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Author(s): Renisch, Dennis; Düllmann, Christoph E.; Abrosimov, Roman; Eberhardt, Klaus; Kindler, Birgit; Lommel, Bettina; Lukacova, Jana; Mokry, Christoph; Oberstedt, Stephan; Pohjalainen, Ilkka; Runke, Jörg; Schwab, Tanyel; Sirleaf, Christopher

Title: Actinide and lanthanide thin-layer developments using a drop-on-demand printing system

Year: 2023

Version: Published version

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Please cite the original version:

Renisch, D., Düllmann, C. E., Abrosimov, R., Eberhardt, K., Kindler, B., Lommel, B., Lukacova, J., Mokry, C., Oberstedt, S., Pohjalainen, I., Runke, J., Schwab, T., & Sirleaf, C. (2023). Actinide and lanthanide thin-layer developments using a drop-on-demand printing system. In D. Schumann, C. Stodel, & M. Gott (Eds.), 30th Conference of the International Nuclear Target Development Society (INTDS2022) (Article 04001). EDP Sciences. EPJ Web of Conferences, 285.
<https://doi.org/10.1051/epjconf/202328504001>

Actinide and lanthanide thin-layer developments using a drop-on-demand printing system

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Abstract. Actinide and lanthanide thin layers with specific requirements regarding thickness, homogeneity, chemical purity, mechanical stability, and backing properties are applied in a multitude of physics and chemistry experiments. A novel target preparation method, the so-called “Drop-on-Demand” (DoD) technique, based on a commercial nanoliter (nL) dispenser is applied since a few years in the Nuclear Chemistry unit at Johannes Gutenberg University Mainz. The wetting behaviour of the nL droplets on the substrate’s surface is a key parameter determining the spatial distribution of the deposited material after evaporation. By switching from aqueous to organic solvents as well as by substrate surface modifications, the wetting behaviour can be influenced. Recent investigations on this influence and applications of the DoD method are presented. The produced actinide deposits were characterized by optical and scanning electron microscopy, by α spectroscopy as well as by radiographic imaging.

1 Introduction

Radioactive targets and sources are needed for a variety of physics experiments. The applications range from targets for laser [1] and mass spectroscopic investigations of actinides [2], over myon-based experiments for the determination of nuclear charge radii [3] to recoil sources where the daughter nuclides are to be used for atomic physics [4], nuclear physics [5] and chemical [6] experiments, to targets used for superheavy element production in heavy ion induced fusion reactions [7].

The requirements of the target properties are as diverse as the applications. In addition to the desired nuclide and quantity, the layer thickness, homogeneity, geometry, chemical form, mechanical stability and the substrate used are the most important parameters. All these parameters have to be tailored to the requirements of the individual experiment, so that no single, general specification for “the optimum target” can be given. Accordingly, the fabrication methods must also be flexibly adapted. For many applications, electrochemical deposition, such as molecular plating [8], is a viable method. Disadvantages of molecular plating include the need to use a conductive substrate, the difficulty of obtaining a chemically well-defined layer and limitations in the applicable geometry.

At the Johannes Gutenberg University Mainz, the Drop-on-Demand (DoD) technique has been used for several years as a complementary target fabrication method [9]. The DoD system essentially consists of a commercial nanoliter (nL) dispenser (PipeJet® Nanodispenser from BioFluidix), which is mounted above movable x-y stages, jointly controlled by a versatile control system.

The substrate is positioned on the movable stages. A self-written LabView-based software allows printing any geometries. The printing solution, in which the radioisotope of interest is dissolved, is filled into a reservoir at the dispenser. Aqueous as well as organic solutions can be used. By combining different solvents and different backings (metals, polymers, carbon substrates, etc.), these surfaces can be modified [10,11] and different wetting behavior of the individual drops can be achieved. This also has to be adapted and optimized for the respective target, depending on whether individual, separated deposits are required or whether the backing needs to be covered over as large an area as possible.

