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Electrodeposition source preparation for ^{238}U alpha source: Parameter settings

Report for EMRP MetroFission project

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1. Introduction

A proper uranium source for alpha spectrometry must be thin and uniform and have a homogeneous activity distribution in order to obtain high energy resolution spectra and avoid low energy tailing. To meet these requirements, electrodeposition is one of the most common methods for preparing alpha sources for high resolution spectroscopy. The spectral properties (resolution, tailing) are more important in nuclear data metrology than in any other type of measurement (e.g. environmental analysis, geological studies). For a high quality alpha source many parameters should be optimized. The following settings were studied: type of the electrolyte, type of the electrode, surface quality of the backings, deposited mass, rotation and shape of the anode, current density, deposition time and the experience of the analyst.

2. Parameter settings

2.1. Electrolytes

To prepare alpha sources inorganic electrolytes, like NH_4-citrate/HCl, Na_2SO_4, $H_2SO_4/(NH_4)_2SO_4/Na_2SO_4$, saturated NH_4NO_3 or NO^-_3/NaF, can be used. From those, the most commonly used, are solutions which contain a mixture of $H_2SO_4/(NH_4)_2SO_4/Na_2SO_4$ at pH 2.1-2.4 [1-3].

2.2. Impurities

If the material in contact with the electrolyte is not chemically resistant, it can be dissolved in the electrolyte and be deposited on the surface of the source during the electrolytic process. This was observed in some cases during our experiment. Using a polyethylene electrodeposition cell often resulted in a polymer deposit on the surface of the source (Figure 1.a.). Impurities in the reagents (e.g. Mn, Fe etc.) may interfere with the deposition of ^{238}U (Figure 1.b.).

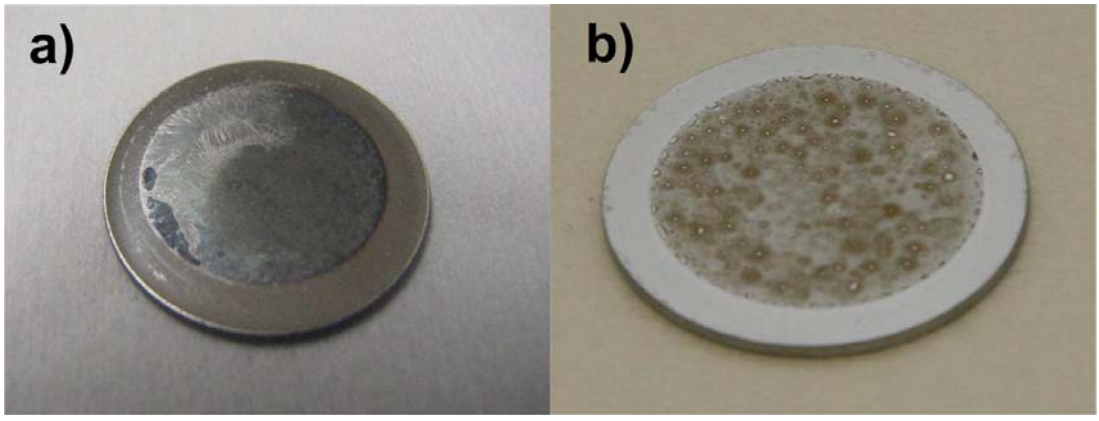

Figure 1. Different impurities on the stainless steel backing: a) polymer deposit using polyethylene electrodeposition cell; b) from iron impurities of the reagents.

If the electronic contact, which is joined to the rotating Pt-anode, is scraping material from the anode, some metal scraps might fall into the electrolyte and be deposited onto the stainless steel backing surface. In order to prevent this, one should choose the right anode material and cover the electrodeposition cell.

2.3. Cathode quality

Surface morphology of the cathode has an impact on the quality of the deposition as it affects the thickness and the homogeneity of the deposited material [4]. A smoother surface - mirror polished – result in more homogeneous uranium deposit, while rougher backing surface with scratches result in less homogeneous sources with poorer resolution. A reason could be that the current density distribution is not homogeneous on rough surfaces. Edges may host nucleation sites for oxygen gas evolution [5].

2.4. Electrolyte-anode material

As platinum (Pt) is used as anode for depositing uranium from an electrolyte solution containing $H_2SO_4/(NH_4)_2SO_4$, some Pt could be dissolved into the solution. Subsequently, it could be deposited onto the stainless steel backing. This process has already been reported [6-8] and leads to a worsening of the spectral quality.

An alternative for a platinum anode can be one of Pt-Rh alloy (90% Pt, 10% Rh), which is more resistant under these circumstances.

