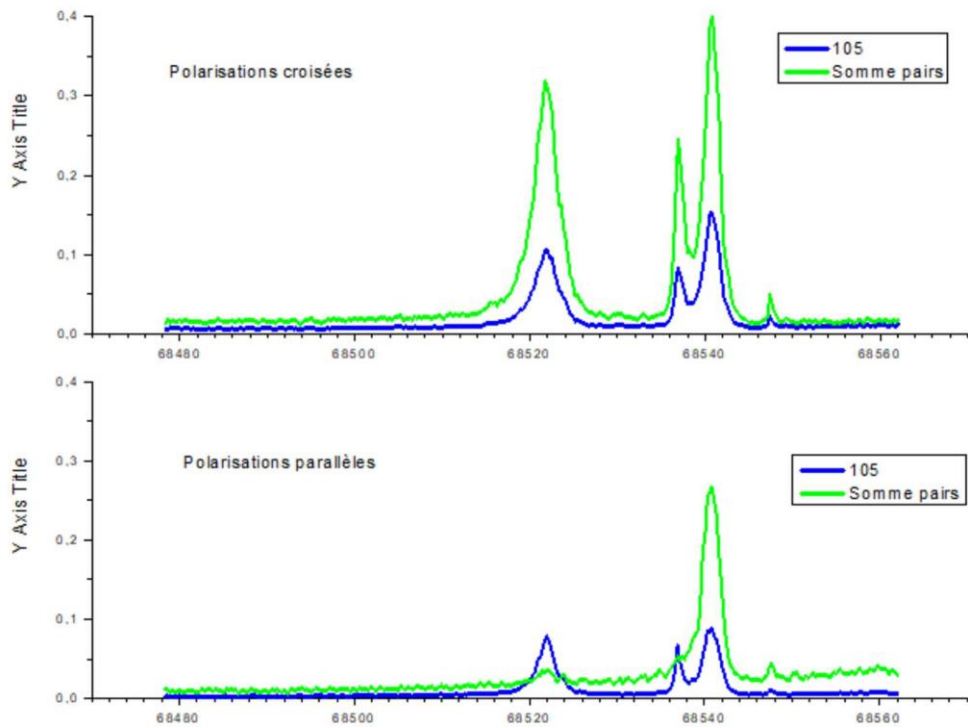


Figure 4: Different autoionizing states versus second laser wavelength scan (upper: cross polarization; lower: parallel polarization and “pairs” = even) showing the selected one at 68522 cm^{-1} .

For the first time in our facilities, we have demonstrated the selective photoionization of even and odd isotopes excited by lasers with parallel polarization (

Figure 4). One can notice that “pairs” is not exactly zero : Could this be the effect of the two photon non selective photoionization [9,10] ?

Since the $1C-R2PI (\lambda_1 + \lambda_2)$ represents a potential limitation of the process, we determined its dependency with the first wavelength pulse energy, and compared it to the dependence of the two color signal as a function of the second laser (the second transition towards the ionization, which gives the following result (Figure 5). The curves show two very different slopes which give hope for a fairly weak $2\lambda_1$ phenomenon, but having not yet been able to obtain saturation of all the parameters, the cross sections are not accessible and hence the conclusions are not definitive.

On the other hand, it seems that the signal of $^{106}\text{Pd}^+$ (and therefore also of other even isotopes) in parallel polarization is linked to direct ionization. Improving the selectivity of ionization will therefore rely on the use of an autoionizing state for which the transition dipole moment with the first stage excited state will be higher.