In the following, the further development of the method is described on the basis of selected examples from recent years, in which DoD produced targets were used, in particular with regard to the use of different solvents for printing.

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2 Experimental results

2.1 Comparison of aqueous and organic solvents

2.1.1 Spontaneous fission sources

For a project in collaboration with JRC Geel, Belgium, to determine fission fragment masses and kinetic energy distributions by means of the double velocity and double energy (2v-2E) method, ^{248}Cm and ^{252}Cf sources are needed. The fission products will be measured in 4 π geometry using the VERDI spectrometer [12]. For high-precision data, the energy loss of the fission products inside the source layer and substrate has to be as small as possible. For this experiment, a rate of about 100 to 1000 fissions/s of ^{248}Cm or ^{252}Cf was requested. The source thus has to be as thin as possible, and a particularly thin substrate is required. The substrate of choice is a 35 $\mu\text{g}/\text{cm}^2$ polyimide (PI) foil, covered with a 50 $\mu\text{g}/\text{cm}^2$ gold coating. Due to the fragility of the foils, mounting into an electrochemical cell is not possible due to the risk of rupture during mounting or dismounting, thus the contactless DoD process was used to fabricate the sources.

For the first attempt to produce a suitable source, ^{252}Cf was printed from an aqueous solution. This involved printing of 221 drops, 20 nL each, 1 mm apart, onto a PI substrate. The source contained a total of 330 kBq α activity and 10 kBq spontaneous fission (sf) activity. The relatively high hydrophobicity of the substrate led to single, spherical droplets, resulting in comparatively thick deposits after drying. The sources were tested at JRC Geel, where it was found that the energy loss within the source material was significantly greater than the energy loss in the substrate. Due to the resulting poor resolution, the sources were not suitable for the desired measurements.

To overcome these limitations, different alcohol-based solvents were tested, in particular ethanol, isopropanol and isobutanol. Preparatory experiments using lanthanide material spiked with ^{243}Am to allow for studying deposit thickness by measure of α particle energy loss showed that an ethanol:water = 72:25 mixture appears to be well suited [13]. In this case, the droplets cover a much larger area than when printing from pure water, but the area to be wetted remains controllable. At higher alcohol content, no defined wetting of the substrate could be obtained. By distributing an identical amount of source material over a larger area, the average film thickness should be significantly smaller than in the previous sources.

^{248}Cm sources were prepared using a printing sequence of 641 drops, 10 nL each, using an ethanol:water = 70:30 mixture as solvent. Fig. 1 shows a microscope image (left) and a radiographic image (right) of one of the finished ^{248}Cm sources. The source contains 8.1(3) μg of ^{248}Cm . An α activity of 1270(38) Bq was measured, corresponding to a spontaneous fission rate of 114(4) Bq. Alpha spectroscopic

measurements show a relatively narrow FWHM of 19 keV, which is close to the intrinsic resolution of the used PIPS detectors [14].

The characterization of the fission fragment energy distributions is ongoing at JRC Geel.

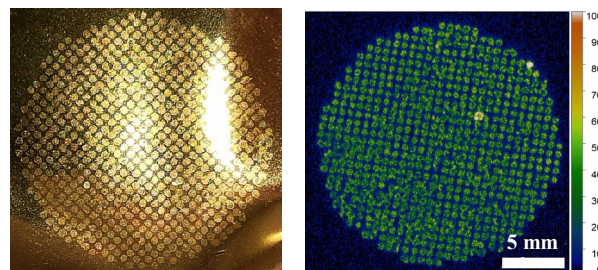


Fig. 1. Microscope image (left) and radiographic image (right) of a 8 μg ^{248}Cm source, printed with the DoD setup from a mixture of ethanol:water = 70:30. The source was produced by placing 641 drops of 10 nL each on a Au coated PI substrate [14].

