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Preparation of high resolution ^{238}U α -sources by electrodeposition from aqueous solution

Report for EMRP MetroFission project

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Table of contents

1. INTRODUCTION.....	2
2. OBJECTIVES.....	2
3. EXPERIMENTAL PROCEDURE.....	2
3.1. Chemicals and backings	3
3.2. Preparation of the electrolytic cell and the backings	3
3.3. Sample/Electrolyte preparation	4
3.4. Electrodeposition	5
3.5. Instruments	6
4. RESULTS AND DISCUSSION.....	6
5. CONCLUSIONS.....	14
REFERENCES.....	16

1. Introduction

The source preparation procedure for high-resolution ^{238}U sources is described in this work. It was done in collaboration between CIEMAT and IRMM within the frame of MetroFission project aiming at the determination of the alpha-emission probabilities of ^{238}U . Metrofission aims to address the measurement challenges posed by 'Generation IV' designs, by testing temperature measurements and materials for suitability, and ensuring sufficient nuclear data and radiation measurement techniques are available.

The demands for source quality in radionuclide metrology are much higher than in applied spectrometry, e.g. for environmental analysis or geological studies. A good uranium source for high-resolution alpha spectrometry must be sufficiently active to achieve good statistical accuracy. 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. Many parameters of the electrodeposition had to be optimised such as the type of electrolyte, material and shape of the platinum anode, material of the cathode (backing), surface quality of the cathode, deposited mass, rotation of the anode, current density and the deposition time.

2. Objectives

The objective of this work was to prepare ^{238}U alpha sources with good spectral properties and relatively high specific activity in order to accurately determine the relative alpha emission probabilities via high-resolution alpha-particle spectrometry. Since source preparation in iso – propanol did not result in satisfactory source quality (too much low energy tailing), we tried to prepare alpha source from aqueous electrolyte solution containing $\text{H}_2\text{SO}_4/(\text{NH}_4)_2\text{SO}_4$ and later from a saturated NH_4NO_3 solution.

3. Experimental procedure

Three different types of electrolyte preparation procedures were used. Two of them are based on Talvitie's and Hallstadius' methods [1, 2] modified according to Tomé and Sanchez [3], while the third is based on experiments carried out at CIEMAT.

Each method consisted of a sample preparation and an electrodeposition phase. The overview of the procedures is presented in Figure 1 and described in more detail below.

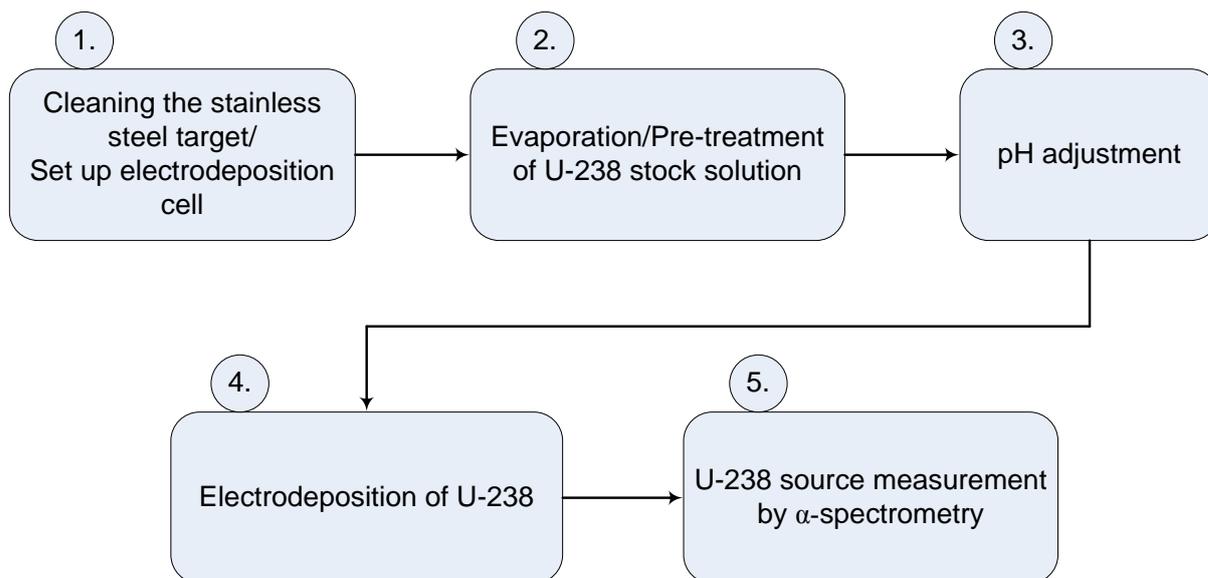


Figure 1. Flow chart of the procedure.

3.1. Chemicals and backings

All chemicals (Na_2SO_4 , NH_4NO_3 , NH_4OH and H_2SO_4) used were analytical grade reagents. The saturated NH_4NO_3 solutions were always freshly prepared by dissolving 19.2 g NH_4NO_3 in 10 cm³ of deionised water.