2.5. Anode geometry

Also, the geometry of the anode is important. The shape of the Pt-electrode influences the current density distribution in the electrolyte during the electrodeposition and thus the homogeneity of the alpha source. Better homogeneity can be obtained by using a spirally wound or meshed disc shape electrode, compared to a pin shaped or cross type electrode [9]. For this reason, rectangular and spiral shaped anodes were tested.

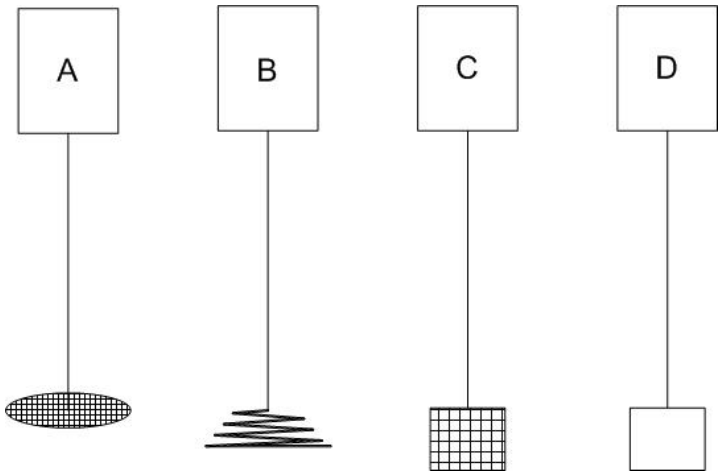

Figure 2. Optimal geometries of the Pt-anode: A) meshed disc, B) spirally wound, C) rectangular grid, D) rectangular without grid.

In Figure 3, autoradiographs are shown of sources prepared with rectangular and spirally shaped anodes respectively. Also shown are activity profiles along a line through the centre of the sources.

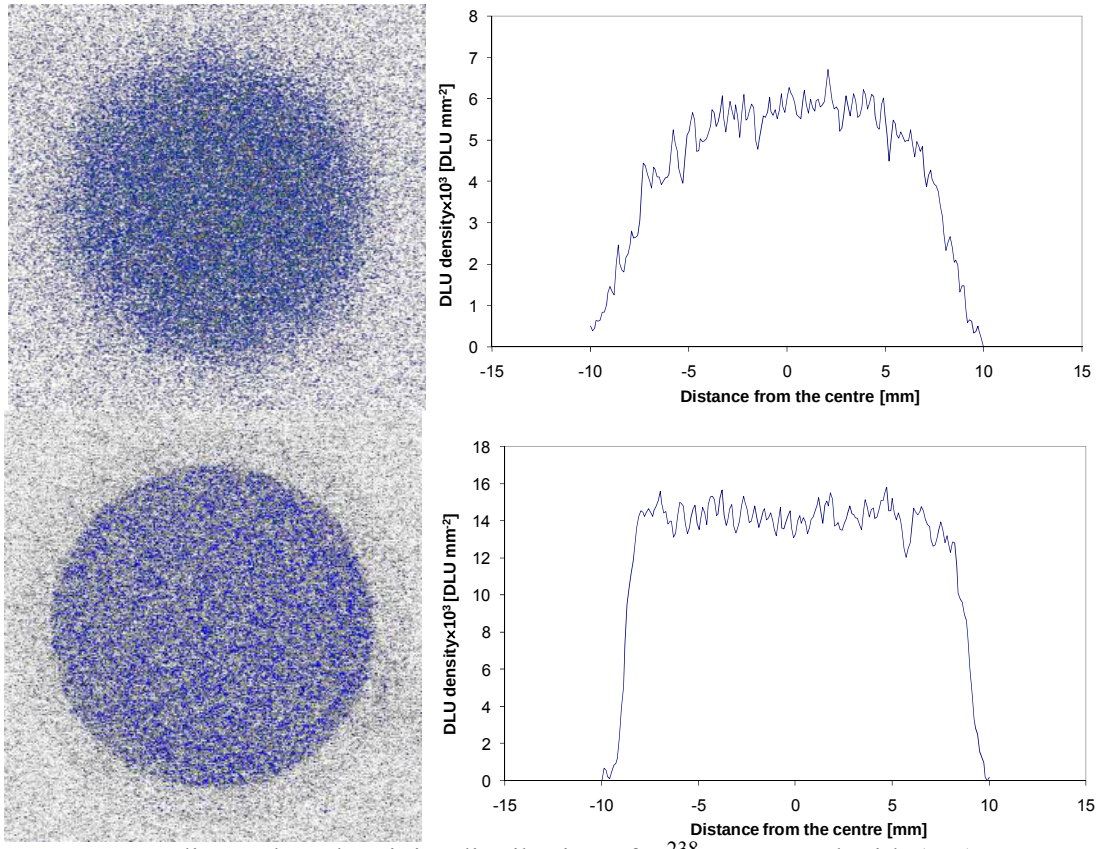

Figure 3. Autoradiograph and activity distribution of a ^{238}U prepared with (top) a rectangular shaped anode and (bottom) a spirally wound anode.