2.1.2 Targets for accelerator-based experiments

At the university of Jyväskylä, the properties of n-deficient Th to Pu isotopes shall be studied at IGISOL [15]. Those isotopes are produced by p-induced reactions on neutron-poor actinide targets, like ^{232}Th or ^{233}U . Thus, nuclides in the range $^{226-229}\text{Th}$, ^{227}Pa , or $^{224-233}\text{Np}$ are accessible. Many fundamental properties of the nuclides, that can be reached this way, have hardly been investigated so far or are based only on extrapolated values. For example, direct mass measurements with the penning trap setup JYFLTRAP [16] would be of great interest to the community.

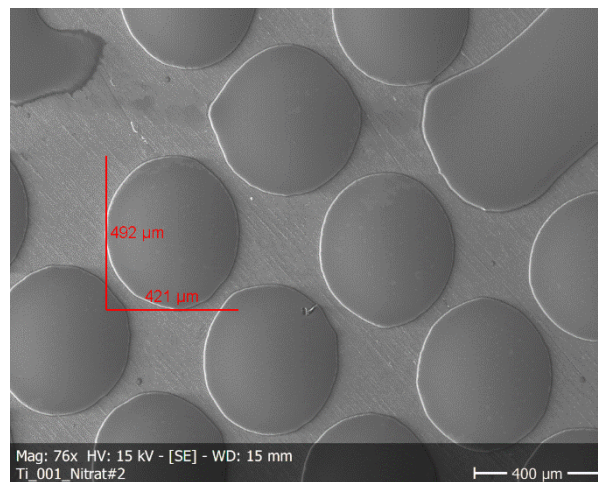


Fig. 2. SEM image of ^{232}Th nitrate depositions on a Ti substrate. 432 drops, 20 nL each, of an aqueous solution were positioned using the DoD system. 174 μg of ^{232}Th were deposited in total.

In the case of ^{232}Th , the target material is available in the form of a mechanically stable self-supporting metal foil. For all other, more exotic actinide isotopes, such as ^{229}Th , ^{233}U , ^{239}Pu , or ^{241}Am , this possibility does not exist because there is not enough material available to produce a self-supporting target. Therefore, other production methods must be used to produce thin films

on suitable backings. ^{232}Th was selected as the first test species to compare the performance of DoD-based targets with that of ^{232}Th metal foil targets and thus to assess the suitability of printed layers for online experiments.

Numerous ^{232}Th targets with average thicknesses ranging from 197 to 592 $\mu\text{g}/\text{cm}^2$ were produced. Various metal foils (Pd, Rh, W, Zr, Pt, Ti, Ni, Au), provided by the GSI target laboratory, were tested as possible backing material. The targets were printed from aqueous nitrate solution and subsequently heat-treated at 550°C in a muffle furnace. Fig. 2 shows a SEM image of one of the targets before irradiation. One can see the ^{232}Th -nitrate deposits on the Ti substrate as well-defined spherical structures. However, large uncovered areas are also clearly visible between the deposits. A selection of these targets could be tested during a beam time in 2018 at JYFL. In addition to the mechanical stability, the yield could also be compared to that from a 3.25 mg/cm^2 ^{232}Th foil.

The results of this beam time were very promising. Reaction products could be obtained from all used DoD targets and all targets withstood the thermal stress in the beam without being visibly damaged. Compared to the solid ^{232}Th film, about 30% of the yield of reaction products was obtained [17]. The yield was presumably limited by insufficient coverage of the irradiated area with target material.