A stock solution of highly enriched ^{238}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 mg mL⁻¹. This stock solution was diluted with 0.75 M HNO_3 lowering the uranium concentration to 1 mg mL⁻¹.

Commercially available mirror polished stainless steel disks were used as source backing.

3.2. Preparation of the electrolytic cell and the backings

Mirror polished stainless steel discs were used as backings. First the protective plastic tape was removed from the backing surface and it was cleaned with acetone. It was ready to place into the electrodeposition cell. The electrodeposition cell used is a polyethylene plastic scintillation vial for methods A and B and a Teflon vial for method C.

- a) In the first approach, a wire was soldered in the middle of a copper support disc. A hole was drilled in the centre of the cap of the vial and the wire was passed through. The stainless steel backing cathode was put on top of the copper support disc and both were fixed in the bottom of the cap.
- b) Later the stainless steel backing disc was fitted in the cap on the top of the wire (electrical connection) without using any copper support in between as is shown in Figure 2.

At the screw-cap side the thread of the vial is covered with Teflon tape in order to make the cell leak tight. The other side of the vial was cut off.

Before using it, the cell was checked for leak tightness by filling it with distilled water. It was left for standing for 10-15 minutes and a visual check was made.

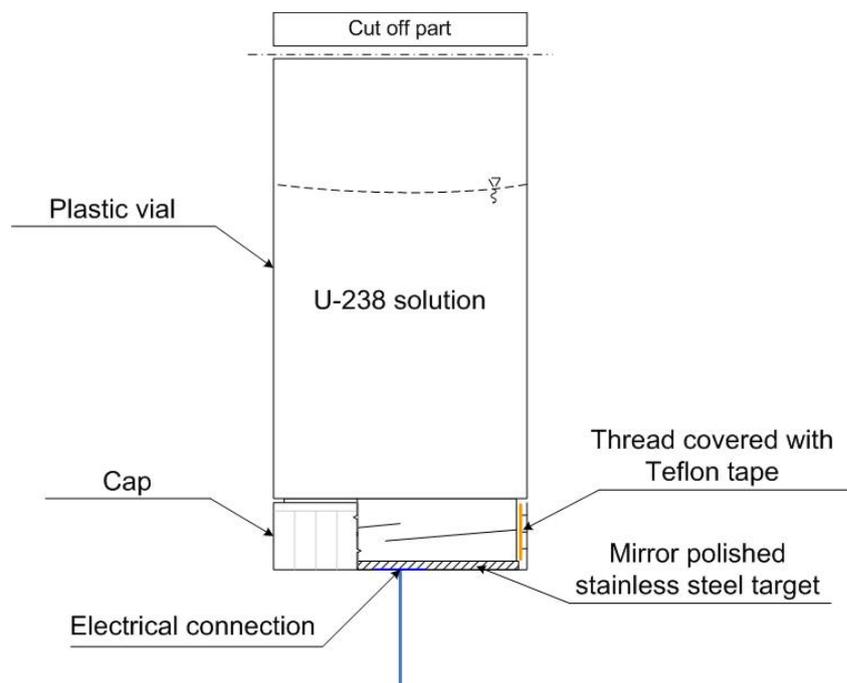


Figure 2. Experimental setup of the electrodeposition cell.

3.3. Sample/Electrolyte preparation

Three different electrolyte solutions were used for the electrodeposition.

- A) a conventionally used solution containing Na_2SO_4 , H_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$ [1 - 3].
- B) a slightly modified version of A containing a mixture of NaHSO_4 , H_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$.
- C) a saturated NH_4NO_3 solution as used at CIEMAT.

A. Na_2SO_4 , H_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$

- 1) An aliquot of ^{238}U stock solution (20-100 μL) was transferred into a 10 mL glass beaker and 0.2 mL of 0.3M Na_2SO_4 was added to prevent adsorption of the uranium to the glass wall.
- 2) The solution was evaporated very carefully to dryness
- 3) The dry residue was redissolved in 300 μL concentrated H_2SO_4 . If necessary, the solution was warmed up in order to dissolve the residue completely. Any loss of H_2SO_4 was avoided.
- 4) 4 mL of distilled water were carefully added (heat production), followed by 2 drops of 0.1 % thymol blue indicator.
- 5) The pH was adjusted to 2.1-2.4 with 25 wt% NH_4OH . This was done slowly, as the reaction is exothermic and the solution needs to cool to room temperature. At pH 2.1-2.4, the colour of the solution changes from red to salmon pink (yellow/yellow orange).

- 6) The solution was transferred into the electrodeposition cell and the glass beaker was rinsed 5 times with 1 mL of 1 wt% H₂SO₄
- 7) The pH was readjusted to 2.1-2.4 by slowly adding 25 wt% NH₄OH as described in step 5.