The autoradiograph images and profiles show that with a spirally wounded anode the ^{238}U is deposited more homogenously over the whole stainless steel backing than with a rectangular one.

2.6. Cathode-anode rotation

Cathode and anode rotation speed are adjustable. Becheril Vilchis et al. [10] showed that the higher the rotation frequency the higher the deposition yield is. Beyond a certain rotation speed some vibrations might occur and foam production starts on the top of the solution, therefore loss of uranium can be expected.

An attempt was made to make a more homogeneous uranium source by rotating the platinum spiral with a speed of 10-12 rpm. An autoradiograph of this ^{238}U source (Figure 4) shows that this attempt failed as most of the activity was concentrated in the centre and did not equally cover the outer parts of the disk.

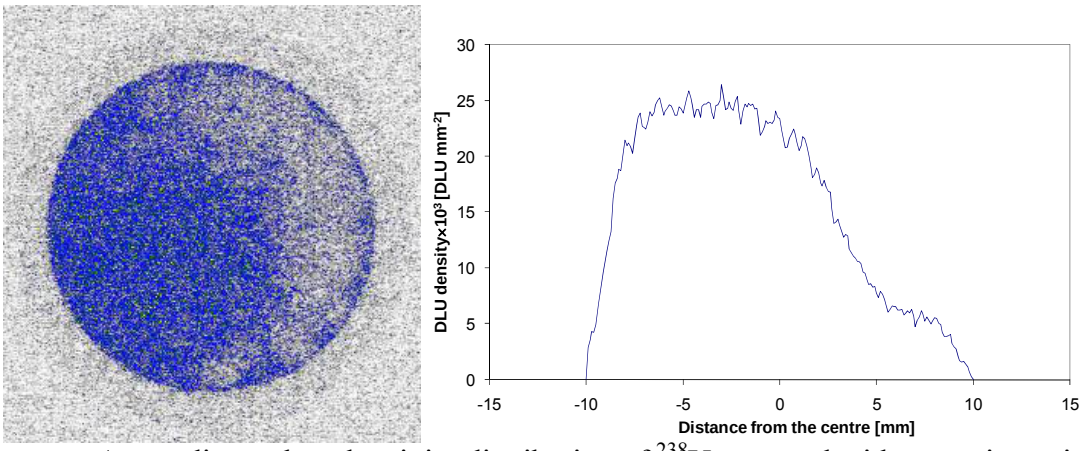

Figure 4. Autoradiograph and activity distribution of ^{238}U prepared with a rotating spirally wound anode.

2.7. Electrolyte pH

The electrodeposition process is very sensitive to the electrolyte pH. It strongly influences the deposition yield of uranium [5]. At a low pH (pH < 2), the deposited uranium layer can be redissolved into the electrolyte. At higher pH (pH > 4), uranium tends to form hydroxide complexes with different stochiometry which inhibit its deposition.

2.8. Temperature control

During the electrodeposition, the temperature rises due to the high current density. Since the ion mobility (i.e. the conductivity of the electrolyte, current) depends also on the temperature, controlling the temperature was important. The electrodeposition cell was immersed into a water bath to keep its temperature stable during the whole process.

2.9. Deposited mass

The deposited mass plays a significant role in the spectral quality. Martin and Hankock [11] found a positive correlation between source mass density and peak width (FWHM), which is 0.63 keV per µg cm^{-2}. Using this heuristic relationship, one finds an attainable resolution of 16.4 keV for a source with a density of 26 µg cm^{-2}. Other researchers [6-8] have demonstrated that suitable alpha sources for common applications can be prepared with a surface mass density of 30 µg cm^{-2}, even up to 40 µg cm^{-2} [12] which is equivalent to 0.371-0.495 Bq ^{238}U activity[1].

At IRMM, we could make sources with reasonable resolution but the deposited mass was far too low to obtain good counting statistics within a reasonable period of time. Using another method with 18.6 mm of source diameter, we were unable to produce good quality sources with the mass of deposited ^{238}U exceeding 100 µg (A = 1.2 Bq). It was concluded that the surface density should be kept below 26 µg cm^{-2} in order to reach a good compromise between energy resolution and counting statistics [13].