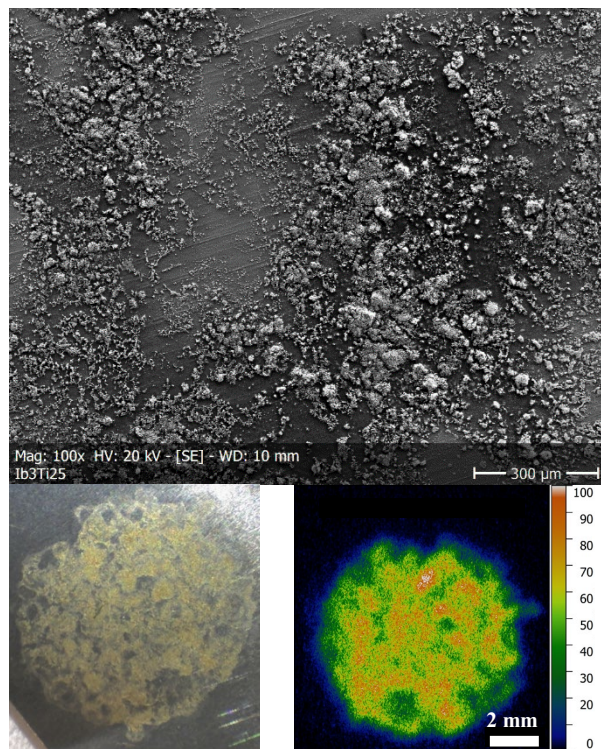


Fig. 3. SEM image (top), microscope image (bottom left) and radiographic image (bottom right) of ^{233}U nitrate depositions on a Ti substrate. 1052 drops, 5 nL each, of an isobutanolic solution were positioned using the DoD system. 61 μg of ^{233}U were deposited in total [18].

In 2019, additional target preparation experiments were performed, this time with ^{233}U as target material, using organic solvents instead of aqueous solutions to

achieve better wetting of the droplets on the substrates. Various alcohols, acetone, and acetonitrile were applied as possible solvents. In particular, printing from pure isobutanolic solution led to a more homogeneous distribution of activity than from aqueous solutions. Finally, 6 targets with film thicknesses in the range of 120 to 180 $\mu\text{g}/\text{cm}^2$ on Ti (25 μm), Pt (20 μm) and Au (20 μm) substrates were sent to Jyväskylä [18]. Originally, experiments with these targets were planned for 2020, but could only be carried out in October 2022.

The ^{233}U targets irradiated in 2022 show a better distribution of the target material on the backing (see fig. 3), although still no completely homogeneous layer could be obtained. However, it can be seen, especially in the radiographic image, that there are only few gaps in the activity distribution where no target material is present at all. In the SEM picture, one can see that the uranyl nitrate formed more small-grained crystallites distributed over the surface.

2.2 Usage of polymer-based solutions

A new idea to increase the homogeneity of the produced layers is the combination of DoD with polymer assisted deposition (PAD). In the PAD process [19,20], a polymer agent is added so that, after drying, a homogeneous polymer film is formed, in which the target material is uniformly distributed. The polymer film is then converted by thermal decomposition, leaving a uniform layer of the target material.

Polyethyleneimine (PEI) was used as the polymer for the initial experiments. PEI offers the advantage that it is readily soluble in water and ethanol and decomposes at relatively low temperatures (< 500°C).

Again, ^{233}U was chosen as the first test species. For this purpose, uranyl nitrate was dissolved in water as well as ethanol and mixed with PEI solutions, which were previously adjusted to a pH in the range of 6.5 - 9.2. Two different PEI solutions were used, one using PEI with a molecular weight of 1800 g/mol and one with 10000 g/mol (Alfa Aesar, 99%). The mixture of a PEI solution with a ^{233}U solution was applied by DoD to the desired substrate (25 μm Ti foils) and then dried under an IR lamp. As a final step, the polymer was decomposed in a muffle furnace at a maximum temperature of 410°C [21].