B. NaHSO₄, H₂SO₄ and (NH₄)₂SO₄

- 1) An aliquot of ²³⁸U stock solution (20 μL) was transferred into a 10 mL glass beaker and 4 mL of 5 wt% NaHSO₄ was added.
- 2) The solution was evaporated to dryness.
- 3) The dry residue was redissolved in 10 mL of 0.75 M H₂SO₄ and again evaporated to dryness.
- 4) The residue was dissolved in 10 mL of 0.75 M H₂SO₄.
- 5) Two drops of 0.1 % thymol blue indicator was added then the pH was adjusted to 2.1-2.4 with 25 wt% NH₄OH. This was done slowly as the reaction is exothermic and the solution needs to cool to room temperature. At pH 2.1-2.4, the colour of the solution changes from red to salmon pink (yellow/yellow orange).
- 6) The solution was transferred into the electrodeposition cell and the glass beaker was rinsed three times with 1 mL of distilled water.

C. Saturated NH₄NO₃

- 1) An aliquot of ²³⁸U stock solution (100 μL) was transferred into a 10 mL glass beaker and evaporated to dryness.
- 2) The dry residue was dissolved in 5 mL saturated NH₄NO₃ solution (1920 g L⁻¹; T = 20 °C) and transferred into the electrodeposition cell.
- 3) The beaker was rinsed with saturated NH₄NO₃ little by little (with 1-2 mL portions).
- 4) The total volume of the electrolyte in the electrodeposition cell was 15 mL.

3.4. Electrodeposition

The set-up used for the electrodeposition procedure, presented in Figure 3, was the same for the 3 methods described above. The distance between the platinum anode and the stainless steel backing cathode was set between 0.5-1 cm.

- 1) The platinum anode was rotating during the electrodeposition (~ 10-12 rpm).
- 2) The following settings were used for the electrodeposition:
 - I = 1 A t = 20 min for "A" and "B" type electrolyte.
 - I = 0.52 A t = 60 min for "C" type electrolyte.
- 3) 1 mL of 25 wt% NH₄OH was added 1 minute before switching off the current.
- 4) The backing was rinsed with distilled water and then with acetone.
- 5) The electrodeposition cell was disassembled.

6) For "A" and "B" type electrolytes, the backing was rinsed with acetone again and dried at ambient temperature for 2-3 minutes and then it was heated on a hot plate in order to fix the deposited ^{238}U onto the stainless steel backing.

For the "C" type electrolyte, the disk was rinsed with ethanol only.

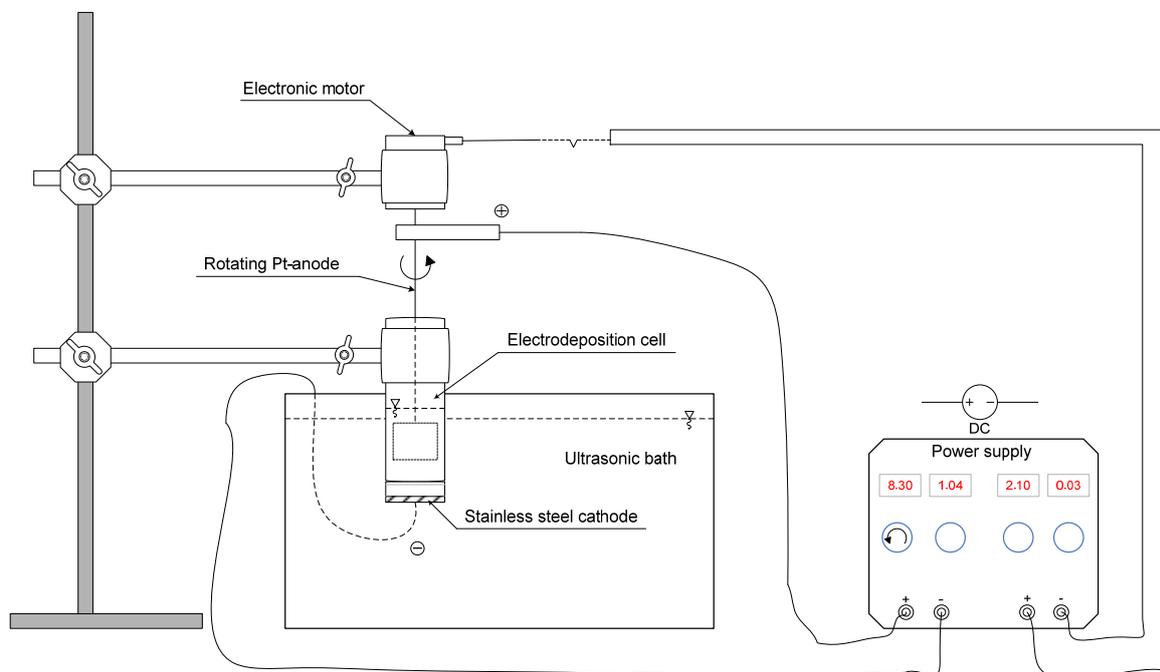


Figure 3. Set-up for the electrodeposition.

