

## Preparation of high-resolution $^{238}\text{U}$ $\alpha$ -sources by electrodeposition from various electrolyte solutions

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**Abstract** – In this paper the source preparation procedure for high-resolution  $^{238}\text{U}$  sources is described. This work was done in a collaboration between CIEMAT and IRMM within the frame of MetroFission, a project of the European Metrology Research Programme, in order to determine the alpha-emission probabilities of  $^{238}\text{U}$ .  $^{238}\text{U}$  was deposited from organic (iso-propanol) and inorganic ( $\text{H}_2\text{SO}_4/(\text{NH}_4)_2\text{SO}_4$ , saturated  $\text{NH}_4\text{NO}_3$ ) electrolyte solutions on metal backings. Preliminary results show that the  $^{238}\text{U}$  source quality is significantly better when making them in saturated  $\text{NH}_4\text{NO}_3$  than in the two other electrolytes. By this method sources of 18,6-22 mm diameter,  $26 \mu\text{g cm}^{-2}$  surface density, 16-18 keV resolution and a peak to valley ratio higher than 50 could be made. This reconciles the inherently opposing requirements of high resolution and sufficient count rate needed to determine the alpha-emission probabilities accurately.

**Keywords:**  $^{238}\text{U}$ , high-resolution alpha-spectrometry, alpha-emission probability, electrodeposition.

### 1. INTRODUCTION

A proper uranium source for alpha spectrometry must be sufficiently active to achieve good statistical accuracy, but also the uranium layer must be thin and homogeneously distributed on a flat and smooth backing in order to minimise energy loss in the source and detect the emitted alpha-particles with optimum energy resolution. In order not to lose too much precious (enriched) uranium, a source preparation technique with high yield is preferred. To meet all these requirements, electrodeposition, one of the most common methods for preparing alpha sources for high-resolution spectrometry, was used. Spectral properties like, energy resolution, low-energy tailing and counting statistics are the most important parameters by which to judge the quality of a source. The demands for source quality in radionuclide metrology are much higher than in applied spectrometry, e.g. for environmental analysis or geological studies.

Our main objective was to prepare  $^{238}\text{U}$  alpha sources by electrodeposition with good spectral properties and relatively high specific activity. Many parameters of the electrodeposition have to be optimised such as for example the type of electrolyte, material and shape of electrode, surface quality of the backing, deposited mass, rotation of the anode, current density and the deposition time.

Three different types of electrolytes were tested. The first one is an organic (iso-propanol) electrolyte [1] while

the other two are inorganic electrolytes:  $\text{H}_2\text{SO}_4/(\text{NH}_4)_2\text{SO}_4$ , based on Talvitie's method [2], and saturated  $\text{NH}_4\text{NO}_3$  [3].

### 2. MATERIALS AND METHODS

#### 2.1. Chemicals and backings

All chemicals (iso-propanol,  $\text{Na}_2\text{SO}_4$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{NH}_4\text{OH}$  and  $\text{H}_2\text{SO}_4$ ) used were analytical grade reagents. The saturated  $\text{NH}_4\text{NO}_3$  solutions were always freshly prepared by dissolving 19,2 g  $\text{NH}_4\text{NO}_3$  in 10  $\text{cm}^3$  of deionised water.

A stock solution of highly enriched  $^{238}\text{U}$  (99,999 wt%) was prepared at IRMM and was in  $\text{UO}_2(\text{NO}_3)_2$  form with a uranium concentration of 20  $\text{mg cm}^{-3}$ . This stock solution was diluted with deionised water (18  $\text{M}\Omega \text{ cm}$ ) lowering the uranium concentration to 1  $\text{mg cm}^{-3}$ .

At CIEMAT, tests on the electrodeposition methods were carried out using a CIEMAT natural uranium standard solution of 6,3  $\text{Bq g}^{-1}$  activity concentration. Since the specific activity of  $^{234}\text{U}$  is much higher than that of  $^{238}\text{U}$ , results can be extrapolated to a pure  $^{238}\text{U}$  solution.

Commercially available aluminium (99,99 %) and mirror polished stainless steel disks were used as source backing.

#### 2.2. Preparation of the electrodeposition cell and the backing

At IRMM, the surface of the backing was rinsed first with deionized water and cleaned with acetone in order to remove any traces of glue and fat.