[1] The specific activity of ^{238}U in natural uranium is considered as 12.4 Bq mg^{-1} [6].

Pictures of the sources made in CIEMAT and IRMM are shown in Figure 5 and the alpha-spectrum of the IRMM source in Figure 6.

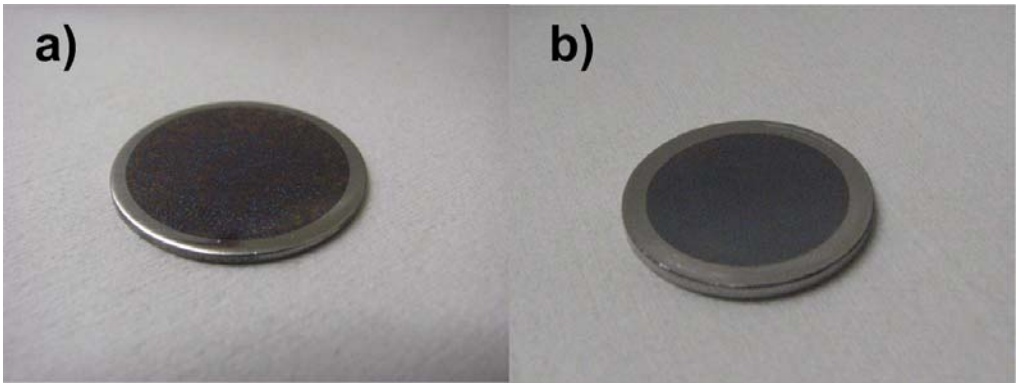

Figure 5. ^{238}U sources prepared: a) from natural uranium solution (CIEMAT); b) from enriched ^{238}U solution (IRMM).

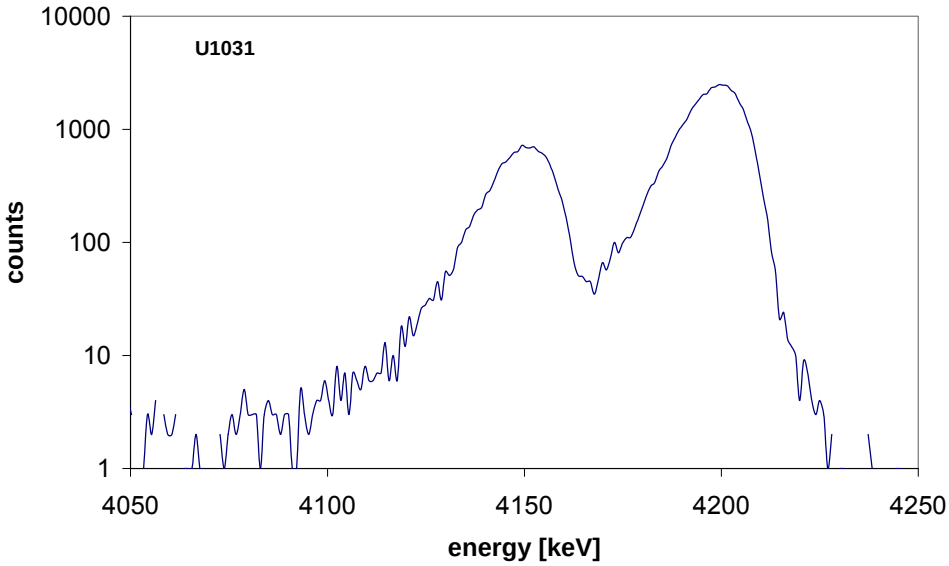

Figure 6. Alpha spectrum of an enriched ^{238}U source (IRMM).

High quality spectra are shown in different papers [6, 10], with energy resolution below 8 keV [6]. However, Garcia-Torano [14] states that, energy resolution values between 8 and 8.5 keV seem to be the lowest limit, both from theoretical and experimental point of view. He claims that such a low resolution is not realistic and might be a result of a possible failure of the software used for the calculation. Apart from the quality of the alpha source, resolution depends on the measurement set-up as well.

2.10. Current density and deposition time

When a high current density is applied in an aqueous electrolyte, gaseous hydrogen is produced at the surface of the stainless steel cathode during the electrodeposition. These hydrogen bubbles might either remove some of the deposited ^{238}U particles into the solution or prevent the ^{238}U to deposite onto the backing surface, resulting in a heterogeneous layer as

shown in Figure 7. Ultrasonic agitation helps removing hydrogen bubbles from the surface resulting in a more uniform alpha source.