3.5. Instruments

For the electrodeposition an Aim & Thurlby Thandar Instruments EL 302 TV power supply was used.

The measurements at IRMM were performed in a vacuum chambers equipped with ion implanted Si detectors, having an active area between 50 and 150 mm². A set of internal baffles prevented the scattering of α -particles from the counter walls into the detector. The solid angle subtended by the detectors was between 0.39 – 1.77 % of 4π sr.

The electronic chain was composed of a temperature stabilised preamplifier, an amplifier, a single channel analyser, a dead time unit, an ADC and a clock. The data were acquired using the DAQ2000 computer software package developed at IRMM [5].

The energy resolution of the measured spectra was determined by fitting the alpha peaks with the DAQ2000 software.

4. Results and discussion

(a) With copper contact disc

Three sources were prepared by using a copper disc in between the wire and the stainless steel backing.

The above mentioned procedure "A" was applied for the production of source U238SS1021. Before switching off the current, 1 mL of 25 wt% NH₄OH was added as described in the procedure. At that moment, dark brown black precipitate appeared in the cell and on the surface of the source backing. The same happened to source U238SS1022; light brown precipitate appeared after adding 25 wt% NH₄OH.

After disassembling the cell, light blue solution was observed between the copper support disc and the thread of the cap. Probably, the solution could pass through the Teflon covered thread and reach the copper disc. There the sulphuric acid dissolved the copper, and the ions passed into the electrolyte solution. Later the electrodeposition cell was used without a copper support disc.

(b) Without copper contact disc

Source U238SS1023 was the first ²³⁸U source that was prepared without a copper disc. No brown or black precipitate was observed. The electrolyte was colourless but the quality of the source was still poor. A metallic grey deposit covered the stainless steel backing. Looking at the Pt-electrode (Figure 4), it can be clearly seen that the electrode was etched by the electrolyte solution. The platinum was first dissolved in the solution then deposited onto the stainless steel backing. Therefore the old Pt-electrode was replaced by a new one.

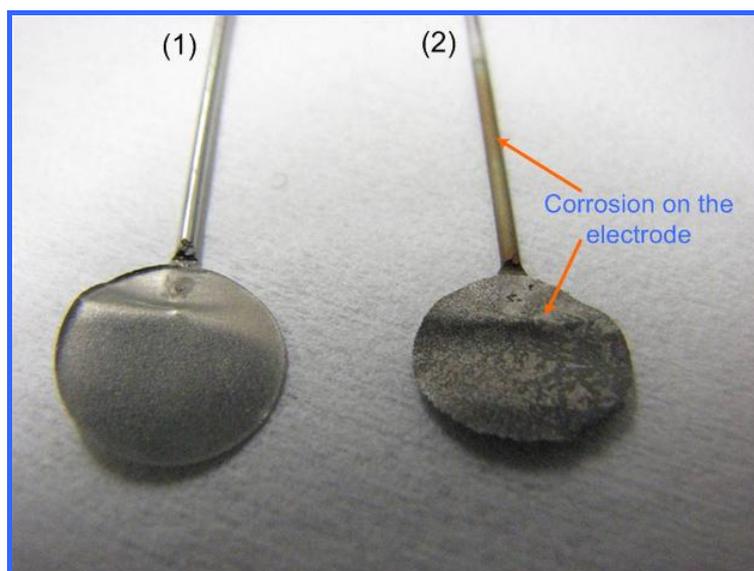


Figure 4. Old "Pt – electrode" (1) before and (2) after the electrodeposition.

Although no deposits were formed on the surface of source U238SS1024, the ²³⁸U distribution was not homogeneous. Some "empty/dead" spaces were observed. It might be due to the H₂ bubbles formed during the electrolytic processes at the cathode. In order to improve the homogeneity of the source, the set-up was immersed in an ultrasonic bath filled with water. Water conducts the ultrasonic waves and cools the cell.

Source U238SS1025 was prepared placing the set-up in an ultrasonic bath. The electrolytic cell and the wire were wrapped in a water tight plastic foil and immersed into an ultrasonic bath during the electrodeposition (Figure 5).