For the method in organic environment the electrodeposition cell was made of polyacetal. The source diameter was initially 6 mm, later increased to 12 mm. The cell used with the inorganic methods was initially a polyethylene plastic scintillation vial (16 mm source diameter). After electrodeposition, polymer traces appeared on the surface of the  $^{238}\text{U}$  source. Therefore the polyethylene vial was replaced by a Teflon vial (18,6 mm source diameter).

At the screw-cap side the thread of the polyethylene vial was covered with Teflon tape in order to make the cell leak tight. For the Teflon electrodeposition cell this was not necessary. The base side of the vials was cut off before use. The cells were visually checked for leakage, by filling them with water.

CIEMAT backings were first cleaned with chloroethylene, and then washed with deionised water. The CIEMAT electrodeposition cells were made of polypropylene and the water tightness was checked before each use. The source diameter on the backings was 22 mm.

### 2.3. Sample preparation and electrodeposition

As it was described earlier, three different methods were used for the electrodeposition. The settings of the different methods are presented in Table I.

#### 2.3.1. Method A

20 cm<sup>3</sup> of iso-propanol was transferred into the polyacetal cell. An aliquot of the <sup>238</sup>U solution was added. Aluminium and stainless steel backings were used. A stable current of 2 · 10<sup>-3</sup> A was applied during 90 minutes by varying the voltage. After the electrodeposition the cell was emptied and the source was rinsed with water and ethanol, then slightly heated up to fix the uranium [1].

#### 2.3.2. Method B

This method is based on the conventionally used electrolyte containing H<sub>2</sub>SO<sub>4</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> [2, 4, 5].

An aliquot of <sup>238</sup>U stock solution (20-100 µL) was transferred into a 10 cm<sup>3</sup> glass beaker and 0,2 cm<sup>3</sup> of 0,3 M Na<sub>2</sub>SO<sub>4</sub> was added to prevent adsorption of the uranium to the glass wall. The solution was evaporated to dryness. The dry residue was redissolved in 0,3 cm<sup>3</sup> concentrated H<sub>2</sub>SO<sub>4</sub> and 4 cm<sup>3</sup> of distilled water was added followed by 2 drops of 0,1 % thymol blue indicator. The pH was adjusted to 2,1–2,4 with 25 % NH<sub>4</sub>OH. The solution was transferred into the electrodeposition cell and the glass beaker was washed 5 times with 1 cm<sup>3</sup> of 1 % H<sub>2</sub>SO<sub>4</sub>. The pH was readjusted to 2,1 - 2,4 by adding 25 % NH<sub>4</sub>OH.

#### 2.3.3. Method C

An 0,1 cm<sup>3</sup> aliquot of enriched <sup>238</sup>U solution (IRMM) or an 0,35 – 0,50 cm<sup>3</sup> aliquot of a natural uranium solution (CIEMAT) was transferred into a 10 cm<sup>3</sup> glass beaker and evaporated to dryness. The dry residue was dissolved in saturated NH<sub>4</sub>NO<sub>3</sub> (1920 g dm<sup>-3</sup>; T = 20 °C) solution and transferred into the electrodeposition cell. The beaker was rinsed with 1 – 2 cm<sup>3</sup> portions of saturated NH<sub>4</sub>NO<sub>3</sub> and finally with 4 cm<sup>3</sup> of deionised water [3].

For *method B* and *C* ultrasonic agitation was applied in order to remove hydrogen bubbles from the backing surface, to obtain a more uniform alpha source.

In case of inorganic electrolytes (method B and C), one minute before switching off the current, 1 cm<sup>3</sup> of 25 % NH<sub>4</sub>OH was added to the solution to prevent the redissolution of the deposited uranium layer. The source was rinsed with deionised water and ethanol, then the electrodeposition cell was disassembled. The disc was rinsed with ethanol once again and dried at ambient temperature.

TABLE I. The setting of the electrodeposition procedures as a function of electrolyte.