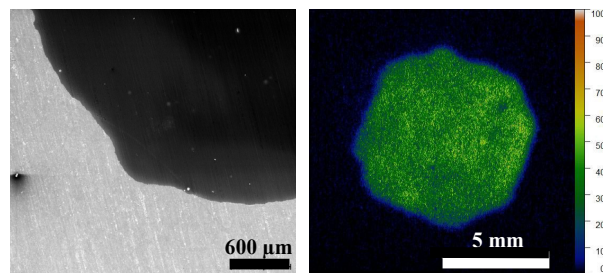


Fig. 4. SEM image (left) and radiographic image (right) of a ^{233}U deposition on a Ti substrate. 69 drops, 20 nL each, of an ethanol based ^{233}U solution containing 25 vol% PEI (1800 g/mol) were positioned using the DoD system and treated at 410°C in a muffle furnace afterwards. The deposited areal thickness of ^{233}U is 0.3 $\mu\text{g}/\text{cm}^2$ [21].

Figure 4 shows a SEM image (left) and a radiographic image (right) of a deposition containing $0.3 \mu\text{g}/\text{cm}^2$ ^{233}U obtained in this way. Compared to all previously discussed DoD methods, an extremely homogeneous layer was obtained here, with no gaps visible in the coating. Also, the original printing pattern is no longer observable because a uniform polymer film formed before the heating procedure.

Thus, this method is extremely promising from the point of view of producing homogeneous, thin layers. However, more optimization steps are necessary before this can be applied. A fundamental problem arose during the actual printing process, as the dispenser tip was regularly clogged due to the high viscosity of the polymer solution, so that it was often not possible to perform a continuous printing sequence. This could be compensated for using the PEI with a molecular weight of 1800 g/mol and using larger dispenser tips ($20 - 75 \text{ nL}$), but the printing process remains more error-prone than printing with aqueous or alcoholic solutions.

A second problem arose with the maximum achievable layer thickness. Layers with $> 10 \mu\text{g}/\text{cm}^2$ could not be achieved so far, because using higher uranium concentrations either changed the printing behavior of the polymer solution, so that a homogeneous film was no longer obtained, or the obtained film no longer adhered to the substrate after the final heating step. There was a tendency to observe that those problems were less pronounced when using the shorter chained PEI. This may be due to incomplete coordination of the dissolved uranyl ions by the PEI, when the uranium concentration is too high. Therefore, an approach for further studies would be to use PEI with even lower molecular weight, but possibly in higher concentration, so that sufficient PEI molecules are available to complex all uranium ions. Possibly, the addition of an additional coordinating agent, e.g., EDTA (ethylenediaminetetraacetic acid), could also positively influence the properties of the polymer film. These ideas will be further investigated in future work.

3 Conclusion & Outlook

The use of organic solvents, like alcohols, acetonitrile, etc., improves the chance of achieving flat deposits and avoiding irregular patterns originating from the surface tension of water droplets, like the so-called coffee ring effect [22].

The best results in terms of uniformity and homogeneity of the deposits have so far been achieved using PEI as polymer-forming agent. So far, this has only been successful up to a low uranium concentration, and the printing process has also been considerably more complex than printing with other solvents due to the properties of PEI. But, there is potential to make further progress by adapting the conditions, for example using PEI with a lower molecular weight but a higher concentration.

Besides changing the solvent, there are other ideas for adjusting the DoD process. For example, chemical or physical pretreatment of the substrate is conceivable.

First attempts for anodic oxidation of Ti substrates to improve the wettability of the surface showed promising results [11]. Another possibility to be investigated in the near future is the pretreatment of substrates with a plasma torch, which should also activate the surface so that increased hydrophilicity is achieved.

The DoD technique has great potential to be a complementary production method for thin films of lanthanides and actinides due to its flexibility in the choice of solvents and substrates. Further studies are needed to identify crucial parameters in the production of homogeneous films, but PAD based attempts show promising results.

We acknowledge the support of the technical staff of the TRIGA Mainz research reactor and the corresponding mechanical workshop as well as of the staff of the JYFL accelerator laboratory and Iain Moore for scientific support during the JYFL beam times.

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