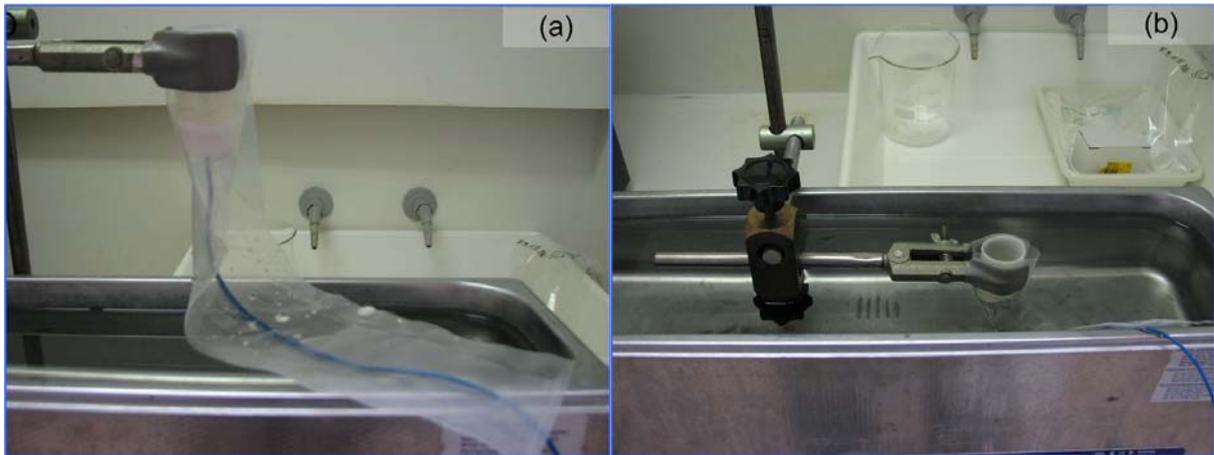


Figure 5. Polyethylene electrodeposition cell (a) wrapped in plastic foil; (b) immersed into the ultrasonic bath.

The quality of the sources improved using the ultrasonic bath. No "empty/dead" spaces were observed on the surface of the backing.

Source U238SS1026, was deposited from the "B" type electrolyte. The quality of the source didn't improve at all; "empty/dead" spaces appeared again. The alpha sources deposited from electrolyte A and B are presented in Figure 6.

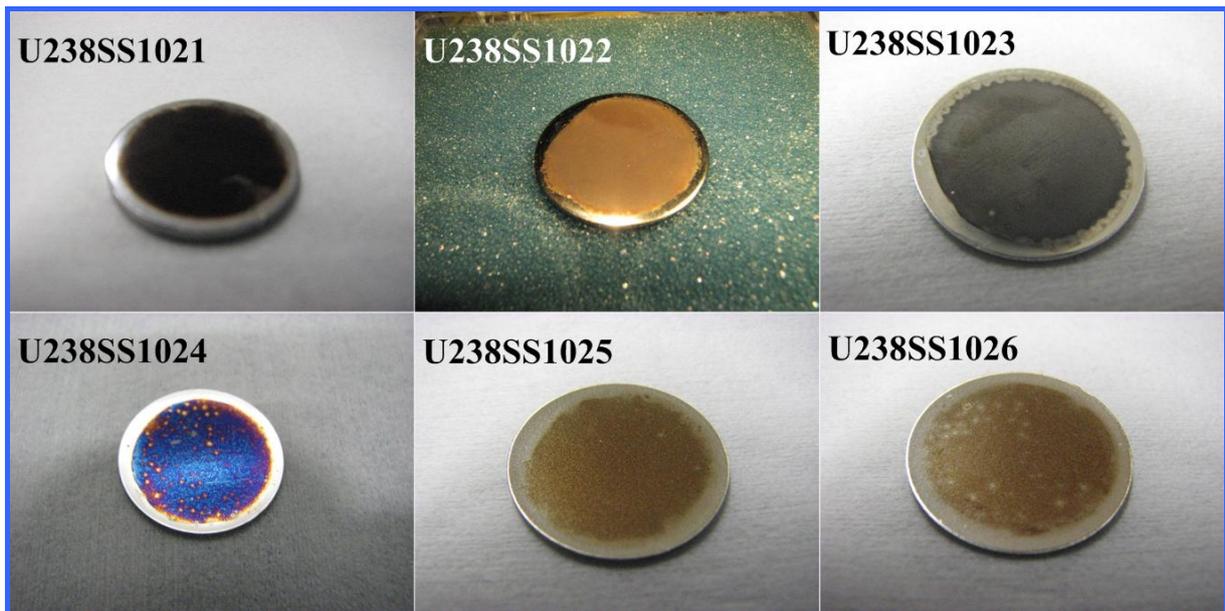


Figure 6. U-238 sources electrodeposited from "A" and "B" type electrolyte.

Source U238SS1027, U238SS1028 and U238SS1029, shown in Figure 7, were electrodeposited from saturated NH_4NO_3 solution. The electrolytic cell and the wire were wrapped in a water tight plastic foil and immersed in the ultrasonic bath during the electrodeposition, but no ultrasonic agitation was applied.



Figure 7. U-238 sources electrodeposited from "C" type electrolyte.

In the case of U238SS1027 and U238SS1028 sources, after the electrodeposition, a polymer like material covered the surface of the stainless steel backing. The backings were rinsed with distilled water and acetone, but this polymer like material remained on the surface. We assumed that it is either from the polyethylene vial, or from the glue from the used tape. For the sources U238SS1028 and U238SS1029 visible blue/gray and brown deposit can be observed. The "crocodile" electrical contact scratched the copper from the upper part of the anode and scrapes fell into the solution.