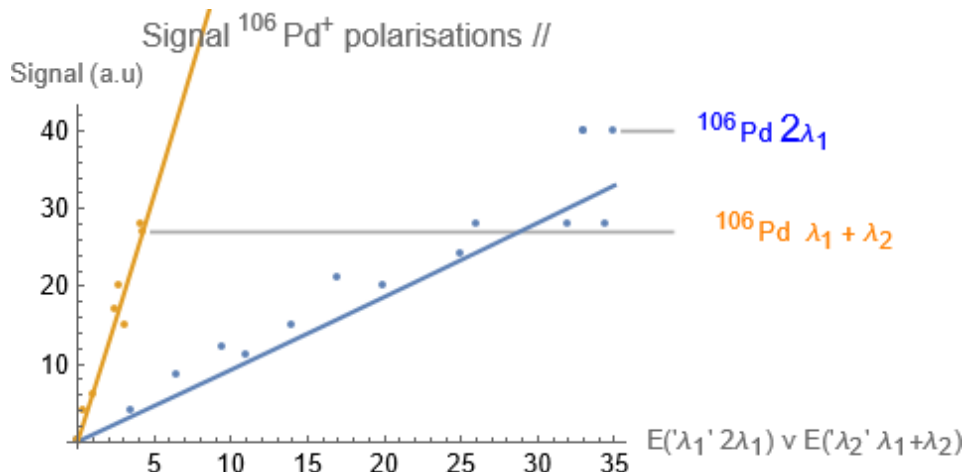
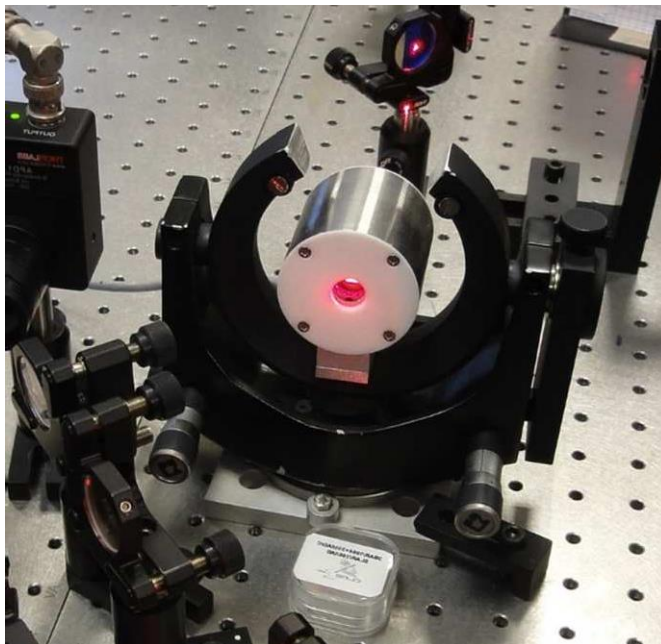


Figure 5 : $^{106}\text{Pd}^+$ Signals as a function of the pulse energy of laser λ_1 (One-color R2PI; blue points) or of laser L_2 (two-color R2PI with $E[\lambda_1] \sim 0.6 \mu\text{J}$), with parallel polarizations)

High power UV laser beam generation

A large flow rate of palladium production requires a very strong fluence perfectly tuned in wavelength. Since the quantum yield of photon production is never unitary, the thermal energy must be removed from the laser system. Liquid evacuation is the best solution and therefore only liquid dye lasers are suitable. However, to generate UV radiation, the dye molecules are too quickly destroyed. The solution adopted is



that of generating a dye laser beam, in the visible range, then doubled in frequency. Frequency doubling in the UV spectrum is a hard point at high average power. The choice of the “ladder” that leads to ionization takes into account this energetic constraint and others like photoionization efficiency, isotopic selectivity and resultant UV optical beams configuration.

So the study of the most appropriate crystal is in progress as well as its UV absorption, its resistance to laser flux and its operating temperature.

Figure 6 : LBO and its oven in test

High power pump laser for palladium

The wavelength proposed previously in the first step at 276 nm requires laser power at 552 nm, i.e. with photons 20 nm less energetic than those of the Nd:YAGs sold commercially (second harmonic 532 nm). Dye absorption efficiencies are not excellent at these wavelengths. To get closer to the yields of copper vapor lasers, it is preferable to build dye pumping lasers emitting at 515 nm and therefore Yb:YAG.



Figure 7: Tangor laser from Amplitude Group to be modified for AVLIS application

Amplitude Laser Group proposes to build that unit starting with a standard brick based on a multipass Yb:YAG slab amplifier (TANGOR). On this laser, it is necessary to increase the pulse energy from 7 mJ to at least 20 mJ at the fundamental wavelength, 1030 nm, or an average power of 400W at the repetition rate of 20 kHz. This will be done by increasing the diameter of the laser beam.

Secondly, in order to maintain high conversion efficiency and to be compatible with the dye laser pumping, the minimum pulse duration is 20ns. This will require the use of Non Critical Phase Matching LBO to compensate for walk off and angular acceptance.

Lastly, in the fibered subsystem, it is necessary to overcome Amplification of Spontaneous Emission (ASE) and Brillouin effect.

Conclusion

France is launching a new project on the reduction of very long-lived nuclear fission products. Among the seven materials composing this set, palladium is a critical element that it is interesting to purify, both due to its price, the tension on supply and demand, but also on the quantity of waste that can be reduced. AVLIS is the process chosen for the separation of its radioactive isotope.

Despite some difficulties, the separation of palladium isotopes by laser is demonstrated and the hints about manageable parasitic phenomena are not prohibitive.

The development of the process faces some difficulties, which are described here. However, the separation of isotopes palladium by laser was achieved and hints about manageable parasitic phenomena were obtained. Finally, the targeted laser technology for the massive production of purified palladium either exists or is under development.

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