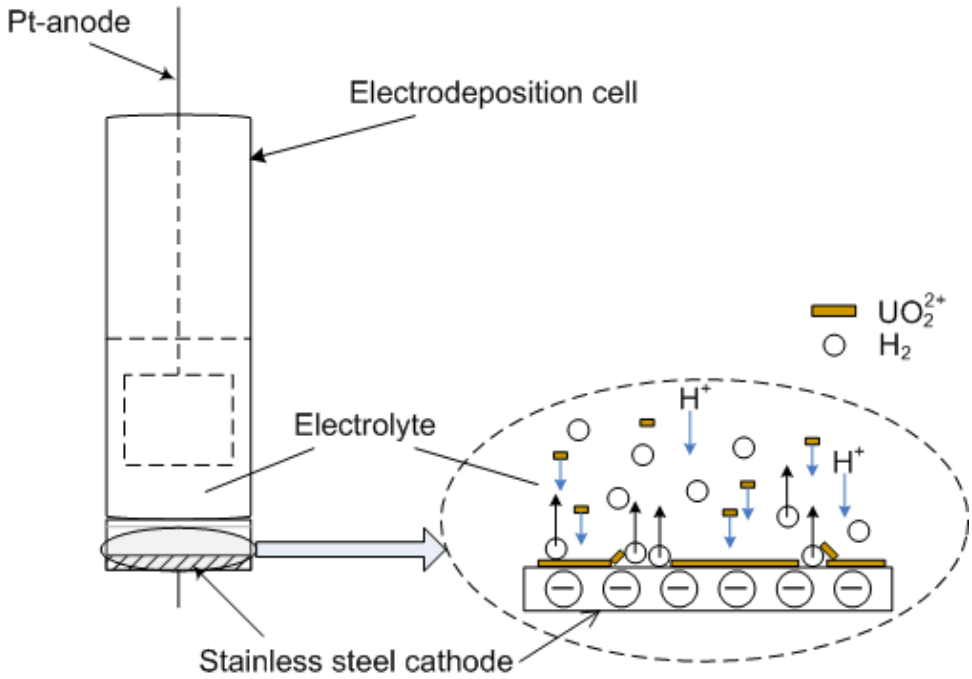

Figure 7. Processes on the anode and cathode.

In addition, a permanent re-dissolution of the deposit might happen in acidic condition; therefore 1 minute before switching off the voltage, the pH must be shifted to alkali by adding 1 mL concentrated NH_4OH.

The typical deposition time for uranium is 60 to 120 min and results in a 60-100% deposition yield. The deposition yield can not be calculated without internal tracer, it can only be estimated.

3. Conclusions

The optimalisation of the all parameters of the electrodeposition leads to the production of very thin and homogeneous alpha sources with high alpha particle energy resolution. The following aspects and parameters were considered and optimised to improve the source quality:

- Mirror polished stainless steel backings are used (flat, no roughness).
- Chemically resistant electrodeposition cells are used (Teflon).
- The current density must be set properly according to the electrolyte used!
- If the Pt-electrode is dissolved and deposited, then Pt/Rh alloy should be used.
- The deposited mass must be below 30 μg cm^{-2}.
- The shape of the anode must be either spiral or meshed type.

- The rotation speed of the anode must be optimized.
- The distance between cathode and anode must be set between 0.5-1 cm.
- The deposition time must be kept between 60 - 80 minutes.
- The electrodeposition cell must be kept at constant temperature.
- Ultrasonic agitation is applied during the electrodeposition.
- Proper electrical connections must be used.

Table 1. Summary of the electrodeposition methods.

	Electrolyte	pH	Current density [mA cm^{-2}]	Dissolved ^{238}U	FWHM [keV]	Pt rotation [r.p.m.]	Pt-shape	Deposition time [min]	Yield [%]	Reference
1	H_2SO_4/Na_2SO_4	3.5-6	0.18-1.4	N.D.	10	Cathode	N.D.	100	97.5	[10]
2	H_2SO_4/Na_2SO_4	2.1-2.4	400-600	N.D.	24.9	No	spiral	60	99	[2]
3	H_2SO_4/Na_2SO_4	2.1-2.4	530	N.D.	18.2		spiral	20	91	[3]
4	H_2SO_4/Na_2SO_4	2.3	400			10-12	rectangular	20	N.D.	[14]
5	NH_4NO_3	5	400	~125 µg	15.3		spiral	60	70-80%	[15]
6	NH_4NO_3	5	200-250		11.4	10-12	rectangular	60	N.D.	[14]
7	NO_3^-/NaF	10-12	1	6.5 Bq U_{nat}	75	Cathode stirring	spiral	180	N.D.	[16]

N.D. – no data available

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Abstract

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