Since the shape of the anode influences the deposition process, the rectangular Pt was replaced by a Pt-spiral as shown in Figure 8. This anode gave more homogeneous deposits. During the electrodeposition, ultrasonic agitation was applied.



Figure 8. Spirally wound (left) and rectangular (right) Pt-electrodes.

A new Teflon electrodeposition cell was used in order to avoid any organic material impurities on the deposit. The opening at the threads side of this vial was larger than the previously used polyethylene vial; so the active diameter on the stainless steel backing increased from 16 mm to 18.6 mm.

Some sources (U238SS1101, U238SS1102, U238SS1103 and U238SS1104) were deposited onto a non treated stainless steel backing while others onto an electro polished stainless steel backing. Images of the sources are shown in Figure 9.

The U238SS1105, U238SS1106 and U238SS1107 sources were prepared by using electro-polished stainless steel backings which had smoother surfaces.

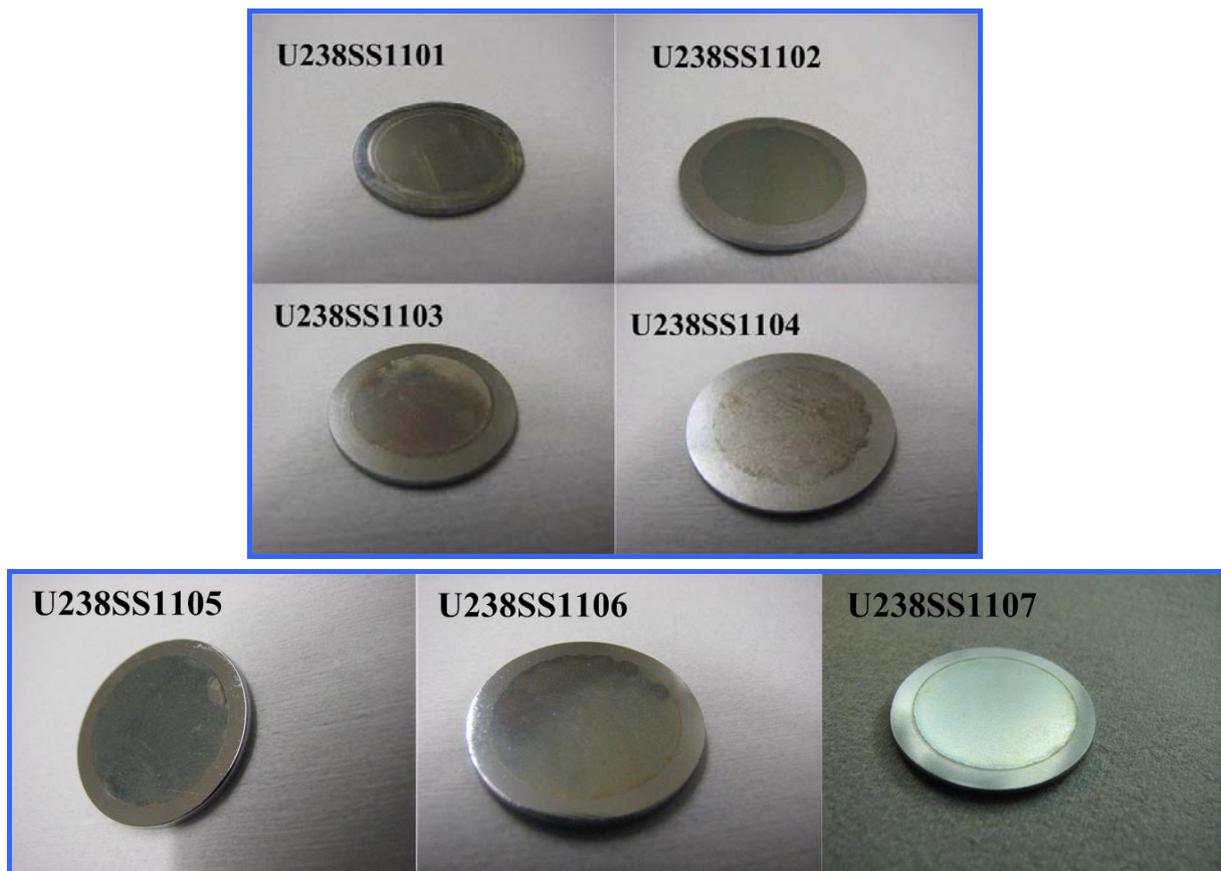


Figure 9. ^{238}U sources prepared by Pt-spiral.

According to the radiograph, the uranium is evenly deposited onto the U238SS1102 and U238SS1105 backings but not onto the U238SS1106. For the latter, a rotating Pt-spiral was applied, but due to the improper electrical contact the current was fluctuating significantly.