	Method A	Method B	Method C
Electrolyte	Iso-propanol	H <sub>2</sub> SO <sub>4</sub> / (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	Saturated NH <sub>4</sub> NO <sub>3</sub>
pH adjustment	no	yes; 2,1-2,4	no
Electrolyte volume (cm <sup>3</sup> )	20	15	15
Anode shape	rectangular	rectangular	spiral
Cathode to anode distance (mm)	10	5-10	6-7
Voltage (V)	300-400	8-10	4,1-4,5 (IRMM) 4,9-5,1 (CIEMAT)
Current (A)	2 · 10 <sup>-3</sup>	1	0,85 (IRMM) 1 (CIEMAT)
Deposition time (min)	90	40	60
Ultrasonic agitation	No	Yes	yes
Source diameter (mm)	6 and 12	16	18,6 (IRMM) 22 (CIEMAT)

### 2.4 Measurement set-up

Measurements were taken at IRMM and CIEMAT using measurement chambers of identical design with temperature stabilization at the level of the preamplifier. Both systems are equipped with ion implanted Si detectors, having active areas between 50 and 150 mm<sup>2</sup>. A set of internal baffles was used to reduce the scattering of α-particles from the counter walls into the detector. The solid angle subtended by the detectors was between 1,0 % and 1,6 % of 4π sr.

At IRMM, the electronic chain was composed of an amplifier, a single channel analyser a dead time unit, an ADC and a clock. The data were acquired using the DAQ2000 software developed at IRMM [6]. At CIEMAT a digital multichannel analyzer, model DSPECPRO from ORTEC was directly connected to the preamplifier output.

The energy resolution of the measured spectra was determined by fitting alpha peaks with in-house built computer packages: DAQ2000 at IRMM [6] and ALPACA at CIEMAT [7].

### 3. RESULTS AND DISCUSSION

The results for five representative sources produced by the three different methods are summarized in Table II.

TABLE II: Overview of the properties of the sources made with the different source preparation methods measured at IRMM.

Source	1031	All016	SS1019	SS1024	SS1111
Produced at	CIEMAT	IRMM	IRMM	IRMM	IRMM
Method	C	A	A	B	C
Backing material	SS	Al	SS	SS	SS
Active area of detector (mm <sup>2</sup> )	100	100	100	150	100
Solid angle (%)	1,5	1,5	1,5	1,6	1,5
Count rate (counts per hour)	31	6,1	9,4	4,4	30,5
FWHM at 4198 Kev (keV)	15,8	12,3	18,6	19,1	15,8
Peak to valley ratio	58	26	16	37	≈60

SS – Stainless steel

Al – Aluminium

The difference in quality between the sources can be explained by reviewing the settings.

#### 3.1. Impurities

If the material in contact with the electrolyte is not chemically resistant, it can be dissolved in the electrolyte and deposited on the surface of the source during the electrolytic process as observed in some cases during our experiment. Using a polyethylene electrodeposition cell often resulted in a polymer deposit on the surface of the source (Fig. 1a). Impurities in the reagents (e.g. Fe) may interfere with the deposition of <sup>238</sup>U (Fig. 1b).

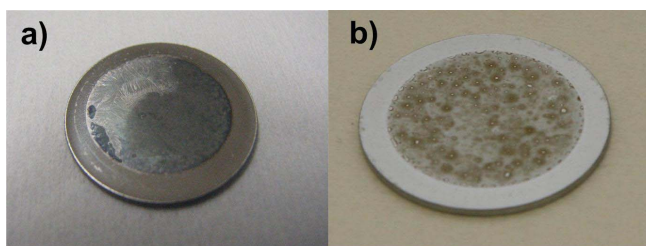


Fig. 1. Different impurities on the stainless steel backing: a) polymer deposit using polyethylene electrodeposition cell; b) from iron impurities of the reagents

#### 3.2. Electrolyte-anode material

As platinum (Pt) is used as anode and uranium is deposited from the electrolyte solution containing H<sub>2</sub>SO<sub>4</sub>/(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution, some Pt could get dissolved into the solution. Subsequently, it could be deposited onto the stainless steel backing. This process has already been

reported [8-10] and leads to a subsequent worsening of the spectral quality.

#### 3.3. 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 spirally wound or meshed disc shape electrode, compared to pin shaped or cross type electrode [12]. For this reason, rectangular and spiral shaped anodes were used.

#### 3.4. Deposited mass

The deposited mass plays an important role in the spectral quality. Martin and Hancock [11] found a positive correlation between source mass density and peak resolution (FWHM), which is 0,63 keV per μg cm<sup>-2</sup>. Using this heuristic relationship, one finds indeed an attainable resolution of 16,4 keV for a source with a density of 26 μg cm<sup>-2</sup>.

Other researchers [8-10] have demonstrated that suitable alpha sources for common applications can be prepared with a surface mass density of 30 (maximum 40 μg cm<sup>-2</sup>).