The U238SS1107 backing looks shinier, but a closer look reveals a smooth wavy surface. Also the surface density of the U238 deposit is higher than optimal. This resulted in an alpha-particle spectrum not having the desired properties, i.e. good resolution without low energy tailing.

Sources U238SS1108, U238SS1109 and U238SS1111 were prepared from the diluted ^{238}U solution. The deposited mass was significantly less than in the previous sources. The surface of the sources was more homogeneous and its colour turned from yellow into light blue resulting in better spectra.



Figure 10. Uranium sources with thin and homogenous deposit.

The properties of the electrodeposited sources are summarized in Table 1 and Table 2.

Table 1. Summary of the ^{238}U source preparation(continues on next page).

Source I.D	^{238}U stock solution [μL]	Cu support disc	Electrolyte	Pt-anode	US	Source quality	Visual observations	FWHM [KeV]
U238SS1021	100	yes	"A"	Old *	No	Thick black residue	Black/dark brown precipitate in the electrolyte	–
U238SS1022	100	yes	"A"	Old*	No	Brown residue	Brown precipitate, Cu-dissolved	–
U238SS1023	50	no	"A"	Old*	No	Gray residue	Transparent electrolyte	–
U238SS1024	50	no	"A"	new [#]	No	Thin deposit with "empty/dead" spaces	Shiny brown surface; Empty spaces on the backing	20.3
U238SS1025	20	no	"A"	new [#]	Yes	Good, uniform deposit	No empty spaces	
U238SS1026	20	no	"B"	new [#]	No	Thin deposit with "empty/dead" spaces	Empty spaces on the backing	Spectra looks good, but activity is low
U238SS1027	100	no	"C"	new [#]	No	Very thin deposit	Polymer traces on the backing	11.4
U238SS1028	200	no	"C"	new [#]	No	Visible bluish - grey deposit	After drying polymerlike traces on the backing	- Peak to valley not bad
U238SS1029		no	"C"	new [#]	No	Inhomogeneous deposit	Visible bluish and brown deposit	-
U238SS1101	100 ^a	no	"C"	Spiral	Yes	Visible thin deposit	Yellow film covers the backing	Bad resolution
U238SS1102	100 ^a	no	"C"	Spiral	Yes	Very thin and uniform deposit	No polymer, metallic gray	Bad resolution
U238SS1103	30 ^a	no	"C"	Spiral	Yes	Thin light yellow deposit	Inhomogeneous deposit	Bad resolution
U238SS1104	110	no	"C"	Spiral	Yes	light brown and gray deposits	Inhomogeneous deposit	Bad resolution
U238SS1105	20 ^a	no	"C"	Spiral	Yes	light blue deposit on the source	Very thin deposit	Resolution is reasonable, good peak to valley ratio

Table 1. Summary of the ^{238}U source preparation(continued from the previous page).

Source I.D	^{238}U stock solution [μL]	Cu support disc	Electrolyte	Pt-anode	US	Source quality	Visual observations	FWHM [KeV]
U238SS1106	20 ^a	no	"C"	Spiral/rotating	Yes	one part of the deposit is yellow, the other part is light blue; electropolished backing	Inhomogeneous deposit	Bad peak/valley and resolution
U238SS1107	15 ^a	no	"C"	Spiral	Yes	Shiny homogeneous surface; electropolished backing	Some yellow deposits, grains	
U238SS1108	80	no	"C"	Spiral	Yes	homogeneous deposit	Light blue coloured deposit	Good resolution and Peak to valley ratio
U238SS1109	75	no	"C"	Spiral	Yes	homogeneous deposit	Light blue coloured deposit	Good resolution and Peak to valley ratio
U238SS1110	75	no	"C"	Spiral	Yes	inhomogeneous deposit	Scratches on the backing	
U238SS1111	70	no	"C"	Spiral	Yes	homogeneous, thin deposit	Light blue	The best resolution and peak to valley ratio

*-"O"-shaped anode; #– Rectangular shaped anode; ^a-from the original ^{238}U solution (20mg/ml)

Table 2. Overview of the properties of the sources made with the different source preparation methods. The measurements were performed in one set-up at IRMM.

Source	1031	SS1024	SS1111
Produced at	CIEMAT	IRMM	IRMM
Method	C	A	C
Active area of detector (mm^2)	100	150	100
Solid angle (%)	1.5	1.6	1.5
Count rate (counts per hour)	31	4.4	30.5
FWHM at 4198 keV (keV)	15.8(5)	19.1(5)	15.8(5)
Peak to valley ratio	≈ 60	≈ 40	≈ 60

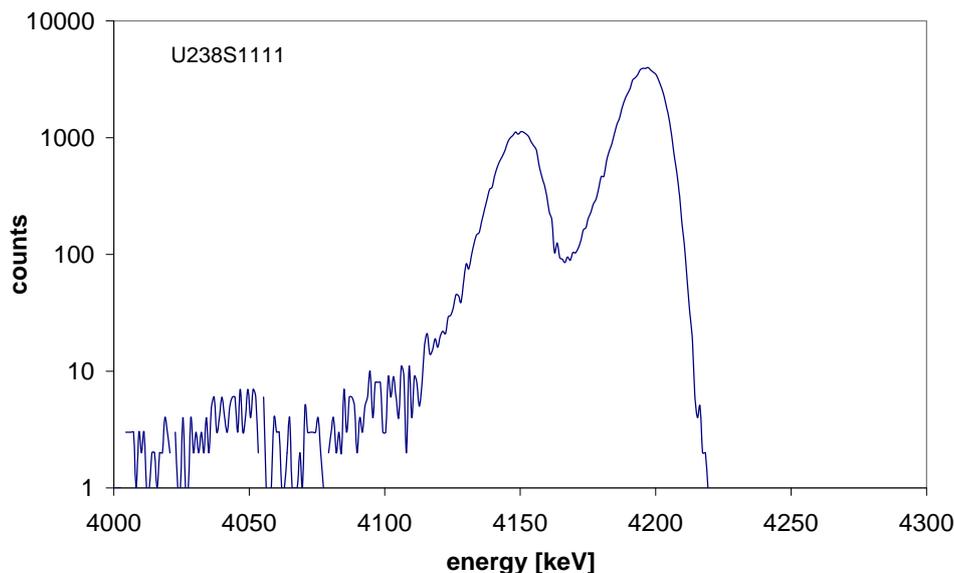


Figure 10. Alpha spectrum of an enriched ^{238}U source (IRMM).

In Figure 11, the autoradiograph and the activity profile along a line through the centre of the U238SS1111 source are shown. The source was prepared with a spirally shaped anode.

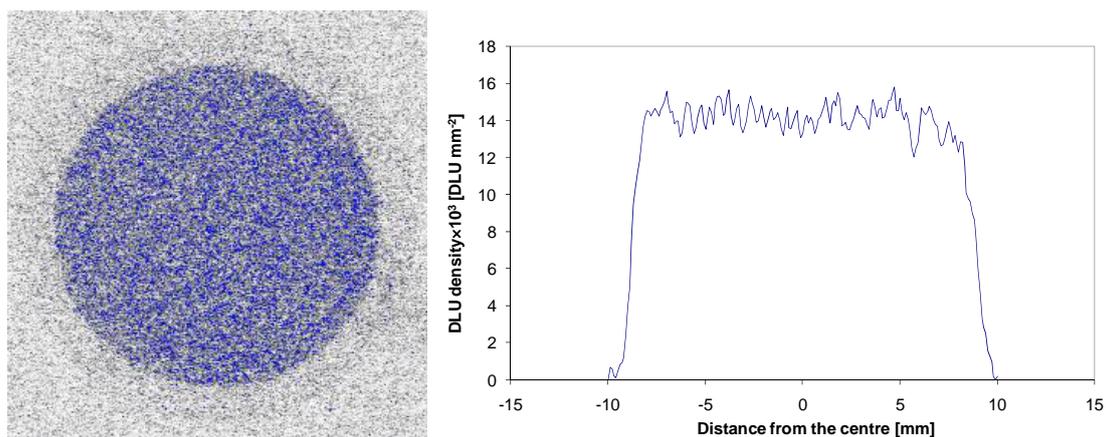


Figure 11. Autoradiograph (left) and activity distribution (right) of a ^{238}U source prepared with a spirally wound anode.

The autoradiograph image and profile show that using a spirally wound anode the ^{238}U isotope is deposited homogeneously over the whole stainless steel backing.

5. Conclusions

Electrodeposition procedures were optimised for the production of ^{238}U sources for high-resolution alpha-particle spectrometry. Two different inorganic electrolytes were tested with respect to attainable resolution for sources of about 1 Bq activity. Several tests show that the best energy resolution was achieved with sources produced in saturated NH_4NO_3 , deposited onto polished stainless steel backings using a spirally wound platinum anode.

Our best sources have a diameter of about 20 mm and a maximum surface density of $26 \mu\text{g cm}^{-2}$. The resolution of the alpha sources is between 16 and 18 keV and 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 of ^{238}U more accurately.

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Abstract

The source preparation procedure for high-resolution ^{238}U sources is described in this work. For preparing alpha sources for high-resolution spectrometry many parameters of the electrodeposition had to be optimised such as the type of electrolyte, material and shape of the platinum anode, material of the cathode (backing), surface quality of the cathode, deposited mass, rotation of the anode, current density and the deposition time. This work was done in collaboration between CIEMAT and IRMM within the frame of MetroFission project aiming at the determination of the alpha-emission probabilities of ^{238}U . Metrofission aims to address the measurement challenges posed by 'Generation IV' designs, by testing temperature measurements and materials for suitability, and ensuring sufficient nuclear data and radiation measurement techniques are available.

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