At IRMM, using method A 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 method C with 18,6 mm of effective backing diameter, we were unable to produce good quality sources with mass of deposited <sup>238</sup>U exceeding 100 μg (A=1,2 Bq). It was concluded that the surface density should be kept below 26 μg cm<sup>-2</sup>.

At CIEMAT, several mass densities were checked and it was concluded that the range between 20 and 26 μg cm<sup>-2</sup> is the most appropriate.

Pictures of sources made in CIEMAT and IRMM are shown in Fig.2 and the associated alpha-spectra in Figs. 3-4.

### 4. CONCLUSION

Electrodeposition procedures were optimised for the production of <sup>238</sup>U sources for high-resolution alpha-particle spectrometry. Three different electrolytes were tested with respect to attainable resolution for sources with about 1 Bq activity. Several tests show that the best energy resolution was achieved with sources produced in saturated NH<sub>4</sub>NO<sub>3</sub>, compared to iso-propanol or H<sub>2</sub>SO<sub>4</sub>/(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>.

Our best sources have a diameter of about 20mm, and a maximum surface density of 26 μg cm<sup>-2</sup>. The resolution of the alpha sources is between 16 and 18 keV, the peak to valley ratio is about 60. The method reconciles the inherently opposing requirements of high resolution and sufficient count rate needed to determine the alpha emission probabilities more accurately.

### ACKNOWLEDGEMENT

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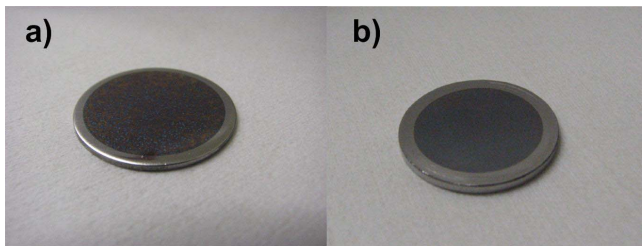


Fig. 2. <sup>238</sup>U sources prepared: a) from natural uranium solution (CIEMAT); b) from enriched <sup>238</sup>U solution (IRMM)

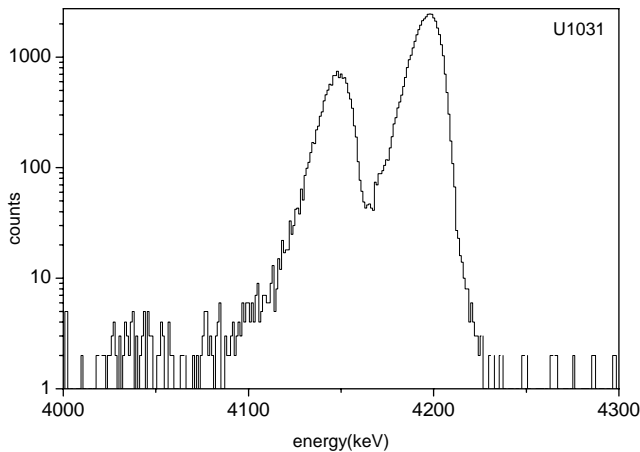


Fig. 3. <sup>238</sup>U peaks in an alpha spectrum of a natural uranium source (CIEMAT)

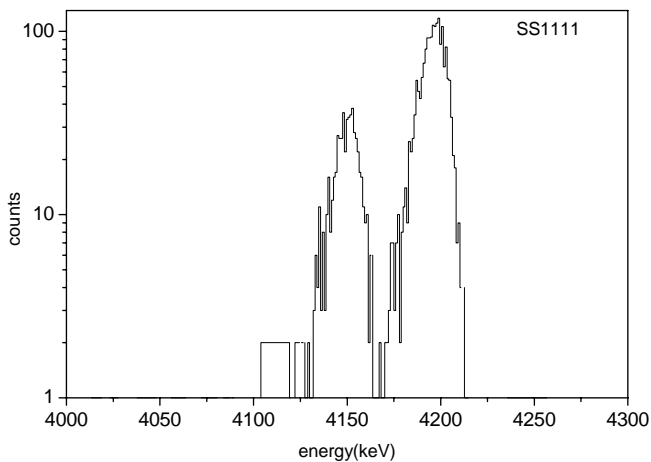


Fig. 4. Alpha spectrum of an enriched <sup>238</sup>U source (IRMM)

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